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Interchain interactions in conjugated materials: The exciton model versus the supermolecular approach

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Correlated quantum-chemical techniques are applied to the description of electronic excitations in interacting conjugated chains. The focus is on the magnitude and conjugation-length dependence of the splitting of the lowest optically allowed excitonic state, which is induced by interchain interactions. We first examine cofacial dimers formed by linear polyene chains of various lengths and use two strategies to compute the exciton coupling energy. One is based on molecular exciton theory, which assumes that the excited-state wave functions of the isolated chains remain unperturbed by the intermolecular forces; in the other, the supermolecular approach, the wave functions are obtained from molecular orbital calculations performed for the whole system and are therefore not constrained to a single chain. We find that the two techniques lead to consistent results, provided an appropriate form for the interchain Coulomb interactions is adopted in the excitonic model. In particular, both formalisms indicate a peak behavior for the evolution of the exciton splitting energy with the length of the interacting conjugated chains. As an illustration, the chain-length dependence of the Davydov splitting is evaluated in the case of oligothiophenes on the basis of the experimental x-ray crystal structures; the results are compared to recent polarized absorption data. © *2000 American Institute of Physics.* [S0021-9606(00)70710-0]

I. INTRODUCTION

Since the discovery that a conjugated organic polymer, poly(paraphenylene vinylene) (PPV), can be used as the active component in light-emitting diodes (LED),[1] much effort has been devoted to the synthesis of new electroluminescent conjugated materials, the characterization of their photophysical properties by means of both experimental and theoretical tools, and the manufacturing of stable polymer-based devices with optimal performance. Significant improvements have resulted from this interdisciplinary research work, as exemplified by recent reviews on the topic.[2–4] For the achievement of highly efficient devices, the conjugated polymer has to fulfill a number of requirements, the most obvious one being to display high luminescence quantum yields in the solid state.

Several strategies have been proposed in order to improve the electroluminescence (EL) quantum yields of organic conjugated polymers.[3] These aim at insuring: (i) a balanced injection for holes and electrons (through a proper choice of emissive material and electrodes[5]); (ii) an efficient electron-hole capture within the emissive layer (by using hole- and electron-transport materials in multilayer architectures[6]); (iii) a strong radiative decay for the singlet excitons generated in the conjugated material (by control of microscopic order and sample purity[7]); and (iv) an efficient coupling of the excitons to photon states allowed by the device structure (for instance, through the use of metallic mirrors[8]). Whether or not polymer LED applications will flourish on the marketplace in the future partly depends on the understanding of the fundamental issues quoted above.

In this context, quantum-chemical calculations can help in providing structure–property relationships that are useful for the engineering of materials with improved characteristics. For instance, VEH (valence effective Hamiltonian) calculations have shown that it is possible to modulate the position of the frontier molecular orbitals of PPV by grafting electroactive groups on the conjugated segments;[9] such theoretical results provide a simple tool not only to control the match between the electronic levels of the conjugated material and those of the metallic electrodes used in LED devices, but also to tune the color of the emitted light. Substitutional effects have been successfully exploited by the Cambridge group, who has reported a high EL quantum efficiency for a cyano-substituted PPV polymer.[6]

If up to now most of the theoretical investigations related to the photophysics of conjugated organic polymers have been carried out on isolated chains (which mimics the situation in inert matrices or dilute solutions), there is a growing interest for the simulation of the corresponding properties in the solid state (films or crystals). In the field of polymer-based light-emitting diodes, this interest is motivated by an attempt to rationalize the generally observed decrease in luminescence quantum efficiency when going from solutions to films.[10–12] The lower emission quantum yield in the solid state is often ascribed to the presence of low-lying excited states with weak (or vanishing) radiative coupling to the ground state. Such low-lying weakly allowed (or even forbidden) excited states can result from the presence of impurities or defects (traps) in the sample but also from interchain interactions between conjugated chromophores, even if the latter are intrinsically very strong emitters.

Conjugated polymers usually consist of a distribution of finite segments with various conjugation lengths. Therefore, in most cases, the conjugated materials should not be viewed as quasi-one-dimensional infinite objects but rather as an ensemble of interacting finite-size segments.[13] In that respect, they display similarity with the well-known family of organic molecular crystals.[14] As a matter of fact, the terminology used in the field of molecular solids to depict the nature of electronic excitations (Frenkel excitons, charge-transfer excitons,...) is nowadays widely adopted by the conjugated polymer community. It is then logical to try and apply the basic theories that have been developed for molecular crystals to the description of excited states in conjugated polymers. Among these theories, the molecular exciton approach has been extensively used to predict the changes in optical absorption and luminescence properties of conjugated compounds that occur when interchain interactions are switched on.[14]

In traditional molecular exciton theory,[14] the excited-state wave functions of the molecules in the aggregate (or crystal) are assumed to be unaffected by the intermolecular forces. Such an approximation is expected to be valid for weak (e.g., van-der-Waals-like) interactions. In this case, the spectroscopic properties of the cluster can be obtained through a first-order perturbation treatment, with the unperturbed isolated-chain wave functions as zero-order functions and the interchain Coulomb operator as the perturbation. Different approximations can be considered to solve this problem, such as the widely used dipole approximation described in the next section. When applicable, molecular exciton theory allows the estimation of the energy splitting of the excited states responsible for the single-chain optical transitions, which arises because of the intermolecular interactions; it also provides useful information on the absorption cross section (oscillator strength) and polarization of the electronic excitations appearing in the solid.[14,15]

In the strong interaction limit, the excited states likely spread out over several molecules and a proper description of the electronic structure then requires the building of delocalized wave functions. This approach is known as the supermolecular approach, since it is then required to perform the calculation of the excited-state electronic structure by considering the ensemble of interacting conjugated units as a single entity.[16] An important asset of this technique is that it inherently accounts for charge-transfer excitations among different chains, which is not the case in exciton theory, unless the basis set is augmented.

Here, we apply both formalisms (exciton theory and supermolecular approach) to the description of the lowest electronic excitations, first in the simple case of dimers of linear polyenes arranged in a face-to-face configuration. We have made this choice of system in order to be able to discuss the evolution of the energy splitting associated with the 1^1B_u excited state, as a function of both interchain separation and conjugation length. The point dipole and the atomic transition density[17] exciton models are tested against the delocalized supermolecular approach. With the results of these calculations in hand, we then investigate the evolution with oligomer size of the Davydov splitting in model clusters of oligothiophene single crystals.

