

Influence of Electric Fields on the Electron Transport in Donor–Acceptor Polymers

Förster, A.; Günther, F.; Gemming, S.; Seifert, G.;

Originally published:

February 2017

Journal of Physical Chemistry C 121(2017)7, 3714-3723

DOI: <https://doi.org/10.1021/acs.jpcc.6b11230>

Perma-Link to Publication Repository of HZDR:

<https://www.hzdr.de/publications/Publ-25540>

Release of the secondary publication
on the basis of the German Copyright Law § 38 Section 4.

Influence of Electric Fields on the Electron Transport in Donor-Acceptor Polymers

Anja Förster,^{†,‡} Florian Günther,^{†,‡,¶} Sibylle Gemming,^{‡,¶,§} and Gotthard Seifert^{*,†,‡}

Theoretical Chemistry, TU Dresden, 01062 Dresden, Germany, Center for Advancing Electronics Dresden (cfaed), 01062 Dresden, Germany, Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Bautzner Landstraße 400, 01328 Dresden, Germany, and Institute of Physics, TU Chemnitz, 09107 Chemnitz, Germany

E-mail: gotthard.seifert@chemie.tu-dresden.de

Abstract

The influence of an electric field on different properties of the donor-acceptor polymer diketo-pyrrolo-pyrrole bithiophene thienothiophene (DPPT-TT) that are essential for the charge transport process are studied. The main focus is on whether the transport in DPPT-TT-based organic transistors can be tuned by electric fields in the gate direction. The considered electric fields are in the range of $10^8 - 10^{10} \text{ V m}^{-1}$. We show that strong electric fields ($\sim 10^9 \text{ V m}^{-1}$) which are parallel to the polymer backbone can influence the reorganization energy in a Marcus-type approach. Weaker electric fields parallel to the polymer backbone result in minimal changes to the reorganization energy. The coupling element of DPPT-TT shows a pronounced affinity to be influenced by electric fields in the charge transport direction independent of the field strength.

*To whom correspondence should be addressed

[†]Theoretical Chemistry, TU Dresden, 01062 Dresden, Germany

[‡]Center for Advancing Electronics Dresden (cfaed), 01062 Dresden, Germany

[¶]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, Bautzner Landstraße 400, 01328 Dresden, Germany

[§]Institute of Physics, TU Chemnitz, 09107 Chemnitz, Germany

Introduction

In recent years organic field-effect transistors (OFETs) have become a research topic of high interest.¹⁻⁶ Their low production costs and easy processing at low temperatures together with their high flexibility make them ideal materials for e-papers, flexible, high-resolution displays, electronic identification tags, sensors and many more applications.⁷⁻¹² One limiting factor of OFETs is the carrier mobility μ of the semiconducting organic materials. Polymers with charge carrier mobilities above $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are desired.¹³

One group of polymers that are of special interest are donor-acceptor polymers. As their name suggests, they combine electron-deficient (acceptor units) and electron-rich regions (donor units). Experimental investigations of a wide variety of donor and acceptor combinations were carried out with the aim to find combinations which possess high carrier mobilities.^{16,17} Theoretical studies, on the other hand, mainly investigate the transfer rate t . The Einstein relation connects the experimentally measurable carrier mobility with the theoretically accessible transfer rate t .¹ Thus the transfer rate t gives a first quantitative insight to the field effect mobilities of donor-acceptor polymers.^{14,18}

¹In detail, the diffusion constant D in the Einstein relation is directly dependent on the transfer rate t .

The transfer rate t can be estimated using Marcus theory:^{19–21}

$$t = \frac{T_{ij}^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{\lambda}{4k_B T}\right). \quad (1)$$

The transfer rate t is defined by the coupling element T_{ij} of the molecules i and j and the reorganization energy λ . Both the coupling element and the reorganization energy are dependent on an applied electric field ε . Other parameters that influence the transfer rate t are the temperature T and the Boltzmann constant k_B .

The intramolecular reorganization energy λ depends on the energy difference between the neutral and charged polymer chains (see below eq. 2 and fig. 1). It describes the reorganization of the atoms in the neutral and charged polymer chain due to the transfer of the charge between two chains.

$$\begin{aligned} \lambda &= \lambda_1 + \lambda_2 \\ \lambda &= [E_0(\pm 1) - E_{\pm 1}(\pm 1)] + [E_{\pm 1}(0) - E_0(0)] \\ &\quad (\text{cf. fig. 1}) \end{aligned} \quad (2)$$

The energy of a molecule in eq. 2 is denoted as $E_{\text{geo}}(\text{charge})$. The value in brackets gives the total charge of the system when the energy was calculated and the value of the index denotes for which charge the geometry was optimized.

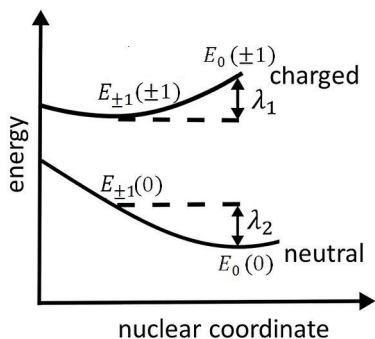


Figure 1: Scheme of the reorganization energy composition.

There are different approaches to determine the coupling element T_{ij} (cf. Ref. 22–25). One approach is to use Koopmans’ theorem together with the orbital splitting in an molecular orbital (MO) picture of the dimer system (cf. eq. 3). There, the definition of the coupling element is

based on the splitting of the monomer’s highest occupied molecular orbital (HOMO) ψ_{HOMO} or the lowest unoccupied molecular orbital (LUMO) ψ_{LUMO} into HOMO and HOMO-1 or LUMO and LUMO+1 due to the overlap of the orbitals when the dimer is formed (cf. fig 2). That the results from this method are in good agreement with other approaches to calculate the coupling element was shown in references 26 and 27.

$$\begin{aligned} T_{elec} &= 0.5 * (E_{\text{LUMO}+1} - E_{\text{LUMO}}) \\ T_{hole} &= 0.5 * (E_{\text{HOMO}} - E_{\text{HOMO}-1}) \end{aligned} \quad (3)$$

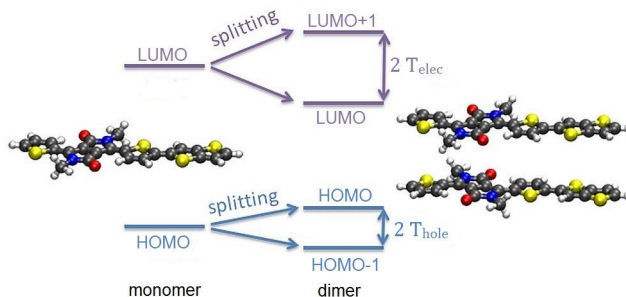


Figure 2: (Color online) Scheme of the coupling element composition.

Both the reorganization energy and the coupling element can be influenced by an electric field because it polarizes the molecule. This gives the opportunity to control the electron transport inside OFETs via gate-induced electric fields, but also raises the question whether electric field effects should be considered in the Marcus transport calculations. Thus, we investigate the influence of electric fields on the energy of both neutral $E(0)$ and charged $E(\pm 1)$ donor-acceptor polymers. With these energy changes we determine the impact of electric fields on the reorganization energy λ as described in eq. 2. The influence of an electric field on the coupling element manifests itself in changes of the HOMO and LUMO orbitals. In a final step we estimated the coupling element T_{ij} and the transfer rate t as a function of the applied electric field.

For this purpose we consider electric fields up to $1.29 \cdot 10^{10} \text{ V m}^{-1}$. The currently produced OFETs use gate voltages between 1-100 V for system sizes of 1-100 μm ,^{28–32} leading to possible gate-induced electric fields between 10^4 - 10^8 V m^{-1} .

