Effect of an external electric field on the charge transport parameters in organic molecular semiconductors

4 AUTHORS, INCLUDING:

Juan Sancho Garcia
University of Alicante
83 PUBLICATIONS   1,217 CITATIONS

Gilles Horowitz
French National Centre for Scientific Research
235 PUBLICATIONS   11,032 CITATIONS

Jérôme Cornil
Université de Mons
291 PUBLICATIONS   15,333 CITATIONS

Effect of an external electric field on the charge transport parameters in organic molecular semiconductors

J. C. Sancho-García

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

G. Horowitz

ITODYS, CNRS, University Denis-Diderot (Paris 7), 1, Rue Guy-de-la-Brosse, F-75005 Paris, France

J. L. Brédas[a)]

Department of Chemistry, The University of Arizona, Tucson, Arizona 85721-0041 and 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

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 and Department of Chemistry, The University of Arizona, Tucson, Arizona 85721-0041

Internal reorganization energies and interchain transfer integrals are two key parameters governing the charge-transport properties of organic semiconducting materials. Here, in order to model some aspects of device operation in field-effect transistors based on conjugated oligomers, we investigate via semiempirical quantum-chemical calculations the way these two parameters are modified when a static electric field in the range $10^6 - 10^8$ V/cm is applied along the long axis of pentacene and sexithienyl molecules. For the highest fields, a pronounced redistribution of the charges along the oligomer chains occurs, which is accompanied by significant geometric distortions. However, these charge redistribution effects are found not to impact significantly the transport parameters. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1625918]

I. INTRODUCTION

Field-effect transistors based on organic semiconductors (OFETs) are currently attracting tremendous interest[1–9] since such devices are envisioned in a wide range of applications where low cost is of primary importance. Materials used in OFETs can be divided into two classes: polymers and small oligomers. Up to now, the best performances have been achieved with conjugated oligomers, in particular oligothiophenes and oligoacenes. These compounds have the same crystalline structures, made of stacked layers wherein molecules pack in a herringbone fashion with their long axes parallel to one another. Such a lamellar structure gives rise to highly anisotropic charge transport at room temperature: charge mobility is much higher within the layers than across them. This feature confers to these materials a two-dimensional character with regard to transport.

A field-effect transistor, see Fig. 1, consists of a semiconducting thin film contacted by two parallel planar electrodes, the source and the drain. A third electrode, the gate, separated from the semiconductor film by an insulating layer, induces a conducting channel within the semiconductor, the channel conductivity being modulated by the gate voltage. In this structure, current from source to drain flows parallel to the film; due to the two-dimensional character of transport

described above, the highest mobilities are generally obtained when the molecules orient perpendicularly to the insulator–semiconductor interface.

Two issues should be highlighted. First, the depth of the conducting channel is very limited. This can be estimated by resolving Poisson's equation at the insulator–semiconductor interface; it leads to an effective thickness of typically one or two molecular layers. In conventional semiconductors, the three-dimensional character of charge transport is preserved over such a narrow channel, so that only minor corrections have to be brought to the isotropic charge transport model. In contrast, since a conducting channel made of molecules lying perpendicular to the substrate is highly anisotropic, a theoretical description of the charge distribution in the channel cannot be performed using an effective medium approximation, where the semiconductor film is treated as an uniform material. More reliable approaches require the combination of conventional electrostatics and quantum mechanics to describe the charge distribution within the molecule. The second important issue is related to the geometry of the device. Since the distance between source and drain is much larger than the thickness of the insulator, the electric field felt by the molecules is dominated by that developed by the gate voltage, which is transverse to the conducting channel, over that generated by the drain voltage, parallel to the channel. As a consequence, the charge carriers are submitted to a strong electric field perpendicular to the drift direction within
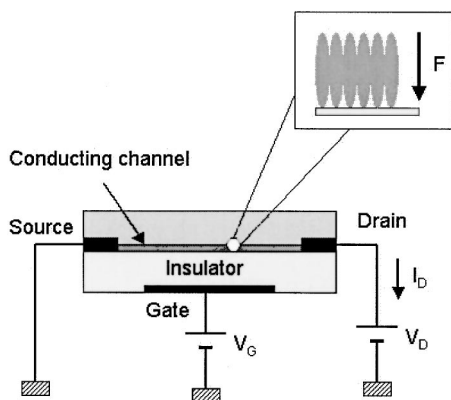
FIG. 1. Architecture of a typical organic field-effect transistor.

