

Intrachain versus Interchain Electron Transport in Poly(fluorene-*alt*-benzothiadiazole): A Quantum-Chemical Insight

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*Poly(9,9-di-n-octylfluorene-*alt*-benzothiadiazole) [F8BT], displays very different charge-transport properties for holes versus electrons when comparing annealed and pristine thin films and transport parallel (intrachain) and perpendicular (interchain) to the polymer axes. The present theoretical contribution focuses on the electron-transport properties of F8BT chains and compares*

the efficiency of intrachain versus interchain transport in the hopping regime. The theoretical results rationalize significantly lowered electron mobility in annealed F8BT thin films and the smaller mobility anisotropy ($\mu_{\parallel}/\mu_{\perp}$) measured for electrons in aligned films (i.e. 5–7 compared to 10–15 for holes).

1. Introduction

Conjugated polymers with regularly alternating electron-donor and electron-acceptor units have attracted significant interest over the last few years. Careful choice of the two building blocks allows the emission properties of the copolymers to be tuned over the whole visible range for applications in light-emitting displays.^[1] Such structures also open the way to design low-bandgap polymers (bandgap < 1.5 eV) which extend the spectral absorption of light in organic solar cells. In this context, a great deal of interest has been devoted to fluorene-based copolymers and in particular to chains incorporating a benzothiadiazole (BT) unit as comonomer. This is the case in the widely studied poly(9,9-di-*n*-octylfluorene-*alt*-benzothiadiazole) [F8BT], which has a dioctyl-substituted fluorene unit as donor and a BT unit as acceptor (see chemical structure in Figure 1); note that a similar copolymer in which the fluorene unit is replaced by two bridged thiophene rings was recently synthesized by Müllen and co-workers.^[2] The charge-transport properties of F8BT chains have been characterized in field-effect transistors,^[3,4] but detailed understanding of the mechanisms of hole versus electron transport is still missing. The optical properties of this polymeric green emitter have

been also investigated,^[5–7] and the performance of F8BT in light-emitting transistors was recently assessed.^[8] The morphology^[9] and electronic properties^[10] of polymer blends incorporating F8BT chains have been investigated in depth.

Recent quantum-chemical calculations of the electronic structure of F8BT oligomers performed at the semi-empirical Hartree–Fock INDO (intermediate neglect of differential overlap) level reveal that the HOMO level is fully delocalized along the polymer backbone due to the relatively small energy gap (ca. 0.65 eV) between the HOMO levels of the two building blocks.^[11,12] In contrast, the LUMO is strongly localized on the BT unit (92% in a F8BT unit, with a torsion angle of 0°) due to the large gap (ca. 1.55 eV) between the LUMO levels of the two comonomer units (see Figure 1). Hole transport in F8BT chains is thus expected to be similar to that typically observed with homopolymer chains: holes can migrate very efficiently along the polymer backbone in the absence of chemical defects and/or strong fluctuations in the torsion angles between adjacent units,^[13] while charge transfer between two chains is the limiting step. The situation is radically different for electron transport due to strong localization of the LUMO level, which suggests a priori that electrons can only hop between BT units of adjacent F8BT chains.

One of the key quantities that determines the efficiency of charge hopping between two sites is the coupling between the electronic levels, also referred to as the transfer integral.^[14,15] This can be estimated—as a first approximation—for

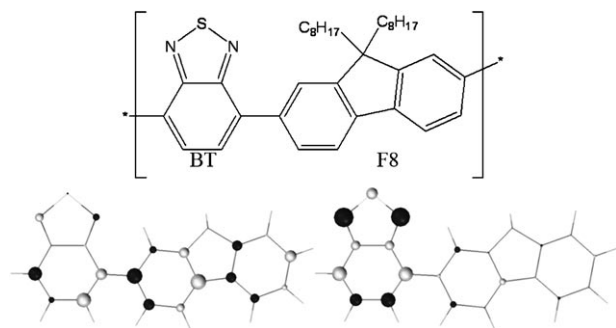


Figure 1. Top: Chemical structure of poly(9,9-di-*n*-octylfluorene-*alt*-benzothiadiazole), F8BT. Bottom: LCAO pattern of the HOMO and LUMO levels of an F8BT unit. The size and color of the balls reflect the amplitude and sign of the LCAO coefficients, respectively.