We consider electric fields up to 10^{10} V m⁻¹ because we expect the system size to further decrease to 0.1 μ m. This reflects also that Wang et al. reported that electric fields $>10^7$ V m⁻¹ are needed to lead to significant changes in the carrier mobility.³¹ We further include the influence of electric fields along the source-drain direction in our investigation. We thus can study, which orientation of donor-acceptor polymers result in the best possible tuning via electric fields with respect to source, drain and gate contacts.

Model System and Computational Details

Model System

As an example we study the donor-acceptor polymer diketo-pyrrolo-pyrrole bithiophene thienothiophene (DPPT-TT) — see fig. 3. We choose DPPT-TT because it possesses the highest electron mobility for DPPT-containing polymers^{13,32} and the hole mobility can reach values above 10.5 cm² V⁻¹ s⁻¹.³³ In DPPT-TT, DPP is the acceptor unit and thienothiophene the donor unit.

Our DPPT-TT model system differs slightly from the DPPT-TT polymer that is used in the experimental studies.^{16,34–38} We investigate a DPPT-TT monomer instead of a DPPT-TT polymer and saturate the open ends of the monomer with hydrogen atoms as shown in fig. 3. The monomer unit possesses a dipole moment of 0.61 Debye. This smaller system size also affects the absolute value of the reorganization energy of optically excited long polymer chains.¹⁵ However, in the framework of this study only the relative changes of the reorganization energy due to an applied electric field are of interest. For a detailed discussion see Ref. 39.

For simplification we replace the large pendant 2-octyldodecyl groups by methyl groups. This does not influence the final results because the pendant groups do not contribute to the transport process. The thiophene rings can have two different

orientations in DPPT-TT, the cis and trans configurations (see fig. 3). At the density-functional level of theory (see section) the cis configuration is by 7.3 kcal mol⁻¹ (= 0.32 eV) energetically more favorable than the trans configuration.

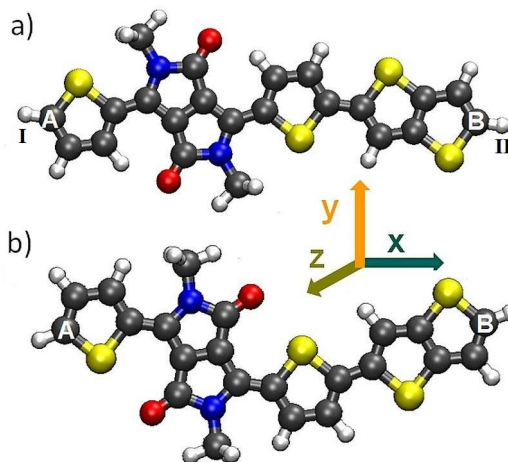


Figure 3: (Color online) The two configurations of DPPT-TT: cis (a) and trans (b). The coordinate axis defines the position of the monomers with regard to the direction of the applied electric fields.

The two configurations are oriented in the coordinate systems as follows (cf. fig. 3): The x -direction is defined parallel to the polymer backbone. In detail, the two carbon atoms (A and B in fig. 3) that connect the basis units of the polymer define the x -direction. The y -direction is defined transversal to the polymer backbone and the z -direction is perpendicular to the polymer backbone.

Inside the OFET the DPPT-TT can have three fundamentally different orientations: end-on, edge-on or face-on (cf. fig. 4). All other orientations are combinations of those. Therefore, gate-induced electric fields can act on DPPT-TT in three different directions: parallel or vertical to the polymer backbone, as well as perpendicular to the polymer backbone plane. With reference to the coordinate system in fig. 3, gate-induced electric fields act on the DPPT-TT polymer from the x -, y - or z -direction.

Zhang et al. showed that in the as-cast film DPPT-TT assembles in the edge-on and face-on orientations. In the annealed film DPPT-TT changes to an

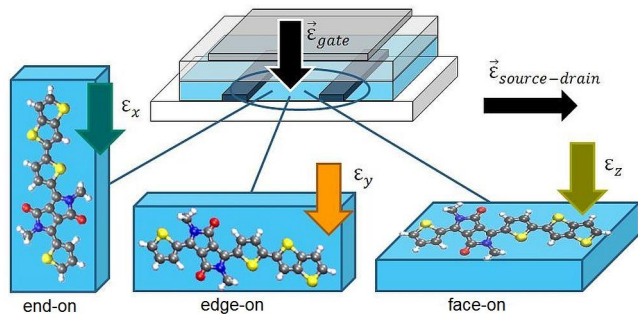


Figure 4: (Color online) Orientation of DPPT-TT inside the OFET. The arrows indicate the direction from which the gate-induced electric field acts on the DPPT-TT polymer. The black arrow in the upper right corner indicates the direction of source-drain-induced electric fields.

exclusively edge-on orientation.¹⁶ Besides these two experimentally encountered orientations, we also include gate-induced electric fields for end-on oriented DPPT-TT polymers for three reasons:

(i) In the end-on orientation the gate-induced electric field (x -direction) acts on DPPT-TT along the polymer backbone and thus, it is the direction with the largest spatial interaction cross section for the electric field. Also, Ma et al.⁴⁰ showed that it is possible to change the orientation preference of poly(3-butylthiophene) (P3BT) by functionalizing the ends with semifluoroalkyl chains. Through the functionalization the orientation of P3BT changed from edge-on to end-on. In another study Ma et al. successfully demonstrated that the functionalizing with semifluoroalkyl chains can also be used for changing the orientation of poly(3-hexylthiophene) (P3HT).⁴¹ Ma and coworkers predict that the functionalizing with semifluoroalkyl chains to change the orientation of the polymers can also be applied to various semi-crystalline semiconducting polymers. Therefore, it should be possible to adapt this process for DPPT-TT to obtain an end-on orientation of this polymer inside OFETs.

(ii) We study DPPT-TT as an example for donor-acceptor polymers. Other donor-acceptor polymers can assemble in the end-on orientation. Ma et al.⁴¹ showed that the hole mobility of P3BT with semifluoroalkyl chains changes from $3.6 \cdot 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $1.1 \cdot 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when its

orientation is changed to end-on. The activation energy of transport is also lowered from 133 meV to 80 meV. Their results also showed an improvement of the hole mobility of P3HT when it is changed to the end-on orientation. Thus the end-on orientation with its distinctly unique behavior should not be neglected.

(iii) In the experimentally encountered edge-on and face-on orientations an electric field in the x -direction resembles a source-drain-induced electric field (as indicated by the black arrow in the upper right corner of fig. 4). Therefore, if we study the influence of electric fields from all three directions, we address both the influence of gate-induced electric fields, as well as the influence of weaker source-drain-induced electric fields for all three orientations of DPPT-TT and whether they need to be taken into account when calculating the Marcus transfer rate.

The coupling element for the transport in z -direction is calculated by investigating the dimer. The two DPPT-TT monomers are aligned as shown in fig. 2. This means that the upper DPPT-TT (cf. fig. 2) is rotated by 180° with regard to the lower DPPT-TT monomer. According to reference 39 it is the stacking configuration with the highest value of the coupling element for the electron transport. The distance between the two monomers in z -direction is 3.4 Å. The hydrogen atoms I and II (cf. fig. 3) of both monomers are directly on top of each other.

