

Quantum-Chemical Characterization of the Origin of Dipole Formation at Molecular Organic/Organic Interfaces

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Recent experiments have reported a vacuum level shift at the interface between organic materials due to the formation of an interface dipole layer. On the basis of quantum-chemical calculations, this paper sheds light on the factors contributing to the formation of an interface dipole between an electron donor and an electron acceptor, considering as model system a complex made of tetrathiafulvalene (TTF) as a donor and tetracyanoquinodimethane (TCNQ) as an acceptor. The results indicate that the interface dipole is governed both by charge-transfer and polarization effects and allow for disentangling of their respective contributions. Two regimes of charge transfer can be distinguished depending on the strength of the electronic coupling: a fractional charge transfer occurs in the strong coupling regime while only integer charges are transferred when the coupling is weak. The polarization contribution can be significant, even in the presence of a pronounced charge transfer between the donor and acceptor molecules. The values of ionization potential and electron affinity of the donor and acceptor molecules may experience shifts as large as several tenths of an eV at the interface with respect to the isolated compounds.

1. Introduction

The field of organic electronics has experienced a rapid progress during the last decade. Applications envisioned for organic semiconductors encompass light-emitting devices (LEDs), solar cells, field-effect transistors and sensors. Many of these devices incorporate several components; this is especially the case in solar cells in which π -donor (D) and π -acceptor (A) compounds are used under the form of a bilayer or a homogeneous blend to dissociate excitations into free charge carriers at their interface.^[1] This also applies to light-emitting devices that are generally made of several layers with specific functions (hole/electron transporting layers, exciton blocking layers, emitting layers). Since key mechanisms such as exciton dissociation in solar cells or charge recombination in LEDs occur at the interface between organic semiconductors, a deep understanding of electronic processes at

organic/organic interfaces will prove very useful to develop new strategies towards devices with enhanced efficiencies.

A central issue is to determine the way the frontier electronic levels of two adjacent organic layers align ones with respect to the others at the interface. The Schottky–Mott model is the simplest one that can be applied to organic conjugated materials. In this model, two adjacent organic layers share a common vacuum level. If this holds true, the energetic characteristics of the interface can be designed by tailoring separately the electronic properties of the two materials. This is typically done with organic solar cells by inferring the alignment of the HOMO and LUMO levels of the donor and acceptor units from cyclic voltammetry measurements performed separately for the two compounds. However, recent experimental studies have clearly shown that this picture is usually incorrect.^[2–4] An additional potential is often induced at the donor/acceptor

interface, which shifts the vacuum level of one layer with respect to the other. In the case of organic/organic interfaces, this additional potential is associated with the formation of an interface dipole layer (IDL). When approximating the IDL by two infinite charged plates, the magnitude of the vacuum level shift (VLS) originating from the charge distribution is given in this simple model by:

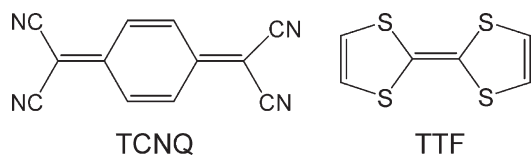
$$VLS = \frac{M_z}{\epsilon\epsilon_0 S} \quad \text{or} \quad VLS[V] = \frac{M_z[D]}{\epsilon S[\text{\AA}^2]} \times 37.6 \quad (1)$$

where M_z is the component of the dipole moment of a pair of interacting donor/acceptor molecules in the direction perpendicular to the interface and S is the surface area occupied by the donor–acceptor complex at the interface.

Vacuum level shifts at metal/organic interfaces are well documented at both the experimental and theoretical levels.^[2,5–7] In contrast, although there is considerable experimental evidence for vacuum level shifts at organic/organic interfaces, theoretical papers addressing this issue at the quantum-chemical level are still scarce.^[8,9] While the description of a well-ordered interface would preferentially require calculations on an infinite system using periodic conditions, this approach is not relevant for

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Scheme 1. Chemical structures of TCNQ and TTF.

interfaces between rather amorphous materials that are generally characterized at the experimental level.

