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We report a detailed quantum-chemical characterization of the electronic and optical properties of polyfluorene chains and compare them to those in copolymers containing alternating fluorene and benzothiadiazole or ethylenedioxythiophene units. The introduction of the comonomer can strongly modify the excitonic properties as well as the efficiency of charge- and energy-transfer processes. The choice of the comonomer is thus critical in targeting specific optical properties while maintaining good transport properties. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Since the first report of electroluminescence in a conjugated polymer,[1] many experimental and theoretical efforts have been devoted to improving the performance of polymer-based light-emitting devices.[2] Low-resolution matrix displays have now reached the stage of commercialization.[3] Conjugated polymers are also widely investigated for use in organic transistors[4–6] as well as in photodiodes and solar cells,[7–9] where light is absorbed by the material and converted into an electric current. However, these devices usually suffer from the low charge mobilities achieved in polymer films.[5]

Polyparaphenylenevinylene (PPV) was the first polymer involved in a light-emitting device.[1,10] Interest has now shifted to polymers of high purity and high stability in view of commercial applications. Among these, polyfluorenes and fluorene-containing copolymers emerge as promising materials for light-emitting displays since the color of the emitted light can span the entire visible range as a function of the nature of the comonomer unit. This has stimulated recent experimental and theoretical studies aimed at better understanding the electronic and optical properties of these systems[11–20] and assessing their performance in electro-optic devices.[21–23] Interestingly, polarized electroluminescence has also been reported for liquid crystalline polyfluorenes obtained by derivatizing the conjugated backbones with long saturated side-chains.[24]

Quantum-chemical calculations can prove useful to provide good insight into the electronic and optical properties of conjugated chains and to design materials matching specific requirements prior to chemical synthesis. We exploit them here to describe the nature of the lowest singlet and triplet excited states in polyfluorene (F) chains and in copolymers containing alternating fluorene units and benzothiadiazole units (BT), a copolymer recently synthesized at Dow,[21] or ethylenedioxythiophene (EDOT) units (see Fig. 1). We analyze how the electronic and optical properties of polyfluorene chains as well as the efficiency of charge and energy transfer processes in thin films are impacted by the nature of the comonomer.

II. THEORETICAL METHODOLOGY

Since the electronic and optical properties of conjugated oligomers saturate rapidly with chain length,[25] we have considered oligomers of F, FBT, and FEDOT containing from one to four repeat units. In the absence of structural information, we have assumed the oligomers to be planar; this is reasonable since: (i) solid-state packing tends to significantly reduce the torsion angles between adjacent units (this is the case of oligophenylenes[26]); and (ii) electronic and optical properties are weakly affected by small changes in torsional angles.[27]

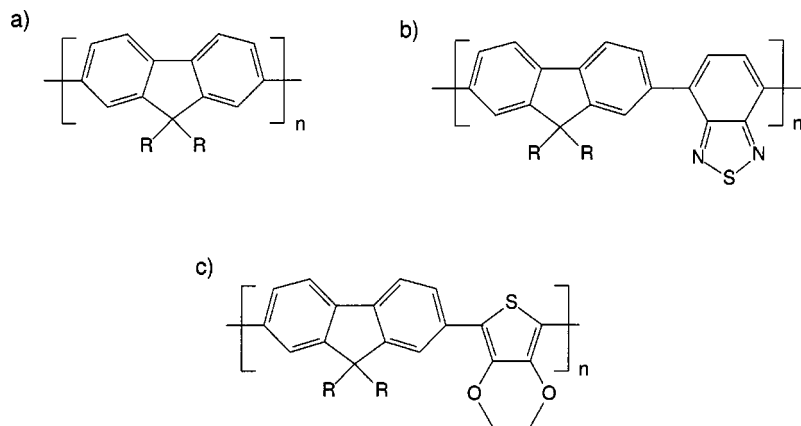[a]Electronic mail: jlbredas@u.arizona.edu

FIG. 1. Chemical structure of: (a) polyfluorene; (b) poly(fluorene-co-benzothiadiazole); and (c) poly(fluorene-co-ethylenedioxythiophene).

