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Optical Signature of Delocalized Polarons in Conjugated Polymers**

By *David Beljonne, Jérôme Cornil, H(■ Sirringhaus, P■ J. Brown, M■ Shkunov, Richard H. Friend*, and *Jean-Luc Brédas*■Missing first names, please■

Quantum-chemical calculations, incorporating both electron–phonon and electron–electron effects, are performed on two-chain model aggregates to assess the influence of interchain interactions on the nature of the singly charged species (polarons) in organic conjugated polymers. In symmetric cofacial dimers with fixed intermolecular distances, our theoretical approach leads to polarons fully delocalized over the two conjugated chains. Such a delocalization strongly affects the geometric and electronic relaxation phenomena induced by charge injection, which in turn leads to a dramatic spectral redistribution of the linear absorption cross section. Optical signatures for delocalized polarons in conjugated materials are identified from our theoretical description and compared to experimental data from optical charge modulation spectroscopy; these are fingerprints for the degree of interchain order, a decisive factor in the achievement of high charge carrier mobilities in polymer-based field-effect transistors.

1. Introduction

Light-emitting diodes (LEDs), solar cells (SCs), and field-effect transistors (FETs) are among the most attractive applications envisioned for organic conjugated polymers in the near future. For such applications, the degree of structural order within the active organic material has been recognized as one of the key parameters in the definition of optimal device performance. While interchain interactions are usually detrimental to electroluminescence quantum efficiency in LEDs (due to the formation of low-lying excited states with vanishing or weak optical coupling to the ground state),[1,2] charge transport in SCs and FETs obviously requires good contacts between adjacent conjugated chains in the solid. This is achieved for instance in the high-quality pentacene and tetracene single crystals grown by Batlogg and co-workers, for which ambipolar transport has been demonstrated with mobilities up to 10^4–$10^5\ cm^2\ V^{-1}\ s^{-1}$ at low temperature.[3]

The inherent disorder in organic conjugated polymers has long prevented the achievement of charge-carrier mobilities comparable to those of molecular crystals or amorphous silicon. Such a challenge has recently been met with a regioregular substituted poly-3-hexylthiophene (RR P3HT), which displays room-temperature mobilities of up to $0.1\ cm^2\ V^{-1}\ s^{-1}$.[4,5] Films of RR P3HT were successfully used in a FET device to drive a light-emitting diode based on a luminescent polymer, thereby providing the first demonstration of an all-organic display pixel.[5] Self-organization in this polymer results in a lamellae structure with two-dimensional sheets built by strongly interacting conjugated chains (with interchain distance on the order of 3.8 Å). In contrast to most molecular crystals in which the preferential direction for charge transport is perpendicular to the chain axes,[6,7] the migration of the charges along the polymer chains contributes to transport in the RR P3HT films. However, since the conjugation length is small compared to the device dimensions, interchain polaron hopping is likely to limit the transport properties. Therefore delocalization of the charged species over several adjacent chains has been conjectured to lie at the origin of the high mobilities reported in the ordered P3HT samples.[4,5]

The nature of the charge carriers in RR P3HT has been investigated experimentally using optical charge modulation spectroscopy (CMS)[8] and photoinduced absorption (PiA).[9] These studies have pinpointed substantial differences between the optical signatures of polarons in the microcrystalline materials, as compared to chemically doped polythiophene in solution. Such differences were attributed to delocalization of the polaronic species over several adjacent polythiophene chains, which is consistent with the high transport properties within the two-dimensional conjugated sheets.[4,5]

[*] (■Please check titles of all authors■)
Prof. J.-L. Brédas,[+] Dr. D. Beljonne,[+] Dr. J. Cornil
Laboratory for Chemistry of Novel Materials
Center for Research in Molecular Electronics and Photonics
University of Mons-Hainaut
Place du Parc 20, B-7000 Mons (Belgium)
E-mail: jlbredas@u.arizona.edu

Dr. H. Sirringhaus, Dr. P. J. Brown, Dr. M. Shkunov, Prof. R. H. Friend
Cavendish Laboratory, University of Cambridge
Madingley Road, Cambridge CB3 0HE (UK)

[+] Second address: Department of Chemistry, The University of Arizona, Tucson, AZ 85721-0041, USA.