The approach adopted in this paper is to characterize the electronic interactions leading to the formation of an interface dipole at an organic/organic interface by performing quantum-chemical calculations on a model system made of a single donor and a single acceptor molecule, with various geometric arrangements. This choice is primarily motivated by the fact that the largest interactions are expected to occur between the molecules facing each other at the interface; of course, predicting the absolute values of the vacuum level shifts would require an explicit account of the contribution arising from the long-range electronic interactions. We focus here, in particular, on a complex made by a strong donor (tetrathiafulvalene, TTF) and a strong acceptor (tetracyanoquinodimethane, TCNQ, see chemical structures in Scheme 1), since the VLS between TTF and TNCQ layers has been recently characterized experimentally by Ultraviolet Photoelectron Spectroscopy (UPS) and estimated to be on the order of 0.6 eV.^[10]

2. Interface Dipole: Charge Transfer and Polarization Components

The formation of an interface dipole between two organic layers originates from several dominant effects:

i) when the neutral state (DA) is more stable than any charge-transfer excited state (D^+A^- or D^-A^+), the formation of the interface dipole might stem from the admixture of a charge-transfer (CT) character in the ground-state wavefunction describing the donor/acceptor interface. Such a partial charge transfer in donor/acceptor complexes is a well-known phenomenon described previously at the theoretical level.^[11–14] At the second order of perturbation theory, the ground-state wavefunction of a donor–acceptor complex acquires some charge-transfer character due to the admixture of terms corresponding to excited CT states:

$$\Psi(D, A) = a\Psi_0(D, A) + \sum_i b_i\Psi_i(D^+A^-) + \sum_i c_i\Psi_i(D^-A^+) \quad (2)$$

where $\Psi_0(D, A)$ is an antisymmetrized product of the unperturbed wavefunctions of the donor and acceptor molecules; $\Psi(D^+A^-)$ [$\Psi(D^-A^+)$] is the wavefunction of a CT state corresponding to a charge transfer from [to] the donor to [from] the acceptor. The first-order correction coefficients (b_i

and c_i) to the wavefunction Ψ_0 are equal to $V_i/\Delta E_i$, with V_i the electronic coupling between the ground-state (GS) and the charge-transfer excited state CT_i , and ΔE_i the corresponding energy separation. Accordingly, the charge transfer admixture in the ground state is given by:

$$q \div \sum_i \pm \left(\frac{V_i}{\Delta E_i} \right)^2 \quad (3)$$

where the sign is determined by the direction of the charge transfer. It is usually assumed that $ci \ll bi$, since the $\Psi_i(D^-A^+)$ states are lying at much higher energies, so that a back charge transfer (from the acceptor to the donor) is generally less efficient. From Equation 3, it is clear that the amount of charge transferred at the interface is controlled not only by the difference in electronegativities (which is closely related to ΔE)^[15] but also by the electronic coupling between the two molecules. The electronic coupling V is very sensitive to the mutual orientation of the molecules and exponentially decreases with the distance between the molecules (due to the exponential decay of the overlap between the wavefunctions).^[16]

ii) the interfacial dipole layer may be formed by a polarization of the electronic cloud within the molecules, which is induced by interactions between all permanent and induced multipoles. This contribution can be described (in the basis of the molecular orbitals of the isolated molecules) by the admixture of locally excited states in the ground-state wavefunction:

$$\Psi(D, A) = a\Psi_0(D, A) + \sum_i b_i\Psi(D_0A_i^*) + \sum_i c_i\Psi_i(D_i^*A_0) \quad (4)$$

where D_0 [A_0] and D^* [A^*] stand for the unperturbed ground and excited states of the isolated donor [acceptor]. This mixing results from the fact that the singly excited configurations D^*A and DA^* built from the molecular orbitals of the isolated units are not orthogonal to the ground-state wavefunction calculated for the whole dimer. In the case of the single-point SCF calculations performed here, the difference between the ground and excited CT state (ΔE_i in Eq. 3) corresponds to the energy difference between the occupied and unoccupied one-electron levels involved in the CT state, together with a Coulomb term describing the attraction between the hole on one molecule and the electron on the other molecule.

iii) at small intermolecular distances, the wavefunctions of two neighboring molecules may overlap significantly, thus opening the way to Pauli repulsion effects. For instance, this interaction is responsible for the well-known “pillow effect” observed for molecules deposited on metals.^[17–19]

In the present work, we do not make a distinction between electrostatic and exchange interactions since we expect the exchange effects to be relatively small for the systems under study. Therefore, we attribute to polarization the difference between the total dipole and the dipole due to the charge transfer.

