

Effect of Electronic Polarization on Charge-Transport Parameters in Molecular Organic Semiconductors

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Abstract: Theoretical investigations of charge transport in organic materials are generally based on the “energy splitting in dimer” method and routinely assume that the transport parameters (site energies and transfer integrals) determined from monomer and dimer calculations can be reliably used to describe extended systems. Here, we demonstrate that this transferability can fail even in molecular crystals with weak van der Waals intermolecular interactions, due to the substantial (but often ignored) impact of polarization effects, particularly on the site energies. We show that the neglect of electronic polarization leads to qualitatively incorrect values and trends for the transfer integrals computed with the energy splitting method, even in simple prototypes such as ethylene or pentacene dimers. The polarization effect in these systems is largely electrostatic in nature and can change dramatically upon transition from a dimer to an extended system. For example, the difference in site energy for a prototypical “face-to-edge” one-dimensional stack of pentacene molecules is calculated to be 30% greater than that in the “face-to-edge” dimer, whereas the site energy difference in the pentacene crystal is vanishingly small. Importantly, when computed directly in the framework of localized monomer orbitals, the transfer integral values for dimer and extended systems are very similar.

Introduction

Molecular organic semiconductors are currently the object of much interest because of their applications in new generations of (opto)electronic devices.^{1–5} A detailed understanding of the charge-transport mechanism in these materials is therefore of interest from both fundamental and practical points of view,^{6–8} since charge transport is a critical component of device operation in, for instance, organic light-emitting diodes, solar cells, or field-effect transistors.

The challenge for theory is to explain how chemical composition, geometric structure, and packing affect the transport properties. It was shown, for instance, that pentacene, one of the most studied and promising organic semiconductors, crystallizes in different phases depending on growth conditions

and film thickness.^{9–16} At least four¹³ pentacene crystalline polymorphs have been reported in the literature. Recent studies on pentacene monolayers¹⁷ indicate that this variety is even larger. The electronic, optical, and transport properties of different morphologies, despite similar geometric parameters, vary substantially.^{18–22}

The relationship between charge-transport properties and geometric structure can be understood by considering the electronic Hamiltonian in a simple tight-binding approximation:⁷

$$H = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m \neq n} t_{mn} a_m^\dagger a_n \quad (1)$$

Here, a_m^\dagger and a_m are the creation and annihilation operators,

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respectively, for an electron on molecular site m , ϵ_m is the electron site energy, and t_{mn} is the transfer integral (electronic coupling). Whether a bandlike or hopping transport mechanism is operative, the charge-transport characteristics depend on both parameters.^{6,7,23–28} For instance, the carrier mobility in the hopping regime is controlled by the intersite electron-transfer (ET) rate k_{ij} , given in the semiclassical approximation by^{6–8,29}

$$k_{ij} = t_{ij}^2 \sqrt{\frac{\pi}{\hbar^2 k_B T \lambda_{ij}}} \exp\left(-\frac{(\Delta E_{ij} - \lambda_{ij})^2}{4\lambda_{ij} k_B T}\right) \quad (2)$$

Here, λ_{ij} is the reorganization energy and $\Delta E_{ij} = \epsilon_i - \epsilon_j$, where ϵ_i and ϵ_j are the energies of the initial and final states. The intermolecular overlap of the electronic wave functions and thus the transfer integral depend delicately on the intermolecular distance and orientation.³⁰ While charge transport also depends on ΔE_{ij} , and this dependence was recently included in band-structure calculations of oligoacene systems, the origin of ΔE_{ij} was solely attributed to the geometric differences of the two molecules present in the unit cell.^{23,24} We show here that there is another contribution to ΔE_{ij} that results from the polarization of the localized electronic states by intermolecular interactions. We demonstrate that this contribution can be very large and, like the electronic coupling, is also very sensitive to the details of the system environment.