The ground-state geometries of the oligomers have been optimized at the semiempirical Hartree–Fock Austin Model 1 level;[28] this choice is justified by previous theoretical studies for phenylene-based[29] and oligoethylenedioxythiophene[30] chains. On the basis of the optimized geometries, we have calculated the electronic structure of the oligomers using the spectroscopic version of the semiempirical Hartree–Fock INDO (intermediate neglect of differential overlap) Hamiltonian developed by Zerner and co-workers.[31] The excited states of the oligomers have been characterized by coupling the INDO hamiltonian to a single configuration interaction (SCI) scheme. The INDO/SCI method has been parametrized to reproduce the optical absorption spectra of organic molecules, using the Mataga–Nishimoto potential[32] to evaluate the two-center two-electron integrals. However, here we have estimated the energy of the lowest triplet excited state of the chains using the Ohno–Klopman potential,[33] which reduces the screening between electrons and provides a much better agreement with experimental data. The CI active space has been built by promoting a single electron from one of the highest M occupied levels to one of the lowest N unoccupied levels; M and N are chosen here to be equal to the number of π-occupied and π-unoccupied levels in the oligomer, respec-

tively (for instance $M=6$ and $N=6$ in the fluorene monomer while $M=11$ and $N=10$ in the FBT monomer).

III. RESULTS AND DISCUSSION

Figure 2 describes the evolution of the INDO-calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies as a function of the inverse number of monomer units in F, FBT, and FEDOT. As is usual in π-conjugated systems, the energy of the frontier electronic levels evolves linearly with inverse chain length in the three systems. While similar energies are obtained for the LUMO of the F and FEDOT oligomers, the introduction of BT units lowers significantly the LUMO of the longest oligofluorene chains by some 1.1 eV. The high electron affinity of FBT chains should thus ensure efficient electron injection and low charge trapping in devices, as suggested by recent time-of-flight measurements.[17] Turning to the evolution of the HOMO levels, we find that while similar energies are calculated in F and FBT chains, the HOMOs of the longest FEDOT chains are destabilized by about 0.45 eV with respect to the fluorene chains. This reduction in the
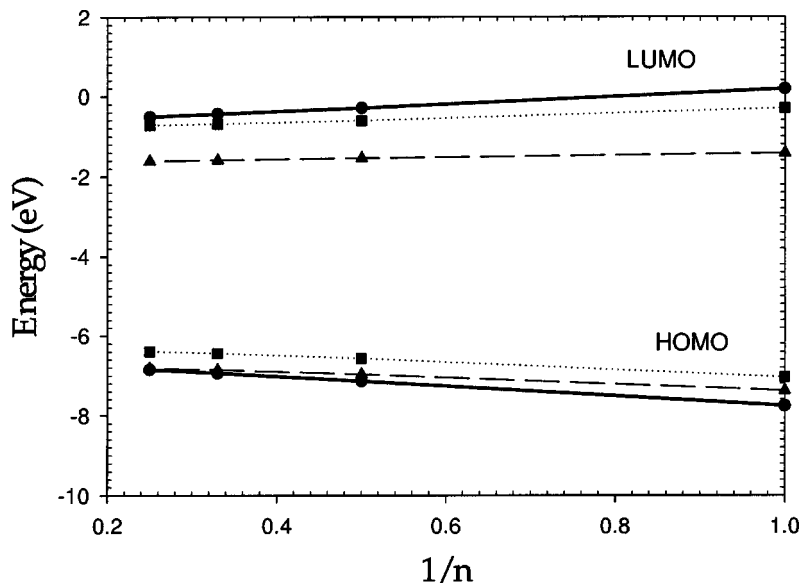