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hole (electron) transport as half the splitting of the HOMO (LUMO) levels in a neutral dimer made of the two interacting molecules. A large amplitude of the transfer integral translates into a large hopping rate and hence into a high mobility value.^[16] Herein we discuss, on the basis of quantum-chemical results, the relative efficiency of intrachain versus interchain electron transport in F8BT in the hopping regime. The results show that interchain transport strongly depends on the relative position of the interacting BT units. Moreover, despite the large separation between two adjacent BT units on the same chain (ca. 13 Å between the centers of the BT units), the corresponding transfer integral is significant as a result of through-bond coupling via the bridging fluorene units.

2. Interchain Transport

In the case of interchain transport, the transfer integral t between the LUMO levels of two BT units (ϕ_1 and ϕ_2 , respectively) has been directly computed at the INDO level by expanding the molecular orbitals ϕ_1 and ϕ_2 into atomic contributions [Eq. (1)]

$$t = \langle \phi_1 | h | \phi_2 \rangle = \sum_{\mu} \sum_{\nu} C_{1\mu} C_{2\nu} \langle \chi_{\mu} | h | \chi_{\nu} \rangle \quad (1)$$

where $C_{1\mu}$ ($C_{2\nu}$) corresponds to the linear combination of atomic orbitals (LCAO) coefficient of the atomic orbital χ_{μ} (χ_{ν}) in the molecular orbital ϕ_1 (ϕ_2). The matrix element $\langle \chi_{\mu} | h | \chi_{\nu} \rangle$ is implemented in the INDO method using Equation (2)

$$\langle \chi_{\mu} | h | \chi_{\nu} \rangle = \frac{1}{2} (\beta_A + \beta_B) \bar{S}_{\mu\nu} \quad (2)$$

where β_A and β_B are two parameters depending on the chemical nature of atoms A and B, and $\bar{S}_{\mu\nu}$ is the overlap factor between the atomic orbitals χ_{μ} and χ_{ν} corrected by empirical factors.^[17] The choice of INDO is motivated by the fact that this approach is, in our experience, the best compromise between accuracy and computing time when dealing with the electronic properties of organic conjugated materials.^[14,18] INDO generally yields transfer integrals in good quantitative agreement with results provided by ab initio Hartree–Fock and DFT calculations.^[19,20]

We first calculated the transfer integral for electrons between two BT units and between two F8BT units in a cofacial geometry, in which they are exactly superimposed; the octyl chains are replaced by hydrogen atoms, and the intermolecular separation is fixed to the shortest possible distance of 4.2 Å. Note that all geometries are optimized with the semi-empirical Hartree–Fock Austin Model 1 (AM1) method.^[21] The values obtained for BT (395 cm⁻¹) and F8BT

(415 cm⁻¹) are very similar, that is, the transfer integral for electrons is governed by the BT unit, as expected from the localization pattern of the LUMO level. In contrast, the values obtained for holes when comparing two F8 and two F8BT units (863 vs 714 cm⁻¹) are marginally different as a result of delocalization of the HOMO level over the conjugated backbone. This motivated us to calculate the interchain transfer integrals for electrons exclusively between isolated BT units.

The molecular packing of F8BT chains is not yet fully resolved at the atomic level. X-ray diffraction data only point to a periodicity of four polymer chains along the π -stacking direction.^[3] Accordingly, we calculated the interchain transfer integral for a large number of geometric configurations, assuming that the BT units of adjacent chains lie in parallel molecular planes, separated by a typical intermolecular distance of 4 Å. We considered dimers in which the BT units point in the same direction (SYN) and in opposite directions (ANTI). The spatial evolution of the electronic coupling was analyzed by mapping the transfer integrals over a grid obtained by translating one BT unit by up to 2 Å along the x-axis and by up to 6 Å along the y-axis (see Figure 2). Such degrees of translation typically match the size of one BT unit. Sixty-five data points were generated for the ANTI dimers but only 35 data points for SYN dimers, since positive and negative translations along the y-axis are equivalent for the SYN dimers, in contrast to the ANTI dimers.