Here, without losing any generality, we will restrict our study to hole transport. However, it is important to note that it is now well established, on both experimental³¹ and theoretical³⁰ grounds, that hole and electron transport can both be very significant in a number of organic semiconductors. While it was long thought that organic semiconductors were almost exclusively p-type, the development of efficient n-type organic semiconductors opens the way to ambipolar devices.³²

Methodology

Within a simple tight-binding model, the total valence bandwidth (W) results from the interaction of the HOMO (highest occupied molecular orbital) levels of all molecules. For instance, in the case of an infinite one-dimensional stack, $W = 4t$. In the same approximation, the interaction of monomer HOMOs leads to a level splitting $2t$ in a dimer. This result provides a simple and often reliable way to estimate the transfer integrals, since it involves the investigation of a dimer rather

than an infinite system. Thus, the absolute value of the transfer integral related to hole transport can be obtained from the energy difference, $t = (E_H - E_{H-1})/2$, where E_H and E_{H-1} are the energies of the HOMO and HOMO-1 orbitals taken from the closed-shell configuration of a dimer.^{8,26–28,33–35} We show below that the application of this simple approach is restricted by several conditions.

Following Siebbeles and co-workers,^{32,36} we define one-electron dimer states in terms of localized monomer orbitals. Assuming that the dimer HOMO and HOMO-1 result from the interaction of only monomer HOMOs (Ψ_i), the orbital energies of the dimer are described by the following secular equation:

$$\mathbf{HC} - \mathbf{ESC} = \mathbf{0} \quad (3)$$

where \mathbf{H} and \mathbf{S} are the system Hamiltonian and overlap matrices in the basis of monomer HOMOs:

$$\mathbf{H} = \begin{pmatrix} e_1 & J_{12} \\ J_{12} & e_2 \end{pmatrix} \quad (4)$$

$$\mathbf{S} = \begin{pmatrix} 1 & S_{12} \\ S_{12} & 1 \end{pmatrix} \quad (5)$$

The matrix elements that enter eq 4 have the form

$$e_i = \langle \Psi_i | \hat{H} | \Psi_i \rangle \quad (6)$$

$$J_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle \quad (7)$$

The matrix elements e_i and J_{ij} have the same physical meaning as the parameters ϵ_i and t_{ij} in eqs 1 and 2; however, these two sets are *not* identical. Indeed, while monomer orbitals Ψ_i used to derive e_i and J_{ij} are nonorthogonal, eqs 1 and 2 are given in an orthogonal basis. An orthonormal basis set that maintains as much as possible the initial local character of the monomer orbitals can be obtained from Ψ_i by means of Löwdin's symmetric transformation.³⁷ In a symmetrically orthonormalized basis, eq 4 takes the form

$$\mathbf{H}^{eff} = \begin{pmatrix} e_1^{eff} & J_{12}^{eff} \\ J_{12}^{eff} & e_2^{eff} \end{pmatrix} \quad (8)$$

where

$$e_{1(2)}^{eff} = \frac{1}{2} \frac{(e_1 + e_2) - 2J_{12}S_{12} \pm (e_1 - e_2)\sqrt{1 - S_{12}^2}}{1 - S_{12}^2} \quad (9)$$

$$J_{12}^{eff} = \frac{J_{12} - \frac{1}{2}(e_1 + e_2)S_{12}}{1 - S_{12}^2} \quad (10)$$

In this way, e_i^{eff} and J_{ij}^{eff} are now identical to ϵ_i and t_{ij} . (We note that neglecting to apply the orthogonalization procedure³⁵ leads to J_{ij} values which can differ from the J_{ij}^{eff} values by as much as a factor of 2.)

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Equation 3 expressed in the orthonormal basis becomes a standard eigenvalue problem:

$$\mathbf{H}^{\text{eff}}\mathbf{C} = E\mathbf{C} \quad (11)$$

The resulting energy splitting (absolute value) between the dimer HOMO and HOMO-1 levels writes

$$\Delta E_{12} = \sqrt{(e_1^{\text{eff}} - e_2^{\text{eff}})^2 + (2J_{12}^{\text{eff}})^2} \quad (12)$$

Equation 12 indicates that the transfer integral ($J_{ij}^{\text{eff}} \equiv t$) can be estimated as one-half of ΔE_{12} when (1) the site energies e_i (e_i^{eff}) are equal and (2) the HOMO and HOMO-1 orbitals of the dimer contain contributions that come exclusively from the monomer HOMOs. We also note that when the transfer integral is derived from ΔE_{12} , it is explicitly assumed that an orthogonal localized (diabatic) basis set is used and the derived transfer integral should be interpreted as an effective quantity that accounts for both J_{ij} and S_{ij} .