FIG. 2. INDO-calculated HOMO and LUMO energies of F (solid lines), FBT (dashed lines), and FEDOT (dotted lines) oligomers as a function of the inverse number of monomer units.
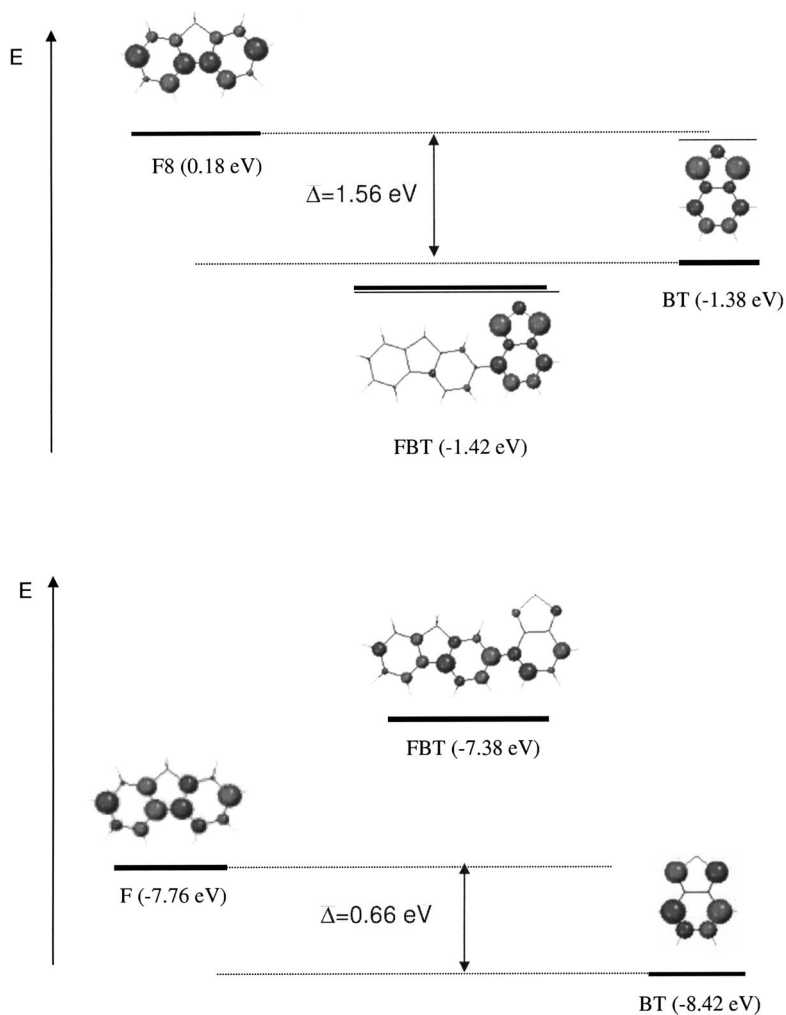
FIG. 3. Energies and shapes of the HOMO (top) and LUMO (bottom) orbitals of fluorene (F), benzothiadiazole (BT), and FBT, as calculated at the INDO level; the size and color of the circles describe the amplitude and sign of the LCAO (linear combination of atomic orbitals) coefficients associated with the π-atomic orbitals.

HOMO–LUMO gap observed when going from F to FBT and to FEDOT will impact the optical properties of the chains (*vide infra*).

The results of Fig. 2 can be easily rationalized by analyzing how the nature of the frontier electronic levels of the fluorene chains is affected by the incorporation of BT or EDOT units. In FBT, the HOMO remains delocalized along the conjugated backbone; the shapes of the LUMOs become drastically different, being localized on the BT units in the copolymer and delocalized in the fluorene chains. This is rationalized by the fact that the energy separation between the LUMO of F and BT monomer is large (1.56 eV) and leads to weak interactions between the two building blocks; in contrast, the separation between the corresponding HOMO levels is smaller (0.66 eV) and promotes stronger interactions between the two units, thus giving rise to a delocalized HOMO level in the FBT monomer (described as the antibonding interaction between the HOMO of the individual units, see Fig. 3). The strong localization of the LUMO level in the FBT copolymer is expected to reduce significantly the intrachain mobilities for electrons. In contrast, a delocalized character prevails for both the HOMO and LUMO levels when replacing BT units by EDOT units (Fig. 4), as a result of the small energy separation between the frontier electronic levels of the two building blocks (0.31

and 0.27 eV for the HOMO and LUMO levels, respectively). The choice of the comonomer is thus critical in defining the shape of the frontier electronic levels and all the resulting properties (such as intrachain charge mobilities) in fluorene-based alternating copolymers.

