J. Am. Chem. Soc. **1998,** *120,* 1289−1299 1289

Influence of Interchain Interactions on the Absorption and Luminescence of Conjugated Oligomers and Polymers: A Quantum-Chemical Characterization

J. Cornil,[†,‡,§] D. A. dos Santos,[†] X. Crispin,[†] R. Silbey,[‡] and J. L. Brédas*[,†,§]

Contribution from the Laboratory for Chemistry of Novel Materials,
Center for Research on Molecular Electronics and Photonics, University of Mons-Hainaut,
Place du Parc 20, B-7000 Mons, Belgium, Department of Chemistry and Center for Materials Science and
Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Institute for
Polymers and Organic Solids, University of California, Santa Barbara, California 93106-5090

Received October 31, 1997

Abstract: Correlated quantum-chemical calculations are used to investigate the influence of interchain interactions on the absorption and emission of π-conjugated chains. The results are discussed in relation to the utilization of conjugated materials as active elements in electro-optic devices; they provide guidelines on how to prevent a substantial decrease in luminescence yield in solid films. In high-symmetry cofacial configurations, interchain interactions lead to a blue shift of the lowest optical transition compared to that calculated for an isolated chain; the appearance of an additional red-shifted component is expected when positional disorder is considered. The absence of any significant oscillator strength in the transition between the ground state and the lowest excited state in highly symmetric complexes implies that the luminescence emission will be strongly quenched. This picture is, however, modified when one takes account of the relaxation processes which occur in the lowest excited state. The nature of the most stable photogenerated species and the role played by chemical impurities are also addressed.

I. Introduction

Organic conjugated polymers have been thoroughly investigated in the context of their insulator-to-conductor transition upon chemical or electrochemical doping.[1] Since the first report of electroluminescence in poly(paraphenylenevinylene), PPV,[2] renewed interest has focused on the use of these compounds as active components in electro-optic devices. The combination of the semiconducting properties and high luminescence efficiency of conjugated oligomers and polymers has opened the way to the development of polymer light-emitting diodes,[2−4] light-emitting electrochemical cells,[5] and solid-state lasers.[6−8] Although the achievement of an understanding of the photophysics of these systems is thus of importance, detailed structure−property relationships are still lacking,[9] partly because the experimental results are sensitive to the nature and/or quality of the samples.[10]

In recent years, the theoretical methods of quantum-chemistry and solid-state physics have provided significant insight into the electronic and optical properties of isolated conjugated chains (oligomers and polymers). These calculations, supported by a wide range of experimental measurements, have established that the primary photoexcitations in isolated chains of (for example) PPV and its substituted derivatives are polaron−excitons, weakly bound electron−hole pairs coupled to local deformations of the conjugated backbone.[11,12] The radiative decay of these excitations competes with nonradiative routes and takes place from the lowest excited state, in agreement with Kasha's rule.[13] In the absence of significant intermolecular interactions (for example, in dilute solutions or when the conjugated compounds are incorporated in inert matrixes), the luminescence efficiency is relatively high and the luminescence decays with a natural lifetime of approximately a nanosecond.[14]

For substituted PPV chains in solution, the decay of the fluorescence signal was reported to be equivalent to that of the picosecond photoinduced absorption features.[15−18] In such a

---

[†] University of Mons-Hainaut.

[‡] Massachusetts Institute of Technology.

[§] University of California.

(1) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.

(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(3) Braun, D.; Heeger, A. J. Thin Solid Films **1992**, *216*, 92. Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *1982*, 18.

(4) Gymer, R. W. *Endeavour* **1996**, *20*, 115.

(5) Pei, Q.; Yu, C.; Zhang, Y.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086.

(6) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B.; Andersson, M. R.; Pei, Q.; Heeger, A. J. *Science* **1996**, *833*, 273.

(7) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* **1996**, *382*, 695.

(8) Frolov, S. V.; Gellermann, W.; Ozaki, M.; Yoshino, K.; Vardeny, Z. V. *Phys. Rev. Lett.* **1997**, *78*, 729.

(9) *Primary Photoexcitations in Conjugated Polymers: Molecular Exciton versus Semiconductor Band Model*; Sariciftci, N. S., Ed.; World Scientific Publisher: Singapore, in press.

(10) Denton, G. J.; Tessler, N.; Harrison, N.; Friend, R. H. *Phys. Rev. Lett.* **1997**, *78*, 733.

(11) Brédas, J. L.; Cornil, J.; Heeger, A. J. *Adv. Mater.* **1996**, *8*, 447.

(12) Harrison, N. T.; Hayes, G. R.; Philipps, R. T.; Friend, R. H. *Phys. Rev. Lett.* **1996**, *77*, 1881.

(13) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals*; Oxford University Press: New York, 1982.

(14) Greenham, N. C.; Samuel, I. D. W.; Hayes, G. R.; Philipps, R. T.; Kessener, Y. A. R. R.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1995**, *241*, 89.

(15) Schwartz, B.; Hide, F.; Andersson, M. R.; Heeger, A. *J. Chem. Phys. Lett.* **1997**, *265*, 327.

S0002-7863(97)03761-X CCC: $15.00

case, the formation of singlet intrachain polaron−excitons was invoked in order to rationalize the excited-state dynamics; the measured photoinduced absorption spectra then reflect the nature of the optical transitions between the lowest singlet B_u state and higher-lying A_g states.

In many cases, the results of electronic structure calculations based on isolated chains are in good agreement with relevant experimental data.[19] However, intermolecular interactions have been shown to dramatically alter the electronic and optical properties from those characteristic of a single chain.[15−18,20−29] It is thus essential not to rely exclusively on the simple assumption that interchain interactions are of secondary importance and that most of the properties are governed by intrachain interactions. The need to incorporate the effect of the surroundings was clearly recognized in the field of nonlinear optics in order to rationalize the interconnection between the nature of the medium and the amplitude of the hyperpolarizabilities.[30] Quantum-chemical calculations have further illustrated that the nonlinear optical response is affected by interactions between adjacent chromophores;[31−34] this was shown experimentally to be at the origin of a strong second-harmonic generation signal in centrosymmetric dyes.[35]

Various manifestations of interchain coupling have been demonstrated in recent experimental investigations of the photoluminescence properties of conjugated chains. For example, in cyano-substituted poly(paraphenylenevinylene), the radiative lifetime of the luminescence is significantly increased compared to other PPV derivatives without any substantial change in the quantum efficiency;[24,25] in poly(2-methoxy-5-((2′-ethylhexyl)oxy)paraphenylenevinylene), MEH−PPV, a dramatic decrease in the fluorescence quantum yield was reported in the solid state;[16,20,21] in poly(2-butyl-5-(2′-ethylhexyl)-1,4-paraphenylenevinylene), BuEH−PPV, and MEH−PPV, there is no correlation between the dynamics of the fluorescence signal and that of the picosecond photoinduced absorption features.[15] These studies indicate that intermolecular interactions give rise to the appearance of new *interchain* species; their nature and origin are, however, a matter of controversy.

Here, we report the results of correlated quantum-chemical calculations performed on interacting conjugated chains. Our goal is to better understand the way interchain coupling affects the electronic and optical properties with respect to those calculated for isolated chains, and hence to understand the effect of interchain interactions on the absorption and emission. Since we hope to clarify the nature of the most stable photogenerated species by comparing the results of the calculations to the data reported in the literature, we must also address the influence of disorder and defects/impurities. These issues are relevant to the development of new materials with high quantum efficiency for photoluminescence in the solid state, and hence for the design of light-emitting devices with enhanced performance.

We emphasize that the present calculations do not allow us to distinguish between dimers (for which the wave functions of two adjacent chains overlap in the ground state, due for example to packing effects) and excimers (where overlap occurs only upon photoexcitation).[26] In contrast to other recent theoretical work,[36,37] we make a clear distinction between excimers (where no net charge separation is observed) and interchain polaron pairs, also referred to as interchain excitons (where a positive polaron is bound by Coulomb attraction to a negative polaron on an adjacent chain).

This paper is organized as follows. We first focus on the electronic and optical properties of highly symmetric complexes formed by two identical PPV oligomers. We mainly discuss the results obtained for the two-ring oligomer, i.e., stilbene; we then consider longer chains and extrapolate to polymer chains (note that such extrapolations are qualitative due to the fact that a stilbene unit is smaller than the typical delocalization lengths encountered in the corresponding polymer[38] and in most conjugated chains, typically between 10 and 20 conjugated units). The discussion of the emission properties of such complexes is extended to situations where geometry relaxation phenomena have time to take place in the lowest excited state. We then analyze the influence of (i) increasing the number of units in interaction, (ii) varying the relative positions of the oligomers, and (iii) chemical impurities.