The influence of interchain interactions on the optical absorption spectrum has been investigated by Blackman and Sabra in the case of doped polyacetylene[10] at the one-electron SSH (Su–Schrieffer–Heeger) level.[11] These authors have demonstrated that, for strong interchain coupling, charge delocalization occurs and is accompanied by a dramatic change in the energies and relative intensities of the spectral transitions within the bandgap. Earlier local density functional theory (DFT) calculations by Vogl and Campbell on the crystal structure of polyacetylene suggested, on the basis of the magnitude of the interchain transfer integrals, that charges injected in perfect crystals would fully delocalize over a large number of conjugated chains and that therefore polarons would not be stable.[12] Similar DFT band-structure calculations on poly(-*para*-phenylenevinylene) (PPV) have lead to the same conclusions.[13] An electron or hole injected in polyacetylene or PPV would then behave as a free charge carrier, without any lattice distortion. It was argued that the experimental observation of polarons in conjugated polymers reflects disorder in the films, which localizes the charge species.[12,13]

In this work, we apply correlated quantum-chemical methods, including both lattice relaxation and electron correlation effects, to the description of the optical properties of a polaron in a two-chain aggregate. The spectroscopic signatures of interchain interaction effects are identified and compared to optical charge modulation spectra recorded for low- and high-regioregular substituted polythiophenes.

2. Results and Discussion

Our theoretical approach first involves the computation of the geometric and electronic structures of a single conjugated chain carrying a positive charge. We have considered PPV since: i) it is a prototype for non-degenerate ground-state conjugated polymers; ii) it is the most actively studied light-emitting polymer; and iii) the parameters for PPV in the semiempirical Hamiltonians used in our quantum-chemical calculations are very reliable. We stress that the general picture provided by our theoretical results is not sensitive to the exact chemical structure of the interacting chains (PPV or polythiophene (PT)). (■OK?■(

We have performed quantum-chemical calculations on oligomers of increasing size but only report here on the results obtained for a five-ring oligomer (denoted hereafter as PPV5). We first focus on isolated chains. Ground-state geometry optimization of the PPV5 molecule in its neutral and singly charged states has been carried out at the Austin model 1[14]/full configuration interaction (AM1/FCI) level (four molecular orbitals (MOs) were included in the CI active space[15]). Figure 1 shows the bond-length deformations associated with the formation of a positive polaron on PPV5. Charge injection induces the appearance of a slight quinoid character on the phenylene rings, together with a decrease of bond-length alternation in the vinylene linkages. These deformations are more pronounced around the center of the molecule and typically extend over three repeat units (~20 Å).
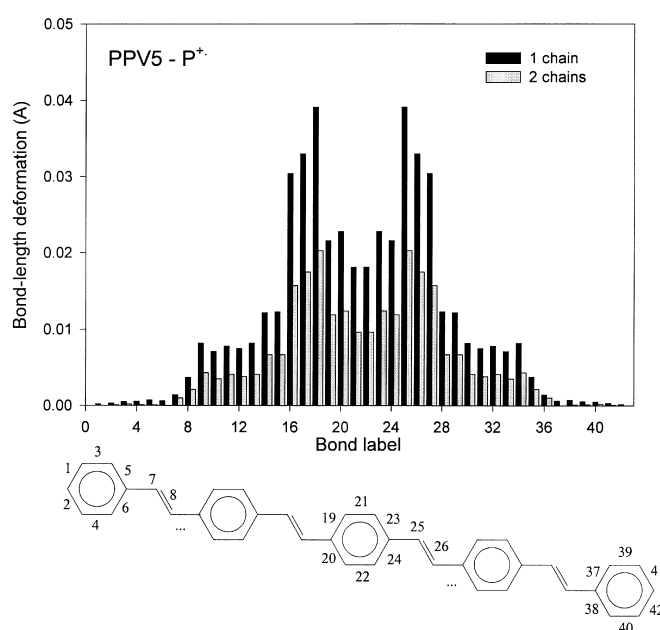

Fig. 1. Differences (in Å) between the AM1/FCI calculated bond lengths in the neutral and singly charged states of PPV5, in the isolated molecule (black) and in the dimer (gray). The structure and bond labeling of the five-ring oligomer is shown below.