Figure 5 illustrates the evolution of the energies of the lowest singlet and triplet excited states in F, FBT, and FEDOT as a function of the inverse number of monomer units. The transition energies between the ground state and the lowest singlet excited state decays linearly with inverse chain size in the three systems, although the slope is less pronounced for the FBT chains. This is most likely due to the less efficient interactions between adjacent units in the copolymer, as evidenced by the localization of the LUMO level. The lowest optical transition is mostly described as a HOMO to LUMO transition at the INDO/SCI level (except in the fluorene monomer where the lowest excited state at 4.30 eV is forbidden while the second excited state at 4.36 eV, included in the plot of Fig. 5, is described by a mixing of several configurations). The contribution of additional configurations, however, progressively increases when the chains elongate, as is usually observed with other conjugated oligomers.[34] Linear extrapolation of the transition energies yield at the scale of long conjugated chains transition energies of 2.24, 2.42, and 3.08 eV for FBT, FEDOT, and F
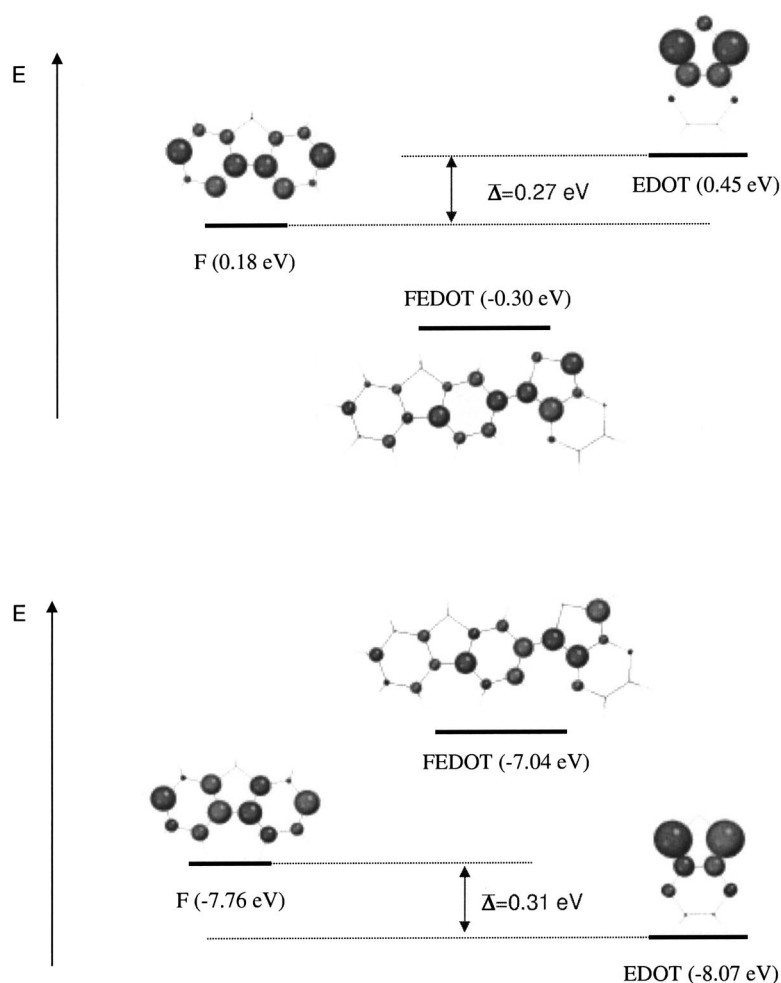
FIG. 4. Energies and shapes of the HOMO (top) and LUMO (bottom) orbitals of fluorene (F), EDOT, and FEDOT, as calculated at the INDO level; the size and color of the circles describe the amplitude and sign of the LCAO coefficients associated to the π-atomic orbitals.

chains, respectively; this is in good agreement with experimental values of 2.65 and 3.25 eV obtained for thin films of FBT and F, respectively;[12] the redshift calculated in going from F to FEDOT is also supported by experimental absorption spectra obtained for statistical fluorene-based copolymers incorporating EDOT units.[35] The small theoretical un-

derestimations can be attributed to the fact that the chains are imposed to be planar, which neglects possible torsions between adjacent units (that would lead to higher transition energies). The results point to a significant bathochromic shift, of about 0.84 eV, when going from F to FBT chains, which is consistent with the change in color of the emitted
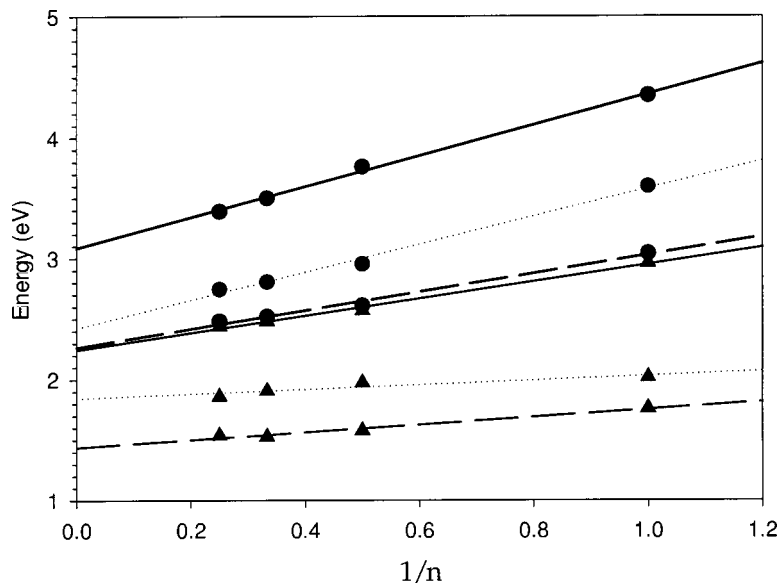

FIG. 5. INDO/SCI-calculated evolution, as a function of the inverse number of monomer units, of the energies of the lowest singlet (circles) and triplet (triangles) states in F (solid lines), FBT (dashed lines), and FEDOT (dotted lines) chains.

light from blue to green;[12] similarly, the introduction of the EDOT units reduces the energy of the lowest optical transition by 0.66 eV.