II. Theoretical Methodology

The ground-state geometry of the complexes formed by planar PPV oligomers (hereafter denoted PPVx, where x is the number of phenylene rings so that $x = 2$ corresponds to the stilbene molecule) is optimized by means of the semiempirical Hartree−Fock Austin Model 1 (AM1) method;[39] this technique has been shown to provide geometric parameters in very good agreement with experimental X-ray data.[40] Note that, in each case, we find that the ground-state geometry of the molecular units is not affected by intermolecular interactions.

To investigate the emission properties of the complexes, we determine their equilibrium geometry in the lowest excited state by coupling the AM1 formalism to a limited configuration interaction (CI)

---

[16] Rothberg, L. J.; Yan, M.; Papadimitrakopoulos, F.; Galvin, M. E.; Kwock, E. K.; Miller, T. M. *Synth. Met.* **1996**, *80*, 41.

[17] Graupner, W.; Leising, G.; Lanzani, G.; Nisoli, M.; De Silvestri, S.; Scherf, U. *Phys. Rev. Lett.* **1996**, *76*, 847.

[18] Pauck, T.; Hennig, R.; Perner, M.; Lemmer, U.; Siegner, U.; Mahrt, R. F.; Scherf, U.; Müllen, K.; Bassler, H.; Gobel, E. O. *Chem. Phys. Lett.* **1995**, *244*, 171.

[19] Beljonne, D.; Cornil, J.; dos Santos, D. A.; Shuai, Z.; Brédas, J. L.; in ref 9, in press.

[20] Yan, M.; Rothberg, L. J.; Kwock, E. K.; Miller, T. M. *Phys. Rev. Lett.* **1995**, *75*, 1992.

[21] Antoniadis, H.; Rothberg, L. J.; Papadimitrakopoulos, F.; Yan, M.; Galvin, M. E. *Phys. Rev. B* **1994**, *50*, 14911.

[22] Hsu, J. W. P.; Yan, M.; Jedju, T. M.; Rothberg, L. J.; Hsieh, B. P. *Phys. Rev. B* **1994**, *49*, 712.

[23] Rumbles, G.; Samuel, I. D. W.; Magnani, L.; Murray, K. A.; DeMello, A. J.; Crystall, B.; Moratti, S. C.; Stone, B. M.; Holmes, A. B.; Friend R. H. *Synth. Met.* **1996**, *76*, 47.

[24] Samuel, I. D. W.; Rumbles, G.; Collison, C. J. *Phys. Rev. B* **1995**, *52*, 11573.

[25] Samuel, I. D. W.; Rumbles, G.; Collison, C. J.; Crystall, B.; Moratti, S. C.; Holmes, A. B. *Synth. Met.* **1996**, *76*, 15.

[26] Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765. Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389.

[27] Gierschner, J.; Egelhaaf, H. J.; Oelkrug, D. *Synth. Met.* **1997**, *84*, 529.

[28] Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Lih, J. J.; Gustafson, T. L.; Epstein, A. J.; Fu, D. K.; Marsella, M. J.; Swager, T. M.; MacDiarmid, A. G.; Hamaguchi, H. *Phys. Rev. Lett.* **1996**, *76*, 1513.

[29] Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Gobel, E. O.; Müllen, K.; Bässler, H. *Chem. Phys. Lett.* **1995**, *240*, 373.

[30] Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Bredas, J. L.; Pierce, B. M. *Science* **1994**, *265*, 632.

[31] McWilliams, P. C. M.; Soos, Z. G. *J. Chem. Phys.* **1991**, *95*, 2127.

[32] Di Bella, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 5842.

[33] Brouyère, E.; Persoons A.; Brédas, J. L. *J. Phys. Chem.* **1997**, *101*, 4142.

[34] Chen, S.; Kurtz, H. A. *J. Mol. Struct.; Theochem* **1996**, *388*, 79.

[35] Ashwell, G. J.; Jefferies, G.; Hamilton, D. G.; Lynch, D. E.; Roberts, M. P. S.; Bahra, G. S.; Brown, C. R. *Nature* **1995**, *375*, 385.

[36] Conwell, E. M.; Perlstein, J.; Shaik, S. *Phys. Rev. B* **1996**, *54*, 2309.

[37] Conwell, E. M. *Trends Polym. Sci.* **1997**, *5*, 218.

[38] Pichler, K.; Halliday, D. A.; Bradley, D. D. C.; Burn, P. L.; Friend, R. H.; Holmes A. B. *J. Phys. Condens. Matter* **1993**, *5*, 7155.

[39] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[40] Cornil, J.; Beljonne, D.; Brédas, J. L. *J. Chem. Phys.* **1995**, *103*, 843.

scheme (as developed in the AMPAC package[41]). The number of molecular orbitals used to generate the configurations are chosen in a way that ensures the absence of significant evolution in the calculated parameters when additional electronic levels are involved; the CI configurations are selected on the basis of their energy and the strength of their electronic couplings (as set by default in AMPAC[41]). The reliability of this AM1/CI approach to describe the geometry relaxations in the lowest excited state is supported by the excellent agreement observed for trans-polyenes between the AM1/CI results[42] and those afforded by highly correlated ab initio Complete Active Space Self-Consistent-Field (CAS−SCF) calculations;[43] the adequacy of the AM1/CI technique is also confirmed by the excellent agreement between the calculated relaxation energies in the lowest excited state of PPV oligomers and the corresponding experimental values extracted from a detailed analysis of the vibronic progressions observed in the photoluminescence spectra of these compounds.[44] Note that in these excited-state calculations, we only optimize the bond lengths and bond angles formed by the carbon atoms of the conjugated backbone; the parameters involving hydrogen atoms are frozen and set to the values calculated in the ground state. The interchain distances between the planes of the interacting units are varied in a range going from 3.5 to 30 Å; a much more elaborate treatment of the correlation effects would be required to provide accurate determinations of the optimal interchain separation in the lowest excited state. Here, we have chosen to depict various regimes of interaction by simply tuning the amplitude of the interchain interactions (or, in other words, of the interchain transfer integrals, denoted “t perpendicular” in condensed-matter physics terminology). Note that, in the present formalism, the π-electrons are exchanged between the interacting units at short interchain distances, in contrast to models exclusively based on solvation/polarization effects.[45]

On the basis of the optimized geometries, we compute the lowest optical transitions of the complexes and their related intensities with the help of the semiempirical Hartree−Fock Intermediate Neglect of Differential Overlap (INDO) Hamiltonian coupled to a Single Configuration Interaction (SCI) scheme. We use the INDO parametrization developed by Zerner and co-workers[46] and express the electron−electron repulsion term via the Mataga−Nishimoto potential.[47] To be size-consistent,[48] the CI basis includes all the possible singly excited configurations generated from the occupied and unoccupied π-levels.[49] The use of a SCI approach is validated by the absence of significant weight arising from doubly and higher excited configurations in the description of the lowest excited states that are investigated in this paper[50] (an overall description of higher excited states of interacting systems would require a much more elaborate treatment of the correlation effects[19]). All the calculations were performed on IBM RISC-6000 workstations.

The emission spectra are simulated with the same approach, except that the calculations are then performed on the basis of the relaxed geometry in the lowest excited state. An earlier study has shown that the INDO/SCI-calculated vertical transition energies associated to the absorption and emission processes of isolated PPV oligomers compare very well with the experimental values reported for the molecules dispersed in an inert matrix.[44] Note that highly correlated calculations establish that the first excited state of stilbene which is strongly optically coupled to the ground state is not the lowest in energy.[51,52] In contrast to the results provided by an INDO/SCI approach, a forbidden optical transition described by a mixing of two excitations between a localized level and a delocalized level lies below the energy of the intense symmetry-allowed absorption peak. All calculations, however, are consistent with the fact that, as soon as lattice relaxations in the excited states are considered, photoluminescence takes place from the strongly coupled excited state, as expected from the experimental observations.[44] We thus emphasize that an exact ordering of the lowest two excited states would not modify the conclusions drawn in this study regarding the absorption and emission of interacting chains and that the primary goal of the calculations performed on stilbene units is to provide a qualitative picture of the influence of interchain interactions between conjugated segments (for which the lowest excited state is most generally the one strongly coupled to the ground state).