II. EXCITON THEORY AND SUPERMOLECULAR APPROACH

In the following, we consider the case of a cofacial in-phase dimer built by two polyene chains (hereafter referred to as chain 1 and chain 2) with N sites (carbon atoms) and separated by an intermolecular distance d. The total Hamiltonian for such a dimer writes,[14]

$$H_{\mathrm{tot}}=H_1+H_2+H_{12}, \tag{1}$$

with H_1 (H_2) the Hamiltonian for isolated chain 1 (2) and H_{12} the term representing the interchain interactions. In the exciton approximation, the intermolecular interactions are assumed to be weak with respect to the intrachain interactions and the two-chain excited-state wave functions are taken as a linear combination of the isolated-chain unperturbed wave functions.

For two identical chains,

$$|\Psi^{\pm}\rangle=\frac{1}{\sqrt{2}}(|\psi_1^*\rangle|\psi_2\rangle\pm|\psi_1\rangle|\psi_2^*\rangle), \tag{2}$$

where $|\psi_1^*\rangle$ (eigenfunction of H_1) denotes the wave function for the excited state localized on chain 1 and $|\psi_2\rangle$ (eigenfunction of H_2) is the ground-state wave function for chain 2; $+/-$ corresponds to the symmetric/antisymmetric combination of the equivalent $|\psi_1^*\rangle|\psi_2\rangle$ and $|\psi_1\rangle|\psi_2^*\rangle$ wave functions. Note that $|\psi^{\pm}\rangle$ is not an eigenfunction of H_{tot}, because of the presence of the H_{12} interaction operator in the complete Hamiltonian.

In the case of a symmetric dimer, the energy splitting between the two excited states described by Eq. (2) is given to first order by[14]

$$\begin{aligned}W&=\langle\Psi^+|H_{\mathrm{tot}}|\Psi^+\rangle-\langle\Psi^-|H_{\mathrm{tot}}|\Psi^-\rangle\\&=2\langle\psi_1^*\psi_2|H_{12}|\psi_1\psi_2^*\rangle=2|\beta|.\end{aligned} \tag{3}$$

This expression can be easily generalized to the bandwidth of a one-dimensional crystal when only nearest-neighbor interactions are retained: $W=4|\beta|$ in this case.[14] The computation of W (or β) first requires building the ground-state and excited-state wave functions for the isolated molecules [$|\psi_1^*\rangle$, $|\psi_1\rangle$, $|\psi_2^*\rangle$, and $|\psi_2\rangle$ in Eq. (3)]. Here, these wave functions are obtained by combining the Hartree–Fock semiempirical intermediate neglect of differential overlap (INDO)[18] Hamiltonian to a single configuration interaction (SCI) scheme,

For chain 1: $|\psi_1\rangle = |\mathrm{HF}_1\rangle$;

$$|\psi_1^*\rangle = \frac{1}{\sqrt{2}} \sum_{i_1 a_1} Z_{i_1 a_1} (a_{1\uparrow}^+ i_{1\uparrow} + a_{1\downarrow}^+ i_{1\downarrow}) |\mathrm{HF}_1\rangle, \tag{4}$$

where $|\mathrm{HF}_1\rangle$ is the Hartree–Fock ground state for molecule 1 (which is not modified by configuration interaction due to Brillouin theorem) and Z_{ia} corresponds to the configuration interaction expansion coefficient associated with an electronic configuration built by promoting one electron from the occupied molecular orbital (MO) i to the virtual MO a.

If the exchange interaction terms are neglected (which is reasonable for singlet states), the interchain Hamiltonian in Eq. (1) is the Coulomb interaction between a site on chain 1 and a site on chain 2. Substituting (4) into (2), it is possible to show that the exciton coupling energy corresponds to the electrostatic interaction between the transition electron densities associated with the unperturbed localized $\pi-\pi^*$ excitations,[17]

$$\beta = \sum_{m=1}^{N} \sum_{p=1}^{N} \frac{q_1^m q_2^p}{r_{mp}}, \tag{5}$$

where $m(p)$ runs over all sites of chain 1 (2); r_{mp} is the distance between sites m and p; and $q_1^m(q_2^p)$ denotes the transition electronic density on site $m(p)$ for molecule 1 (2). The transition density is calculated for the $1^1A_g \rightarrow 1^1B_u$ excitation of a single polyene chain and satisfies the following relationships:[17]

$$\sum_{m=1}^{N} q_1^m = 0 \quad \text{and} \quad \sum_{m=1}^{N} q_1^m \mathbf{r}_1^m = \langle 1A_g | \hat{\mu} | 1B_u \rangle = \boldsymbol{\mu}_1, \tag{6}$$

where $\boldsymbol{\mu}_1$ is the $^1A_g \rightarrow {}^1B_u$ transition dipole moment on chain 1.

Equation (5) corresponds to a multicentric monopole expansion of the transition electronic density,[17] which provides the exact solution for the exciton splitting energy within exciton theory (to first order). Different degrees of approximation to estimate β in (5) lead to various models, the most simple and popular one being the point-dipole model. The point-dipole approximation is based on the assumption that the interchain distance is larger than the length of the individual chromophores,[19] so that Eq. (5) can be simplified to a two-center form with the transition dipoles $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ located on the centers of each interacting molecule,

$$\text{for parallel chains: } \beta = \frac{\boldsymbol{\mu}_1 \boldsymbol{\mu}_2}{d^3}. \tag{7}$$

In the supermolecular approach, the full Hamiltonian, H_{tot}, is diagonalized, which provides molecular orbitals that can become delocalized over the entire dimer. The excited states are then built from this delocalized MO basis by applying a similar SCI formalism as before (note that the CI active space has doubled),

$$|\psi_{\mathrm{tot}}\rangle = |\mathrm{HF}_{\mathrm{tot}}\rangle; |\psi_{\mathrm{tot}}^*\rangle = \frac{1}{\sqrt{2}} \sum_{ia} Z_{ia} (a_\uparrow^+ i_\uparrow + a_\downarrow^+ i_\downarrow) |\mathrm{HF}_{\mathrm{tot}}\rangle, \tag{8}$$

where $i(a)$ now denoting a delocalized occupied (empty) molecular orbital. As mentioned above, a major advantage of this approach is that it accounts for charge-transfer (CT) excitations between the two chains, which is not the case in the excitonic molecular models. If interchain distances are large compared to the molecule size, CT excited states lie well above the Frenkel localized excited states. However, for small d values, CT and Frenkel excitations can be expected to mix significantly.