3. Computational Methodology

The choice of the computational method is guided by its performance in predicting the induced dipole moment in donor/acceptor complexes. For the sake of comparison, we will discuss below the results obtained at the semi-empirical Hartree–Fock Austin Model 1 (AM1),^[20,21] ab initio Hartree–Fock (HF) and density functional theory (DFT) levels. The hybrid B3LYP^[22,23] and BHandHLYP functionals introducing 20% and 50% of exact Hartree–Fock exchange, respectively, were used in the DFT calculations, as implemented in Gaussian03.^[24] The possibility of complete intermolecular charge transfer was studied with a multideterminant ansatz and discarded for our system, see Section 4.1 for the corresponding calculations and the Supporting Information for a derived analytical model. We used a split-valence 6-31G(d)^[25] basis set for most HF and DFT calculations; the performance of the 6-31+G(d) basis set was also tested. A basis set incorporating polarization functions is expected to be sufficient for the description of the polarization component.

The Mulliken charge partitioning scheme exploited in this study might prove a rather crude approximation, especially when the basis set is augmented with diffuse functions.^[26] However, we are confident that the Mulliken charges summed over the individual molecules are meaningful in our case since: i) the intermolecular overlap is relatively small for the intermolecular distances considered in this study (≥ 3.5 Å) and ii) we used in most cases the 6-31G(d) basis set which does not contain diffuse functions. In addition, a natural population analysis (NPA) performed with the DFT–BHandHLYP/6-31G(d) approach that we have favored (vide infra) has produced charge distributions similar to those provided by a Mulliken population analysis. All these considerations have motivated the use of Mulliken charges throughout this study to quantify the amount of charge transfer between the D/A molecules. The dipole moments and Mulliken charges reported hereafter were corrected for basis set superposition error, using the counterpoise correction of Boys and Bernardi,^[27] except for the AM1 results and the calculations performed in the presence of an electric field.

4. Results and Discussion

4.1. Partial versus Integer Charge Transfer in the Ground State

An important issue triggered by recent experimental data^[8,28] is to know under which conditions an integer charge transfer can be promoted at the D/A interface. In order to resolve this issue theoretically, it is vital to realize first that an inherent problem of single-determinantal calculations is related to their tendency to favor partial charge transfer, as illustrated below. To do so, let us consider donor and acceptor units that are largely separated; the energy of the lowest CT state can be expressed in good approximation as the difference between the ionization potential (IP) of the donor and the electron affinity (EA) of the acceptor corrected by a Coulomb term:

$$E_{CT} = [IP(\text{donor}) - EA(\text{acceptor})] - \frac{e^2}{4\pi\epsilon\epsilon_0 R} \quad (5)$$

where R is an average distance between the hole (localized on the donor) and the electron (localized on the acceptor). From Equation 5, it is clear that the CT state becomes the ground state when the Coulomb attraction term is larger than the gap between the ionization potential of the donor and the electron affinity of the acceptor. In other words, if the HOMO(D)–LUMO(A) gap is very small, an electron jump can be energetically favorable, even for an intermolecular distance so large that the orbital overlap can be neglected. It is worth stressing that such a full electron transfer results in an open-shell singlet configuration (since the HOMO of the donor and LUMO of the acceptor are singly occupied) that cannot be properly described with a single-determinantal approach, based typically on restricted Hartree–Fock (RHF) or Density Functional Theory (DFT) calculations, that imposes either two- or zero-electron occupation of molecular orbitals.

In order to model theoretically the charge-transfer behavior of molecular dyads at an arbitrary HOMO(D)–LUMO(A) gap and intermolecular distance, as well as its description by various methods, we have applied an external electric field in a direction perpendicular to the molecular planes. The results are collected in Figure 1, where an increasing field corresponds to a decreasing gap or distance that facilitates the charge transfer. We provide in the Supporting Information a simple analytically solvable formulation of the model and a more detailed discussion of