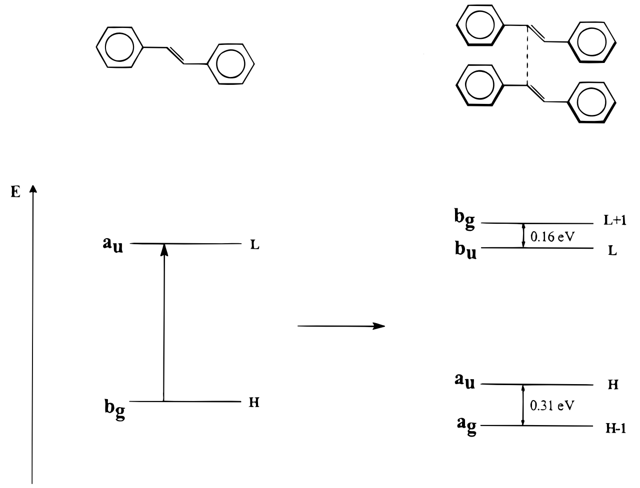


Figure 1. Schematic representation of the one-electron structure of a single stilbene molecule and that of a cofacial dimer formed by two chains separated by 4 Å. The INDO-calculated energy split of the HOMO and LUMO levels when going from the isolated molecule to the dimer is also given.

III. Results and Discussion

III.1. Absorption Properties of Highly Symmetric Complexes. III.1.a. Interacting Stilbene Units. The first complexes we have considered are cofacial dimers where one PPV oligomer is exactly superimposed on top of another one; see the top of Figure 1. Such a configuration is expected to maximize the interaction between adjacent chains and hence to give rise to the largest energy splitting of the lowest excited state.[53] In fact, the energy splitting between the lowest two excited states is calculated to be 0.27 eV in a cofacial dimer formed by two stilbene units separated by 4.5 Å, while values of 0.09 and 0.14 eV are obtained for two stilbene molecules aligned along the chain axis and along the in-plane transverse axis, respectively (the closest distance between two carbon atoms of adjacent chains being also fixed at 4.5 Å). The different interaction strengths in these three configurations are intimately related to the relative strengths of the overlap between the wave functions of the adjacent strands, as illustrated in the following discussion. Moreover, we note that the chain separations are not identical in these three directions in actual samples and that the most efficient intermolecular interactions in the solid state are expected to originate from the superposition of molecules

---

[41] Ampac 5.0, 1994, Semichem, 7128 Summit, Shawnee, KS 66216.

[42] Cornil, J.; Beljonne, D.; Brédas, J. L. *Synth. Met.* **1997**, *84*, 1629.

[43] Serrano-Andres, L.; Lindh, R.; Roos, B. O.; Merchan, M. *J. Phys. Chem.* **1993**, *97*, 9360.

[44] Cornil, J.; Beljonne, D.; Heller, C. M.; Laurich, B. K.; Smith, D. L.; Bradley, D. D. C.; Müllen, K.; Brédas, J. L. *Chem. Phys. Lett.* In press.

[45] Moore, E.; Gherman, B.; Yaron, D. *J. Chem. Phys.* **1997**, *106*, 4216.

[46] Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111.

[47] Mataga, N.; Nishimoto, K. *Z. Phys. Chem.* **1957**, *13*, 140.

[48] Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry*; MacMillan: New York, 1982.

[49] Similar results can also be obtained with a lower CI basis rather than provided by a full SCI approach within the π-framework, however, only when the correct balance is kept between the size of a cluster and the size of the corresponding CI.

[50] The INDO-calculated ground-state stabilization is negligible in all cases with respect to the shift calculated for the lowest two excited states.

[51] Soos, Z. G.; Ramasesha, S.; Galvao, D. S.; Etemad, S. *Phys. Rev. B* **1993**, *47*, 1742.

[52] Molina, M.; Merchan, M.; Roos, B. O. Submitted for publication.

[53] Cornil, J.; Heeger, A. J.; Brédas, J. L. *Chem. Phys. Lett.* **1997**, *272*, 463.

Table 1. INDO/SCI-Calculated Transition Energies, Intensities, and CI Descriptions of the Lowest Two Excited States (S_1 and S_2, respectively) of a Cofacial Dimer Formed by Two Stilbene Molecules for Various Interchain Distances

interchain distance (Å)	excited state	transition energy (eV)	intensity (arb. units)	CI description
30	S_1	4.097	0.0	−0.7 H → L+1 − 0.7 H−1 → L
	S_2	4.100	2.5	0.7 H → L+1 − 0.7 H−1 → L
15	S_1	4.087	0.0	−0.7 H → L+1 − 0.7 H−1 → L
	S_2	4.112	2.5	0.7 H → L+1 − 0.7 H−1 → L
10	S_1	4.068	0.0	−0.7 H → L+1 − 0.7 H−1 → L
	S_2	4.131	2.5	0.7 H → L+1 − 0.7 H−1 → L
7	S_1	4.034	0.0	0.67 H → L+1 − 0.66 H−1 → L −0.21 H−1 → L+1 + 0.21 H → L
	S_2	4.164	2.5	0.69 H−1 → L + 0.69 H → L+1
6	S_1	4.014	0.0	−0.68 H → L − 0.67 H−1 → L+1 −0.17 H → L+1 + 0.17 H−1 → L
	S_2	4.183	2.5	0.69 H−1 → L + 0.69 H → L+1
5	S_1	3.985	0.0	−0.71 H → L + 0.68 H−1 → L+1
	S_2	4.210	2.4	0.69 H → L+1 − 0.68 H−1 → L
4	S_1	3.870	0.0	0.87 H → L − 0.47 H−1 → L+1
	S_2	4.235	2.3	O.77 H → L+1 − 0.56 H−1 → L
3.5	S_1	3.437	0.0	0.97 H → L
	S_5[a]	4.161	1.8	0.93 H → L+1

[a] Note that, at 3.5 Å, the lowest intense optical transition involves the fifth excited state.

(with the plane of the units not necessarily parallel, such as in the herringbone-like structure observed in sexithienyl crystals[54]).

First, we focus on the electronic and optical properties of cofacial dimers formed by two stilbene units, with interchain distance ranging between 3.5 and 30 Å. Table 1 summarizes the CI description of the lowest two excited states of these complexes as well as their transition energies and related intensities. For chain separations between 30 and 8 Å, we find the LCAO coefficients of a given molecular orbital to be localized on a single unit, as intuitively expected (a more detailed discussion of the origin of the symmetry breaking is given below). In this weak coupling regime, the electronic and optical properties of the complexes can be understood on the basis of the dipole−dipole interaction model. Indeed, the CI calculations indicate that the lowest two optical transitions in these dimers correspond to destructive and constructive interactions of the intrachain transition dipole moments, respectively; the intensity is concentrated in the second excited state corresponding to the constructive component, as also established by the molecular exciton model described by Kasha.[55,56] The energy splitting between the two excited states increases as the interchain distance is decreased and reaches a value close to 0.1 eV at 8 Å, although the LCAO coefficients of a given molecular orbital are still localized on a single chain ("t perpendicular" is therefore still very small). Note that the stabilization of the lowest excited state can be considered as the result of the polarization effects induced by the presence of the adjacent chain; a detailed analysis of such effects is certainly a relevant issue[45] but is, however, beyond the scope of the present paper.

In this range of interchain distances, the CI description of the excited states reflects that there is equal probability of finding the exciton on one chain as on the other. However, because of the very low transfer rate between the two units typically expected in a regime of weak interchain coupling, at any given time, the exciton is localized on a single chain; as a result, the luminescence takes place as in the isolated molecule and is not quenched by the intermolecular interactions. In this regime of interchain separation, the results thus describe the photoluminescence properties characteristic of molecules in dilute solutions or dispersed in inert matrixes.

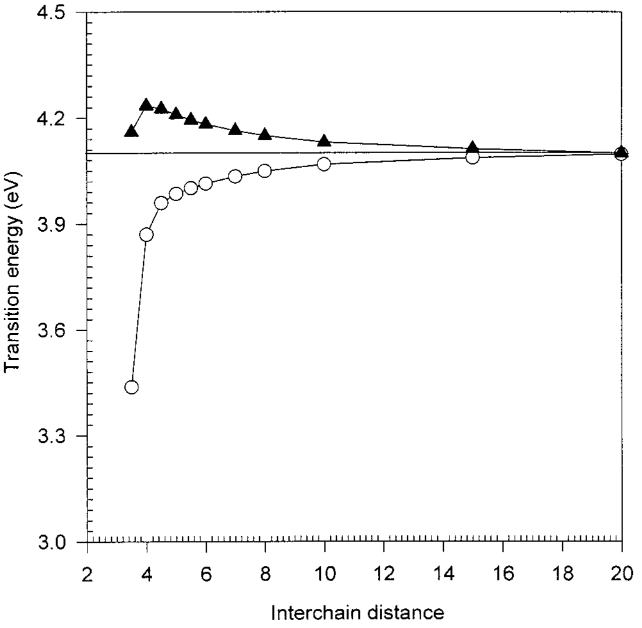


Figure 2. INDO/SCI-calculated transition energies of the lowest two optical transitions of a cofacial dimer formed by two stilbene molecules as a function of the interchain distance. The horizontal dashed line refers to the transition energy of the isolated molecule. Note that the upper value reported at 3.5 Å corresponds to the transition to the fifth excited state, which provides the lowest intense absorption feature.