Computational Details

We employ the density functional theory (DFT) program package GAMESS US^{42,43} to study the effect of electric fields on DPPT-TT. In detail, we used the B3LYP functional⁴⁴ as different benchmarks⁴⁵⁻⁴⁷ indicate that it is a well suited functional to study such systems. We performed a study on the influence of the basis set on the results. Our analysis shows that the large 6-31g(d,p) and the small 3-21g Gaussian basis set lead to identical trends with regard to energy changes of the neutral monomer due to an applied electric field. Further, for electric fields in

the y - and z -direction the differences between the 6-31g(d,p) and the 3-21g Gaussian basis set is below 1 kcal mol^{-1} ($= 0.043 \text{ eV}$). Therefore for these two directions there also is a qualitative agreement between the two basis sets. This is in agreement with the study of Chen et al.,⁴⁷ where also no dependence of the trends on the basis set was found for electric field free calculations. With regard to the coupling element we found that the deviation between the 6-31g(d,p) and the 3-21g basis set is below 15 meV when no electric field is applied and that the quantitative changes through the applied electric field are nearly identical. Further, the charge relocalisation inside the DPPT-TT monomer due to an applied electric field is also identical for both basis sets (cf. fig. S2 of the SI). Therefore, we use the 3-21g basis set throughout this study.

We performed energy calculations and geometry optimizations with the standard GAMESS US settings, except for the gradient convergence tolerance that was changed to $0.5 \cdot 10^{-3} \text{ Ha bohr}^{-1}$. This consequently changed the root mean square gradient to $0.16 \cdot 10^{-3} \text{ Ha bohr}^{-1}$. The convergence criterion for the self-consistent field (scf) cycles was 10^{-5} Ha . We studied the influence of the electric fields on the reorganization energy and the coupling element by applying a uniform electric field in the range of $0\text{-}13 \cdot 10^9 \text{ V m}^{-1}$ along the x -, y - and z -directions. In the supporting information we shortly discuss why negative electric fields were not taken into consideration and show exemplarily the effect for negative fields in fig. S1, which is an extension of fig. 5b.

Results and Discussion

Reorganization energy

We first discuss the dependence of the reorganization energy on the applied electric field. In accordance with eq. 2 the influence of the electric field on the energy of the charged and neutral monomer has to be studied. We use the neutral monomer to investigate both the cis and trans configurations to

determine if one of the two isomers is more susceptible to an applied electric field. We study the effect of the electric field by analyzing the energy difference ΔE between the energy of the molecule without an applied electric field (E^0) and when an electric field is applied ($E \neq 0$) (cf. eq. 4). We further subtract the electric work $U_E = \epsilon q \Delta x$ from ΔE . This procedure ensures that the electric work from the movement of the center of charge Δx when an electric field ϵ is applied does not contribute to the energy change ΔE . For more details refer to the SI.

$$\Delta E = E^{\neq 0} - E^0 - U_E \quad (4)$$

Electric Field Dependence of the Neutral Cis and Trans Configurations

In a first step, we investigate the effect of an applied electric field on neutral monomers. Fig. 5 shows the energy changes of the neutral cis and trans configurations due to an applied electric field (cf. eq. 5) and fig. S1 of the SI shows the reaction to negative electric fields.

$$\begin{aligned} \Delta E_{\text{cis}} &= E_{\text{cis}}^{\neq 0} - E_{\text{cis}}^0 - U_E \\ \text{and } \Delta E_{\text{trans}} &= E_{\text{trans}}^{\neq 0} - E_{\text{trans}}^0 - U_E \end{aligned} \quad (5)$$

There are three major conclusions that can be drawn from the results:

(i) The influence of the electric fields in gate direction on edge-on and face-on oriented DPPT-TTs (y - and z -direction) are by a factor of three and ten, respectively, weaker than an electric field of the same strength to end-on oriented DPPT-TTs. This means that the influence of electric fields perpendicular to the polymer backbone are nearly negligible in comparison to the electric fields oriented along the polymer backbone.

(ii) The change in energy is below 0.4 eV if currently available gate-induced electric field strengths ($0.5\text{-}2.6 \cdot 10^9 \text{ V m}^{-1}$) are considered. This is a first indication that effects of gate-induced electric fields will have to be considered in the transport description of DPPT-TT in particular and of donor-acceptor polymers in general only for

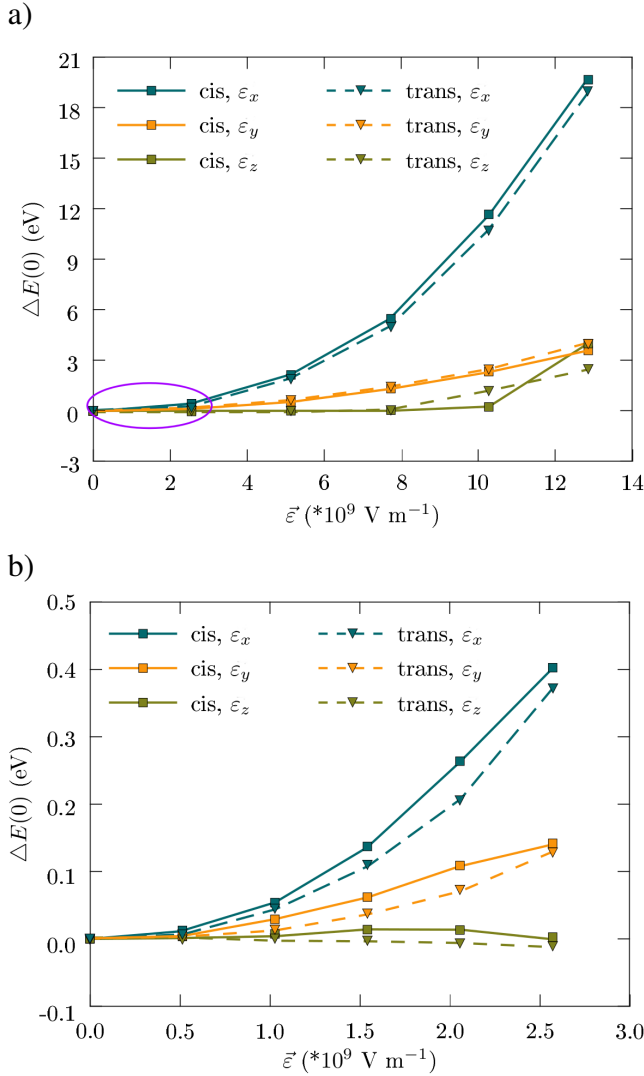


Figure 5: Electric field influence on the energy of neutral monomers (cf. eq. 5). a) Differences between the cis and trans configuration. b) Zoom into the circled region of a).

devices that are smaller than today's devices. This also means that the weaker source-drain-induced electric fields will not influence the transport.

(iii) The maximum energy difference between the cis and trans configuration is about 0.25 eV and 0.90 eV for electric fields applied in the y- and z-direction², respectively, and thus, practically negligible. Only for the x-direction along the polymer backbone a distinct difference between the two configurations can be seen. And even then, very strong fields above $7 \times 10^9 \text{ V m}^{-1}$ are necessary to yield a considerable deviation between the

²Neglecting the outlier for the cis configuration with an electric field in z-direction at $12.9 \times 10^9 \text{ V m}^{-1}$.

two configurations. This independence on the configuration is in agreement with previous studies on donor-acceptor polymers without an applied electric field.³⁹

The slightly different behavior of the two configurations for electric fields perpendicular or parallel to the polymer backbone can be explained with the structure of the two configurations. For electric fields in the y- and z-direction, the neighboring atoms in the direction of the electric field are nearly identical for both the cis and trans configuration. Only when the electric field is applied in the x-direction the neighboring atoms in the direction of the electric field are noticeably different. For example the sulfur atom of the left thiophene ring in the cis configuration has nitrogen as its next neighbor in x-direction, whereas the same sulfur atom in the trans configuration has a carbon atom as its nearest neighbor in x-direction (cf. fig. 6). That this has an influence on the charge distribution is already noticeable when no electric field is applied. While the atomic charges for most atoms of DPPT-TT are identical for the cis and the trans configuration, there is a large discrepancy ($\geq 0.05 e$) for the sulfur atoms of the thiophene rings and the two hydrogen atoms of the same rings that face the oxygen atoms in the cis configuration (cf. purple circles in fig. 6). Thus, one can conclude that the slightly different reactions of the trans and cis configuration under strong electric fields are due to their different nearest neighboring atoms during an internal polarization process for an applied electric field in x-direction.