FIG. 3. Illustration of the potential energy curves of an organic semiconductor in its ground state (GS) and singly charged state (+1); the reorganization energy components are indicated in the presence (λ_1'' and λ_2'') or absence (λ_1 and λ_2) of the static electric field F (see text for detail). The thick horizon bars represent the distorted geometries in the presence of the electric field.

the channel and parallel to the oligomer long axes.

The main goal of this contribution is to investigate the way key parameters controlling transport at the molecular level are affected upon application of gate voltage. We focus here on the pentacene and sexithienyl oligomers (see chemical structures in Fig. 2) and describe their hole transport properties (we note that the intrinsic electron transport characteristics are often difficult to measure in conjugated materials due to extrinsic effects, such as oxygen trapping[4]).

This paper is organized as follows: Sec. II describes the nature of the two main parameters controlling transport at the molecular scale in organic thin films. Section III presents the theoretical approach we use to compute them. We discuss in Sec. IV the impact of the applied static electric field on these two parameters.

II. CHARGE TRANSPORT PARAMETERS

In the thin films used in OFET devices, it is expected that charge transport takes place in the hopping regime: localized charge carriers jump from one chain to the next, the latter being initially in the neutral state and the former in the ionized state. From a chemical standpoint, this can be described as a self-exchange electron-transfer reaction:

$$M_1 + M_2^+ \xrightarrow{k^{ET}} M_1^+ + M_2 \tag{1}$$

and the corresponding charge-transfer rate can be estimated to first approximation[10] from semiclassical Marcus theory[11] as

$$k^{ET} = \frac{4\pi^2}{h} \frac{1}{\sqrt{4\pi\lambda k_B T}} t^2 e^{-\lambda/4k_B T}, \tag{2}$$

where λ is the reorganization energy and t is the electronic coupling between adjacent chains (interchain transfer integral); T denotes the temperature, and h and k_B are fundamental constants.
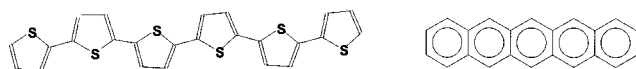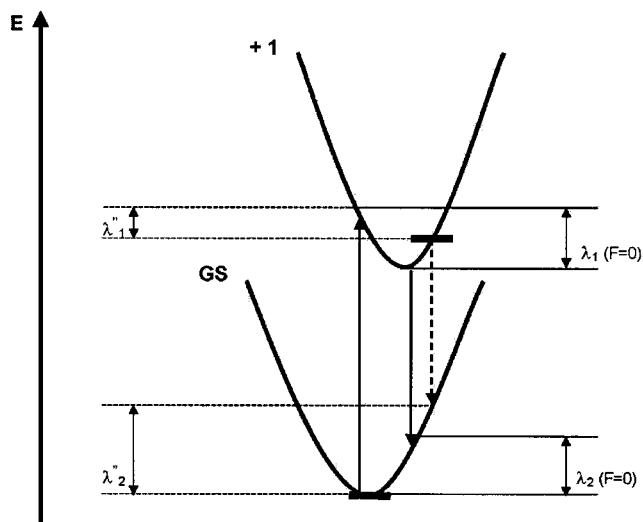

FIG. 2. Chemical structure of sexithienyl (left) and pentacene (right).

The reorganization energy includes two contributions associated to the charge hopping;[12] one arises from the geometric changes within the molecules (internal part, λ_i) while the other relates to the polarization changes of the surrounding medium (external part, λ_e). The changes in geometry and charge distribution induced by the application of the gate electric field are expected to modify mainly the transfer integral and the internal part of the reorganization energy, on which we focus below. Note that, in addition to λ_e, we also neglect at this stage the source–drain potential that forces the charges to drift along the channel by creating an electric field parallel to the hopping direction (this would require the introduction of a free energy term in the transfer rate[13,14]).