Upon decreasing the interchain separation, a critical distance is reached around 7 Å below which the molecular orbitals of the dimer start to delocalize over the two chains; they become entirely symmetric below 5 Å. The interaction between the originally degenerate HOMO and LUMO molecular orbitals of the isolated units leads to the formation of four nondegenerate levels that constitute the frontier orbitals of the complex. We present in Figure 1 the relative positions and symmetry of the levels calculated for the stilbene molecule and for the cofacial dimer with the two chains separated by 4 Å. In contrast to the situation in an isolated unit, the HOMO and LUMO orbitals have the same parity in the complex, as is also the case for the HOMO-1 and LUMO+1 levels. As a result, the lowest optical transition (that is described by a mixing of the H → L and H-1 → L+1 excitations) is forbidden according to the selection rules; the entire oscillator strength is concentrated in the transition to the second excited state (that is characterized by a mixing of the H → L+1 and H-1 → L excitations). The splitting between the two optical transitions continuously increases as the interchain distance is decreased; see Figure 2. Furthermore, at short distances the splitting is not symmetric with respect to the transition calculated for the isolated molecule. Referring to perturbation theory,[57] this can be explained by the fact that the first-order correction leads to a symmetric splitting whereas the second-order correction induces an identical stabilization of the two states. On the basis of the INDO/SCI calculations, we estimate the latter correction to be on the order of 0.045 eV at 4 Å and much smaller at larger interchain separations. We also note that the lowest optical transition calculated for chain separations between 5 and 7 Å is described by a mixing of

---

(54) Horowitz, G.; Bachet, B.; Yassar, A.; Lang, P.; Demanze, F.; Fave, J. L.; Garnier, F. *Chem. Mater.* **1995**, *7*, 1337.

(55) McRae, E. G.; Kasha, M. *J. Chem. Phys.* **1958**, *28*, 721.

(56) Kasha, M. *Radiation Res.* **1963**, *20*, 55.

(57) Soos, Z. G.; Hayden, G. W.; McWilliams, P. C. M.; Etemad, S. *J. Chem. Phys.* **1990**, *93*, 7439.

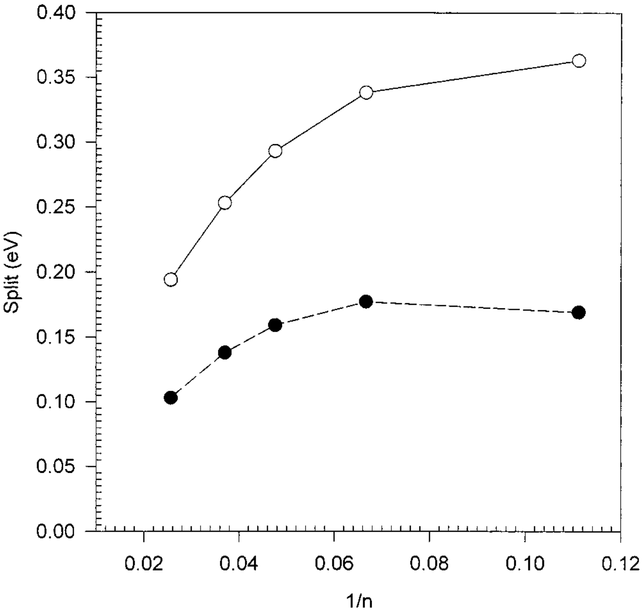


Figure 3. Evolution of the INDO/SCI-calculated splitting between the lowest two optical transitions of cofacial dimers formed by two PPV chains as a function of the inverse number of bonds (1/*n*) along the conjugated backbone of the oligomer. The theoretical results are reported for interchain distances of 4 (open circles) and 6 Å (filled circles).

excitations taking place between the four frontier molecular orbitals of the dimer, due to the lack of symmetry in the wave function of these levels. This range of interchain distances can thus be considered as a transition domain between the regime of weak intermolecular interactions (>7 Å) and that of strong interchain couplings (<5Å).

Analysis of the one-electron structure also reveals that the splitting of the HOMO and LUMO levels is not equal (0.31 and 0.16 eV at 4 Å, respectively, see Figure 1), as is also noticed in previous three-dimensional band-structure calculations.[58] This rationalizes the fact that the H → L+1 and H → L-1 configurations have different weights in the description of the second excited state at short interchain distances. This lack of electron−hole symmetry also indicates that the overlap of the HOMO levels is larger than that of the LUMO levels; hence, the width of the valence band for a one-dimensional stacking of stilbene units should be larger than that of the conduction band. Such a behavior might have strong implications for the transport properties in conjugated systems, since it is consistent with the typical observation that hole mobility is larger than electron mobility. A simple way to rationalize the fact that the HOMO levels have larger overlap than the LUMO levels for cofacial π-dimers is that there are more nodal surfaces in the LUMO wave function than in the HOMO. The overlap of the molecular orbitals is made up of a sum of many atomic overlaps with a product of LCAO coefficients. The more nodal surfaces, the more cancellation of terms is possible due to the signs of the products of coefficients.

III.1.b. Influence of Chain Length. The energy splitting between the lowest excited states calculated for cofacial dimers formed by longer PPV oligomers that are separated by 4 Å is shown in Figure 3. The results demonstrate that the general picture provided by the calculations performed on stilbene units holds true for longer chains. Going from the two-ring to the three-ring oligomer, we find the critical distance, below which the wave functions start to be delocalized over the two chains, to be larger. In both cases, it roughly corresponds to the oligomer length. This result is consistent with earlier theoretical analyses which have shown that models based on dipole−dipole interactions break down when the intermolecular distance is smaller than the size of the interacting units;[57,59,60] however, it appears that the critical distance saturates around 14 Å in longer chains; it is reasonable to expect that this distance is related to the average separation between the electron and the hole in the excited state.

Table 2. INDO/SCI-Calculated Transition Energies (in eV) of the Lowest Absorption Feature of PPV Oligomers Containing from 2 to 7 Phenylene Rings and of the Lowest Two Optical Transitions of Cofacial Dimer Formed by Two Chains Separated by 4 Å[a]

	PPV2	PPV3	PPV4	PPV5	PPV7
$S_0 \rightarrow S_1$ isolated	4.098	3.562	3.329	3.210	3.095
$S_0 \rightarrow S_1$ dimer	3.870	3.351	3.155	3.058	2.972
$S_0 \rightarrow S_2$ dimer	4.235	3.689	3.448	3.309	3.166
splitting $S_1 - S_2$	0.365	0.338	0.293	0.251	0.194
interaction energy	0.228	0.211	0.174	0.152	0.123

[a] We also report the splitting (in eV) calculated between the two transitions of the dimer together with the interaction energy (in eV) defined as the stabilization of the lowest excited state when going from the single molecule to the dimer.

Note that the splitting tends to decrease nonlinearly with chain length, as illustrated in Figure 3. Such behavior is supported by previous calculations performed by using perturbation theory[57] (without explicit account of transfer integrals) but in stark contrast with the molecular exciton model, which predicts the splitting to be proportional to the oscillator strength, and hence to increase with chain length.[55] Though reduced, the energy separation between the lowest two excited states is expected to be significant (and larger than the second-order correction in perturbation theory) for interacting units with lengths corresponding to the typical effective conjugation lengths encountered in polymer films. In contrast, for polymers that can be effectively described as infinite chains, such as MEH−PPV in highly drawn and oriented polyethylene,[61] the splitting would become vanishingly small. The evolution is then dominated by the second-order stabilization of the excited state levels; this would result in a red shift of the lowest optical transition, as suggested for infinite *trans*-polyacetylene chains on the basis of highly correlated calculations.[57] Two aspects should be borne in mind: (i) all the shifts and splittings discussed so far are expected to be larger when increasing the number of neighboring chains, as discussed below, and (ii) the splitting decreases with chain length because of the delocalization of the wave function on a single chain. The argument based on perturbation theory goes as follows for the systems we have considered: the normalized coefficients decrease with chain length L (as $L^{-1/2}$); the relevant matrix element is a sum of terms containing a product of four coefficients (proportional to L^{-2}); this sum is dominated by diagonal terms, the number of which is proportional to L, leading to the sum being proportional to L^{-1}.