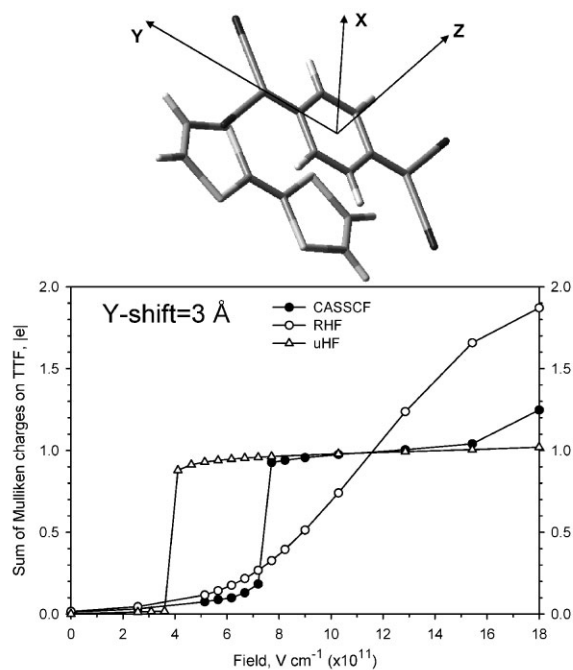


Figure 1. Top: Representation of the TTF/TCNQ dimer with the definition of the three Cartesian axes. Bottom: Evolution of the calculated charge transferred between TTF and TCNQ (RHF – open circles; CASSCF – filled circles; uHF – open triangles) as a function of the amplitude of an external electric field applied in a direction perpendicular to the planes of the two molecules for a TTF/TCNQ dimer with an intermolecular distance fixed at 3.5 Å; we have considered here a geometry characterized by a strong electronic coupling between the two molecules (the TTF molecule is translated by 3 Å along the Y axis).

the results of our calculations for electron transfer between non-overlapping molecular orbitals.

In the framework of a closed-shell (*spin-restricted* single-determinantal) ansatz, which is the basis of standard Hartree–Fock or DFT treatment of molecular systems in the ground state, a partial charge transfer is observed between the donor and acceptor units, see Figure 1. The expected full, practically stepwise-like, charge transfer is automatically recovered in the framework of a superior, more variationally flexible CAS-SCF approach, in which a multi-determinantal ansatz is employed to take into account the possible quasi-degeneracy of frontier MOs (i.e., non-dynamic correlation). This demonstrates an important discrepancy introduced by a closed-shell ansatz: the significant intermolecular charge transfer is an artefact resulting from an orbital mixing occurring to compensate the impossibility of single-electron occupation of the molecular orbitals. A *spin-unrestricted* Hartree–Fock (uHF) open-shell solution, allowing for single MO occupations, also appears to restore the stepwise full-electron transfer, though at a different electric field (Fig. 1). However, this solution (that requires a specially engineered initial guess) is not a remedy since it is highly spin-contaminated: $\langle S^2 \rangle$ exceeds 1.5 in the region after the jump for a “singlet”. The unrestricted hybrid DFT BHandHLYP/6-31G(d) solution that partially recovers a full-electron jump, though conserving some gradual character of the charge transfer (Fig. 2), is also spin-contaminated and thus does not offer any radical improvement in comparison to the spin-restricted formalism, especially in the regions of intermediate charge transfer.

From this methodological study, we conclude that applying a closed-shell, Hartree–Fock or DFT, approach in the case of a weakly overlapping D–A pair can be reliable only as long as the predicted charge transfer does not exceed a certain threshold. We will show hereafter that this is the case in this work.

When the HOMO(D)–LUMO(A) gap is large enough to preclude a full electron transfer at large intermolecular distance (as it is typically the case for complexes made of small molecules),

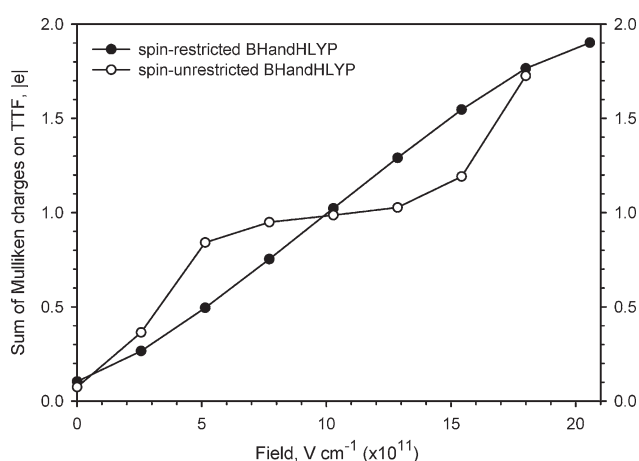


Figure 2. Evolution of the intermolecular charge transfer driven by an homogeneous external electric field in a TCNQ-TCNQ cofacial dyad (Y shift of 3 Å), as obtained either from spin-restricted (filled circles) or spin-unrestricted hybrid DFT (using the BHandHLYP functional and a 6-31G(d) basis set).