On the basis of the optimized geometry of the charged species, the one-electron energy levels were calculated using both the AM1 and INDO[16] (■please explain INDO■(semiempirical approaches. A simplified representation of the one-electron diagrams typically obtained by these two techniques is given in Figure 2. Removal of one electron from a conjugated chain induces the appearance of two electronic (polaronic) levels within the previously forbidden HOMO–LUMO (HOMO = highest occupied MO, LUMO = lowest unoccupied MO) gap.[17] The localized character of these gap levels is easily identified from the electronic density computed at the INDO level for the PPV5 molecule, see Figure 3. Similar results are obtained with the AM1 method.
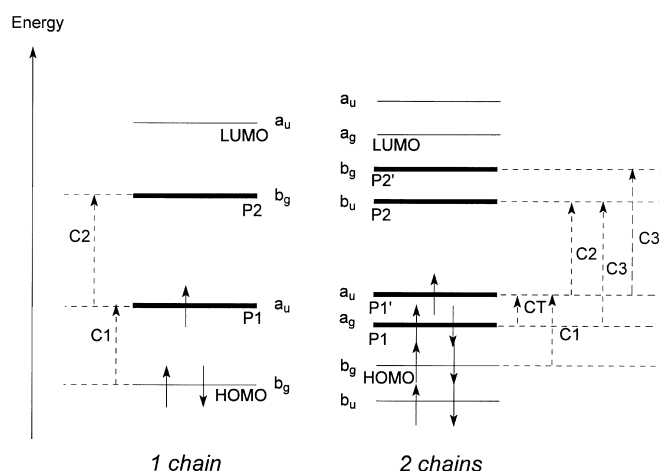

Fig. 2. Schematic representation of the one-electron energy diagram for a polaron localized on a single conjugated chain (left), and delocalized over two cofacial chains (right). The symmetry of the orbitals and the relevant electronic excitations are indicated.
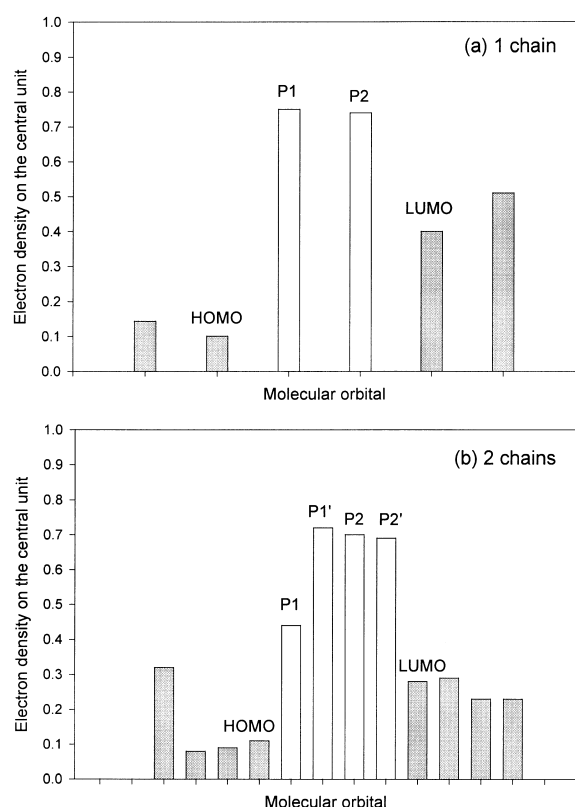
Fig. 3. a) INDO molecular electron density (square of the atomic coefficients) over the central part of the PPV5 molecule (central phenylene ring plus the two adjacent vinylene linkages) in its singly charged state. b) Same for the singly charged PPV5 cofacial dimer. Sum over all atoms is 1.
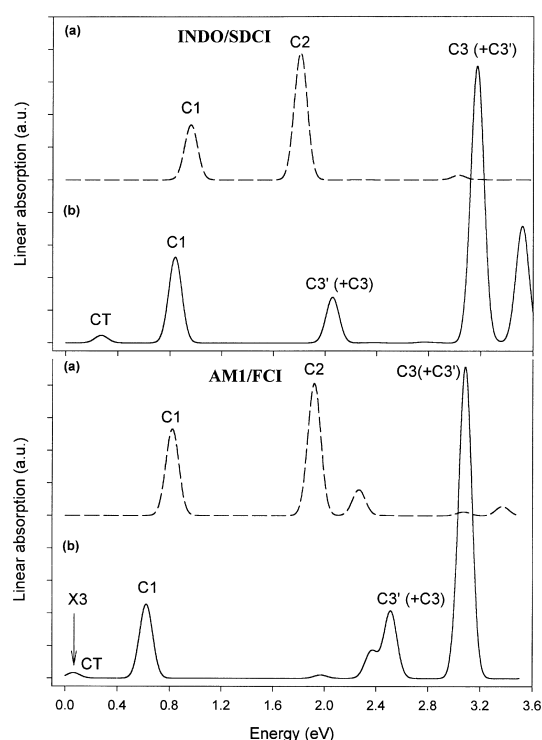