We report in Table 2 the lowest transition energies calculated for the cofacial dimers at 4 Å and those of the corresponding isolated oligomers (estimated from cofacial dimers with huge interchain separations in order to avoid size-consistency effects). The results indicate that the stabilization of the lowest excited state decreases when the chain length increases. Intermolecular

---

[58] Gomes da Costa, P.; Dandrea, R. G.; Conwell, E. *Phys. Rev. B* **1993**, *47*, 1800.

[59] Coulson, D. A.; Davies, P. L. *Trans. Faraday Soc.* **1952**, *48*, 777.

[60] Sternlicht, H. *J. Chem. Phys.* **1964**, *40*, 1775.

[61] Hagler, T. W.; Pakbaz, K. J.; Voss, K. F.; Heeger, A. J. *Phys. Rev. B* **1991**, *44*, 945.

interaction effects are thus expected to be higher in molecular materials than in actual polymer films, assuming that the interchain distances are comparable.

Two important conclusions can be drawn regarding the absorption and emission properties of conjugated oligomers interacting strongly in a high-symmetry configuration:

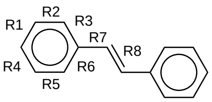
(i) The lowest symmetry-allowed optical transition involves the second excited state (or even a higher-lying excited state at very short interchain distances) and is blue shifted with respect to that of the isolated molecule. This is fully consistent with the results of recent experimental studies.[27,62−64] This blue shift might, however, be masked by additional effects related, for example, to changes in chain conformation when going from solutions to films; this would lead generally to a red shift of the lowest optical transition, due to an increase in planarity of the conjugated backbone. Note also in Figure 2 that the lowest optical transition at interchain distances below 4 Å is red shifted with respect to that calculated at 4 Å.

(ii) Since the splitting between the lowest two optical transitions increases as the interchain distance is lowered and the lowest excited state is not optically coupled to the ground state, we expect that, in the absence of relaxation phenomena, intermolecular interactions would strongly reduce the luminescence efficiency, however more so in molecular materials than in polymers since the splitting induced by intermolecular interactions decreases with growing chain length. These trends are consistent with recent experimental studies[65,66] showing that highly delocalized conjugated chains do not undergo concentration quenching, as typically observed with dyes; this is why conjugated polymers emerge as highly promising materials for the design of solid-state lasers.[65]

III.2. Photoluminescence Properties of Highly Symmetric Complexes. The picture presented above does not take into account the large electron−phonon coupling typical of conjugated systems. This coupling generally makes the equilibrium geometry in the lowest excited state different from that in the ground state.[67−69] It is therefore of prime interest to evaluate the possible influence of lattice relaxations in the lowest excited state, on the emission properties of the interacting units. This approach assumes that such relaxation phenomena have sufficient time to occur (i.e., that the excited-state relaxation time scale is fast compared to the excited-state lifetime).

We first discuss the AM1/CI calculations performed on cofacial dimers formed by two widely separated stilbene molecules. As expected, one chain displays a geometry typical of the ground state of the stilbene molecule, while the second chain has a geometry characteristic of the lowest excited state of the single unit. In the range of large interchain distances, the transition moment associated to the molecule in the relaxed conformation is very close to that calculated for the isolated system, thus indicating that intermolecular interactions do not significantly affect the emission. When the distance between the chains is decreased, the chain initially having the ground-state geometry starts to be affected by lattice relaxations; the latter become increasingly pronounced as the two molecules approach. However, the major relaxation phenomena always take place over a single chain (reminiscent of those associated with the formation of an intrachain polaron−exciton). The C−C bond lengths in a cofacial dimer formed by two stilbene molecules are collected in Table 3 for various interchain distances.

Table 3. Ground-State and Lowest-Excited State AM1/CI-Optimized C−C Bond Lengths (in Å) in a Cofacial Dimer Formed by Two Stilbene Molecules Separated by 3.5, 4.0, and 4.5 Å, Respectively[a]



	3.5 Å	4 Å	4.5 Å	∞
ground state				
R1	1.397	1.396	1.396	1.395
R2	1.388	1.390	1.391	1.392
R3	1.415	1.410	1.409	1.407
R4	1.394	1.394	1.394	1.394
R5	1.391	1.392	1.393	1.394
R6	1.411	1.406	1.404	1.402
R7	1.432	1.442	1.447	1.453
R8	1.366	1.355	1.350	1.344
lowest excited state				
R1	1.401	1.403	1.403	1.404
R2	1.383	1.381	1.381	1.380
R3	1.424	1.427	1.429	1.430
R4	1.394	1.394	1.393	1.393
R5	1.388	1.388	1.388	1.387
R6	1.420	1.424	1.425	1.426
R7	1.412	1.406	1.404	1.403
R8	1.388	1.395	1.398	1.400

[a] We also report in the right column the geometric parameters obtained for single molecules.

In a recent study, we have shown that because of an increase in the spatial extent of the polaron−exciton, the amplitude of relaxation energy in the lowest excited state of isolated PPV oligomers is reduced when the chain length is increased.[44] Similarly, the progressive delocalization of the polaron−exciton over the two interacting chains is accompanied by a decrease in relaxation energy (and thus in the Huang−Rhys factor[44]) in the lowest excited state of the dimer. This is illustrated in Figure 4. Note that the mostly intrachain character of the polaron−exciton, already suggested in previous calculations,[70] can be understood as driven by the Coulomb attraction between the electron and the hole; the latter is maximized when the two charges are located on the same chain.

This self-localization of the electron−hole pair is further supported by a detailed analysis of the INDO/SCI wave function $\Psi(x_e, x_h = l)$ of the lowest excited state of a cofacial dimer formed by two five-ring PPV oligomers. We present in Figure 5 the results of the INDO/SCI simulation of the cofacial dimer first excited-state wave function $|\Psi(x_e, x_h = 16, \text{chain I})|$, assuming an intermolecular distance of 4 Å; here, $|\Psi(x_e, x_h = 16, \text{chain I})|$ represents the probability amplitude to find the electron on a given site x_e assuming the hole is centered on the middle of one chain of the dimer (carbon site 16, see Figure 5), which is denoted as chain I (the other chain being referred to as chain II). As illustrated in the figure, the first excited state in the dimer is characterized by a strong intrachain character;

---

(62) Deloffre, F.; Garnier, F.; Srivastava, P.; Yassar, A.; Fave, J. L. *Synth. Met.* **1994**, *67*, 223.

(63) Hamano, K.; Kurata, T.; Kubota, S.; Koezuka, H. *Jpn. J. Appl. Phys.* **1994**, *33*, L1031.

(64) Liang, K.; Farahat, M. S.; Perlstein, J.; Law, K. Y.; Whitten, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 830.

(65) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res.* **1997**, *30*, 430.

(66) Bazan, G. C.; Miao, Y. J.; Renak, M. L.; Sun, B. J. *J. Am. Chem. Soc.* **1996**, *118*, 2618.

(67) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698.

(68) Brédas, J. L.; Street, G. B. *Acc. Chem. Res* **1985**, *18*, 309.

(69) Beljonne, D.; Shuai, Z.; Friend, R. H.; Brédas, J. L. *J. Chem. Phys.* **1995**, *102*, 2042.

(70) Gomes da Costa, P.; Conwell, E. M. *Phys. Rev. B* **1993**, *48*, 1993.

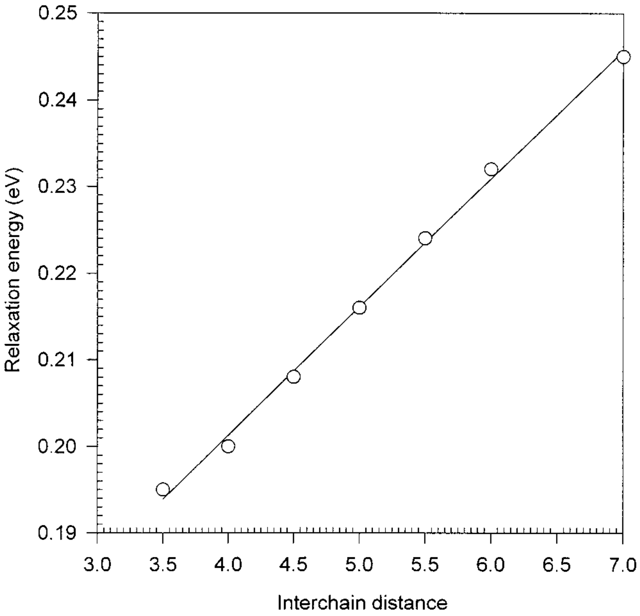


Figure 4. Evolution of the AM1/CI-calculated relaxation energy in the lowest excited state of a cofacial dimer formed by two stilbene molecules as a function of interchain distance. The solid line is the result of a linear regression through the theoretical data.

its wave function presents a Gaussian shape with maximum close to the position of the hole in chain I. The probability of finding the electron on chain II, i.e., or of creating an interchain exciton, p_{IT}, is only 6.7% when the PPV5 molecules are separated by 4 Å. Note that the small contribution to the first excited-state wave function on chain II is also characterized by a Gaussian shape with its maximum located around the middle of the chain, i.e., in the region that is closest to the hole site on chain I. The probability p_{IT} evolves exponentially as a function of the intermolecular distance *R*, as shown in the inset of Figure 5; the value of p_{IT} drops from 28.1% when *R* is equal to 3.5 Å to only 0.6% for an interchain distance of 4.5 Å.