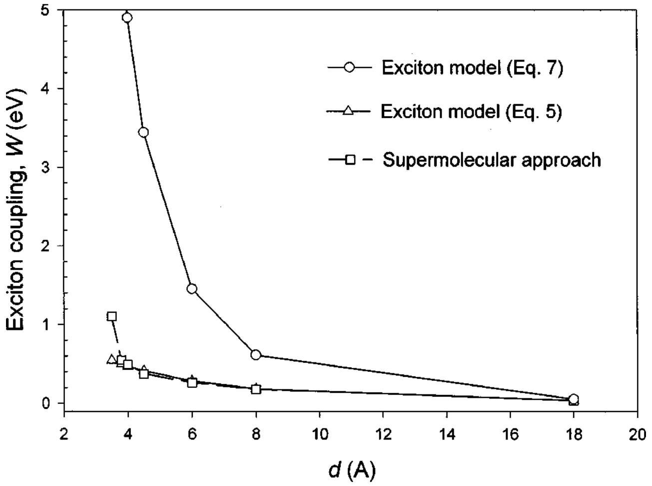

FIG. 1. Evolution with interchain separation, d, of the exciton coupling energy, W (in eV), in a cofacial dimer built by two 16-site polyene chains, as obtained on the basis of: (i) the exciton model and the point-dipole approximation (solid line, circles); (ii) the exciton model and using the atomic transition densities (solid line, triangles); and (iii) the supermolecular approach (dashed line, squares).

III. INTERCHAIN SEPARATION DEPENDENCE OF EXCITON SPLITTING

First, we have applied the two formalisms (exciton model and supermolecular approach) to calculate the exciton splitting energy associated with the optically allowed $1^1A_g \rightarrow 1^1B_u$ transition in cofacial dimers built by polyene chains with $N=16$. The evolution with intermolecular separation of the splitting energy is displayed in Fig. 1. The following conclusions can be drawn:

(i) The exciton model in the point-dipole approximation largely overestimates the exciton splitting for short interchain separations, d; as expected, a more reliable estimate of this splitting is obtained within this approach when d becomes comparable to or larger than the actual chain length (~18 Å for a 16-site polyene).

(ii) When the transition densities are inserted into Eq. (5) the exciton coupling energy calculated in the framework of exciton theory is in excellent agreement with the value obtained from the full SCI calculation on the dimer (supermolecular approach), for *d* larger than 4 Å; for smaller *d* values, the two sets of results slightly deviate, a feature that is attributed to increasing contributions from charge-transfer excitations in the description of the lowest excited states.

IV. CHAIN-LENGTH DEPENDENCE OF EXCITON SPLITTING

A. Cofacial polyene dimers

Next, we have investigated the evolution of the exciton coupling energy with the size of the individual conjugated polyene chains; segments containing up to 80 carbon atoms (40 carbon–carbon double bonds) have been considered. Our aim here is twofold: (i) to check the validity of the exciton approach in predicting quantitative values for the splitting, by comparison to the results provided by the supermolecular approach; and (ii) to extract useful information regarding the effects of interchain interactions on the luminescence properties of the conjugated chromophores. Note that, since we apply a full SCI treatment, the results are size-consistent.

For parallel molecules and in-phase bond alignment, as considered here, intermolecular interactions in the dimer lead to a splitting of the 1^1B_u state into a low component which is symmetry-forbidden with respect to the ground state and a high component which is dipole-allowed[15,16] (note that in single polyene chains, the lowest excited state is not the 1^1B_u state, but the one-photon forbidden $2\,^1A_g$ state; as a consequence, polyenes are weak light emitters even when interchain interactions are negligible[20]). In general, it can be concluded that, if the energy separation between the two components of the splitting is much larger than *kT*, a sizable quenching of the luminescence is expected as a result of the intermolecular interactions. It is thus highly desirable to be able to evaluate correctly the magnitude of the coupling energy and its chain-length dependence.

The point-dipole approximation [Eq. (7)] would predict an *increase* of the exciton splitting with size of the interacting units, since the transition dipoles grow with conjugation length. On the other hand, quantum-chemical calculations performed for oligo(phenylenevinylene)s indicate a decrease in splitting with chain length;[16] such a behavior is: (i) supported by earlier calculations using perturbation theory applied to different orders;[21–23] and (ii) in agreement with the evolution of the Davydov splitting when going from quaterthienyl to sexithienyl single crystals, as determined experimentally from polarized absorption measurements.[24] On the basis of either Su–Schrieffer–Heeger[21] or Pariser–Parr–Pople[22] descriptions of linear conjugated chains and including Coulomb interchain interactions to first order, Spano and co-workers have shown that the magnitude of the exciton coupling first increases linearly with chain length for oligomer sizes smaller than the interchain separation, reaches a maximum, and then decreases for longer conjugated segments.