The internal reorganization energy λ_i can be split into two (nearly equivalent) contributions, λ_1 and λ_2, which can be estimated from a set of four energy values, as sketched in Fig. 3,[15]

$$\lambda_1 = E_{M_2^+//M_1} - E_{M_2^+}, \tag{3}$$

$$\lambda_2 = E_{M_1//M_2^+} - E_{M_1}. \tag{4}$$

In these equations, E_{M_1} and $E_{M_2^+}$ are the energies of the neutral molecule and radical-cation in their equilibrium structure, respectively, while $E_{M_2^+//M_1}$ is the energy of the radical-cation frozen in the neutral geometry, and $E_{M_1//M_2^+}$ is the energy of the neutral molecule adopting the radical-cation geometry. The internal reorganization energy reflects the price to be paid to accommodate the geometric distortions accompanying charge hopping. It is clear that materials displaying small reorganization energies are highly desirable[16–19] to promote good transport properties. On the other hand, the transfer integrals t reflect the strength of the electronic interactions between adjacent chains and should be maximized to ensure high charge mobilities.

III. COMPUTATIONAL APPROACH

Our goal is to examine the evolution of λ_i and t as a function of an external electric field applied along the long axes of pentacene and sexithienyl chains. This electric field is meant to simulate that due to gate voltage. We have varied the amplitude of the applied electric field between $10^6 - 10^8$ V/cm.

To a good approximation, the electric field F_s at the semiconductor–insulator interface is given by $\epsilon_s F_s = \epsilon_i F_i$.[20] Here, F_i is the (uniform) electric field in the insulator; ϵ_s and ϵ_i are the permittivities of the semiconductor and insulator, respectively. The equation can also be written as $F_s = F_i(k_i/k_s)$, where k_s and k_i are the dielectric constants. The dielectric constant of most organic semiconductors ranges between 2 and 4. Thus, the upper electric field at the semiconductor–interface is limited to the breakdown field (also called dielectric strength) of the insulator. Typical values for the latter do not exceed 10^7 V/cm.[21] However, the upper value of F_s can be raised by at least one order of magnitude by using high k insulators, such as titanates, which can have dielectric constants above 100.

The reorganization energies, with and without field, have been calculated with the semiempirical Hartree–Fock Austin Model 1 (AM1) (Ref. 22) method, as implemented in the MOPAC (Ref. 23) package; AM1 has been parameterized to reproduce the ground-state geometry of organic molecules and it is our experience that it also provides accurate cationic geometries in π-conjugated molecules. In all cases, the geometries of the neutral and singly charged systems [treated within the restricted open-shell (ROHF) formalism] have been kept coplanar since this is the conformation expected in the solid state. At this stage, it is useful to note the following: (i) we have chosen not to use a DFT-based (density functional theory) approach due to the known limitations of DFT calculations dealing with charge delocalization in charged conjugated systems;[24–26] and (ii) we are interested in the qualitative evolution of λ_i as a function of applied external field rather than its absolute value.

The transfer integrals t have been estimated on the basis of the semiempirical Hartree–Fock intermediate neglect of differential overlap (INDO) method,[27] as implemented in ZINDO. This technique has been used successfully over the past few years to determine the electronic properties of conjugated systems and the impact of interchain interactions.[28,29] In previous studies,[30] we have evaluated the transfer integrals for holes as half the splitting of the HOMO energy level when going from an isolated chain to an interacting dimer made of two molecules in their ground-state geometry. However, such an approach cannot account for the geometric deformations induced by the application of the electric field. Therefore, here, we have computed the transfer integrals as half the splitting of the HOMO levels at the transition state for hole-transfer reaction; the geometry of this transition state is built by imposing to each chain bond lengths that are the average between the AM1 values calculated for the neutral and singly-charged states.

TABLE I. Evolution of the internal reorganization energy, λ_i (meV), as a function of the amplitude of the electric field (in V/cm), as calculated at the AM1 level.

	Pentacene	Sexithienyl
0	233	510
10^6	233	510
5.10^6	233	510
10^7	233	510
5.10^7	227	507
10^8	215	494

IV. RESULTS AND DISCUSSION

The evolution of the AM1-calculated reorganization energy as a function of the applied electric field is reported in Table I for pentacene and sexithienyl. *A priori*, the charge confinement induced by the electric field is expected to impact significantly the value of the internal reorganization energy, especially in the high-field regime. Actually, the λ_i values are found to be hardly affected; they change by less than 1 meV in the $10^6 - 10^7$ V/cm field range and decrease by only a few meV for the highest fields considered in our work. The origin of such a negligible influence will be discussed below.