The above results thus indicate that the equilibrium geometry in the lowest excited state is not symmetric with respect to the two chains; the selection rules are therefore relaxed. Although the transition dipole moment between the ground state and the lowest excited state remains small, the luminescence is no longer entirely quenched by symmetry constraints and is red shifted with respect to that in the isolated molecule. This is illustrated in Figure 6 where we present the absorption and emission spectra simulated for (i) two stilbene molecules with a huge interchain separation and (ii) a cofacial dimer formed by two stilbenes separated by 4 or 5 Å. (Note that, contrary to what was recently suggested by other theoretical calculations,[71] the emission does not take place from the second excited state.) On the basis of these considerations, the significant increase in radiative lifetime observed in recent experimental studies[24,25] could possibly be attributed to (i) the weak coupling between the ground state and the lowest excited state, which yields small radiative decay rates, and (ii) the fact that the polaron−excitons tend to migrate toward regions where the chains are strongly interacting (i.e., the low-energy domains of the samples) before light emission occurs.[28,29]

Since the excitation is equally likely to be on either molecule in the pair, one might suppose that the correct quantum description of the excited states is a linear combination of the two possibilities, thereby restoring the symmetry and the selection rules. That is, the two asymmetric states can be written approximately as $\Psi_a = \phi_{1e}(R_e)\phi_{2g}(R_g)$ and $\Psi_b = \phi_{1g}(R_g)\phi_{2e}\cdot(R_e)$, where we have explicitly noted that the equilibrium geometry of the two molecules is different. The symmetrized states would then be $[\Psi_a \pm \Psi_b]/2^{1/2}$, with an energy splitting of $2\langle\Psi_a|H|\Psi_b\rangle$. Note that these combinations go beyond the Born−Oppenheimer approximation. When considering a condensed phase environment, other effects can be large, leading to self-localization and symmetry breaking. When the dimer is put into a condensed phase, there will be a *different* solvent shift for Ψ_a and Ψ_b. If this difference is larger than the energy splitting, then the symmetry will be broken, and the correct description of the states will be Ψ_a and Ψ_b and not $[\Psi_a \pm \Psi_b]/2^{1/2}$. Because of the large geometry change between Ψ_a and Ψ_b, the energy splitting will be small; therefore, the difference in solvent shift will dominate, leading to symmetry breaking and relaxation of the selection rules.

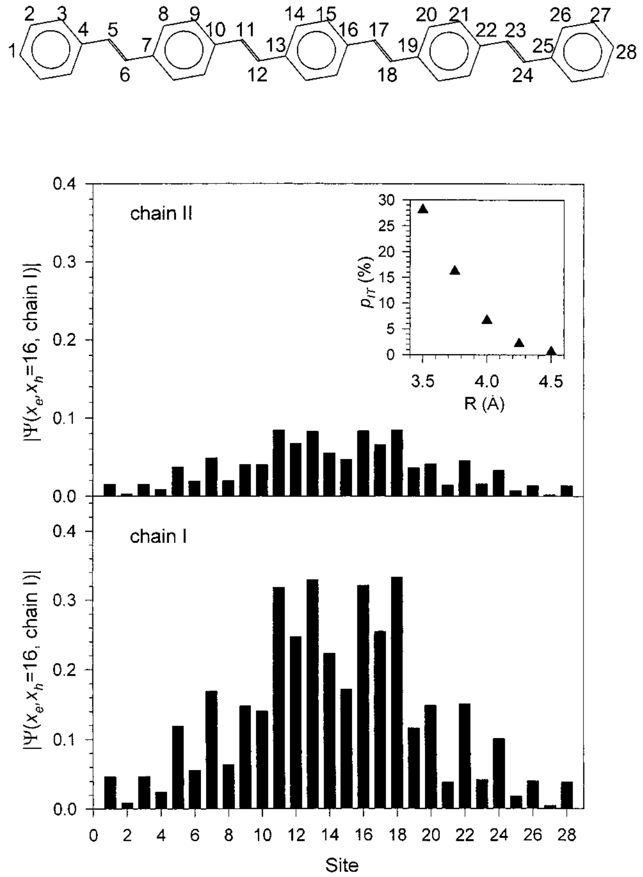


Figure 5. INDO/SCI simulation of the first singlet excited-state wave function in a cofacial dimer formed by two five-ring PPV oligomers, $|\Psi(x_e, x_h = 16, \text{chain I})|$, assuming an intermolecular distance of 4 Å. $|\Psi(x_e, x_h = 16, \text{chain I})|$ represents the probability amplitude to find an electron in a given site x_e assuming the hole is centered on 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 labeling is represented in the top panel. The inset shows the evolution of the probability to create an interchain exciton, p_{IT}, as a function of the intermolecular distance *R*. The *R* values are given in Å.

We conclude that strong interchain couplings do not necessarily imply a substantial reduction in luminescence efficiency. As a matter of fact, a decrease in radiative decay rate increases the relative importance of multiple nonradiative decay channels; conversely, the effectiveness of some nonradiative decay routes is decreased by the confinement of the polaron−excitons in the strongly interacting regime (for example migration to a defect

---

[71] Fagerstrom, J.; Stafstrom, S. *Phys. Rev. B* **1996**, *54*, 13713.

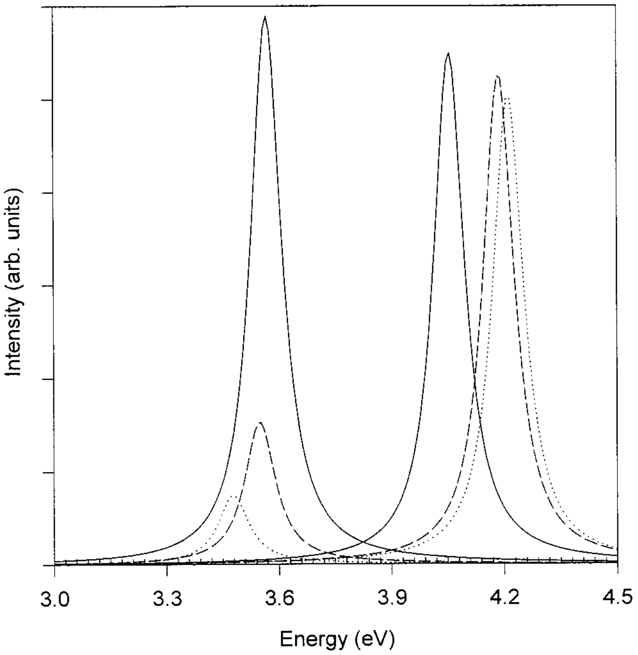


Figure 6. INDO/SCI-simulated absorption and emission spectra of two stilbene molecules with a huge interchain distance (solid lines) and those of a cofacial dimer formed by two stilbene chains separated by 5 (dashed lines) and 4 Å (dotted lines), respectively.

site). The actual luminescence efficiency thus results from the balance of these contributions.

The results of the calculations also indicate that in the regime of strong interactions the shorter the interchain distance, the larger the red shift of the emission peak, as shown in Figure 6. Simultaneously, the amplitude of the transition dipole moment between the ground state and the lowest excited state is reduced, due to the fact that the wave functions become increasingly symmetric. The red shift and the attenuation of the emission appear to be consistent with recent experimental measurements of the photoluminescence spectra of PPV[72] and cyano-substituted PPV[73] as a function of an applied external pressure, i.e, effectively as a function of interchain distance.