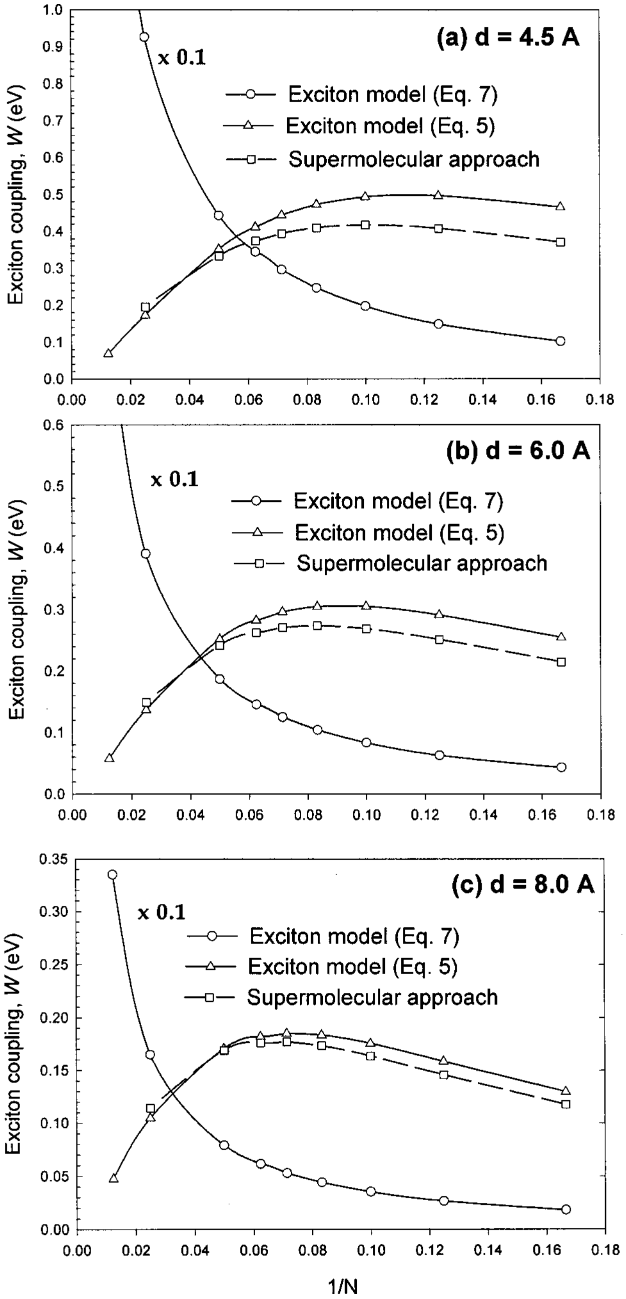

FIG. 2. (a) Evolution with the inverse number of sites in the conjugated segment, 1/*N*, of the exciton coupling energy, *W* (in eV), in cofacial polyene dimers with an interchain separation $d = 4.5$ Å, as obtained on the basis of: (i) the exciton model and the point-dipole approximation (solid line, circles); (ii) the exciton model and using the atomic transition densities (solid line, triangles); and (iii) the supermolecular approach (dashed line, squares); (b) same as (a) for $d = 6.0$ Å; (c) same as (a) for $d = 8.0$ Å. Note that, for the sake of clarity, the *W* values calculated in the point-dipole approximation are multiplied by a factor 0.1.

In Fig. 2, we display for several interchain distances the 1/*N* evolution (with *N* denoting the number of carbon sites in the polyene chains) of the exciton coupling energy, calculated: (i) on the basis of the exciton model, in the point-dipole approximation [Eq. (7)]; (ii) on the basis of the exciton model, by using the atomic transition densities [Eq. (5)]; and (iii) on the basis of the supermolecular approach (full SCI calculation on the dimer). It is clear from Fig. 2 that the point-dipole model provides an erroneous estimate of the coupling energy for long conjugated chains, both qualitatively (the coupling always increases with *N*) and quantitatively (the splitting energy is largely overestimated). In con-

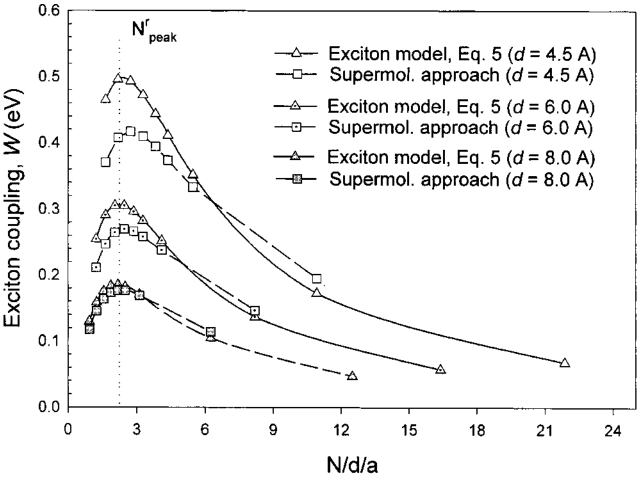

FIG. 3. Evolution with the ratio $N/d/a$ (with N the number of sites, d the interchain distance, and a an average unit cell length here taken to be 1.23 Å) of the exciton coupling energy, W (in eV), in cofacial polyene dimers, as obtained on the basis of: (i) the exciton model and using the atomic transition densities (solid line, triangles); and (ii) the supermolecular approach (dashed line, squares).

trast, when the more realistic interchain Coulomb potential of Eq. (5) is used in the calculations, the computed exciton coupling is in reasonable agreement with the value obtained by means of the supermolecular approach, especially in the large interchain separation regime. When the distance between the interacting chains decreases, the values calculated for the exciton splitting energy in the two formalisms slowly diverge (the difference amounts to ~0.08 eV for $N=8$ and $d=4.5$ Å); this is due mainly to charge-transfer excitations that start mixing with the low-lying intrachain transitions in the supermolecular calculations but are not included in the exciton model.[25] Note also that a possible origin for the differences between the two sets of results is related to the fact that the perturbation associated with intermolecular interactions is limited to first order in Eq. (3) (this limitation is obviously not present in the SCI supermolecular approach). Second-order corrections to the excitation energies, as computed in the excitonic model, have indeed been shown to be sizable in weakly alternated conjugated structures.[23]

In agreement with the results of Spano and co-workers,[21,22] the calculated chain-length dependence of the splitting shows a peak behavior (except in the point-dipole approximation) with a maximum at $N=N_{\mathrm{peak}}$; N_{peak} shifts to longer chain lengths when the interchain separation is raised: $N_{\mathrm{peak}}\approx 8$ for $d=4.5$ Å; $N_{\mathrm{peak}}\approx 10-12$ for $d=6.0$ Å; and $N_{\mathrm{peak}}\approx 14$ for $d=8.0$ Å. In the limit of very large electronic alternation along conjugated rings (decoupled repeating units), McIntire *et al.* have derived an analytical expression for the coupling energy and found that N_{peak} is proportional to the ratio d/a (with a the average carbon–carbon bond length).[21] Figure 3 shows the evolution of the splitting energy that we have calculated as a function of the ratio $N^r=Na/d$. Note that here a is set to 1.23 Å, which is about the average value between the lengths of the single and double carbon–carbon bonds projected onto the polyene chain axis; the total length of the chains is thus $L=(N-1)a$, with N the number of carbon atoms. All curves peak at about the same $N^r_{\mathrm{peak}}(\approx 2.2)$ value; this immediately leads to $N_{\mathrm{peak}}=N^r_{\mathrm{peak}}d/a\approx 2.2\,d/a$. Our results on weakly alternated polyenes are thus consistent with the findings of Spano and co-workers[21] and show that the ratio between the conjugation length ($\sim Na$) and the interchain separation (d) is the decisive factor in determining the maximum amplitude of exciton splitting.