We display in Fig. 4 the evolution of the AM1-calculated net charge per ring as a function of the amplitude of the applied electric field for singly-charged pentacene and sexithienyl molecules. No significant charge displacement is observed until a field of 10^8 V/cm is applied; at this stage, a charge transfer is observed between the two halves of the molecules and leads to the migration of positive charges towards the extremity of the molecule close to the negative pole of the field. According to the AM1 calculations, the charge transfer induced by the field is larger in sexithienyl than in pentacene ($0.39|e|$ flowing from one half of the molecule to the other half, vs $0.13|e|$, respectively, at a field of 10^8 V/cm). This feature can be attributed to the higher polarizability of sexithienyl compared to pentacene; AM1 calculations give static longitudinal polarizability components of 126.1 and 77.6×10^{-24} esu, respectively. A small charge migration is also induced in the neutral state upon application of intense electric fields, see Fig. 4.

Since the introduction of charges leads to geometry relaxations along the conjugated backbone (as a result of the strong electron-vibration coupling characteristic of conjugated materials[31]), we have analyzed the way the geometry of the singly charged molecules is altered under the influence of the electric field. To do so, we consider as the most relevant parameter the field evolution of the degree of bond-length alternation (BLA) along the backbone; it is defined at site i as the difference between the lengths of the $(i, i+1)$ and $(i, i-1)$ C–C bonds. The BLA pattern in the neutral pentacene molecule is on the order of 0.075 Å at the ends and keeps decreasing towards the middle of the molecule where it vanishes, see Fig. 5. Going to the singly-charged state leads to a marked equalization of the C–C bond lengths over the whole molecule. The BLA pattern of the charged state is hardly affected upon application of a field of 10^7 V/cm, which is consistent with the absence of any significant charge transfer. In contrast, a nonsymmetrical C–C
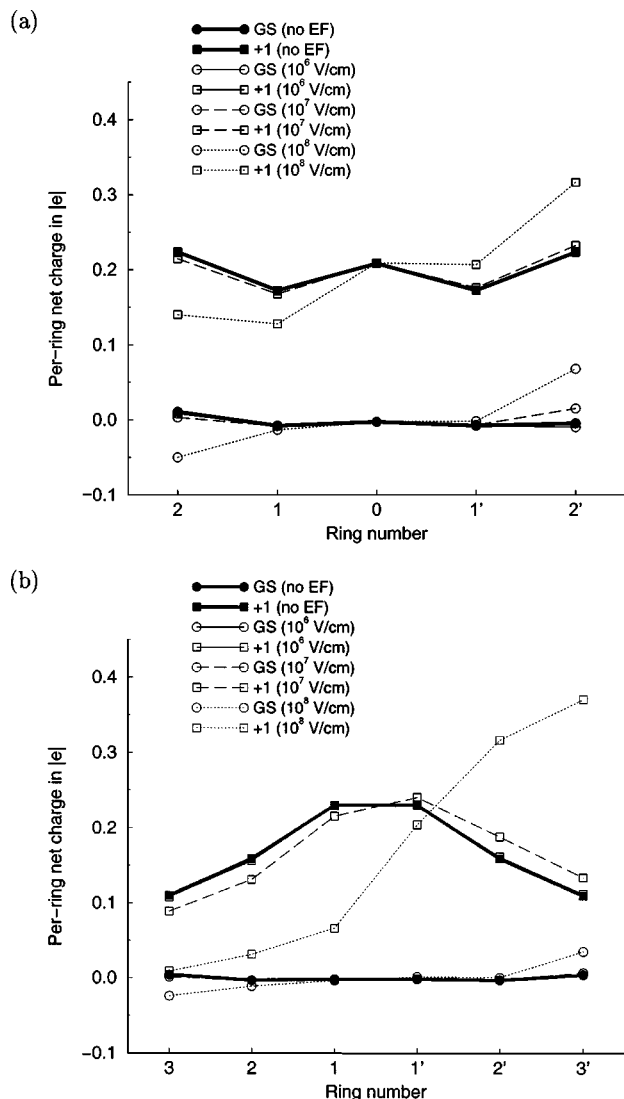
(a)

(b)

FIG. 4. AM1-calculated evolution of the net charge per ring in neutral [ground state (GS)] and singly-charged (+1 state) pentacene (a) and sexithienyl (b) under the influence of a longitudinal electric field of increasing amplitude. The charges have been obtained by a Mulliken population analysis.