Fig. 4. Top: Linear absorption spectra of the singly charged PPV5 single molecule (a) and cofacial dimer (b), simulated on the basis of the INDO/SDCI description of the excited states. Bottom: Similar results from AM1/FCI calculations. Gaussian functions with 0.05 eV width at half maximum have been used to convolute the spectra.

The AM1-optimized geometry of the charged species is then used as input for the computation of the excited states, which is performed at two different levels: i) the AM1/FCI formalism, as adopted for geometry optimization, but considering a larger configuration interaction expansion (including up to 16 molecular orbitals) to ensure convergence of the spectroscopic properties; and ii) an INDO/SDCI (■please explain SDCI■(method where all single excitations over the electronic π levels and a limited number of double excitations (over 16 MOs) were involved. As seen from Figure 4, most of the optical absorption cross section of the charged species is shared between two excited states mainly described in terms of the C1 and C2 electronic transitions shown in Figure 2. Denoting HOMO as the highest doubly occupied level, P1 as the lowest (singly occupied) polaronic level, and P2 as the highest (empty) polaronic level, C1 and C2 correspond to single HOMO → P1 and P1 → P2 excitations, respectively.[18]

The presence of two dominant absorption bands is in good agreement with experimental data on monoionic oligo(phenylenevinylene) solutions.[19] For the five-ring oligomer studied here, two main optical transitions are measured around 0.72 and 1.63 eV, which compare well with both the AM1/FCI (0.82 and 1.92 eV) and INDO/SDCI (0.96 and 1.81 eV) results. The chain-length evolution of the positions and relative intensities of these electronic transitions is also well reproduced by both formalisms.[20]

Next, the influence of interchain interactions on the optical response of singly charged polarons has been assessed by considering a cofacial aggregate formed by two five-ring PPV chains separated by 4 Å. This configuration is similar to that encountered in the microcrystalline domains of RR P3HT.[8] For such a symmetric cofacial arrangement, the INDO and AM1 approaches lead to molecular orbitals completely delocalized over the two conjugated chains, which carry half a unitary charge each. To determine the ground-state geometry of the two-chain system in its singly oxidized state, we apply the same AM1/FCI approach as in the single chain case (while doubling the active space to eight molecular orbitals for size consistency; the interchain separation is kept frozen during the geometry optimization. The lattice deformations in the aggregate, as provided by this approach, are compared to those calculated for the isolated molecule in Figure 1. Since the perturbation induced by charge injection in the individual chains of the dimer is weaker than in the single-chain case, the bond-length modifications are less pronounced in the aggregate (especially around the center of the molecule) and extend in a symmetric way over the two conjugated chains. Note that very similar geometries are obtained on the basis of the INDO/SDCI bond orders when using conventional bond-order/bond-length (BOBL) relationships.[20]