It is useful to have a closer look at the atomic transition density diagrams, since these are directly related to the splitting energy, see Eq. (5). In Fig. 4, we display the transition densities associated with the excitation from the ground state to the lowest optically allowed excited state (1^1B_u) of polyenes of various lengths. Those diagrams represent the way the electronic density gets polarized along the conjugated segment upon excitation.[26] From Fig. 4, we see that the shape of the transition density distributions evolves qualitatively with chain length in the following manner: In short compounds, most of the π density moves from one half of the chain toward the other half; in long chains, the electronic density polarizes via local charge migration from one carbon atom to its first neighbors. Such an evolution results from the interplay between finite size effects, which are very important in short polyenes, and delocalization effects that dominate in long chains: the relative contributions from chain ends to the global polarization of the π-electronic cloud, which is induced by electronic excitation from the ground state to the ^1B_u excited state, decrease with increasing oligomer size.

We rationalize the peak behavior of the exciton splitting as follows. First, when the chain length is small compared to the interchain separation, the molecule can be regarded as a single point object and the point-dipole approximation is valid; the exciton coupling increases with N. When d becomes comparable to the size of the chromophores, it is no longer possible to consider the molecule as a whole, in a nonlocal fashion, as in the point-dipole model; the evolution of the coupling energy can then be understood from a local analysis of the atomic transition density distributions. In Eq. (5), the splitting energy arises from the superimposition of contributions associated with interactions between equivalent sites (diagonal terms, with $m=p$) and interactions between close neighbors (nondiagonal terms with $m=p\pm 1, m=p\pm 2,...$), see Fig. 5(a). The diagonal terms are always positive and decrease monotonically with N. The sign and absolute value of the nondiagonal interaction terms depend on the separation $(m-p)$ between the two sites and the oligomer length, see Figs. 5(b) and 5(c). From Fig. 4, we can expect larger positive contributions arising from short-range (small $m-p$ separation) interactions in molecules of intermediate size compared to either small compounds or extended conjugated chains. As a matter of fact, the absolute value of the sum over all nondiagonal terms shows a dip in its evolution with chain length, as displayed in Fig. 5(a). The evolution of the nondiagonal contributions is mainly responsible for the computed chain-length dependence of the exciton coupling energy.

Simple arguments related to delocalization of the wave functions indicate that, in the limit of strong interchain interactions, the splitting energy W should be inversely propor-

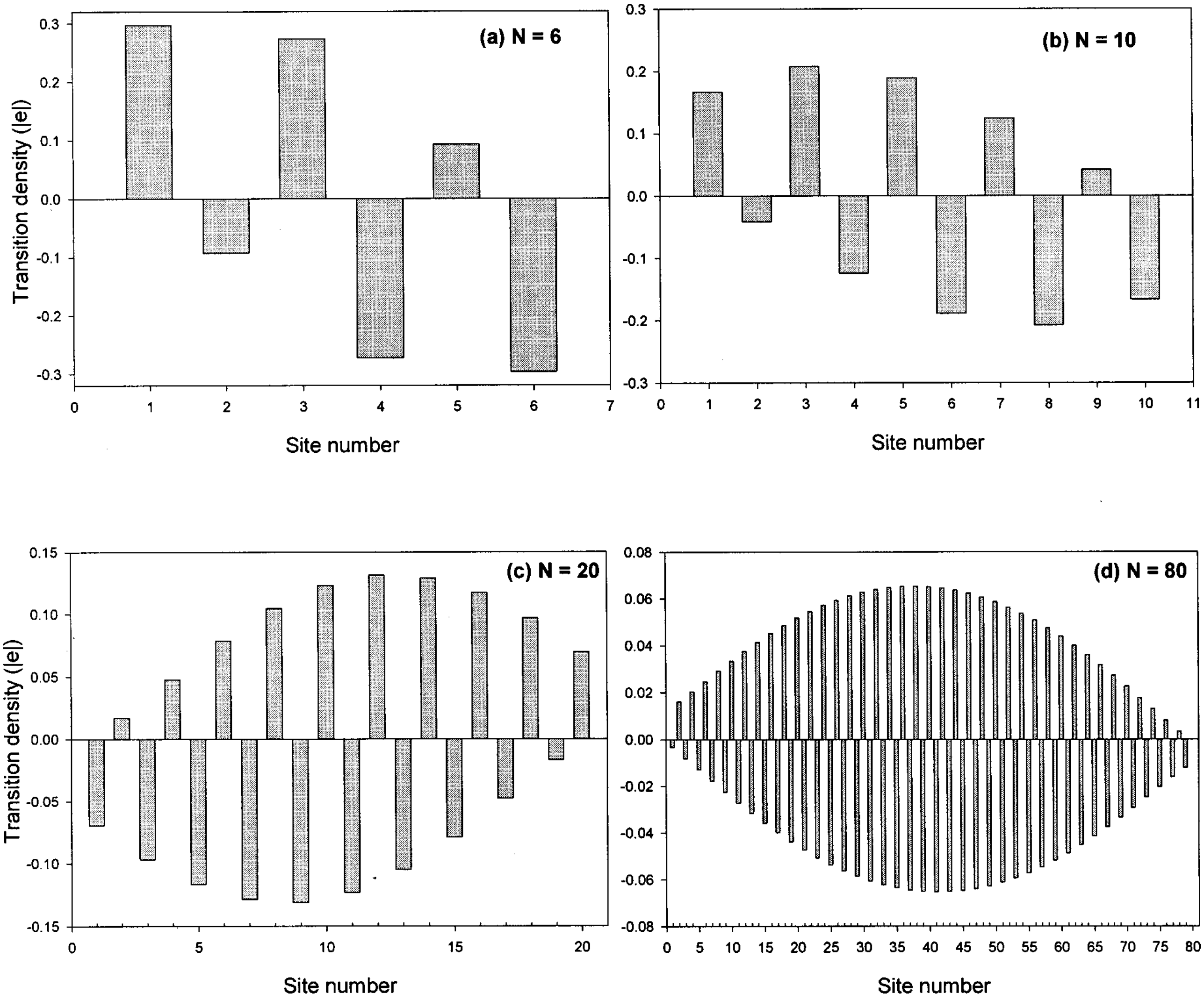

FIG. 4. INDO/SCI $1^1A_g \rightarrow 1^1B_u$ atomic transition densities for polyene single chains, with $N=6$(a), 10 (b), 20 (c), and 80 (d). The site numbers along the chain axis are given on the *x*-axis.