The fact that ΔE_{12} can be affected by site energies was largely overlooked in the literature, especially when dealing with systems formed from identical monomers. The common assumption that the site energies of identical monomers are the same is incorrect when the monomers are not equivalent. This can be easily understood based on symmetry considerations: the energy difference $e_1 - e_2$ ($e_1^{\text{eff}} - e_2^{\text{eff}}$) vanishes only if the matrix elements H_{11} and H_{22} , which define the site energies, can be obtained from one another by a symmetry transformation; i.e., the dimer is symmetric. Otherwise, when the molecules are not equivalent by symmetry, the molecules polarize each other differently and Δe^{eff} is nonzero. In this case, as we show below, the energy-splitting approach can drastically overestimate the transfer integral.

Computational Methods

Most calculations were carried out at the density functional theory (DFT) level using the B3LYP functional in conjunction with the 6-31+G* basis set. Some of the largest calculations were performed at the Hartree–Fock level of theory with the smaller 6-31G* basis set. We found that the neglect of diffuse functions and the lack of electron correlation in the Hartree–Fock model have a relatively small effect on site energy differences but may have a significant effect on transfer integrals (see Table S2 and subsequent discussion in the Supporting Information). In addition, we also carried out calculations (at the 6-31+G*/B3LYP level) on an ethylene dimer where the atoms of one monomer were replaced with point charges (without basis functions), fitted to reproduce the monomer electrostatic potential. Full details of computations, including geometrical parameters, are presented in the Supporting Information. All computations were performed with the developmental version of the MPQC package.³⁸

Results and Discussion

As a first example of how J_{12}^{eff} and Δe^{eff} depend on the intermolecular parameters, we consider a π -stacked ethylene dimer with a fixed 5 Å center-to-center distance and in which one monomer is tilted around its longitudinal molecular axis. Figure 1 illustrates the evolution of J_{12}^{eff} and Δe^{eff} as a function of the tilt angle. As seen from Figure 1, ΔE_{12} varies only slightly with the angle and is maximal at the face-to-edge configuration.

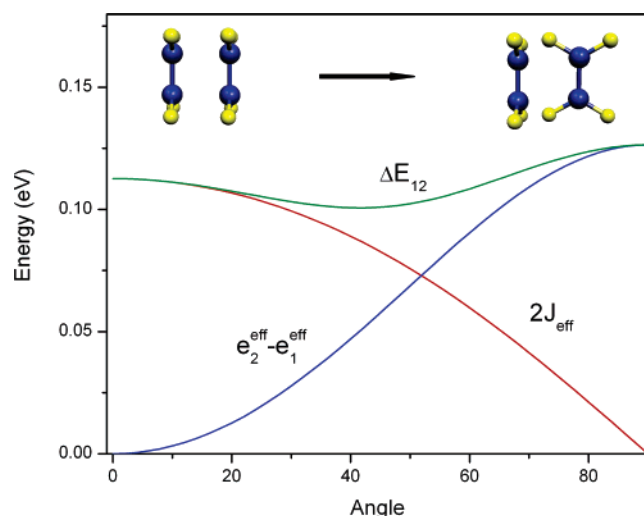


Figure 1. Evolution of the transfer integral and the difference of site energies as a function of the tilt angle in the ethylene dimer.

The transfer integral gradually decreases with the tilt angle from its maximum value at the cofacial orientation to exactly zero when the system reaches the face-to-edge configuration. In contrast, Δe^{eff} reveals the opposite trend. As a consequence, in the face-to-edge configuration, Δe^{eff} is the *sole* contribution to the energy splitting, ΔE_{12} .

A recent study of charge transport in a series of oligo-heterocycle-based molecular systems by Hutchison et al.²⁸ presents an even more significant enhancement of ΔE_{12} upon going from the cofacial to the perpendicular orientation. The enhancement in the energy splitting upon increase in the tilt angle was explained by the increase in overlap (and thus transfer integral) resulting from the reduction of the nearest-contact intermolecular distance. However, our preliminary calculations indicate that the enhancement of ΔE_{12} is due to an increase in the polarization-driven site-energy splitting, Δe^{eff} , and has little to do with the transfer integral. A full investigation of oligo-heterocycles based on our present methodology is now in progress, and detailed results will be reported elsewhere.