a partial charge transfer between the two molecules can be induced when their orbitals start to overlap significantly; as described above, some CT character can be introduced in the ground state via mixing with excited CT states. The amount of mixing varies smoothly with the intermolecular distance. If the molecules in strong interaction are closed-shell systems whose electronic ground state is correctly described within a single-determinantal approach (RHF or DFT), the charge transfer in the closed-shell supermolecule should then be reasonably assessed at the same theoretical level.

The previous considerations are illustrated in Figure 1 where we compare the field evolution of the charge transferred in a TTF-TCNQ dimer, with the two molecules separated by 3.5 Å and the TTF molecule shifted by 3 Å along the Y axis, as provided by RHF and a multideterminantal CASSCF (Complete Active Space – Self Consistent Field) approach; the active space in CASSCF includes the HOMO and HOMO-1 levels of TTF and the LUMO of TCNQ that are the most relevant in describing the charge transfer (vide infra). The minimal active orbital space is chosen to take into account the quasi-degeneracy of the essential MOs (non-dynamic correlation) only and stress its importance. The CASSCF results show that a gradual increase of the electric field up to $7 \times 10^{11} \text{ V cm}^{-1}$ is accompanied by a *gradual charge transfer* between the molecules up to $\sim 0.18 |e|$. A further increase in the field strength promotes an almost sudden jump to the CT state, whose abruptness is due to very weak overlap between the MOs of different molecules that makes crossing of the “neutral” and CT states possible. In contrast, RHF predicts a gradual charge transfer from 0 to ~ 2 electrons, thus yielding a completely unsatisfactory description at high field intensity. However, both CASSCF and HF predict a partial CT at low field values (when the HOMO(D)–LUMO(A) energy gap is initially large), thus validating the use of a mono-determinantal approach to describe the small charge transfer processes typically observed in molecular organic/organic interfaces. Note that the largest amount of charge transferred between the TTF and TCNQ molecules is $\sim 0.12 |e|$ in our calculations (as it will be shown below), thus fitting into the weak charge transfer regime. This justifies our choice of spin-restricted methods in the rest of this work.

There is also an issue regarding partial versus full charge transfer at the interface in the two different models used so far to describe the dipole formation at organic/organic interfaces: namely, the charge neutrality level (CNL) model and the integer charge transfer model. The CNL model^[29,30] can be briefly outlined as follows: i) the interaction between the isolated molecules and a given metallic surface, leading to a broadening of the molecular levels, is first characterized at the theoretical level; on that basis, a continuous density of states (DOS) projected on the molecular orbitals is generated; ii) the projected DOS is then integrated until the number of electrons in the molecule is reached, at an energy defined as the so-called charge neutrality level (CNL); and iii) the alignment of the charge neutrality levels of two organic materials governs the direction and amount of the *fractional* charge transfer at the donor/acceptor interface. This approach was quite successful in predicting the values of the vacuum level shift at metal/organic and molecular organic/organic interfaces^[9,31] despite the fact that this model ignores polarization effects and specific interactions between the donor

and acceptor units and that the electronic level broadening is expected to be strongly reduced at organic/organic interfaces.

In parallel, recent ultraviolet photoelectron spectroscopy (UPS) measurements on interfaces between polymers and various inorganic and organic materials have suggested the existence of two distinct level alignment regimes depending if an integer charge transfer occurs at the interface or not. When there is no charge transfer, a vacuum level alignment is observed at the interface. A VLS is induced by an apparent full charge transfer driven by the alignment of polaronic levels at organic/organic interfaces and by the alignment of the polaronic levels with the Fermi level of the substrate at metal/organic interfaces.^[28,32–35] The authors stressed that the full charge transfer is likely related to the weak coupling between the donor and acceptor materials, in agreement with our previous theoretical considerations.