Analysis of the two maps demonstrates that the largest electronic couplings (up to 600 cm⁻¹) are obtained for the SYN structures with relatively small x and y displacements. The transfer integrals reach vanishingly small values when a spatial overlap is not preserved between the two BT units. This is consistent with measurements showing that electron transport is reduced on annealing of F8BT thin film or when low molecular weight polymer is used, which both lead to an apparent alternating structure of the BT units in neighboring chains (Figure 3).^[3] Calculations on a BT dimer on the basis of the alternating structure lead to an electronic coupling for non-overlapping BT units as small as 0.9 cm⁻¹ (see Configuration 1 in Figure 3). Interestingly, the same coupling is increased by up to 40 cm⁻¹ for the same configuration when transfer is mediated via the F8 units. This demonstrates that the small delocali-

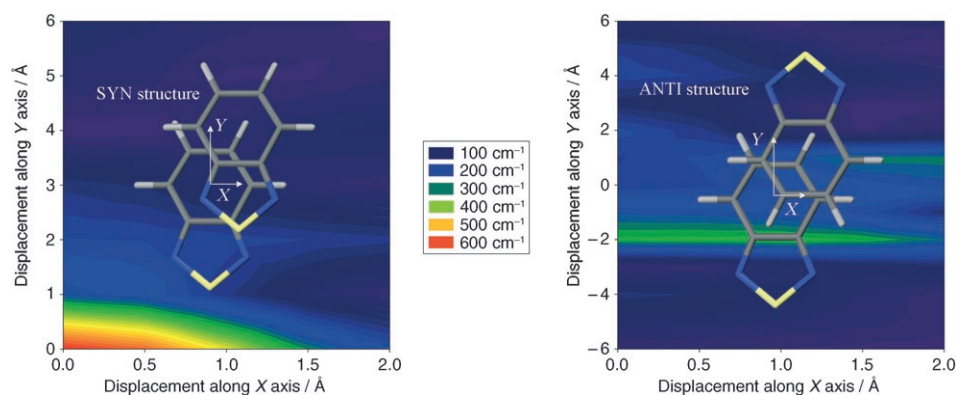


Figure 2. Evolution of the electronic coupling (in cm⁻¹) as a function of the relative position of the BT units in SYN (left) and ANTI (right) dimers. The y-axis corresponds to the long axis of BT; the origin (0,0) refers to a structure in which the geometric centers of the two BT units are perfectly superimposed.

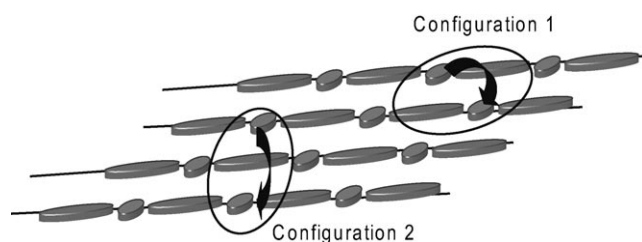


Figure 3. Illustration of the proposed packing structure for low molecular weight F8BT chains or for annealed F8BT thin films. We also show two possible paths for interchain electron transfer considered in our calculations.

zation of the LUMO on the fluorene units helps to establish better communication between BT units of adjacent chains in an alternating configuration. Note, however, that the transfer rate in this geometry remains much smaller than those obtained for quasicofacial geometries owing to the square dependence of the transfer rate with respect to the transfer integral.^[14] Similarly, the smallest transfer integrals reported in Figure 2 are also slightly increased when the role of the F8 units is taken into account. The results further show that interchain transfer between two BT units separated by an intermediate fluorene unit (see Configuration 2 in Figure 3, in which the geometric centers of the three molecules are exactly superimposed) yields a coupling of only 4 cm^{-1} , which suggests that this pathway is very inefficient (note that the corresponding value is increased to 4.5 cm^{-1} when a three-state model is considered; see below). The transfer integrals computed within the widely used Koopmans formalism as half the splitting of the LUMO levels (as was done in a previous study)^[11] are generally significantly larger than the present values. This is explained by the fact that the permanent dipole moment of the BT units leads to an offset in the energies of the LUMO level prior to their interaction in asymmetric dimers.^[22] These electrostatic effects do not assist charge-transfer processes and should thus be subtracted to provide reliable values for the transfer integrals, as is automatically done in our approach calculating the direct coupling between two units.