The significant polarization-induced ΔE_{12} (which results from Δe^{eff}) in the face-to-edge dimers of these nonpolar species should not be surprising. A simple rationalization is that the positively charged hydrogens of the “edge” molecule lower the energy of the mainly π -type HOMO of the “face” molecule. To test this hypothesis, we computed orbital energies of each ethylene in the dimer where the other molecule was represented by point charges derived from the monomer calculation. The site energies estimated in this way along with those derived from the quantum-mechanical (QM) calculations (using eq 9) of the dimer are compared in Figure 2. The site energy of the “face” molecule decreases with the tilt, while the site energy of the “edge” molecule remains mostly constant. Although the values of the site energies computed with the two methods differ to some extent, the qualitative behaviors are similar. The good agreement between QM and mixed QM/electrostatic results underscores the mainly classical origin of Δe (Δe^{eff}).

In our next example, we have studied the dependence of J_{12}^{eff} as a function of the intermolecular distance, R . Figure 3 compares the charge-transfer parameters obtained for a cofacial pentacene dimer with those obtained for a tilted dimer, as encountered in the pentacene crystal. The dependence of the

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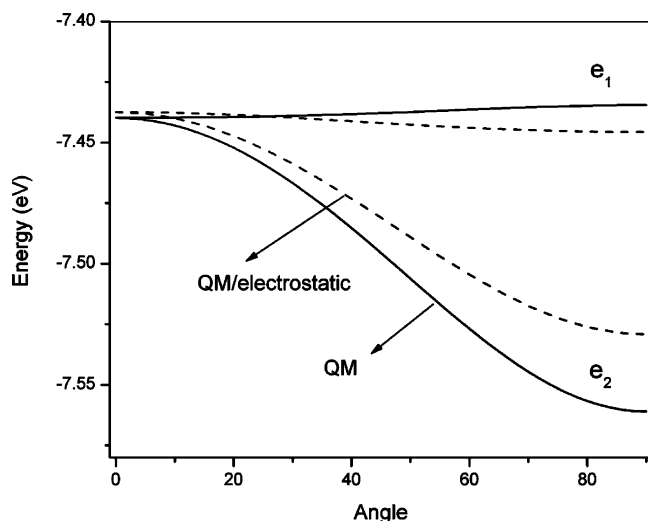


Figure 2. Comparison of site energies in the ethylene dimer derived from quantum mechanical (QM) and mixed QM/electrostatic calculations (see text for details).

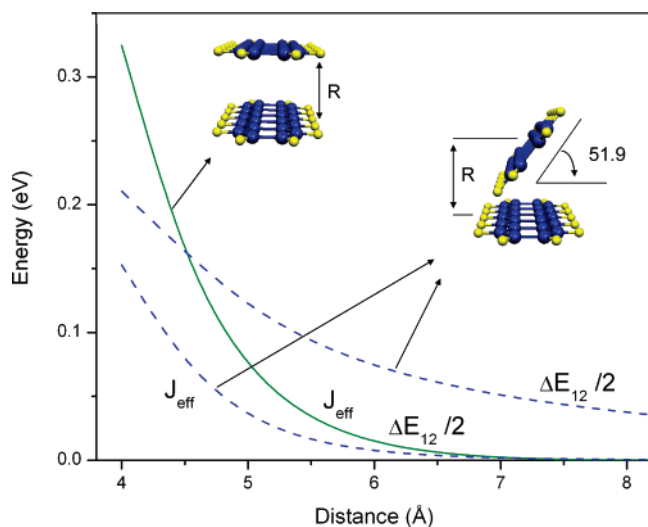


Figure 3. Evolution of the effective transfer integral as a function of intermolecular center-to-center distance (R) of the cofacial and tilted dimers computed by means of eq 10 (J_{eff}) and the dimer energy splitting approach ($\Delta E_{12}/2$). The two approaches are equivalent for the cofacial dimer but differ qualitatively for the tilted dimer.

transfer integrals on the intermolecular separation for analogous pentacene dimers was also recently discussed by Deng and Goddard²⁷ but simply in the framework of the energy-splitting method (which again, as we show below, can lead to misleading results). As evident from Figure 3, for all considered distances, the electronic coupling derived for a cofacial dimer is larger than that in the tilted dimer. In both cases, J_{12}^{eff} exhibits the same (essentially exponential) dependence on intermolecular distance; this result is not surprising, since the electronic coupling is driven by the orbital overlap which, regardless of the monomer–monomer orientation, decays exponentially with distance. For the cofacial dimer, the estimates of J_{12}^{eff} based on eq 10 and on the energy-splitting method are identical. In contrast, in the case of the tilted dimer, the energy-splitting method overestimates the coupling. For instance, for $R = 8 \text{ \AA}$, the energy-splitting method predicts a J_{12}^{eff} value of 60 meV while the actual value is smaller than 1 meV. Moreover, the energy-splitting approach in general would predict a qualitatively