These various experimental data can be reconciled in the following way: when there is a significant overlap between the orbitals of the interacting molecules, a partial charge transfer is always a natural consequence of their orbital mixing; the charge transferred is expected to be small at interfaces built with molecules owing to the generally large HOMO(D)–LUMO(A) energy gap. When the energy difference between the relevant ionization and affinity levels becomes small, a full electron transfer becomes an option when the interaction between the two molecules is very weak; this situation is likely to be more easily encountered with polymer chains due to their reduced bandgaps and to the presence of long alkyl chains preventing close contact between the donor and acceptor units. There is no charge transfer if the HOMO(D)–LUMO(A) energy gap is large and the interactions between the two molecules are weak.

The vacuum level shift observed experimentally at interfaces between donor and acceptor organic materials has been so far ascribed to charge-transfer processes while the role of polarization effects has been overlooked. In the next sections, we report the results of quantum-chemical calculations on TTF/TCNQ molecular dyads where the two molecules are strongly interacting and hence where only partial charge transfers are expected. We will show hereafter that a VLS as large as 0.6 eV (i.e., the experimental value measured for a TTF/TCNQ interface)^[10] can be reached by combining the dipole induced by the partial charge transfer and the additional dipole promoted by polarization effects.

4.2. Dipole in the TTF/TCNQ Complex: The Choice of the Computational Method

Figure 3 (top) shows the evolution of the M_z component of the dipole moment in a TTF/TCNQ dimer as a function of the degree of translation of the TCNQ molecule along its main molecular axis (Y axis), as calculated at different levels of theory (using a 6-31G(d) basis set in the ab initio HF and DFT calculations). The initial geometry of the isolated molecules was first optimized at the B3LYP/6-31G(d) level and the dimer was then built in a cofacial geometry by fixing the separation between the molecular planes at 3.5 Å. The results show that the amount of charge transferred critically depends on the chosen computational approach and on the relative position of the two interacting molecules.

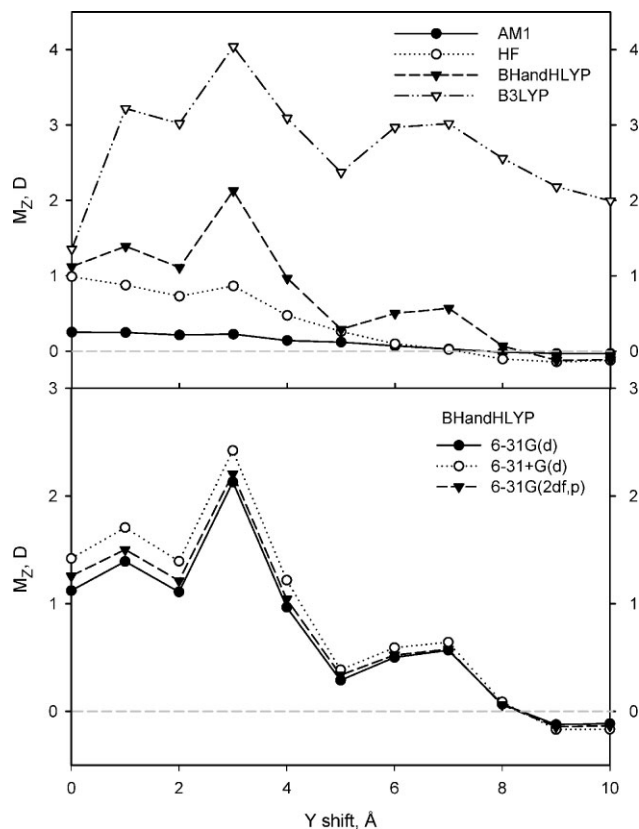


Figure 3. Evolution of the total dipole moment in the direction normal to the molecular planes (M_z) as a function of the degree of lateral translation of the TTF molecule along the Y axis, as obtained with different computational methods (top) and as obtained at the BHandHLYP level with different basis sets (bottom). The distance between the molecular planes is fixed at 3.5 Å.

The magnitude of the charge transfer is governed by the calculated energy gap between the frontier orbitals of the donor and acceptor as well as by their electronic coupling. The Hartree–Fock (HF) method yields very large HOMO/LUMO gaps; this is partly due to the overestimation of the energies of the unoccupied levels. Moreover, the energy of a charge-transfer state calculated at the Hartree–Fock level for an isolated complex is larger than the value expected in a condensed medium (i.e., at the interface) due to the neglect of the polarization of the surrounding medium.^[36] These two effects should lead to an overestimation of the energy of the CT states and hence to a reduced charge transfer with Hartree–Fock. In contrast, hybrid DFT was shown to provide electronic HOMO/LUMO gaps for *isolated* molecules much smaller than Hartree–Fock-based values and actually close to experimental optical gaps in a condensed medium;^[37] thus incorporating artificially medium polarization effects, which proves very useful in the present context.