3. Intrachain Transport

We first calculated the transfer integral for electrons between two BT units connected by a fluorene moiety, considering all possible relative orientations of the two BT units and the coplanarity of the entire system (see Table 1). In the three cases, the transfer integral is as large as the highest values found for interchain transport (ca. 500 cm^{-1}) and is weakly affected by the relative orientations of the BT units. Note that the approach based on the direct evaluation of the transfer integral is not applicable when the two BT units are covalently bound. We thus calculated the transfer integrals here as half the splitting of the LUMO levels in the entire BT–F8–BT system; the impact of the permanent dipoles is expected to be weak due to the high symmetry of the system and the large separation between BT units. This approach has been validated for systems in which a saturated spacer connects two conjugated moieties.^[23,24] However, the need for a three-state model

Table 1. INDO-calculated electronic coupling for electron transfer in a fully planar BT–F8–BT system with different relative orientations of the BT units.

System	Electronic coupling [cm^{-1}]
	517
	525
	492

should be considered for conjugated bridges due to the strong decrease in the energy difference between the frontier orbitals of the donor/acceptor (BT) units and of the bridge (F8). To validate the use of the splitting approach, we also computed the electronic coupling for a fully planar BT–F8–BT system in a three-state model by feeding the results of our INDO calculations into the expression recently introduced by Voityuk [Eq. (3)]^[25]

$$t = \left| \frac{(E_2 - E_1)}{2} \right| (Q_{d1} + Q_{d2}) + \left[E_3 - \frac{(E_2 - E_1)}{2} \right] (Q_{d1} - Q_{d2}) \quad (3)$$

where E_1 and E_2 are the energies of the lowest two unoccupied orbitals mostly localized on the BT units, and E_3 is the energy of the lowest unoccupied orbital mostly localized on the bridging F8 unit; note that the large energy difference between the lowest two unoccupied levels of F8 (0.7 eV) does not require the use of a four-state model; Q_{d1} and Q_{d2} are the charges on the BT units in the electronic levels E_1 and E_2 , respectively (Q_{d1} and Q_{d2} are equal to 0.44 and 0.48 $|e|$, respectively, in the present case). In so doing, we obtain a value of 527 cm^{-1} for the first system reported in Table 1 instead of 517 cm^{-1} from the splitting approach, that is, the correction introduced by a three-state model is negligible.

The rate of charge hopping between two adjacent BT units can be estimated to a good approximation by using semi-classical Marcus theory [Eq. (4)]^[26]

$$k_{\text{hop}} = \frac{2\pi}{\hbar} t^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp \left[-\frac{\lambda}{4k_B T} \right] \quad (4)$$

where λ is the total reorganization energy, which consists of two contributions, namely, an internal component λ_i that reflects the changes in the geometry of the two BT units during the electron-transfer reaction ($\text{BT}_1^- + \text{BT}_2 \rightarrow \text{BT}_1 + \text{BT}_2^-$), and an external component λ_s that describes the changes in the nuclear reorganization of the surrounding medium during the transfer. The λ_i value can be estimated as the sum of the energies required to promote 1) the initially charged molecule from its equilibrium geometry to that characteristic of the neu-