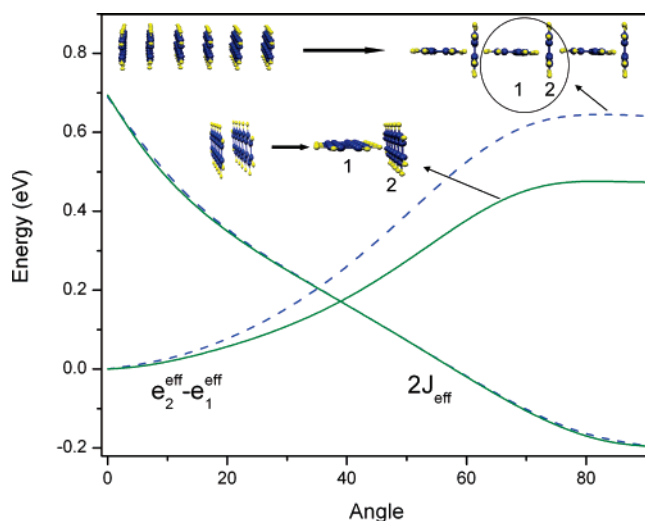


Figure 4. Evolution of the transfer integral and the difference of site energies as a function of the tilt angle in an isolated pentacene dimer and a six-monomer pentacene stack.

incorrect dependence of J_{12}^{eff} on R . This failure is due to the fact that for R larger than 5–6 \AA , the ΔE_{12} energy term is dominated by Δe^{eff} ; due to its electrostatic nature, this contribution decays with R much more slowly than the overlap and, consequently, the transfer integral.

It is clear that the parameters obtained from dimer calculations might be of limited usefulness for explaining charge transfer in larger systems, such as thin films or crystals, because the polarization in the dimer might not reflect the polarization in the larger structure. The straightforward way to describe larger structures is to use the Hamiltonian of the full (infinite) system. Such a Hamiltonian, however, can only be computed for a periodic system. We will therefore approximate the full system by a small subset M . Equations 6 and 7 become

$$e_i = \langle \Psi_i | \hat{H}_M | \Psi_i \rangle \quad (14)$$

$$J_{ij} = \langle \Psi_i | \hat{H}_M | \Psi_j \rangle \quad (15)$$

For a reliable description of the local electrostatic fields when computing the site energies and the transfer integral between two given sites (i and j), the subset M must include the sites of interest as well as at least all nearest neighbors. We first consider a prototypical one-dimensional arrangement of pentacene. The evolution of J_{12}^{eff} and Δe^{eff} as a function of the tilt angle in an isolated pentacene dimer and a six-monomer stack are shown in Figure 4. Our calculations indicate that the transfer integrals for the isolated and embedded dimers, for any dimer configuration, practically coincide at all values of the tilt angle. The situation is quite different for the site energies. In the face-to-face orientation, all molecules are equivalent, and there is no net polarization contribution; Δe^{eff} is therefore zero in the isolated dimer and the one-dimensional structure. In a tilted pentacene dimer, as in the ethylene dimer, the site energy of the “face” molecule is much more strongly affected by polarization than that of the “edge” molecule. Thus, on going from cofacial to perpendicular orientation, the site energy changes from -4.74 eV to -5.08 and -4.61 eV for the “face” and “edge” molecules, respectively. In the six-molecule stack, each of the two molecules is affected by at least two nearest

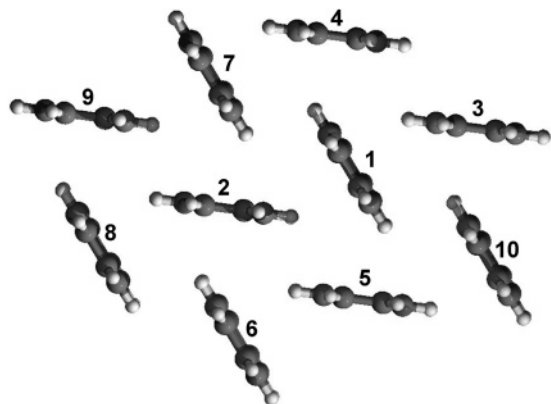


Figure 5. The fragment of a pentacene crystal¹⁴ used to compute the charge-transfer parameter (**1** and **2** are the target molecules).

neighbors. As a result, Δe^{eff} increases from 0.47 to 0.64 eV on going from the dimer to the stack.