The evolutions of the energies of the lowest triplet excited state as a function of inverse chain lengths are also linear. The slopes are consistently smaller than for the corresponding singlet excited states; this originates from the strong spatial confinement of the triplet excitons which makes them less sensitive to chain length effects.[36] The description of the triplet excited states is dominated in all cases by a HOMO to LUMO transition. Extrapolation to infinite chains yields triplet energies of 2.27, 1.84, and 1.44 eV for F, FEDOT, and FBT chains, respectively; this is in very good agreement with the value of 2.2–2.3 eV reported recently for polyfluorene chains in solution.[16,37] Interestingly, the exchange energy, defined as the difference between the energies of the lowest singlet and triplet excited states, amounts to 0.8 eV in the F and FBT chains and 0.6 eV in FEDOT chains, thus matching the results usually obtained for a vast series of conjugated polymers.[38]

We have also analyzed the characteristics of the electron–hole pairs in the lowest singlet and triplet excited states of F, FEDOT, and FBT chains. To do so, we have generated from the INDO/SCI results a two-dimensional grid where each point (x_i, y_i) represents the probability $|\psi(x_i, y_i)|^2$ of finding the electron in the π-atomic orbital on site x_i and the hole in the π-atomic orbital on site y_i and vice versa; the brightest regions refer to the highest probabilities.[39] In the F and FEDOT chains, the bright zones are mostly concentrated along the diagonal and are attenuated around the chain ends, as illustrated in Fig. 6 for the tetramer of F; this points to the fact that the electron and the hole are always very close to one another and that this confined exciton explores mostly the central part of the oligomer. The finite width of the bright zones observed along vertical lines reflects that the average separation between the electron and the hole is much smaller than the length of the four-ring oligomer.

The shape of the exciton is drastically different in the FBT copolymer where we calculate a probability of 40% to find the two particles on the BT units, 46% to have one particle on BT and the other on F, and 14% of getting the two particles on the fluorene moieties. This behavior is correlated to the localization of the LUMO wave function on the BT units, leading to an excitonic wave function mostly centered around the BT units, as sketched in Fig. 6(b). The exciton displays similar shapes in the lowest triplet excited state though being more confined, as evidenced by a smaller electron–hole separation on average in F and FEDOT and by a probability of finding the two carriers on the BT units close to 70% in the FBT copolymer.

The choice of the comonomer can also be critical in defining the efficiency of interchain charge- and exciton-transfer processes. Polymer thin films are generally characterized by a large amount of statistical disorder and a broad distribution of effective chain lengths; charge transport there is usually described by a thermally assisted hopping mechanism where charges jump from chain to chain.[40] The rate of charge hopping between two adjacent chains, and thus the

mobility, depends on their electronic coupling, i.e., on the interchain transfer integral t.[41,42] As we have shown earlier, t for holes and electrons can be estimated in good approximation as half the splitting of the HOMO and LUMO levels, respectively, when considering a system made of two interacting chains.[43,44] Since x-ray diffraction studies indicate that polyfluorene chains stack in a staggered way in order to accommodate the long saturated alkyl chains attached to the bridging carbon atoms,[19] we have analyzed the way the interchain transfer integrals t of F and FBT chains are affected by the translation of one chain with respect to the other.

We describe in Fig. 7(a) the evolution of the HOMO and LUMO splittings in systems made of two tetramers of F chains separated by 4 Å, when translating one chain along its main axis up to the length of one repeat unit. We observe strong oscillations in the electronic splittings (varying typically in a range between 0 and 250 meV) as a function of the degree of translation; this reflects the changes in the nature of the interaction between the wave functions of the two adjacent chains when their relative positions are varied.[44,45] The progressive diminution of the splittings calculated at the various maxima is simply due to the reduction in the spatial overlap of the two chains as the translation proceeds; it is expected to attenuate when dealing with long conjugated backbones. Interestingly, despite the fact that the splittings, and hence the expected mobilities, are in general larger for holes than for electrons, the calculations demonstrate that the small shift of one chain can lead to the opposite behavior, as observed in Fig. 7(a) for a translation of about 1 Å. Note that similar pictures prevail for FEDOT and F chains due to the fact that their frontier electronic levels are delocalized. In contrast in FBT [see Fig. 7(b)], while a similar evolution is observed for holes, a markedly different picture is obtained for the electrons. In the latter case, the electronic splittings are significant only when the F and BT units of one chain overlap similar units of the adjacent chain; in contrast, they reach vanishingly small values when a BT unit faces a F unit due to the localization of the LUMO level on the BT units. Thus, a staggered layout of FBT chains might be highly detrimental to the electron transport properties.