These considerations are supported by the results of the electronic structure calculations based systematically on the same B3LYP/6-31G(d) input geometry (see Fig. 3, top). AM1 yields the smallest induced dipole moment; the negligible charge transfer occurring between the donor and acceptor is rationalized by the overestimation of the energy of the CT states and by a smaller

polarization component due to the use of a minimal basis set. B3LYP calculations predict the largest amount of charge transfer, with a maximum observed for a shift of 3 Å ($q \sim 0.25 |e|$). However, it is worth stressing that with B3LYP the LUMO of TCNQ is found to be lower in energy than the HOMO of TTF. This is certainly due to an insufficient admixture of the Hartree–Fock exchange (20%), which leads to the strong underestimation of HOMO–LUMO gaps in both TTF and TCNQ molecules and the corresponding gap relevant for charge transfer.

At the BHandHLYP level (incorporating 50% of Hartree–Fock exchange), the maximum charge transfer is $\sim 0.12 |e|$ for a shift of 3 Å; the M_z component of the dipole moment reaches 2 D, which yields an estimate for VLS of 0.75 eV on the basis of Equation 1 (with $S = 100 \text{ \AA}^2$ and $\epsilon = 1$ and by neglecting depolarization effects); note that the choice of $\epsilon = 1$ is driven by the fact that it does not make too much sense to screen the interaction between two molecules in close contact with a bulk quantity. This value is in reasonably good agreement with the VLS of 0.6 eV measured experimentally,^[10] thus motivating the choice of the BHandHLYP functional in the following. This is also consistent with a number of theoretical studies showing that the BHandHLYP hybrid functional provides better estimates for the geometries and energies of charge-transfer complexes in comparison to pure density functionals.^[38–40] The performance of different basis sets has been compared at the BHandHLYP level (Fig. 3, bottom). The results show that the inclusion of diffuse functions and of a larger number of polarization functions slightly increases the dipole moment while keeping exactly the same evolution of the charge transfer as a function of the translation.

4.3. Dipole in the TTF/TCNQ Complex: Charge-Transfer and Polarization Components

The consideration of a cofacial TTF/TCNQ complex allows us to separate the charge-transfer versus polarization contributions to the dipole moment in a straightforward way. The charge-transfer admixture in the ground state can be evaluated by summing up the Mulliken charges in each molecule of the dimer and by calculating the dipole moment from these. The remaining part of the total dipole moment obtained from the quantum-chemical calculations is then attributed to the polarization component.

In order to assess the influence of the geometry of the complex on the amount of charge transferred, we have run a series of single-point calculations by shifting the TCNQ molecule along the Y or Z axis, as depicted in Figure 1. An increase in the intermolecular distance (shift along the Z axis) leads to a fast decrease in the amplitude of the induced dipole moment (Fig. 4). Interestingly, we observe that the value of the dipole moment computed from the Mulliken charges decreases almost to zero already for an intermolecular distance of 5 Å; in contrast, the total dipole moment obtained directly from the SCF procedure decreases much slowly when the intermolecular distance is increased from 3.5 to 5 Å and does not reach zero even for an intermolecular distance of 8 Å. This clearly demonstrates that the dipole is induced not only by the charge transfer but also, to a large extent, by polarization effects.

The DFT results show a marked dependence of the charge transferred between the two molecules as a function of the shift

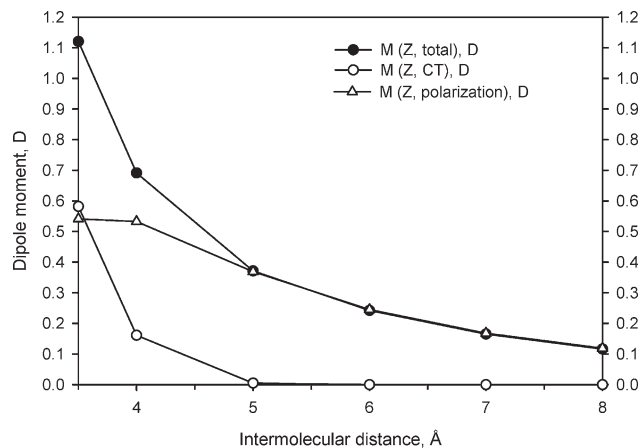


Figure 4. Evolution of the component of the dipole moment normal to the molecular planes obtained from the SCF calculations (filled circles) and from the Mulliken charges (open circles) in a cofacial C_{2v} TTF/TCNQ dimer as a function of the intermolecular distance. The curve with open triangles shows the polarization component of the dipole.