FIG. 5. Evolution, with site position i, of the C–C bond-length alternation (BLA, in Å) in pentacene, as calculated at the AM1 level (see chemical structure on top for site labels).

the induced dipole moment and a destabilizing effect by distorting the geometry away from the equilibrium structure of the cation. We now discuss the way these two effects impact the amplitude of the two reorganization energy components, λ_1 and λ_2, in order to rationalize the evolution of λ_i as a function of applied electric field. We restrict the following discussion to sexithienyl since the same trends are obtained for pentacene.

Table II collects the values of the two components, referred to as λ_1' and λ_2', obtained upon application of the

bond-length alternation pattern appears at a field of 10^8 V/cm; this confirms the strong connections between geometric distortion and charge-transfer upon application of an external electric field.

Figure 6 displays the electric field evolution of the BLA pattern calculated along the backbone of the sexithienyl molecule. When compared to the neutral state in the absence of an external electric field, the BLA pattern of the singly charged system shows the appearance of a quinoid character in the central rings of the oligomer. At 10^8 V/cm, the BLA pattern in the left-hand side of the radical-cation matches exactly the one obtained for the neutral molecule; this confirms that the positive charge has completely transferred to the right side of the chain. An intermediate situation is observed when a field of 10^7 V/cm is applied.

The application of an electric field has two opposite effects on the total energy of the cation: a stabilization effect resulting from the interaction between the electric field and
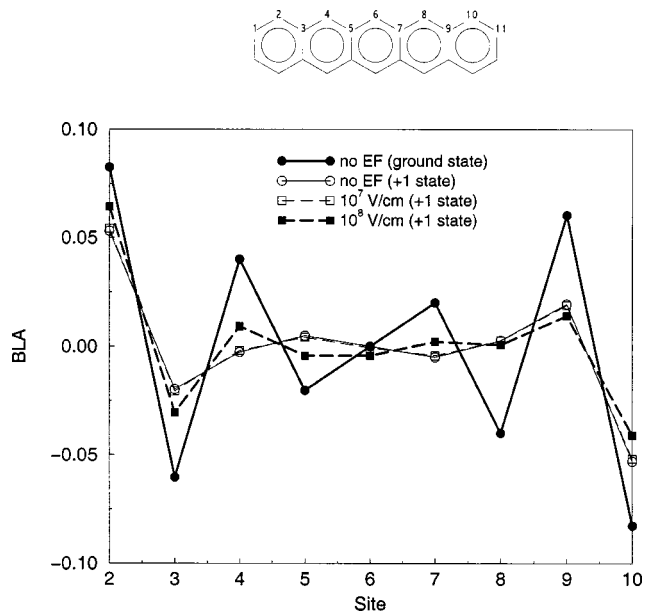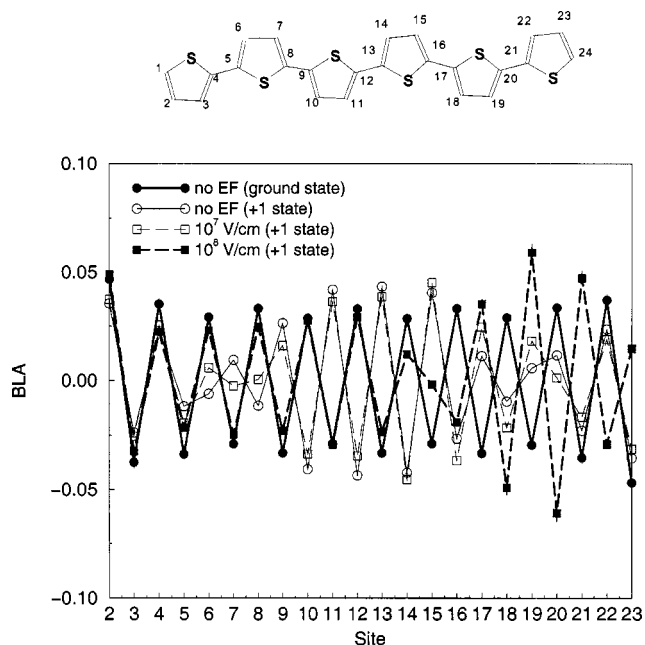

FIG. 6. Evolution, with site position i, of the C–C bond-length alternation (BLA, in Å) in sexithienyl, as calculated at the AM1 level (see chemical structure on top for site labels).