The transfer rate of an exciton between two adjacent chains depends on the optical coupling V_{DA} between the initial and final states, according to Förster theory (note that the Förster mechanism is expected to dominate over the Dexter mechanism when the two excited states involved in the transfer are coupled with a strong transition dipole moment to the ground state, as is the case for the lowest singlet excited states of F and FBT chains). In order to overcome the severe limitations inherent to the point-dipole model used in traditional Förster theory (which works well only when the interchain distance is larger than the size of the interacting units[46]), we have calculated here the optical couplings on the basis of atomic transition densities, as described in previous studies:[47–49]

$$V_{da} = \frac{1}{4\pi\epsilon_0} \sum_m \sum_n \frac{q_d(m)q_a(n)}{r_{mn}},$$

where the summations run over all sites $m[n]$ on the donor [acceptor] chain, r_{mn} denotes the distance between m and n,
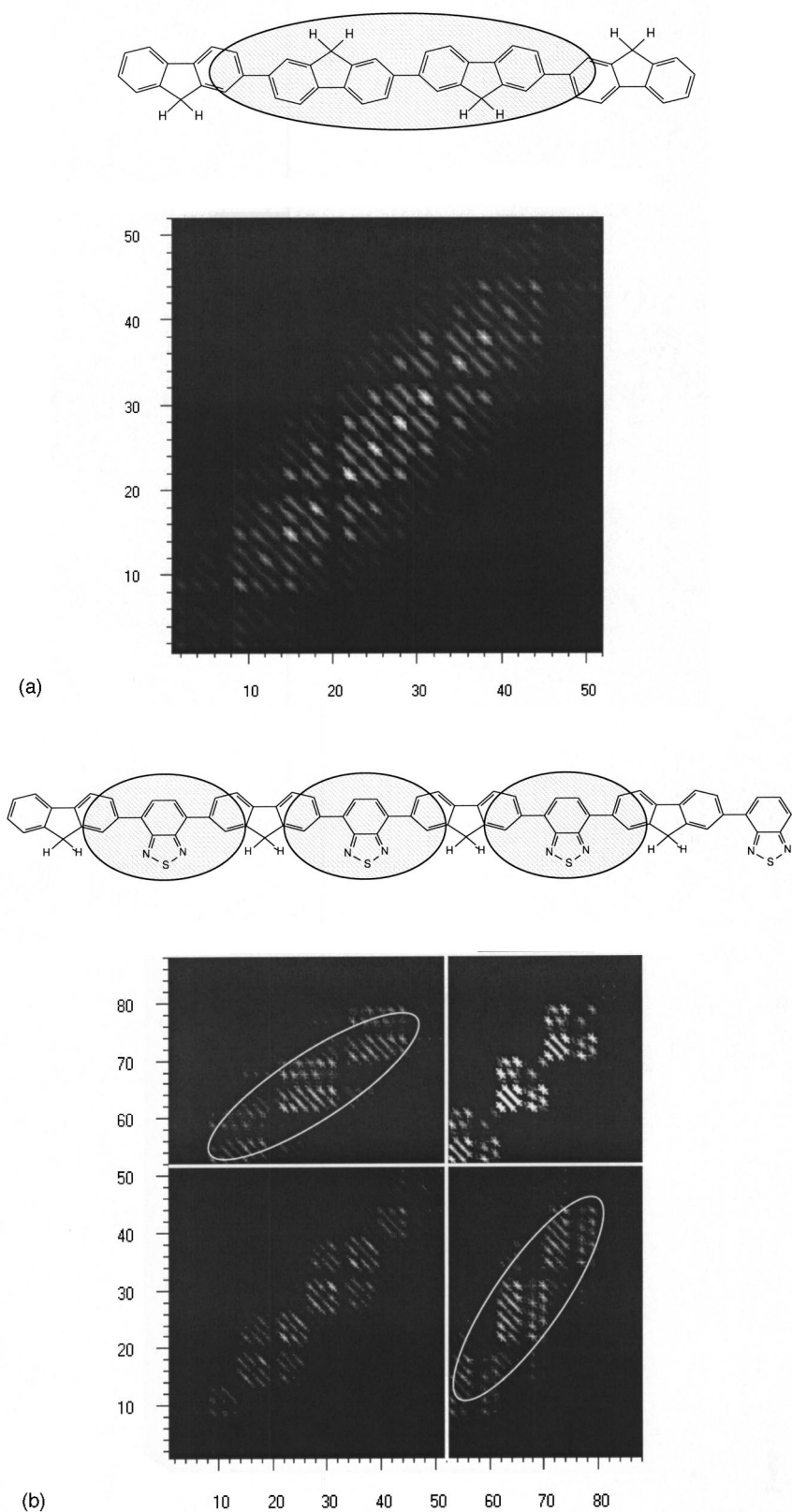
and $q_d(m)$ $[q_a(n)]$ is the INDO/SCI-calculated atomic transition density on site $m[n]$ calculated for the lowest optical transition between the ground state and the lowest excited state.