Finally, we examined polarization effects in a two-dimensional layer found in the pentacene crystal. This structure contains two molecules per unit cell, labeled **1** and **2**. Polarization-driven site-energy splitting is therefore expected. A 10-monomer fragment, shown in Figure 5, was chosen as a suitable approximation to the full crystal environment of molecules **1** and **2**.¹⁴ Compared to only two nearest neighbors in the one-dimensional stack, each molecule now has four nearest neighbors. Each molecule thus participates in four face-to-edge interactions. For example, molecule **1** interacts as an “edge” with molecules **2** and **3** and as a “face” with molecules **4** and **5**. The strengths of these interactions can be estimated as the site-energy splitting due to polarization in corresponding dimers. For all four interactions, the dimer splittings (Δe) are 0.326 eV, within 1 meV of each other. The important consequence is a near-complete cancellation of the polarization effects of the four face-to-edge interactions with a net result of $\Delta e = 0.034$ eV between **1** and **2**; this value is approximately an order of magnitude smaller than that in the isolated dimer of **1** and **2**. The main conclusion is that the site energies of the two types of molecules are nearly identical in the pentacene crystal. As in the one-dimensional case, the transfer integrals calculated for the isolated and embedded dimers practically coincide.

Our results suggest that, depending on the exact topology, the site-energy difference obtained for an isolated dimer can build up or cancel in the crystal. Thus, any deformation of the crystal could significantly affect both the transfer integral and site-energy difference. This aspect should be properly taken into account in any modeling of the charge-transport properties.

Conclusion

Our key finding is that failure to account for polarization effects can impact the computed charge-transport parameters of even nonpolar materials, e.g., pentacene, in a dramatic fashion. In ethylene and pentacene dimers, polarization is the greatest contributor to the site-energy splitting in the “face-to-edge” structures. Such face-to-edge interactions abound in the herringbone-type structures commonly found in organic materials of interest such as oligoacenes or oligothiophenes. To describe the electronic structure of such materials, the effective

one-particle Hamiltonian must take the polarization effects explicitly into account. We presented a straightforward method to include these effects in a tight-binding Hamiltonian. We have also shown that full QM calculations of the site-energy splitting can be well approximated by a mixed QM/electrostatic model.

We demonstrated major differences between the electronic structures of a pentacene crystal and a one-dimensional stack, which can be explained simply in terms of local polarization effects. The net polarization contribution to the site energy difference in the pentacene crystal is small because the two nonequivalent molecules within the unit cell have nearly identical environments. In contrast, the polarization-driven site energy difference in a one-dimensional stack is enhanced with respect to an isolated dimer. Similar examples of significant polarization effects on site energies are likely to occur in other materials.³⁶

Our results also reveal that the energy splitting between the dimer HOMO and HOMO-1 levels could contain a significant contribution from the polarization-induced site-energy difference, Δe , even in the case of chemically identical (but symmetry-distinct) monomers (for instance, a tilted dimer). In this case, as we have shown for ethylene and pentacene dimers, the dimer energy-splitting approach significantly overestimates the transfer integral. We have also shown that the problems arising from the energy-splitting approach can be avoided by computing the transfer integrals directly, in terms of properly orthogonalized monomer orbitals (eqs 7 and 10). Our calculations indicate that the transfer integrals calculated in this way for isolated dimers and for dimers embedded in a crystal environment practically coincide. In contrast to the evolution of the site energy difference, the polarization effects have little impact on the transfer integrals.

Finally, we note that the neglect of polarization effects could also lead to erroneous results when the transfer integrals and/or electron–phonon couplings are derived from a fit of ab initio band-structure calculations to a tight-binding Hamiltonian (eq 1). Computational work to better comprehend these effects is under way.

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Supporting Information Available: Full details of all computations, including the geometrical parameters, are provided as well as a discussion of the dependence of the charge-transfer parameters on the level of theory. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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