Based on the nearly identical reaction of both the cis and trans configuration to applied electric fields, we restrict all further studies on the reorganization energy to the cis configuration as it showed a slightly stronger affinity to be influenced by electric fields than the trans configuration. In addition, the cis configuration is energetically more favorable than the trans configuration. Further, we will restrict our studies to strong electric fields between 10^9 V m^{-1} and 10^{10} V m^{-1} in order to investigate significant changes of the energy.

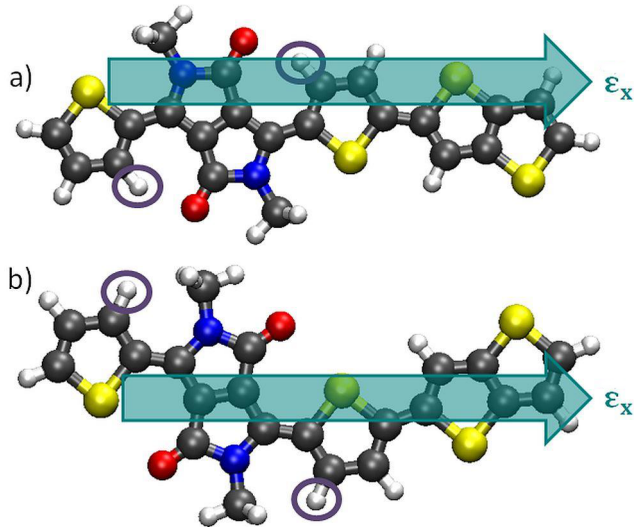


Figure 6: (Color online) Different nearest neighbors for the sulfur atom when an electric field is applied in x -direction. The circled hydrogen atoms are the ones whose atomic charges differ significantly between the cis and trans configuration.

Electric Field Dependence of Charged Monomers

In the second step to calculate the reorganization energy, we investigated how the energy of the cis monomer with a charge of ± 1 is influenced by an applied electric field. To evaluate the influence of the electric field on the charged monomer we follow the same procedure as for the neutral one. We calculate the energy difference of the charged monomer with and without an applied electric field and correct the electric field work U_E (cf. SI).

$$\begin{aligned} \Delta E(+1) &= E^{\neq 0}(+1) - E^0(+1) - U_E \\ \text{and } \Delta E(-1) &= E^{\neq 0}(-1) - E^0(-1) - U_E \end{aligned} \quad (6)$$

The reaction of the charged monomers to an applied electric field in fig. 7 confirms that DPPT-TT is only noticeably affected by applied electric fields in the x -direction when realistic field strengths below $2.6 \cdot 10^9 \text{ V m}^{-1}$ are considered. In this range, the energy changes in the edge-on and face-on oriented polymers are below 0.9 eV and 0.03 eV, respectively. Even for very strong gate-induced electric fields of $12.9 \cdot 10^9 \text{ V m}^{-1}$ the energy changes of 7 eV and 6 eV are rather small in comparison to the effect on the end-on oriented DPPT-TT. There the energy changes

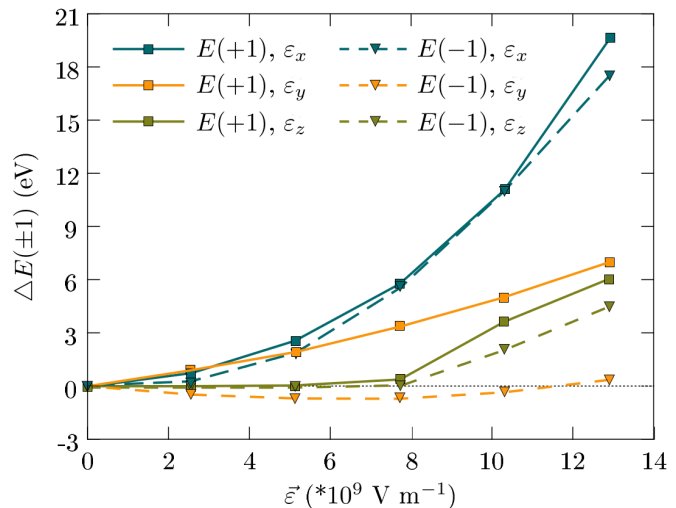


Figure 7: Electric field influence on the energy of charged cis monomers (cf. eq. 6). The straight lines display the positively charged monomers and the dashed lines the negatively charged monomers.

are nearly 19.7 eV and 17.5 eV for the positively and negatively charged monomer, respectively. The results also show that the positively charged monomer is slightly more affected by applied electric fields, but both charged monomers display identical trends as the neutral monomer.

We can conclude that to obtain OFETs that can be tuned via electric fields in gate direction it is necessary to fabricate them with end-on oriented polymers. Further, our results so far indicate that the electron and hole transport are equally influenced by electric fields. However, the required strength of the electric field for noticeable changes is far above the strength of common gate-induced electric fields.

Field-effect corrected Reorganization Energy

We calculated the reorganization energy λ as described in eq. 2. Selected reorganization energies³ are displayed in fig. 8, which demonstrate the influence of electric fields on the reorganization en-

³We note that switching on electric fields further aggravates the convergence problem one encounters when calculating the energy of the neutral monomer in the geometry of the charged monomer and reversed ($E_0(\pm 1)$ and $E_{\pm 1}(0)$).

ergy. The energy changes calculated for the neutral, positive and negative monomers already indicated that DPPT-TT can only be influenced by a very strong electric field along the x -direction, and electric fields from the y - and z -direction do not lead to significant changes. Three major conclusions can be drawn from our obtained results of the reorganization energy.

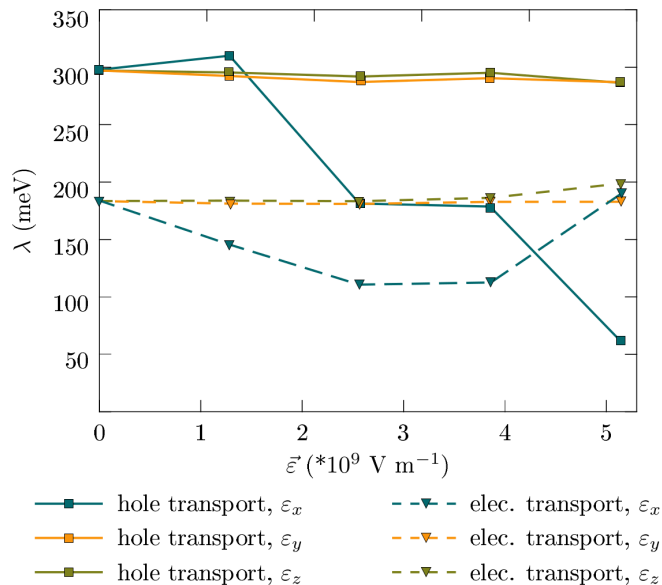


Figure 8: Electric field influence on the reorganization energy.