tral molecule; and 2) the initially neutral molecule from its equilibrium geometry to that characteristic of the radical ion. This has been done here at the DFT level with B3LYP functional and 6-31G** basis set. This approach is known to provide theoretical values in good quantitative agreement with corresponding experimental values extracted from gas-phase ultraviolet photoelectron spectroscopy (UPS) measurements.^[27] These calculations lead to a λ_i value of 0.31 eV for electron transfer between BT units. It is much less straightforward to estimate λ_s , since simple analytical expressions are only available for electron-transfer reactions in isotropic media. We consider here λ_s as a tunable parameter varying in a realistic range extending from 0.2 to 0.4 eV.^[28] By inserting the values of t , λ_i , and λ_s into Equation (3), we obtain hopping rates of $2.2 \times 10^{12} \text{ s}^{-1}$ for $\lambda_s = 0.2 \text{ eV}$ and $2.5 \times 10^{11} \text{ s}^{-1}$ for $\lambda_s = 0.4 \text{ eV}$. The corresponding intrachain mobility in the diffusive regime, which is accessible experimentally for isolated chains in solution via the pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) technique,^[29] can be estimated as Equation (5)

$$\mu = \frac{ea^2}{k_B T} k_{\text{hop}} \quad (5)$$

where k_B is the Boltzmann constant and a the separation between two BT units (12.6 Å). Equation (5) leads to electron mobilities of $1.32 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\lambda_s = 0.2 \text{ eV}$ and $0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\lambda_s = 0.4 \text{ eV}$, which are in the typical range expected for charge transport in the hopping regime.^[16]

We also analyzed the influence of the torsion angle between the F8 and BT units on the transfer integral by considering BT–F8–BT systems in which the two torsion angles vary from 0 to 50° (the latter corresponds to the angle predicted for a gas-phase geometry optimization at the AM1 level); see Figure 4. The results show that the transfer integral evolves as a square-cosine function of the torsion angle, as expected. Note also that these values are weakly affected by the actual direction of rotation applied for each torsion angle. This demonstrates that the amplitude of the transfer integral is primarily governed by the degree of overlap between the p_z atomic orbitals of the carbon atoms forming the bond connecting the BT and F8 units rather than by the relative orientation of the BT units.

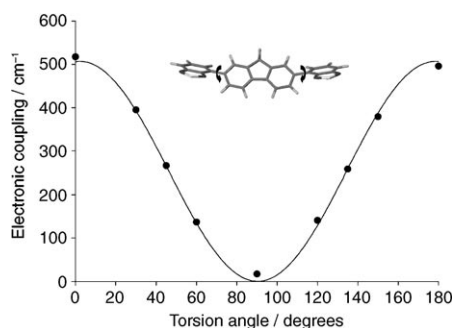


Figure 4. Evolution of the electronic coupling in the BT–F8–BT systems as a function of the torsion angle between F8 and BT units, obtained in the rigid rotor approximation, that is, without reoptimizing the geometry for each torsion angle. The solid line shows a fit of the results to a square-cosine function.

To assess the role of the intermediate F8 unit in assisting electron transfer between BT units, we calculated the transfer integral in fully planar BT–(F8)_n–BT systems in which the two BT units are bridged by different numbers of F8 units, as well as in corresponding systems in which the F8 bridge has been removed and the BT units are terminated by hydrogen atoms. Figure 5 shows that the transfer integrals are virtually zero in

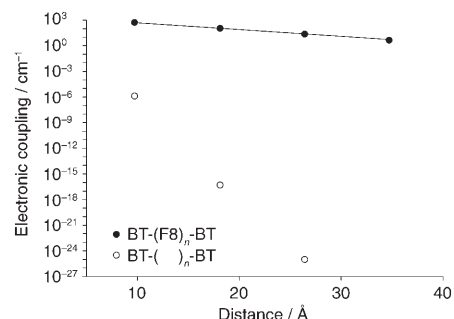


Figure 5. Evolution of the electronic coupling between BT units as a function of the number of bridging F8 units. The x-axis indicates the center-to-center distance between the BT units. The curve with open symbols corresponds to the results obtained without F8 bridge.