III.3. Role of the Number of Units in Interaction. We now go beyond the simple consideration of cofacial dimers and address the changes occurring when the number of units in interaction is increased. To do so, we have calculated the absorption spectrum of one-dimensional stacks containing from 2 to 5 stilbene units in a cofacial conformation separated by 4 and 8 Å, respectively. At 8 Å separation, a complex formed by *n* molecules gives rise to the splitting of the lowest excited state of an isolated unit into *n* nondegenerate levels; such an evolution leads to the formation of an exciton band at the scale of an infinite one-dimensional array of units. As elegantly discussed by Kasha,[55,56] a remarkable feature is the fact that the oscillator strength is concentrated in the highest energy optical transition (corresponding to the fully antiparallel arrangement of the transition dipoles on the individual molecules), which is blue shifted with respect to that of the single molecule. In contrast, the lowest excited state is found not to be significantly optically coupled to the ground state and to be red shifted with respect to the energy calculated for the stilbene molecule. The energy difference between the highest and lowest excited states increases with the number of units but tends progressively to saturate, as would be expected from simple Hückel calculations describing the formation of bands in terms of intrachain or interchain transfer integrals. The same picture holds true at 4 Å except that the strong mixing of the configurations in the CI scheme leads to a very complex description of the optical transitions. We find nevertheless that the red shifted lowest excited state is not optically coupled to the ground state at this intermolecular separation, and we observe the appearance of intense absorption features that are blue shifted with respect to the lowest excited state of the single molecule.

Regarding the emission properties, AM1/CI calculations performed on a complex formed by three stilbene units in a cofacial conformation, with an interchain distance fixed at 4 Å, indicate that the main geometry deformations in the lowest excited state take place over the central unit and affect the adjacent chains to a weaker extent; we can therefore reasonably assume that the wave function of the relaxed electron−hole pair extends mostly over three interacting chains. The INDO/SCI calculations further demonstrate that the lowest excited state of this complex in its relaxed geometry becomes significantly coupled to the ground state; the corresponding transition dipole moment varies as a function of interchain distance in a way similar to that described for the cofacial dimers.

III.4. Role of Positional Disorder. In this section, we address the influence of positional disorder on the optical properties of interacting systems. Since there are, a priori, an infinite number of possibilities to vary the relative positions of the interacting units, we have chosen to investigate the changes occurring in the properties of a highly symmetric complex when basic operations such as translations and rotations are performed. These calculations are expected to suggest new strategies to allow for the ground state to be significantly coupled to the lowest excited state (even in the absence of relaxation effects) and hence to strongly limit luminescence quenching in the solid state.

Starting from a complex containing two or three stilbene units in a cofacial conformation and separated by 4 Å, we have first translated (over a large range of distances) one of the chains along the longitudinal and/or transverse axes while keeping parallel the planes of the units; see Figure 7. The results show that the amplitude of the splitting induced by the interaction decreases as the overlap between the wave functions of the units is reduced. Such translations, however, appear to be very inefficient processes for inducing oscillator strength into the transition between the ground state and the lowest excited state.

We have then modified the original positions of the stilbene units (in a cofacial dimer with an interchain distance fixed at 4 Å) by rotating (i) one molecule in the stacking plane around an axis perpendicular to the molecular planes and passing through the center of the vinylere linkage and (ii) one molecule around its long axis, thus breaking the parallelism of the planes of the two units. This is illustrated in Figure 7.

The results obtained in (i) are displayed in Figure 8. As the angle between the chain axes is increased, the splitting between the lowest two optical transitions is decreased because of the reduced overlap between the wave functions, and a transfer of intensity takes place from the high energy absorption feature to the lowest excited state. This means that in such conformations, intermolecular interactions lead to an intense absorption that is blue shifted with respect to that of the single molecule and also to the appearance of a weaker red shifted absorption feature (or a red tail in the case of highly disordered samples). A supramolecular architecture where the long axes of adjacent chains are perpendicular turns out to be the most efficient

---

(72) Webster, S.; Batchelder, D. N. *Polymer* **1996**, *37*, 4961.

(73) Webster, S.; Batchelder, D. N. To be submitted for publication.

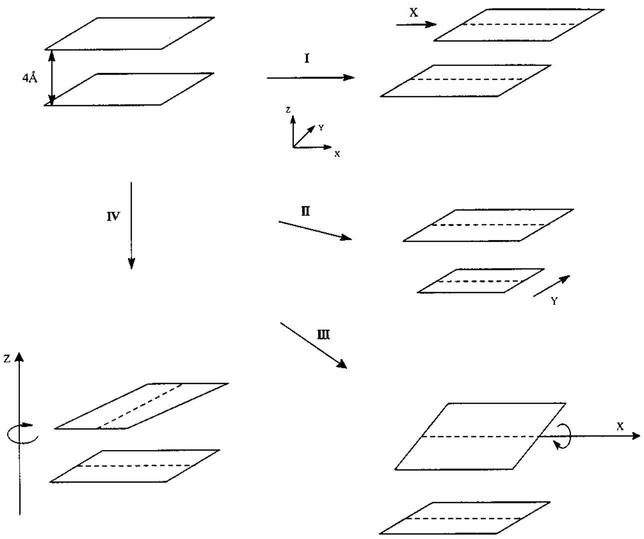


Figure 7. Sketch of the operations applied to a cofacial dimer formed by two stilbene molecules separated by 4 Å when investigating the role of positional disorder. The modifications are induced by (I) the translation of one molecule along the chain-axis direction, (II) the translation of one molecule along the in-plane transverse axis, (III) the rotation of one stilbene unit around its long axis, and (IV) the rotation of one stilbene molecule around the stacking axis while keeping the parallelism between the molecular planes.

configuration to prevent any decrease in luminescence efficiency in condensed media. In that case, we find that the lowest two excited states are degenerate and that the oscillator strength involved in the absorption process is conserved for light emission. Such a perpendicular configuration is encountered in spiro-conjugated molecules.[74] In contrast, in the second type of rotation, since the parallelism of adjacent chain axes is not broken, the optical properties of the complexes at various rotational angles are very similar to those calculated for the cofacial dimer. They are thus characterized by the absence of any significant oscillator strength in the transition between the ground state and the lowest excited state; for instance, this has been observed for the sexithienyl crystal adopting a herringbone structure and confirmed by recent theoretical calculations.[75]

III.5. Polaron Pairs and the Role of Chemical Impurities. Finally, we address the issue of polaron pairs, also referred to as interchain excitons. Experimental studies carried out by the Bell Laboratories group suggested that polaron pairs are the major species generated upon photoexcitation of PPV chains,[76] in contrast to results obtained by the Cambridge group, which demonstrated that the dominant photogenerated species are intrachain polaron−excitons.[12] Such a discrepancy could be attributed to differences in the quality and/or morphology of the PPV films. For example, the photoluminescence efficiency of chains mainly supporting intrachain polaron−excitons is reduced when the interchain distance is decreased, as shown above and measured recently.[72,73] In contrast, the luminescence efficiency is expected to be augmented if polaron pairs are mostly present since short interchain distances would favor the recombination of charge carriers.[36]

We emphasize that the oscillator strength in the transition between the ground state and the charge-transfer state describing

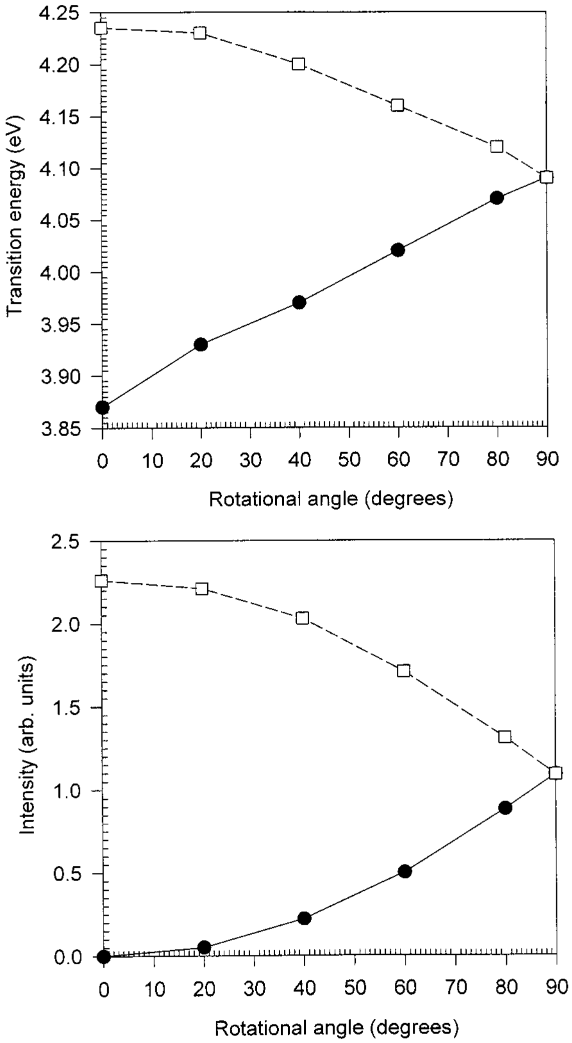


Figure 8. INDO/SCI-calculated evolution of the transition energies (upper part) and related intensities (bottom part) of the lowest two optical transitions of a cofacial dimer formed by two stilbene molecules separated by 4 Å as a function of the dihedral angle between the long molecular axes, when rotating one molecule around the stacking axis and keeping parallel the molecular planes (case IV of Figure 7).