In a cofacial dimer with C_{2h} symmetry, interchain coupling leads to a splitting of all electronic levels into gerade/ungerade symmetry molecular orbital pairs, see Figure 2. The absorption spectrum of the cationic dimer can then be interpreted on the

basis of a one-electron energy diagram, wherein four polaronic levels (one doubly occupied, one singly occupied, and two empty) are pushed within the HOMO–LUMO gap as a result of wavefunction localization. These orbitals, referred to as P1, P1′, P2, and P2′, can be identified from their more localized electron density distribution, shown in Figure 3. Note that the four polaronic levels extend in a symmetric way over the two chains. In contrast, in the SSH calculations of Blackman and Sabra, only two electronic levels are found inside the bandgap, whatever the strength of interchain interactions.[10]

The absorption spectrum of the cationic dimer, as computed at the AM1/FCI level (with up to 26 molecular orbitals in the active space) and INDO/SDCI (with all possible single excitations within the π manifold and double excitations over 22 π orbitals), is shown in comparison to that of the one-chain polaron in Figure 4. Again, it is worth stressing that the optical features discussed below are common to the descriptions provided by the AM1/FCI and INDO/SDCI formalisms. The weaker lattice relaxation in the two-chain aggregate translates into shallower drifts of the polaronic levels inside the gap and a consequent red-shift (by 0.1–0.2 eV) of the absorption band described by the C1 electronic excitation. The nature of the latter transition remains essentially unaffected by interchain interactions.

The most striking feature in the optical spectrum of the singly charged dimer is the appearance of a new intense optical transition located around 3.1 [3.2] eV at the AM1/FCI [INDO/SDCI] level and the emergence of a weak signal, denoted CT, around 0.1 [0.25] eV. Single particle excitations between the four polaronic electronic levels produce two excited states with B_u symmetry (i.e., one-photon symmetry allowed with respect to the ground state), instead of one in the single-chain limit (note that C2 is symmetry forbidden in the dimer). These two B_u excited states result from the configuration mixing between the C3 and C3′ electronic transitions. Constructive combination of these optical excitations leads to the spectral feature around 3.1 eV (i.e., just below the optical gap of the neutral system (~3.2 eV)), which dominates the absorption spectrum of the two-chain aggregate, see Figure 4. Destructive coupling between the same configurations provides the weaker absorption line around 2.4 [2.1] eV (note that this excited state also involves significant contributions from doubly excited configurations).

The charge-transfer (CT) optical transition in Figure 4 is polarized along the interchain packing axis, while all other absorption bands are mainly polarized along the chain axis. The intensity of this absorption feature is controlled by the amount of delocalization in the polaron wavefunction; the overlap between the electron and hole wavefunctions of the CT pair and therefore also the transition moment is maximum for full delocalization over the two conjugated segments, while it is vanishingly small for polarons that would be constrained on isolated chains.[20] In addition, the absorption cross section also depends linearly on the excitation energy of the CT transition, that is to say the energy separation between the two occupied polaronic levels P1 and P1′, which also peaks in the limiting case of complete delocalization. Thus, the optical cross section of this absorption band gives direct information on the

effectiveness of interchain charge delocalization in the conjugated materials.