We report in Fig. 8 the evolution of the optical coupling V_{DA} in systems formed by two parallel trimers of F and FBT

chains, with an interchain distance ranging between 3.5 to 4.5 Å, when one unit is translated along its main axis; the optical couplings typically vary in a range between 0 and 0.2 eV. In the case of polyfluorene chains (or FEDOT chains), the optical splittings, and hence the rate of energy transfer, are found to increase when the interchain distance is lowered
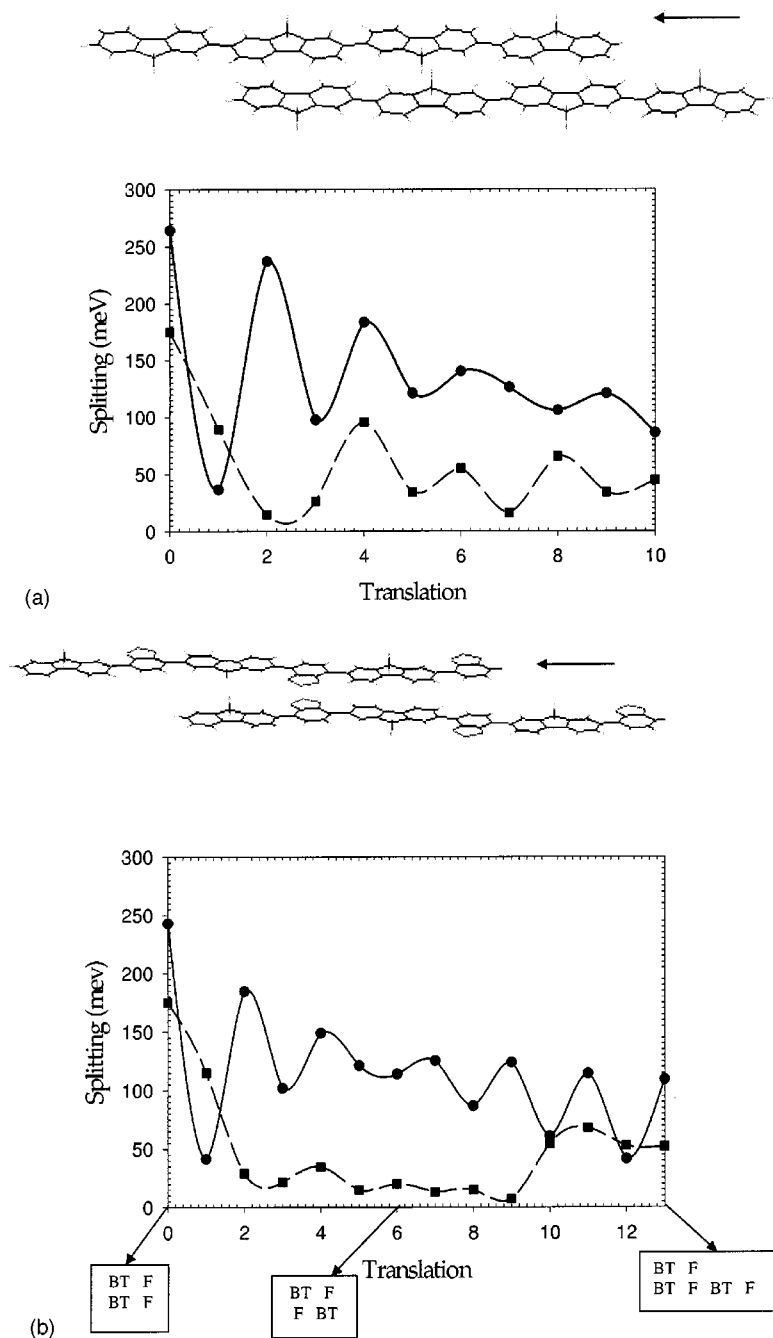
(a)

FIG. 7. INDO-calculated evolution of the electronic splittings of the HOMO (closed circles) and LUMO (closed squares) levels in systems formed by two parallel tetramers of polyfluorene (a) and two parallel trimers of FBT (b), separated by 4 Å, when translating one chain along its main axis up to the length of one repeat unit.