(i) In contrast to the results in the previous two subsections the reorganization energy is already significantly affected by relatively weak electric field values ($<2.6 \times 10^9$ V m $^{-1}$) applied in the x -direction. In order to increase the transport rate a decrease of the reorganization energy is necessary. According to our results, this only happens if the electric field applied in the x -direction has a strength below 3.9×10^9 V m $^{-1}$ for the electron transport or 5.1×10^9 V m $^{-1}$ for the hole transport. This threshold value for the strength of the electric field can be reached in the currently fabricated OFETs. If we exemplarily analyze the changes to the reorganization energy by electric fields of 2.6×10^9 V m $^{-1}$, we find that the reorganization energy for the hole transport changes from 298 meV to 182 meV and for the electron transport from 183 meV to 110 meV. If we insert these changes into eq. 1 and assume that the coupling element T_{ij} remains constant, then an increase in the hole transfer rate to about 430 % and in the electron

transfer rate to 280 % are obtained in comparison with the field-free case.

(ii) Of further interest is the fact that for the end-on orientation the reorganization energy for the electron transport first noticeably decreases before it slightly increases again. At about 3.9×10^9 V m $^{-1}$ the reorganization energy of the electron transport is lower than the one of the hole transport, making electron transport more favorable. However, once we reach an electric field with the strength of 5.1×10^9 V m $^{-1}$, hole transport becomes favorable. This effect can be used to build an OFET that switches between hole and electron transport via the gate voltage and thus via the gate-induced electric field.

(iii) Electric fields in the y - and z -direction, on the other hand, produce only slight changes to either the hole or electron transport's reorganization energy. If we again calculate the increase of the Marcus transfer rate as described in (i) for electric fields of 2.6×10^9 V m $^{-1}$, we gain small increases of 13 % and 7 % for the hole transport in edge-on and face-on DPPT-TTs, respectively, and no changes for the electron transport. Significant changes to the reorganization energy are only observed for electric fields on the order of 10^{10} V m $^{-1}$. This is above the strength of current gate-induced electric fields ($\sim 10^8$ V m $^{-1}$).³⁰ Thus, we can conclude that in the currently fabricated edge-on and face-on orientated OFETs controlling the transport via the gate voltage and therefore, gate-induced electric fields is not possible. In order to control the transport in edge-on and face-on orientated OFETs, the OFETs must become even smaller while the gate voltage remains constant so that we reach the necessary electric field strength of $\sim 10^{10}$ V m $^{-1}$.

In conclusion, when estimating the transport rate by Marcus theory (refer eq. 1), the effects of electric fields on the reorganization energy need only to be taken into consideration for electric fields in x -direction.

HOMO and LUMO

The previous section has shown that only an electric field applied along the x -direction (end-on orientated polymers) is able to influence the reorganization energy of DPPT-TT in such a way that it significantly influences the transfer rate. From the experimental point of view, it is more important to control the transport in the currently produced edge-on and face-on orientated polymers. Thus in the following, we investigate the influence of electric fields on the coupling element T_{ij} . For this purpose, we study how far the HOMO-LUMO-gap is influenced by electric fields and show the changes to the shapes of the HOMO and LUMO in fig. S3 of the SI. It gives a first indication whether the coupling element can be influenced by gate-induced electric fields along the y - and z -direction. Finally we determine the dependence of T_{ij} on an applied electric field.

HOMO-LUMO-gap

First, we investigate how the HOMO-LUMO-gap is affected by an applied electric field and if there is a difference between the cis and trans configuration. In accordance with the study on the reorganization energy we study electric fields along the x -, y - and z -directions. Fig. 9 shows the HOMO-LUMO-gap as a function of the applied electric field.

The most important result is that even for very strong electric fields $\sim 10^{10} \text{ V m}^{-1}$ applied along the y - and z -direction the HOMO-LUMO-gap remains essentially unchanged, with a maximum change of 0.12 eV and 0.06 eV for the cis and trans configuration, respectively. The HOMO-LUMO-gap in the x -direction, on the other hand, is strongly influenced by electric fields above $2.6 \cdot 10^9 \text{ V m}^{-1}$ (fig. 9a), decreasing from 2.2 eV to 0.9 eV. Here, the HOMO-LUMO-gap of the trans configuration is more susceptible to the influence of electric fields than the HOMO-LUMO-gap of the cis configuration.

In the case of weaker electric fields in the x -direction (cf. fig. 9b) the cis and trans configura-

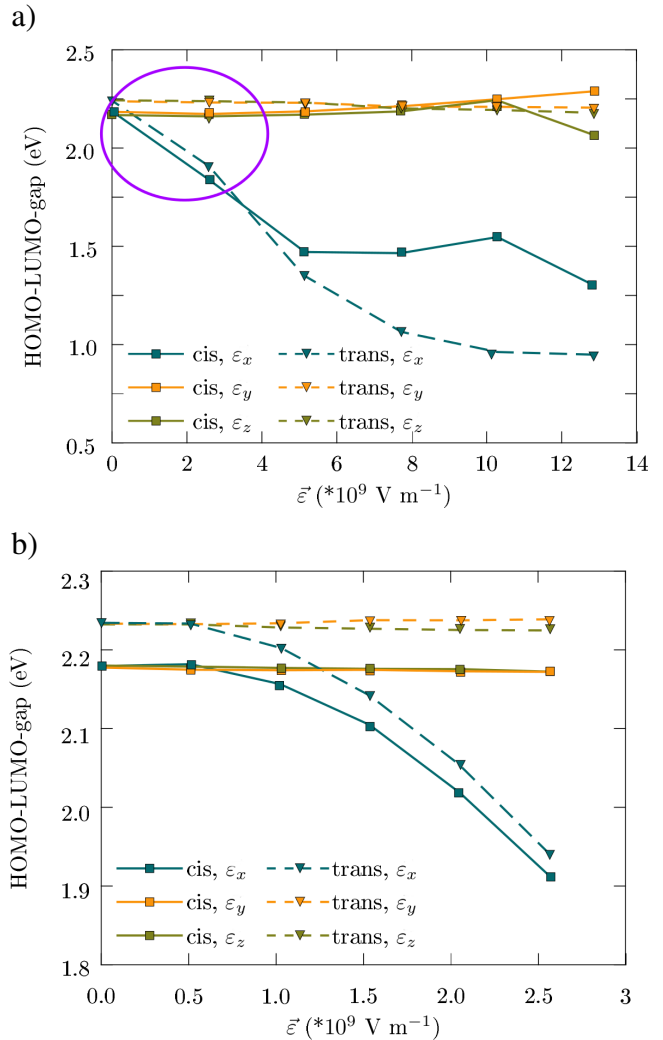


Figure 9: Electric field influence on the HOMO-LUMO-gap a) Differences between the cis and trans configuration. b) Zoom into the circled region of a.

tions show identical trends. Therefore, we ascribe the deviations between the two configurations to the strong field. For electric fields below $3 \cdot 10^9 \text{ V m}^{-1}$ the effect on the HOMO-LUMO-gap is not as pronounced, but still noticeable with a minimum HOMO-LUMO-gap of about 1.9 eV (fig. 9b). Thus, in OFETs with end-on orientated DPPT-TTs it might be possible to influence the HOMO-LUMO-gap via gate-induced electric fields.