tional to N for large N: the relevant matrix element in the definition of the exciton splitting mainly involves a sum of $\sim N$ terms containing a product of four coefficients (proportional to L^{-2}), leading to the sum being proportional to L^{-1} (with L the chain length).[16] On the other hand, we know that for weak intermolecular forces, W should scale as the square of the transition dipole moment, i.e., as the linear polarizability, α. Since α evolves as N^1 in long chains (saturation regime), the splitting energy of weakly interacting conjugated units should also scale as N. To take account of these two opposite limiting behaviors, W can be written as the following scaling relation:

$$W=2\frac{Nm^2}{d^3}\frac{1}{1+2\dfrac{(Nm)^2}{d^3c}}, \tag{9}$$

where $N^{1/2}m(\equiv\mu)$ is the transition dipole for a single chain (m is the transition moment for the repeating unit) with N sites and c is a parameter that depends on d. In the limit $N \gg d/a$, Eq. (9) leads to $W=c/N$ and, when $N \ll d/a$, Eq. (9) is equivalent to Eq. (7). The parameter c can be obtained for each interchain separation from the fit of the calculated chain-length evolution of the exciton splitting (assuming $c \rightarrow 0$ when $d \rightarrow \infty$) at large N and inserted into Eq. (9) to simulate the dependence of W with oligomer size. The simulated evolutions, displayed for different values of d in Fig. 6, are fully consistent with the numerical results obtained on the basis of Eq. (5); in particular, the chain-length dependence of the exciton coupling energy shows the expected peak behavior, with similar N_{peak} values (compare to Fig. 2).

Finally, we would like to comment on the effect of electron correlation on the exciton splitting. Table I reports the coupling energies, as computed from Eq. (5), on the basis of isolated-chain excited states provided by: (i) the single configuration interaction (SCI) formalism; and (ii) the single and double configuration interaction (SDC) technique. In both cases, all occupied π and unoccupied π^* levels are included in the CI active space. The $1^1A_g \rightarrow 1^1B_u$ transition dipole moments are also listed in this table. We find that inclusion of doubly excited configurations in the CI expansion leads to a significant lowering of the transition dipoles and a concomitant large and rigid decrease (by about 50%) in exciton

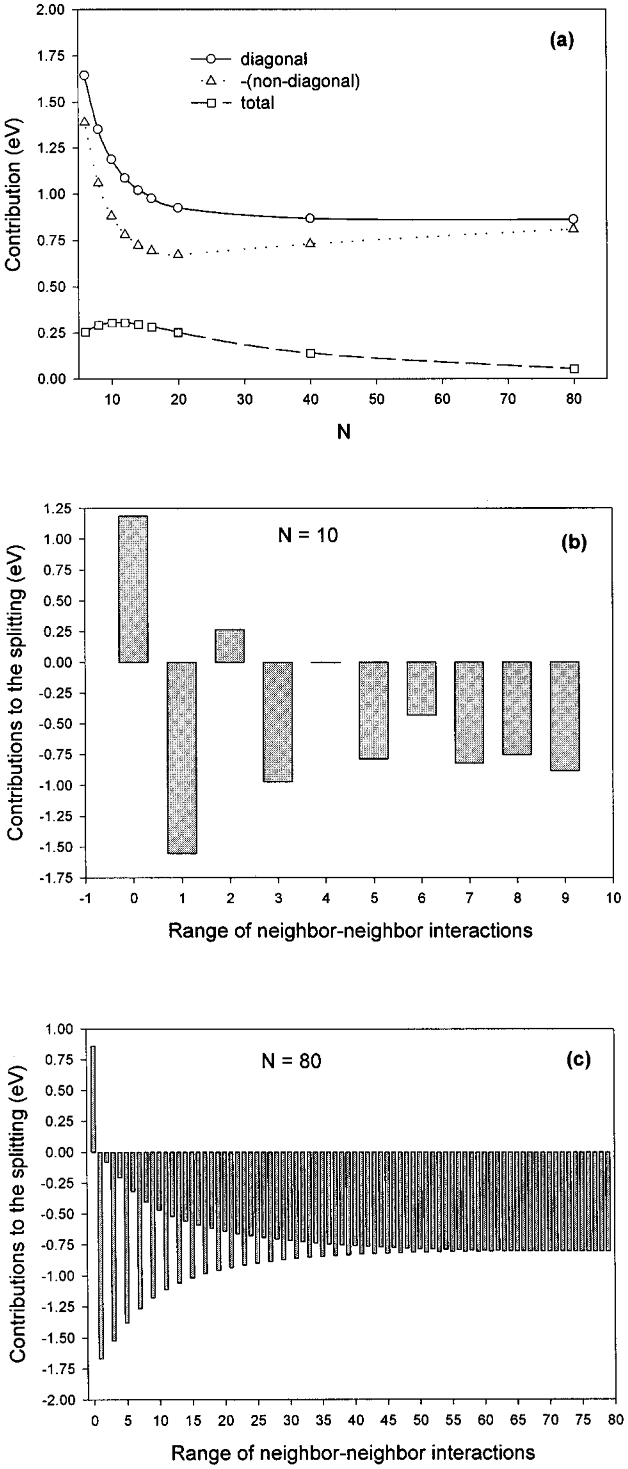

FIG. 5. (a) Evolution with chain length, *N*, of the diagonal contributions and absolute values of the nondiagonal contributions (which are in fact negative) to the exciton coupling energy, *W* (in eV), as obtained from Eq. (5) (for $d=6.0$ Å). (b) Evolution of the nondiagonal contribution to the exciton coupling energy, *W* (in eV), as a function of the range of neighbor interactions retained in Eq. (5) (for $d=6.0$ Å and $N=10$); the diagonal contribution is given at zero abscissa. (c) Same as (b) for $N=80$.