TABLE II. Evolution of the reorganization energy components (in meV, see text for details) in sexithienyl[a] as a function of the amplitude of the electric field (V/cm), as calculated at the AM1 level.

	λ_1'	λ_1''	λ_1	λ_2'	λ_2''	λ_2	$\lambda_i = \lambda_1 + \lambda_2$
10^6	250	248	250	260	262	260	510
5.10^6	249	248	249	261	262	261	510
10^7	249	243	245	259	266	265	510
5.10^7	176	93	204	255	308	303	507
10^8	74	49	140	241	375	354	494

[a]λ_1 and λ_2 are 250 and 260 meV, respectively, in the absence of electric field.

electric field while keeping the geometries frozen in the structures optimized without field. These calculations evaluate the impact of the electrostatic stabilization term. The results indicate a strong reduction of the λ_1' component, associated with the singly charged state, while the λ_2' component slightly decreases. We also report in Table II the values of the two components, referred to as λ_1'' and λ_2'', from a new set of single-point calculations performed in the absence of electric field, at the geometrically distorted structures induced by the electric perturbation; the data show that $\lambda_1'' < \lambda_1$ and $\lambda_2'' > \lambda_2$ when the electric field is high enough to distort significantly the geometry in the singly charged state; this evolution can be qualitatively understood from the potential energy curves drawn in Fig. 3. Combining the two contributions should thus lead to a progressive decrease of λ_1 and a concomitant increase of λ_2 with electric field; this is confirmed by the values provided by the full calculations. However, since the trends for λ_1 and λ_2 are opposite, the total reorganization energy remains nearly unaffected by the application of a static electric field on sexithienyl or pentacene.

We now turn to a discussion of the evolution of the interchain transfer integrals for holes when applying the external electric field. We first consider a cofacial dimer where two pentacene molecules in their ground-state geometry are exactly superimposed on top of one another and separated by 4.0 Å; the HOMO splitting calculated at the INDO level is 0.262 eV. The values obtained for the transition-state geometries (that account for the geometric distortions induced by the electric field, see Methodology section), are modified by only 1–2 meV in the full range of field amplitudes (10^6–10^8 V/cm). These results underline the weak sensitivity of interchain transfer integrals with respect to small geometric distortions. This can be explained by the fact that the global overlap between the HOMO wave functions of the two molecules, which determines the splitting of the HOMO level,[30] is largely governed by the overlap of the face-to-face atoms in the cofacial dimer; it is thus weakly perturbed by small changes in the geometry of the transition state.

Cofacial configurations are, however, seldom encountered in actual crystal structures where lateral displacements of molecules along their long/short axes are frequently observed. In this case as well, insensitivity of the HOMO splitting with respect to the applied electric field is also calculated when considering the staggered chain packing characteristic of crystal structures. The same conclusions apply to the sexithienyl molecule.

V. CONCLUSIONS

We have investigated by means of semiempirical calculations the influence of the electric field generated by the gate of a transistor on the hole transport properties of semiconducting organic layers. To do so, we have applied a static electric field along the long axis of pentacene and sexithienyl molecules in order to mimic the operation of organic transistors where molecules stand perpendicular on the insulating layer. We have characterized the evolution of the internal reorganization energy and hole transfer integral as a function of the amplitude of the static electric field.

The calculations indicate that the charge distribution and geometric structure are left nearly unchanged for electric fields up to 10^7 V/cm. Pronounced charge redistributions and geometric distortions are observed at higher fields and lead to a significant modulation of the two components of the reorganization energy. However, these two components have opposite evolutions, so that the global reorganization energy remains nearly unaffected by the application of the field. The transfer integrals are also calculated to remain nearly constant with field.

We expect that the same conclusions hold true in other organic semiconductors. Thus, it appears that charge confinement effects induced by the gate electric field in organic transistors are not detrimental to the charge transport properties in the semiconducting layer.