Coupling element

The coupling element T_{ij} for holes or electrons can be related to the splitting of the HOMO or LUMO

of the monomer to HOMO-1 and HOMO or to LUMO and LUMO+1 of the dimer, respectively (cf. eq. 3 and fig. 2). For this, we considered a π - π stack of two DPPT-TT monomers in cis configuration as shown in fig. 10. The obtained results are shown in fig. 11 and the following conclusions can be made:

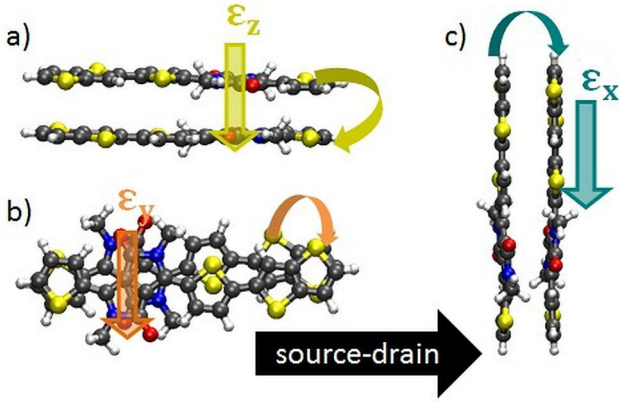


Figure 10: (Color online) Orientation of the coupling element during the transport of the charge in z -direction for the (a) face-on, (b) edge-on and (c) end-on oriented dimers. The curved arrows represent the charge transport, whereas the straight arrows show the direction of the applied (gate-induced) electric field.

(i) The coupling element increases most strongly for an applied electric field in z -direction. This behavior may arise from an enhanced overlap of the frontier orbitals when the electric field is applied parallel to the stacking direction (cf. fig. S4 of the SI). For strong electric fields ($>1.5 \cdot 10^9 \text{ V m}^{-1}$), however, estimating the coupling element T_{ij} according to eq. 3 might not be applicable. The HOMO-1 and HOMO is concentrated on one monomer, whereas the LUMO and LUMO+1 is mainly localized at the other monomer. This leads to a weak to non-existent overlap between the two monomers. Therefore, the corresponding symbols in fig. 11 and fig. 12 are indicated by empty symbols.

If we again calculate the percentage change to the transfer rate for an electric field of $2.6 \cdot 10^9 \text{ V m}^{-1}$, we find that, when assuming a constant reorganization energy, the transfer rate increased to about 700% and 650% of its original value for the electron and hole transport, respectively. These are

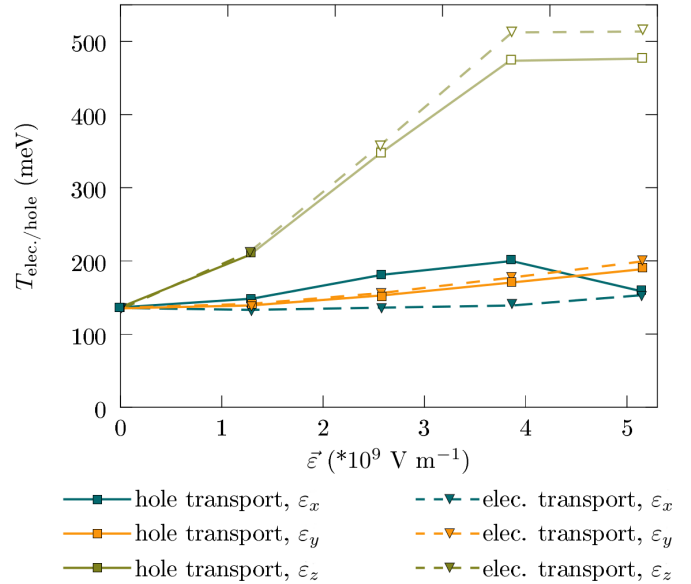


Figure 11: Electric field influence on the coupling element for the transport of the charge in z -direction (cf. fig. 10). The empty symbols indicate the cases of limited applicability of eq. 3.

considerable increases that should be included when calculating the transfer rate.

(ii) If we regard the effect of an electric field in x -direction, we see that the hole transport is slightly more affected by an applied electric field than the electron transport. This is in accordance with the effect of the same electric field on the reorganization energy. At a field strength of $2.6 \cdot 10^9 \text{ V m}^{-1}$ in x -direction the coupling element for the hole transport will increase the overall transfer rate to 180% of the value without an applied electric field. However, the identical field will decrease the reorganization energy so strongly that the transfer rate is increased to 430% of the original value. Thus, an electric field applied in x -direction affects the reorganization energy more strongly than the coupling element.

(iii) At about $4 \cdot 10^9 \text{ V m}^{-1}$ a saturation of the effect of electric fields on the coupling element occurs. For the electric field in y -direction, this means that a maximum increase on the coupling element of 50% can be reached, leading to a doubling of the transfer rate if both the changes to the coupling element and to the reorganization energy are taken into account.

Altogether, we can conclude that the effect of elec-

tric fields ($>10^9 \text{ V m}^{-1}$) on the coupling element should be taken into account when the Marcus transfer rate is calculated, independent of the direction of the electric field.

Transfer rate

Finally we insert the obtained results for the reorganization energy and the coupling element under an applied electric field in eq. 1 to calculate the transfer rate t . We show the result for a temperature of 273.15 K in fig. 12. There it can be seen that electron transport for face-on DPPT-TT is most strongly affected by an applied electric field. As the reorganization energy of the face-on DPPT-TT was not influenced by an electric field in z -direction, the increased transfer rate is solely due to the changes on the coupling element and the changed overlap of the π -orbitals.

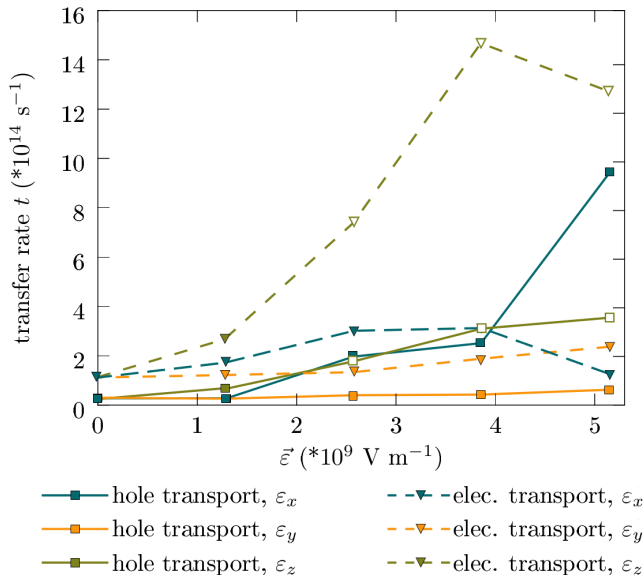


Figure 12: Electric field influence on the transfer rate t . The values were calculated for a temperature of 273.15 K. The empty symbols indicate the cases of limited applicability of eq. 3.

With regard to the hole transfer rate, we conclude that the effect of an electric field applied along the polymer backbone to the reorganization energy equals the effect of an electric field in z -direction on the coupling element. Therefore, one can conclude that the Marcus transfer rate under electric fields in x -direction is dominated by the changes to

the reorganization energy, whereas Marcus transfer rates for electric fields along other directions are dominated by the changes to the coupling element.

If the transfer rate for other transport directions than the here studied z -direction are determined, we find it necessary to study the influence of electric fields along the transport direction on the coupling element. This would be especially advisable if charge transport along the x -direction is investigated. In face-on and edge-on oriented chains, this is the direction of the of weaker source-drain-induced electric fields. Here, we estimate that a significant influence on the coupling element can be observed from such electric fields.

Conclusions

We studied the effect of electric fields on the donor-acceptor polymer DPPT-TT with respect to properties that influence the transport described by the Marcus equation (cf. eq. 1). For this, we considered a monomer model rather than the full polymer chain. We demonstrated that the cis and trans configurations display the same trends regarding the susceptibility to electric fields concerning the total energy and the HOMO-LUMO-gap.