At this stage, it is worth comparing our results to the SSH one-electron picture provided by Blackman and Sabra for delocalized polarons in polyacetylene.[10] Switching on the interchain interactions in the AM1/FCI and INDO/SDCI calculations gives rise to a red-shift of the C1 transition and the smearing out of C2 (for symmetry reasons), two features that are also found at the SSH level. However, electron correlation effects do separate the C3 and C3′ excitations, which are degenerate at the SSH level, into a weak low-lying absorption feature and a strong high-lying one. In addition, the emergence of new spectral lines in the optical spectrum of the dimer, as simulated on the basis of correlated calculations, is not related to the HOMO → P2 and P1 → LUMO single-chain transitions, which would become symmetry allowed in the dimer, but results from the splitting of the P1 and P2 polaronic levels (vide supra) and the appearance of four levels in the original gap. Interchain-polarized excitations, such as the CT band at ~0.1–0.25 eV, were not considered.[10]

The theoretical simulations presented here are consistent with the changes in optical absorption observed experimentally when improving the degree of interchain order in alkyl-substituted polythiophene derivatives.[8,9] Figure 5a shows optical
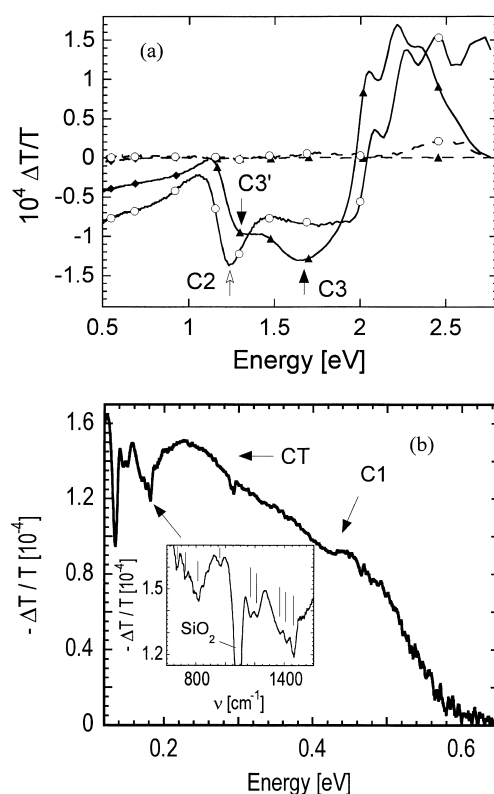

Fig. 5. a) Optical CMS of field-induced charges in the accumulation regime of P3HT FETs in the near infrared and visible range. Spectra are shown for polymers with different microstructures: a polymer with a high percentage of regioregular HT attachments: HT = 96 % (▲) and a polymer with HT < 80 % (○) (solid lines: in-phase signal, broken lines: quadrature signal). b) Optical CMS spectrum in the mid-infrared spectral range for a regioregular poly-3-pentylthiophene FET. Inset: Several reproducible absorption dips due to resonant charge-induced vibrational modes are marked by vertical lines. The strong absorption around 1080 cm⁻¹ is due to some modulation of absorption in the SiO₂ gate insulating layer.

charge modulation spectroscopy of field-induced charge in the accumulation layer of P3HT-based FETs in the near-infrared and visible spectral range.[8] Polymers with a high percentage of regioregular head-to-tail (HT) attachments of the flexible alkyl side chains organize into microcrystalline lamella domains with a preferential orientation of the direction of π–π stacking in the plane of the film. The CMS experiments are performed with unpolarized light at normal incidence and, therefore, are sensitive to transitions polarized both along the polymer chain as well as those polarized along the direction of interchain stacking. The spectrum of the HT = 96 % polymer (▲) is characteristic of high-mobility charge carriers in ordered P3HT lamellae with strong interchain interactions. It exhibits a pronounced charge-induced transition at 1.65 eV (C3) just below the bleaching signal of the neutral polymer absorption and a shoulder at 1.35 eV (C3′).

In contrast, polymers with regioregularity lower than 70–80 %, obtained from the most soluble hexane Soxthlet fraction of as-synthesized P3HT, are amorphous and exhibit mobilities of less than 10^{-5} cm^2 V^{-1} s^{-1}. The spectrum of the HT < 80 % polymer (○ in Fig. 5a) is characteristic of charge carriers in disordered P3HT, in which delocalization of charge carriers over adjacent chains is prevented by strong disorder. The spectra markedly differ from those of highly RR P3HTs. The dominant charge-induced transition is at 1.25 eV (C2), close to where the C3′ shoulder is observed in the highly regioregular polymers. At energies around 1.7 eV no clear transition is resolved. Only a broad background signal is observed, which may be due to contributions from residual ordered domains in the film, but also contains a contribution from an electroabsorption signal. This spectrum is interpreted in terms of the C2 transition of charge carriers confined to short conjugated segments on individual, one-dimensional chains as a consequence of pronounced disorder.