[1] W. Warta and N. Karl, Phys. Rev. B **32**, 1172 (1985).
[2] F. Garnier, Acc. Chem. Res. **32**, 209 (1999).
[3] P. T. Herwig and K. Müllen, Adv. Mater. (Weinheim, Ger.) **11**, 480 (1999).
[4] G. Horowitz, Adv. Mater. (Weinheim, Ger.) **10**, 365 (1998).
[5] E. L. Granstrom and C. D. Frisbie, J. Phys. Chem. B **103**, 8842 (1999).
[6] H. E. Katz, Z. Bao, and S. Gilat, Acc. Chem. Res. **34**, 359 (2001).
[7] T. W. Kelley and C. D. Frisbie, J. Phys. Chem. B **105**, 4538 (2001).
[8] T. M. Pappenfus, R. J. Chesterfield, C. D. Frisbie, K. R. Mann, J. Casado, J. D. Raff, and L. L. Miller, J. Am. Chem. Soc. **124**, 4184 (2002).
[9] K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, and S. Tokito, Angew. Chem., Int. Ed. Engl. **42**, 1159 (2003).
[10] K. Seki, S. D. Traytak, and M. Tachiya, J. Chem. Phys. **118**, 669 (2003).
[11] R. A. Marcus, J. Chem. Phys. **24**, 966 (1965).
[12] R. A. Marcus and N. Sutin, Biochim. Biophys. Acta **811**, 265 (1985).
[13] P. F. Barbara, T. J. Meyer, and M. A. Ratner, J. Phys. Chem. **100**, 13148 (1996).
[14] S. Tanaka and R. A. Marcus, J. Phys. Chem. B **101**, 5031 (1997).
[15] Y. A. Berlin, G. R. Hutchison, P. Rempala, M. A. Ratner, and J. Michl, J. Phys. Chem. A **107**, 3970 (2003).
[16] K. Sakanoue, M. Motoda, M. Sugimoto, and S. Sakaki, J. Phys. Chem. A **103**, 5551 (1999).
[17] M. Malagoli and J. L. Brédas, Chem. Phys. Lett. **327**, 13 (2000).

[18] J. Cornil, V. Lemaur, J. P. Calbert, and J. L. Brédas, Adv. Mater. (Weinheim, Ger.) **14**, 726 (2002).

[19] B. Chao Lin, C. Pyeng Cheng, and Z. P. Michael Lao, J. Phys. Chem. A **107**, 5241 (2003).

[20] This equation is derived under the following assumptions: (1) the whole electric charges lies in the semiconductor and the gate electrode (i.e., there is no charge in the insulator); and (2) the electric field in the insulator is uniform. Applying Gauss' law at both sides of the insulating layer leads to $F_s = -Q_s/\epsilon_s$ at the semiconductor side and $F_i = Q_G/\epsilon_i$ at the gate electrode side, with Q_s and Q_G the respective total charge densities. The equation results from charge neutrality, which imposes $Q_s + Q_G = 0$.

[21] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).

[22] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, J. Am. Chem. Soc. **107**, 3902 (1995).

[23] J. J. P. Stewart, MOPAC 93 (Fujitsu Limited, Tokyo, Japan, 1993).

[24] G. Moro, G. Scalmani, U. Cosentino, and D. Pitea, Synth. Met. **108**, 165 (2000).

[25] F. C. Grozema, L. P. Candeias, M. Swart, P. Th. van Duijnen, J. Wildeman, G. Hadziioanou, L. D. A. Siebbeles, and J. M. Warman, J. Chem. Phys. **117**, 11366 (2002).

[26] V. Geskin, A. Dkhissi, and J. L. Brédas, Int. J. Quantum Chem. **91**, 350 (2003).

[27] M. C. Zerner, G. H. Loew, R. F. Kichner, and U. T. Mueller-Westerhoff, J. Am. Chem. Soc. **102**, 589 (1980).

[28] J. L. Brédas, J. Cornil, D. Beljonne, D. dos Santos, and Z. Shuai, Acc. Chem. Res. **32**, 267 (1999).

[29] J. Cornil, D. Beljonne, J. P. Calbert, and J. L. Brédas, Adv. Mater. (Weinheim, Ger.) **13**, 1053 (2001).

[30] J. L. Brédas, J. P. Calbert, D. A. da Silva Filho, and J. Cornil, Proc. Natl. Acad. Sci. U.S.A. **99**, 5804 (2002).

[31] J. L. Brédas and G. B. Street, Acc. Chem. Res. **18**, 309 (1985).