For the reorganization energy λ , the strongest effect occurs when the electric field is applied in x -direction. We observe a decrease of λ which results in an increase of the transfer rate of up to 430%, assuming that the coupling element remains constant. Based on this, we conclude that the end-on orientation of DPPT-TT might be most suited to tune the transfer via a gate voltage by influencing the reorganization energy. Our investigation shows that very strong electric fields ($>4 \cdot 10^9 \text{ V m}^{-1}$) in the x -direction promise to enable gate-induced switching between hole and electron transport.

Concerning the coupling element, we observe the strongest effect when the electric field is applied parallel to the stacking direction. An increase of the transfer rate up to 700% was noted in case of

an electric field of $2.6 \cdot 10^9 \text{ V m}^{-1}$. This might be one reason why studies without electric fields observe an underestimation of the mobility compared to experimental measurements³⁹. For the directions perpendicular to the stacking, an increase of the coupling is noticed as well, but with a much smaller magnitude. Thus, for tuning the transfer rate via a gate voltage by controlling the electronic coupling, the face-on orientation is best suited.

In summary, we conclude that electric fields are only able to influence the reorganization energy inside donor-acceptor polymers if the electric fields are aligned parallel to the polymer backbone while the coupling element is mostly affected if the electric field is applied in stacking direction. For strong electric fields ($>10^9 \text{ V m}^{-1}$) their effect should be considered when the Marcus transfer rate is calculated, whereas in the limit of small field strengths ($<10^9 \text{ V m}^{-1}$) a treatment without an explicit consideration of electric field effects is sufficient.

Supporting Information

The Supporting information is available free of charge on the ACS Publication website at DOI: (currently unknown).

Polarizability, Mulliken population analysis, charge displacement correction, HOMO and LUMO, HOMO-1 overlap.

Acknowledgments

All authors acknowledge funding from the Center for Advancing Electronics Dresden (cfaed). S. G. acknowledges funding from the Initiative and Networking Funds of the President of the Helmholtz Association via the W3 programme. F. G. and S. G. were supported by the International Helmholtz Research School (IHRs) NanoNet.

The authors acknowledge many inspiring discussions on the experimental background with the cooperation partners within the cfaed, in particular

with the groups of A. Kiriy and B. Voit (Leibniz-Institute for Polymer Research, Dresden).

All authors contributed to the design of the project, to the evaluation of the required theoretical and numerical approaches, and to the discussion of the results. A.F. conducted the numerical simulations and evaluated the calculated data. Both A.F. and F.G. contributed to the analysis of the data and their representation in the manuscript. All authors reviewed the manuscript.

References

- (1) Rovira, C. Bis (ethylenethio) tetrathiafulvalene (BET-TTF) and related dissymmetrical electron donors: From the molecule to functional molecular materials and devices (OFETs). *Chem. Rev.* **2004**, *104*, 5289–5317
- (2) Allard, S.; Forster, M.; Souharce, B.; Thiem, H., Scherf, U. Organic semiconductors for solution-processable field-effect transistors (OFETs). *Angew Chem Int Edit* **2008**, *47*, 4070–4098
- (3) Miskiewicz, P.; Mas-Torrent, M.; Jung, J.; Kotarba, S.; Glowacki, I.; Gomar-Nadal, E.; Amabilino, D. B.; Veciana, J.; Krause, B.; Carbone, D.; et al. Efficient high area OFETs by solution based processing of a π -electron rich donor. *Chem. Mater.* **2006**, *18*, 4724–4729
- (4) Di, C. A.; Zhang, F.; Zhu, D. Multi functional integration of organic field effect transistors (OFETs): Advances and perspectives. *Adv Mater* **2013**, *25*, 313–330
- (5) Jacob, M. V. Organic semiconductors: Past, present and future. *Electronics* **2014**, *3*, 594–597
- (6) Sirringhaus, H. 25th anniversary article: Organic field-effect transistors: The path beyond amorphous silicon. *Adv Mater* **2014**, *26*, 1319–1335
- (7) Gamota, D. R.; Brazis, P.; Kalyanasundaram, K.; Zhang, J. (Eds.) *Printed organic and*

molecular electronics; Springer Science & Business Media, 2013

- (8) Furno, M.; Kleemann, H.; Schwartz, G.; Blochwitz-Nimoth, J. 39.4 L: Late-news paper: Vertical organic transistors (V-OFETs) for truly flexible AMOLED displays. *SID Symposium Digest of Technical Papers* **2015**, *46*, 597–600
- (9) Kudo, K.; Kuniyoshi, S.; Yamauchi, H.; Iizuka, M.; Sakai, M. Vertical channel organic transistors for information tag applications. *IEICE transactions on electronics* **2013**, *96*, 340–343
- (10) Nair, A. K.; Machavaram, V. R.; Mahendran, R. S.; Pandita, S. D.; Paget, C.; Barrow, C.; Fernando, G. F. Process monitoring of fibre reinforced composites using a multi-measurand fibre-optic sensor. *Sensor Actuat B:-Chem* **2015**, *212*, 93 – 106
- (11) Ryu, G. S.; Park, K. H.; Park, W. T.; Kim, Y. H.; Noh, Y. Y. High-performance diketopyrrolopyrrole-based organic field-effect transistors for flexible gas sensors. *Org Electron* **2015**, *23*, 76–81
- (12) Minami, T.; Sato, T.; Minamiki, T.; Fukuda, K.; Kumaki, D.; Tokito, S. A novel OFET-based biosensor for the selective and sensitive detection of lactate levels. *Biosens Bioelectron* **2015**, *74*, 45–48
- (13) Nielsen, C. B.; Turbiez, M.; McCulloch, I. Recent advances in the development of semiconducting DPP-containing polymers for transistor *Adv Mater* **2013**, *25*, 1859–1880
- (14) Ye, Y.; Zhang, M.; Liu, H.; Liu, X.; Zhao, J. Theoretical investigation on the oligothiophenes under the influence of external electric field. *J. Phys. Chem. Solids* **2008**, *69*, 2615–2621
- (15) Gierschner, J.; Cornil, J.; Egelhaaf, H. J. Optical bandgaps of p-conjugated organic materials at the polymer limit: Experiment and theory. *Adv Mater* **2007**, *19*, 173–191
- (16) Zhang, X.; Richter, L. J.; DeLongchamp, D. M.; Kline, R. J.; Hammond, M. R.; McCulloch, I.; Heeney, M.; Ashraf, R. S.; Smith, J. N.; Anthopoulos, T. D.; et al Molecular packing of high-mobility diketo pyrrolo-pyrrole polymer semiconductors with branched alkyl side chains. *J. Am. Chem. Soc.* **2011**, *133*, 15073–15084
- (17) Gao, X.; Geng, H.; Peng, Q.; Ren, J.; Yi, Y.; Wang, D.; Shuai, Z. Nonadiabatic molecular dynamics modeling of the intrachain charge transport in conjugated diketopyrrolo-pyrrole polymers. *J Phys Chem C* **2014**, *118*, 6631–6640
- (18) Yin, S.; Lv, Y. Modeling hole and electron mobilities in pentacene ab-plane. *Org Electron* **2008**, *9*, 852–858
- (19) Marcus, R. A. On the theory of oxidation-reduction reactions involving electron transfer. I. *J Chem Phys* **1956**, *24*, 966–978
- (20) Marcus, R. A. Chemical and electrochemical electron-transfer theory. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155–196
- (21) Marcus, R. A. Electron transfer reactions in chemistry. Theory and experiment. *Rev. Mod. Phys.* **1993**, *65*, 599–610
- (22) Newton, M. D. Quantum chemical probes of electron-transfer kinetics: The nature of donor-acceptor interactions. *Chem. Rev.* **1991**, *91*, 767–792
- (23) Cave, R. J.; Newton, M. D. Calculation of electronic coupling matrix elements for ground and excited state electron transfer reactions: Comparison of the generalized Mulliken-Hush and block diagonalization methods. *J Chem Phys* **1997**, *106*, 9213–9226
- (24) Amini, A.; Harriman, A. Computational methods for electron-transfer systems. *J Photoch Photobio C* **2003**, *4*, 155–177
- (25) Schober, C.; Reuter, K.; Oberhofer, H. Critical analysis of fragment-orbital DFT schemes for the calculation of electronic