(b)

and decrease when the degree of translation is augmented (again the latter is related to the significant reduction in spatial overlap between the two chains as the translation proceeds and is not expected to occur when considering long chains).

In contrast, the evolution calculated for the FBT chains is characterized by a steep decrease in the optical coupling when the BT units of one chain start facing the F units of the adjacent chain, and hence leads to a minimum along the course of the translation. The different evolutions can be explained by the different shapes of the excitons in the lowest excited states of F and FBT chains, the excitonic wave function in FBT being mostly centered around the BT units. As is the case for charge transport, the efficiency of energy transfer processes (that could be exploited for instance in photo-

diodes and solar cells) can thus be strongly impeded by the localization of the LUMO on the BT units in FBT chains.

IV. SYNOPSIS

We have discussed a detailed analysis of the electronic and optical properties of F, FEDOT, and FBT oligomers. We have shown that the strong localization of the LUMO level in FBT leads to pronounced changes in the shape of the excitons as well as in the efficiency of charge-transport and energy-transfer processes, in comparison to the properties obtained for polyfluorene chains. In contrast, the introduction of EDOT units in a polyfluorene backbone, while shifting the emission to the green as for FBT, keeps good energy and charge transfer properties. Quantum-chemical calculations
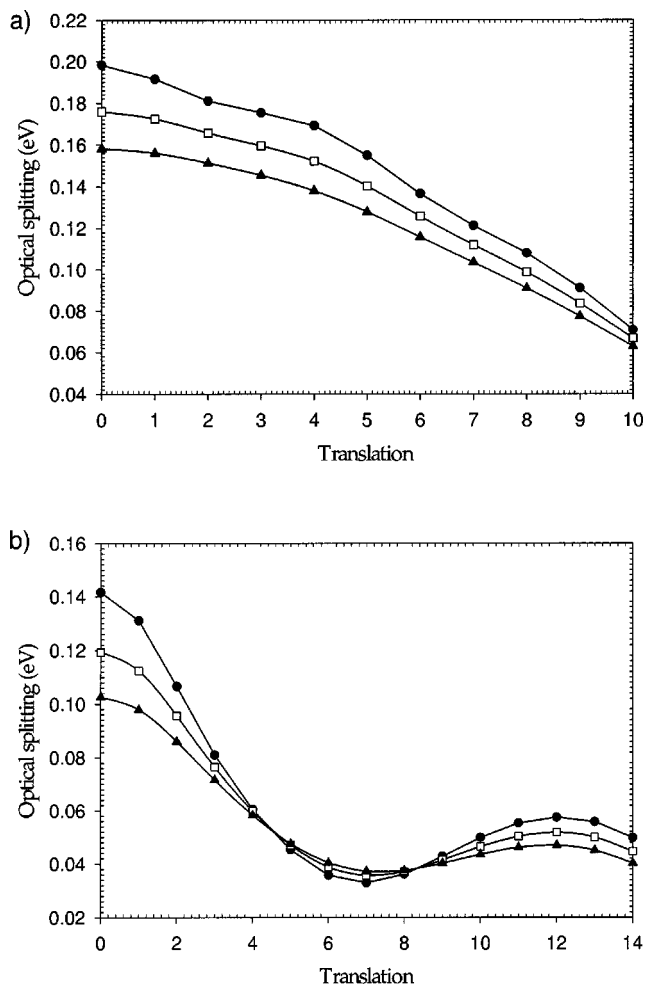
FIG. 8. Evolution of the optical couplings calculated at the INDO/SCI level in systems formed by two parallel trimers of polyfluorene (a) and FBT (b), with the interchain distance fixed at 3.5 Å (closed circles), 4.0 Å (open squares), and 4.5 Å (closed triangles), when translating one chain along its main axis up to the length of one repeat unit.

can thus prove useful to assess the properties of new fluorene-based copolymers prior to chemical synthesis and to design light-emitting polymers with potentially good transport properties.

ACKNOWLEDGMENTS

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