Additional transitions are observed in the mid-infrared spectral range (Fig. 5b). We show here a spectrum obtained for regioregular poly-3-pentylthiophene. Similar spectra were obtained for P3HT.[8] A broad absorption signal (CT) is observed rising beyond the low-energy cutoff of the CMS experiments with a distinct shoulder around 0.35–0.45 eV (that we assign to C1). In PiA experiments on P3HT films extending towards lower energies, the low-energy CT transitions were found to exhibit a peak lying at about 70 meV.[9] The CT transitions are of comparable strength to the C3′ charge-induced transitions in the visible spectral range. They are characteristic of highly microcrystalline P3HT lamella and appear to be the more pronounced, the higher the regioregularity of the polymer.[8] CMS experiments on the very low regioregularity polymers (HT < 80 %) were unsuccessful in this frequency range due to difficulties with fabricating FET devices with operating characteristics that are stable over the duration of the CMS experiment. Note, however, that PiA experiments on P3HT indicate a significant red shift of the C1 optical feature when passing from regiorandom to regioregular samples.[9] At energies below 0.2 eV sharp dips are observed in the charge-induced absorption. They are attributed to antiresonance effects caused by the spectral overlap between the broad electronic CT transitions and sharp vibrational modes of the polymer chain.[21]

3. Summary and Conclusions

To summarize, quantum-chemical calculations, including electron correlation, were performed to probe the influence of interchain interactions on the optical properties of polarons in conjugated materials. We find that interchain coupling in a cofacial dimer leads to a complete delocalization of the polaron wavefunction for close contacts between the conjugated molecules. On the absorption spectrum, this translates into:

- a red-shift of the C1 single-chain lowest polaronic transition,
- the splitting of the interpolaronic absorption band into a weak and an intense component, both located above C2 in the isolated chain,
- the emergence of a low-energy charge-transfer excited state, optically allowed along the packing direction.

These characteristics are consistent with the spectroscopic characterization of two-dimensional polarons in well-ordered polythiophene derivatives. A similar description is expected to hold in the case of a larger number of cofacial interacting molecules as well as for aggregates with lower symmetry (as long as the interchain interactions are strong enough to delocalize the excess charge).[20] Delocalization of the polaron over *N* conjugated chains would result in the formation of a pair of *N*-level polaronic bands inside the gap, a nearly filled band (minus one electron for a positive polaron) and an empty one. Charge-carrier interchain mobilities in conjugated polymers can be related to the width of these bands (which is directly related to the strength of the interchain interactions) and the energy departure from the valence and conduction bands (quantified by the polaron relaxation energy), which can both be monitored by means of spectroscopic tools. Full delocalization of the charges over an infinite number of conjugated chains would lead to vanishingly small geometric relaxation phenomena and hence negligible relaxation energies; very high (band-like) charge-carrier mobilities can then be expected. We also expect that, in this limit, the optical response due to the low-energy charge-transfer excited state will evolve into a Drude-type free-carrier intraband absorption. The optical properties of the regioregular substituted poly-alkylthiophenes of intermediate mobilities investigated here suggest that, although the degree of order allows some spreading of the polaron wavefunction over several chains, such a band-type charge transport and full delocalization is not achieved yet. We also emphasize that polymers offer an advantage over small molecules of smaller polaron relaxation energies, so that the turn-over from polaron-like to band-like transport should in principle occur at a lower degree of interchain order. We believe that this work constitutes a firm theoretical basis for the interpretation of the optical absorption spectrum of polaronic species in interacting conjugated polymer chains and the design of new organic materials with high charge-carrier mobilities.

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