- coupling values. *J Chem Phys* **2016**, *144*, 05410301–05410311
- (26) Pati, R.; Karna, S. P. Ab initio Hartree–Fock study of electron transfer in organic molecules. *J Chem Phys* **2001**, *115*, 1703–1715
- (27) Li, X. Y.; Tang, X. S.; He, F. C. Electron transfer in poly(p–phenylene) oligomers: effect of external electric field and application of Koopmans theorem. *Chem Phys* **1999**, *248*, 137–146
- (28) Fabiano, S.; Musumeci, C.; Chen, Z.; Scandurra, A.; Wang, H.; Loo, Y. L.; Facchetti, A.; Pignataro, B. From monolayer to multilayer N–channel polymeric field–effect transistors with precise conformational order. *Adv Mater* **2012**, *24*, 951–956
- (29) Karpov, Y.; Zhao, W.; Raguzin, I.; Beryozkina, T.; Bakulev, V.; Al-Hussein, M.; Hüßler, L.; Stamm, M.; Voit, B.; Facchetti, A.; et al. Influence of semiconductor thickness and molecular weight on the charge transport of a naphthalenediimide–based copolymer in thin–film transistors. *ACS Appl. Mater. Interfaces* **2015**, *7*, 12478–12487
- (30) Steyrlleuthner, R.; Schubert, M.; Jaiser, F.; Blakesley, J. C.; Chen, Z.; Facchetti, A.; Nehler, D. Bulk electron transport and charge injection in a high mobility n–type semiconducting polymer. *Adv Mater* **2010**, *22*, 2799–2803
- (31) Wang, L.; Fine, D.; Basu, D.; Dodabalapur, A. Electric–field–dependent charge transport in organic thin–film transistors. *J. Appl. Phys.* **2007**, *101*, 054515
- (32) Chen, Z.; Lee, M. J.; Shahid Ashraf, R.; Gu, Y.; Albert-Seifried, S.; Meedom Nielsen, M.; Schroeder, Bob; Anthopoulos, T. D.; Heeney, Ma.; McCulloch, I. et al. High–performance ambipolar diketopyrrolopyrrole–thieno [3, 2-b] thiophene copolymer field-effect transistors with balanced hole and electron mobilities. *Adv Mater* **2012**, *24*, 647–652
- (33) Li, J.; Zhao, Y.; Tan, H. S.; Guo, Y.; Di, C. A.; Yu, G.; Liu, Y.; Lin, M.; Lim, S. H.; Zhou, Y. et al. A stable solution-processed polymer semiconductor with record high–mobility for printed transistors. *Scientific reports, Nature Publishing Group* **2012**, *2*, 754
- (34) Bronstein, H.; Chen, Z.; Ashraf, R. S.; Zhang, W.; Du, J.; Durrant, J. R.; Shakya Tuladhar; P. Song, K.; Watkins, S. E.; Geerts, Y. et al. Thieno [3, 2-b] thiophene–diketopyrrolopyrrole–containing polymers for high–performance organic field–effect transistors and organic photovoltaic devices. *J. Am. Chem. Soc.* **2011**, *133*, 3272–3275
- (35) Kanimozhi, C.; Yaacobi-Gross, N.; Chou, K. W.; Amassian, A.; Anthopoulos, T. D.; Patil, S. Diketopyrrolopyrrole–diketopyrrolopyrrole–based conjugated copolymer for high–mobility organic field-effect transistors. *J. Am. Chem. Soc.* **2012**, *134*, 16532–16535
- (36) Li, Y.; Singh, S. P.; Sonar, P. A high mobility P–type DPP–thieno [3, 2-b] thiophene copolymer for organic thin-film transistors. *Adv Mater* **2010**, *22*, 4862–4866
- (37) Sun, B., Hong, W., Yan, Z., Aziz, H., & Li, Y. Record high electron mobility of 6.3 cm² V⁻¹ s⁻¹ achieved for polymer semiconductors using a new building block. *Adv Mater* **2014**, *26*, 2636–2642
- (38) Li, W.; Lee, T.; Oh, S. J.; Kagan, C. R. Diketopyrrolopyrrole–based p–bridged donor–acceptor polymer for photovoltaic applications. *ACS Appl. Mater. Interfaces* **2011**, *3*, 3874–3883
- (39) Günther, F.; Gemming, S.; Seifert, G. Hopping–based charge transfer in diketopyrrolopyrrole–based donor–acceptor polymers: A theoretical study. *J Phys Chem C* **2016**, *120*, 9581–9587
- (40) Ma, J.; Hashimoto, K.; Koganezawa, T.; Tajima, K. End-on orientation of semiconducting polymers in thin films induced by surface segregation of fluoroalkyl chains. *J. Am. Chem. Soc.* **2013**, *135*, 9644–9647

- (41) Ma, J.; Hashimoto, K.; Koganezawa, T.; Tajima, K. Enhanced vertical carrier mobility in poly (3-alkylthiophene) thin films sandwiched between self-assembled monolayers and surface-segregated layers. *Chem. Commun.* **2014**, *50*, 3627–3630
- (42) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. et al. General atomic and molecular electronic structure system. *J. Comput. Chem* **1993**, *14*, 1347–1363
- (43) Gordon, M.; Schmidt, M.W. In *Theory and Applications of Computational Chemistry: the first forty years*; Dykstra, C. E., G.Frenking, K.S.Kim, G.E.Scuseria, Eds.; Elsevier: Amsterdam, 2005; pp. 1167-1189
- (44) Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys Rev A* **1988**, *38*, 3098–3100
- (45) Sancho-García, J. C.; Pérez-Jiménez, A. J. Accurate calculation of transport properties for organic molecular semiconductors with spin-component scaled MP2 and modern density functional theory methods. *J Chem Phys* **2008**, *129*
- (46) Sancho-Garcia, J. C. Assessment of density-functional models for organic molecular semiconductors: The role of Hartree-Fock exchange in charge-transfer processes. *Chem. Phys* **2007**, *331*, 321–331
- (47) Chen, S.; Ma, J. Charge transport in stacking metal and metal-free phthalocyanine iodides. Effects of packing, dopants, external electric field, central metals, core modification, and substitutions. *J. Comput. Chem.* **2009**, *30*, 1959–1972

electric field effects

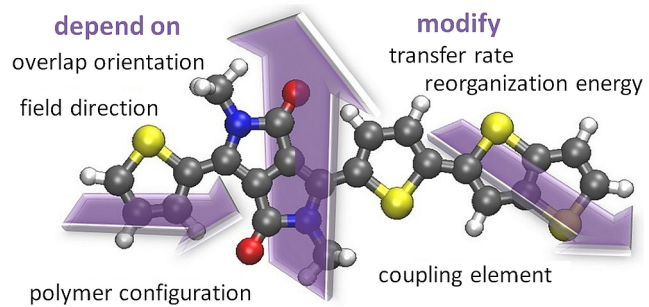


Figure 13: TOC Graphic