a polaron pair is negligible. Therefore, (i) the formation of polaron pairs is highly detrimental to the fluorescence quantum yield, in agreement with experimental studies,[9,21,76] and (ii) polaron pairs cannot be directly generated upon photoexcitation and would therefore have to originate from the dissociation of an intrachain polaron−exciton. However, our calculations demonstrate that the lowest excited state of complexes formed by identical conjugated chains has mostly intrachain character in its relaxed geometry (note that interactions between chains with different conjugation lengths and/or different conformations give rise to energy transfer processes, i.e., a migration of the polaron−excitons toward the lowest-energy domains of the samples[77]). We thus conclude that intrachain polaron−excitons are intrinsically the most stable photogenerated species and that an extra amount of energy is required to dissociate a polaron−exciton into a polaron pair. Therefore, the generation of polaron pairs is associated with *extrinsic* phenomena. That extra energy is required to dissociate the polaron−exciton can be rationalized as follows: (i) there is no one-electron energy gained when

---

[74] Johansson, N.; dos Santos, D. A.; Guo, S.; Cornil, J.; Falhman, M.; Salbeck, J.; Schenk, H.; Arwin, H.; Brédas, J. L.; Salaneck, W. R. *J. Chem. Phys.* **1997**, *107*, 2542.

[75] Beljonne, D. et al. To be submitted for publication.

[76] Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M. *Phys. Rev. Lett.* **1994**, *72*, 1104.

[77] Kersting, R.; Lemmer, U.; Deussen, M.; Bakker, H. J.; Mahrt, R. F.; Kurz, H.; Arkhipov, V. I.; Bässler, H.; Gobel, E. O. *Phys. Rev. Lett.* **1994**, *73*, 1440.

transferring the electron since there is no energy difference between the one-electron levels of the "donor" chain and the "acceptor" chain (i.e., in fact between the LUMO's of the two interacting chains), a typical ingredient involved in the classical description of electron-transfer processes;[78] (ii) no significant elastic energy gain would emerge since the relaxation energy of an intrachain polaron−exciton is found to be very similar to that calculated for two well-separated polarons;[11] and (iii) extra electrostatic energy is required to dissociate the exciton since the Coulomb attraction between the electron and the hole is weaker in a polaron pair than in an intrachain exciton. Note that we have neglected in the previous considerations the influence of polarization effects; these are expected to be strongly in favor of the formation of polaron pairs. In our view, however, the role of polarization is not sufficient to overcome the electrostatic energy cost required for exciton dissocation. If this were the case, an intrachain polaron−exciton could not be stabilized in the solid state.

We suggest that the extrinsic formation of polaron pairs is intimately related to the presence of chemical impurities, either chemically bound to the PPV conjugated segments, such as carbonyl groups,[21] or simply interacting with the chains, such as water or oxygen molecules. In both cases, the external agents are expected to modify the one-electron structure of the PPV chains to which they are connected and to induce interaction processes between chains of different nature. For example, a carbonyl group can be considered as a π-acceptor group attached to a conjugated backbone, leading to an overall asymmetric stabilization of the frontier levels, as shown by earlier calculations.[79−81] The presence of such impurities can thus give rise to photoinduced electron transfer processes between the chains, as observed for example when mixing two differently substituted PPV derivatives[82] or blending conjugated polymers and buckminsterfullerene.[83] Further experimental and theoretical investigations are required to understand the main parameters governing the occurrence of charge and energy transfer between interacting chains.

IV. Synopsis

In this work, we have performed correlated quantum-chemical calculations to clarify the importance of intermolecular interactions on the electronic and optical properties of conjugated chains. The theoretical approach takes into account the full chemical structure of the interacting units and describes the properties of the complexes on the basis of the eigenstates of the Hamiltonian rather than as the product of wave functions associated to each interacting unit, as traditionally done in early studies.

We have first considered cofacial dimers where two stilbene units are superimposed on top of one another, with interchain distances ranging from 3.5 Å to 30 Å. The results indicate that the transition from the lowest excited state to the ground state of such highly symmetric complexes has no oscillator strength and is red shifted with respect to that of the single molecule. The oscillator strength is concentrated in the transition to the second excited state (or in an even higher-lying excited state at 3.5 Å separation) that is located at higher energy than that of the isolated unit; the occurrence of a blue shift of the lowest symmetry-allowed optical transition in such configurations is supported by several experimental studies. The calculations further establish that the energy splitting between the lowest two optical transitions increases when the interchain distance is reduced. We have also shown that the same picture holds true for the longer conjugated segments encountered in polymer samples. Very interestingly, however, the chain-length evolution of the optical properties indicates that a red shift of the lowest optically allowed absorption would prevail in the infinite chain limit, i.e., for chains in which the electronic wave functions are highly delocalized.

Because of the strong electron−phonon coupling in conjugated systems, the emission properties of cofacial dimers are affected by the lattice relaxations which take place in the lowest excited state. The corresponding geometry deformations are localized mostly on a single unit and reminiscent of those calculated for an intrachain polaron−exciton; as a consequence, the optimal geometry is not symmetric with respect to the two chains and lowers the symmetry constraints. When the relaxation phenomena have sufficient time to occur, the luminescence is no longer strictly forbidden and appears red shifted with respect to that of the single molecule. As the interchain distance is decreased, the calculations show the amplitude of this red shift to be increased and the oscillator strength of the transition to be reduced, features which are consistent with recent experimental studies.

To go beyond the idealized case of highly symmetric dimers, we first illustrated that the properties of a cofacial dimer are very similar to those calculated for a one-dimensional stack containing from 2 to 5 units; it thus appears that the number of units in interaction does not alter the dimer picture. We also investigated the changes occurring in the optical properties of high-symmetry complexes when modifying the relative positions of the interacting units by means of translations and/or rotations. These calculations demonstrate that specific configurations are required to break the forbidden nature of the lowest optical transition calculated in highly symmetric complexes (i.e., in the absence of relaxation phenomena). We conclude that a transfer of oscillator strength takes place between the highest energy optical transition and the lowest excited state in configurations with a finite angle between the directions of the long chain axes; this gives rise to the appearance of a weak red shifted feature in the absorption spectra of the complexes.

Consideration of the formation of polaron pairs led to the conclusion that such a process has an extrinsic origin. The decay dynamics of the lowest excited state of any conjugated system is thus sensitive to the relative population of the intrachain polaron−excitons and polaron pairs. Note that the photoluminescence decay is entirely governed by the concentration in intrachain polaron−excitons whereas the decay of the photoinduced absorption features results from the contributions of both intrachain excitons and polaron pairs (that are believed in some cases to absorb in the same spectral range[10]); this rationalizes the fact that the dynamics of these two processes is generally different in solid-state measurements. Note that accurate knowledge of the chain positions is required to provide a quantitative description of the interchain effects.

We believe that our results are of particular interest in the context of light emission from conjugated polymers. Strategies can be developed to prevent a substantial decrease in the luminescence quantum yield in the solid state. Approaches that

---

(78) Marcus, R. A. *Rev. Mod. Phys.* **1993**, *65*, 599.

(79) Brédas, J. L.; Heeger, A. *J. Chem. Phys. Lett.* **1994**, *217*, 507.

(80) Cornil, J.; dos Santos, D. A.; Beljonne, D.; Brédas, J. L. *J. Phys. Chem.* **1995**, *99*, 5604.

(81) Rothberg, L. J.; Yan, M.; Son, S.; Galvin, M. E.; Kwock, E. W.; Miller, T. M.; Katz, H. E.; Haddon, R. C.; Papadimitrakopoulos, F. *Synth. Met.* **1996**, *78*, 231.

(82) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498.

(83) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.

can be followed to improve the luminescence efficiency in electrooptic devices include the following: (i) minimizing the splitting between optically forbidden and optically allowed optical transitions (this can be achieved either by separating the chains by substituents or by using chains with highly delocalized excitations, e.g., highly ordered polymers), and (ii) decreasing the diffusivity of the excitation by forming aggregates that act as trapping sites.

Acknowledgment. We are grateful to Prof. A. J. Heeger and Prof. R. H. Friend for stimulating discussions. The work in Mons 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), and an IBM Academic Joint Study. J.C. is Chargé de Recherches of the FNRS. The work at UCSB was supported by the National Science Foundation under DMR9300366. The work at MIT was partly supported by the National Science Foundation grant to the Center for Materials Science.

JA973761J