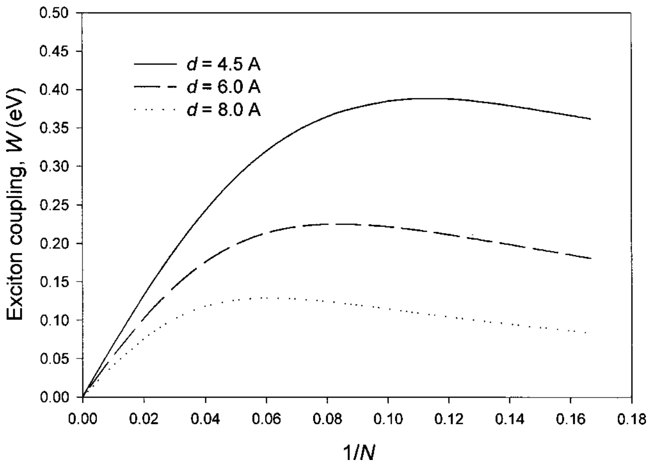

FIG. 6. Evolution with chain length, *N*, of the exciton coupling energy, *W* (in eV), as obtained from Eq. (9) (with $c=6.8$ eV for $d=4.5$ Å; $c=5.4$ eV for $d=6.0$ Å; and $c=4.2$ eV for $d=8.0$ Å).

splitting. Such a decrease results from the electron–electron correlation effects, which tend to reduce the reorganization of the π-electronic density upon excitation from the ground state to the optically allowed excited state.[27] We note that this effect is expected to be less important for conjugated compounds characterized by a larger effective electronic alternation. As an illustration, we give in Table I the coupling energies calculated for stilbene dimers at the SCI and SDCI levels of theory; in this case, taking into account double excitations leads to a reduction of the splitting energy by about 30%.

B. Oligothiophenes single crystals

The magnitude of the exciton coupling energy in quaterthienyl (T_4) and sexithienyl (T_6) single crystals has been recently determined by means of polarized absorption measurements and quantum-chemical calculations based on the supermolecular approach.[24,28] The x-ray structures of both T_4[29] and T_6[30] at low T are characterized by the presence of four molecules per unit cell, which are almost perfectly planar and pack in herringbone fashion, see Fig. 7. Each molecular electronic excited state is split by the crystal field into

TABLE I. Exciton coupling energies in cofacial conjugated dimers, as obtained by the exciton approach [Eq. (5)] with the atomic transition densities provided by the SCI and SD-CI formalisms.

Compound Technique	Single-chain transition dipole, μ_1(D) SCI	SD-CI	Interchain distance, d(Å)	Dimer exciton splitting, W(eV) SCI	SD-CI
Polyene, $N=6$	8.6	6.0	4.5	0.465	0.233
			6.0	0.254	0.127
			8.0	0.130	0.064
Polyene, $N=8$	10.4	7.2	4.5	0.496	0.245
			6.0	0.291	0.143
			8.0	0.158	0.077
Polyene, $N=10$	12.0	8.2	4.5	0.493	0.241
			6.0	0.305	0.148
			8.0	0.176	0.085
Polyene, $N=12$	13.4	9.2	4.5	0.472	0.232
			6.0	0.305	0.149
			8.0	0.184	0.089
Stilbene	9.0	7.3	4.5	0.339	0.209
			6.0	0.204	0.127
			8.0	0.114	0.072

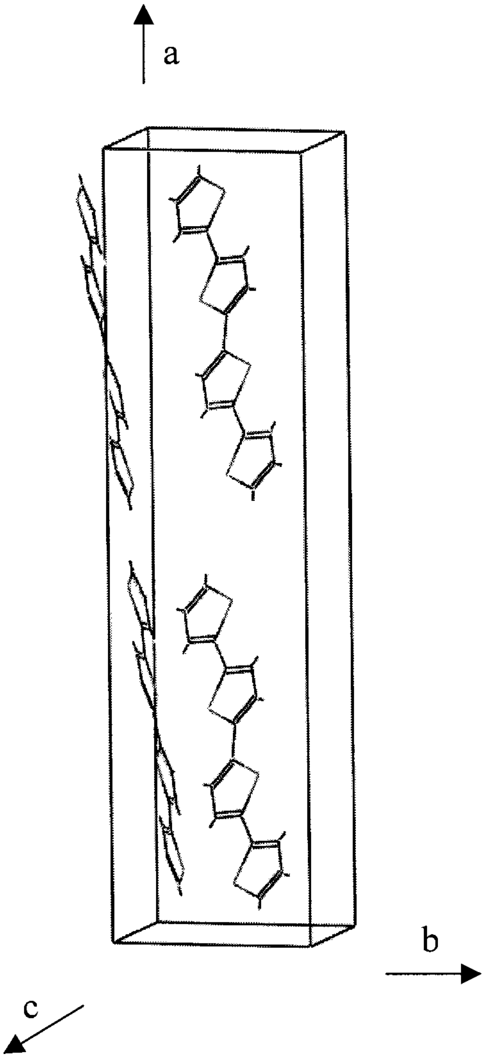

FIG. 7. Crystal structure of the low-temperature phase of T_4 (adapted from Ref. 29). The *a*, *b*, and *c* crystal axes are shown. The arrangement of the four molecules within the unit cell is also representative of the low-temperature phase of T_6[30] and of the crystal structure of T_8.[33] The herring-bone angle is in all cases of 65–66°.

four crystalline levels (Davydov components) belonging to the a_g, a_u, b_g, and b_u irreducible representations of the C_{2h} point group. Due to the layered crystal structure (Fig. 7), the in-plane intermolecular interactions are much stronger than the interactions between layers. This leads to the degeneracy of the homologous gerade and ungerade crystal levels.[28,31] The optically accessible Davydov components, a_u and b_u, are polarized along the *b* axis of the crystal and in the *ac* crystal plane, respectively. The energy difference between the one-photon allowed Davydov components (a_u and b_u crystal levels) gives the Davydov splitting of the corresponding exciton due to the intermolecular interactions in the solid.