the absence of the F8 units (less than 10^{-5} cm^{-1}). In contrast, we observe a dramatic enhancement of the transfer integral as soon as F8 units are introduced between the BT units. The results provided by the splitting approach are once again weakly affected in absolute value when considering a three-state model (see Table 2). This demonstrates that electron transfer between BT units relies on a “through-bond” process, which implies that the lowest unoccupied π orbitals of the fluorene units assist the transfer and enhance its rate by allowing for a small delocalization of the LUMO of BT over the F8 bridge (in the F8BT monomer unit, the weight of the LUMO level on the F8 part is only 8%).^[30] This phenomenon has been well-established through many theoretical and experimental studies probing the rate of electron transfer between donor and acceptor units connected by a saturated or conjugated bridge.^[31,32] However, its high relevance for charge transport processes in conjugated copolymers has rarely been discussed so far. Note that the coupling at 90° is not strictly equal to 0 in Figure 4, since coupling between the BT units is then possible via the σ orbitals of the F8 unit. The transfer integral between the BT units decreases exponentially with increasing number of intervening F8 units [Eq. (6)]

$$t = t_0 \exp(-\beta d) \quad (6)$$

Table 2. Electronic coupling between BT units as a function of the number of bridging F8 units in BT–(F8)_n–BT systems, as provided by two- and three-state approaches.

n	Electronic coupling [cm^{-1}]	
	Two-state	Three-state
1	517	527
2	112	157
3	23	43
4	4	11
5	0	2

where β is the decay factor, estimated to be 0.19 \AA^{-1} for the fully planar systems. This value compares very well with experimentally estimated β values ($0.04 - 0.40 \text{ \AA}^{-1}$ for conjugated hydrocarbon bridges).^[33]

4. Conclusions

We have described at the quantum-chemical level electron transport in F8BT chains as a succession of hopping events between BT units (due to strong localization of the LUMO level on the BT units). The electronic coupling associated with interchain transport strongly depends on the relative positions of the BT units; the largest values are found for quasicofacial structures with the two BT units pointing in the same direction. Interchain transport for F8BT chains in an alternate configuration is much less efficient although it is assisted by slight delocalization of the LUMO level over the fluorene units. In spite of the large separation between adjacent BT units along the conjugated backbone (ca. 13 \AA), the electronic couplings for intrachain electron transport are as large as the highest values found for interchain transport. This is rationalized by a well-documented through-bond coupling phenomenon, which implies that the unoccupied orbitals of the fluorene units assist the electron-transfer process. In contrast, the strong delocalization of the HOMO level over the conjugated backbone suggests that hole transport is very efficient along the backbone and that the limiting step is driven by interchain transfer processes. These results are consistent with recent mobility measurements on aligned F8BT thin films showing that the mobility anisotropy ($\mu_{\parallel}/\mu_{\perp}$) is larger for holes (10–15) than for electrons (5–7).^[4] When F8BT chains are aligned along the transport direction in field-effect transistors, hole transport along the conjugated polymer backbone is significantly faster than interchain hopping between adjacent chains, and a high mobility anisotropy results. In contrast, intrachain electron transport in F8BT is not a very efficient process due to the high-energy barrier introduced by the F8 sites sandwiched between the BT sites, and this rationalizes the smaller anisotropy for electron mobility. It would be of great interest to estimate the actual intrachain versus interchain electron mobilities in F8BT thin films by plugging the calculated Marcus rates into Monte-Carlo simulations^[16] taking the energetic disorder likely to be introduced by the local dipoles supported by the BT units into account explicitly. However, in view of the high sensitivity of the transfer integrals to the relative positions of the BT units, this requires a deep knowledge of the exact packing structure of F8BT chains, which is missing at present.

Acknowledgements

The work in Mons is partly supported by the Belgian Federal Government "Interuniversity Attraction Pole in Supramolecular Chemistry and Catalysis, PAI 5/3"; the European Integrated Project NAIMO (NMP4-CT-2004-500355); and the Belgian National Fund for Scientific Research (FNRS/FRFC). J.C. is an FNRS Research Fellow; A.V.V. acknowledges a grant from "Fonds pour la Forma-

tion à la Recherche dans l'Industrie et dans l'Agriculture (FRIA)". J.S.K. thanks the EPSRC for an Advanced Research Fellowship.

Keywords: electron transfer • electron transport • polymers • quantum chemistry • thin films

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Received: December 19, 2007

Revised: January 10, 2008

Published online on April 3, 2008