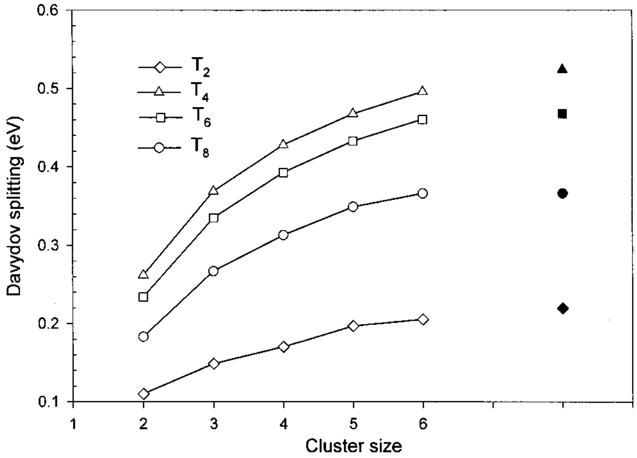

FIG. 8. INDO/SCI computed evolution of the Davydov splitting (in eV) in T_2 (open circles), T_4 (open squares), T_6 (open triangles), and T_8 (open diamonds) with the number of molecules in the clusters, as obtained on the basis of the supermolecular approach. The corresponding Davydov splittings estimated for an infinite cluster, when retaining only nearest-neighbor interactions, are also indicated (closed symbols).

Here, we apply the same supermolecular approach to the calculation of the Davydov splitting in single crystals of bithienyl (T_2)[32] and octathienyl (T_8).[33] The results of these calculations on the T_2,T_4,T_6,T_8 series are compared to the predictions provided by the exciton scheme with the use of atomic transition densities, Eq. (5). Because of the two-dimensional (2D) character of the T_n crystals, we only consider clusters of molecules lying within the same *bc* layer to model the optical properties of the crystals. In Fig. 8, we show the evolution with cluster size of the Davydov splitting, as calculated by the complete INDO/SCI method in oligothiophenes with two, four, six, and eight aromatic rings. As is the case for sexithienyl,[28] the Davydov splitting in T_2, T_4, and T_8 is found to strongly evolve with the number of molecules in the clusters and to converge toward its saturated value for clusters containing about six conjugated chains. We can thus reasonably consider the excitation energies (and the corresponding Davydov splittings) calculated in the largest clusters investigated in this work, to be representative of the crystals. Furthermore, the splittings calculated in the six-chain clusters are close to twice the corresponding values in the two-chain clusters, which indicates that the dominant interactions are between nearest neighbors.

The evolutions with *n* of the Davydov splittings in the T_n crystals, as provided by both the supermolecular approach and the excitonic model [Eq. (5)], are reported in Fig. 9. The splittings reported here are obtained by only retaining nearest-neighbor interactions, i.e., they are set as twice the values calculated for the dimers. As found for cofacial polyenes, the results provided by the two methods are in good agreement and indicate a peak behavior for the chain length dependence of the exciton coupling energy: The Davydov splitting (DS) first increases when going from T_2 to T_4, is maximum for T_4, and then decreases for longer conjugated segments.

Experimentally,[24,28] the DS in oligothiophenes has been demonstrated to slightly decrease (by about 0.037 eV) when passing from T_4(DS$\sim$0.360 eV) to T_6(DS$\sim$0.323 eV), which is consistent with the predicted evolution in Fig. 9. In addition, the DS values computed for T_4 and T_6 are in reasonable agreement (although slightly overestimated) with the spectroscopic results, taking into account the different approximations considered in the calculations. In fact, we have

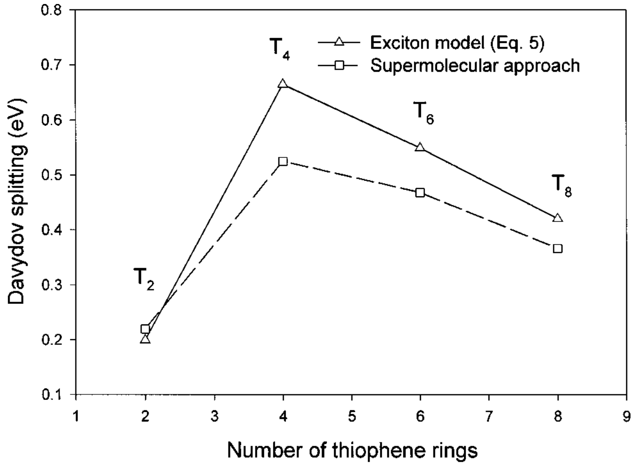

FIG. 9. Evolution with the number of thiophene aromatic rings in the conjugated chain of the Davydov splitting (in eV) in oligothiophene crystals (with only nearest-neighbor interactions), as obtained: (i) on the basis of the exciton model and using the atomic transition densities (solid line, triangles); and (ii) on the basis of the supermolecular approach (dashed line, squares).

shown in the case of T_6 that a better match between theory and experiment can be obtained by considering in the theoretical model the lattice relaxation in the excited states.[28] Another possible explanation for the systematic overestimation of the Davydov splitting by the INDO/SCI formalism is the incomplete inclusion of electron correlation effects; we have seen in the case of cofacial polyenes and stilbenes chromophores that inclusion of double excitations in the CI expansion significantly reduces the DS. Finally, we stress that, as was the case for polyenes, completely erroneous DS values (of a few eV) are evaluated within the point-dipole approximation in oligothiophenes single crystals; the interpretation of experimental results on the basis of such a model[34,35] is thus highly questionable.

V. CONCLUSIONS

We have applied two different formalisms to investigate the influence of interchain interactions on the optical properties of conjugated chains. In the first approach, the molecular exciton theory, the wave functions of the isolated chains are assumed to be unaffected by the interchain interactions and the exciton coupling is obtained from first-order perturbation theory (the perturbation being the intermolecular Coulomb interaction). The second approach, the supermolecular formalism, deals with the complete, fully delocalized wave functions associated with the whole cluster, which allows for the description of charge-transfer excitations.

Two types of architectures have been considered for testing these models: cofacial polyenes and oligothiophene clusters built on the basis of the single crystal x-ray structures. In all cases, a satisfactory agreement is obtained between the results provided by the two techniques, provided a realistic form (multicentric monopole expansion of the transition densities) of the interchain Coulomb potential is used in the excitonic model. In contrast, the widespread point-dipole approximation is found to lead in most cases to unrealistic results (except when the interchain separation is large with respect to the molecular size).

When the interchain separation is smaller than or similar to the actual length of the interacting chromophores (which is most often the case for solid-state materials), each chain experiences the different local contributions to the polarization of the π-electronic cloud which is induced by an electronic excitation taking place on the other chain. As illustrated by the transition density diagrams in Fig. 4, the shape of such a polarization well is intimately related to the size of the conjugated compound, which explains the peak evolution of the exciton coupling energy with oligomer length computed for both polyenes and oligothiophenes. Our results for T_4 and T_6 are consistent with recent polarized absorption measurements recorded on single crystals at low temperature.[24,28]

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