along the Y axis, as illustrated in Figure 5, where the distance between the planes of the TTF and TCNQ molecules has been fixed at 3.5 Å. The geometry for which the centers of mass of the two molecules are exactly superimposed (i.e., a structure with a C_{2v} symmetry and no shift along the Y axis) does not yield the largest charge transfer, as could be intuitively expected. The latter is actually obtained when TCNQ is shifted by 3 Å along the Y axis. Figure 5 also illustrates that there is a full parallelism between the amount of charge transfer and the amplitude of the total dipole moment. In most cases, the charge-transfer contribution dominates the induced dipole at such short intermolecular distances.

The non-monotonic dependence of the amount of charge transferred in the ground state is related to variations in the electronic coupling between the highest occupied levels of the donor and the lowest unoccupied levels of the acceptor (see

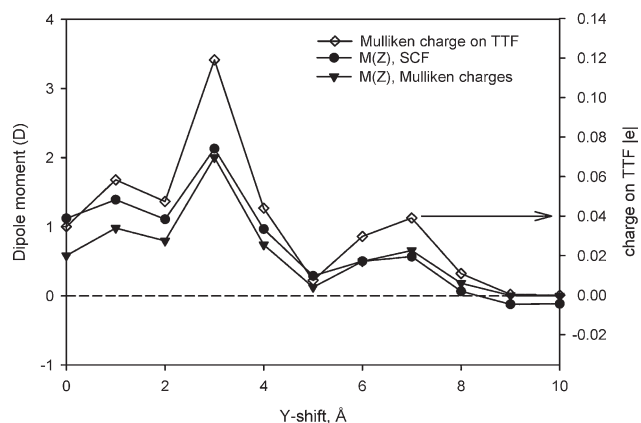


Figure 5. Evolution of the component of the dipole moment normal to the molecular planes in the TTF/TCNQ dimer as a function of the lateral shift between the molecular centers, as provided by the SCF calculations (filled circles) and computed from the Mulliken charges (filled triangles); the total Mulliken charge on the TTF molecule is also shown (open diamonds). The distance between the molecular planes is fixed here at 3.5 Å.

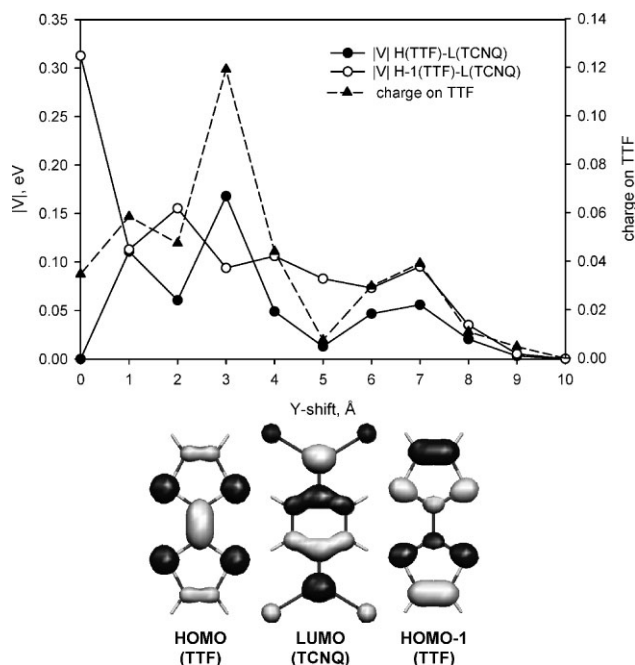


Figure 6. Top: Evolution of the electronic coupling between the HOMO of TTF and LUMO of TCNQ (filled circles) and between the HOMO-1 of TTF and LUMO of TCNQ (open circles), and of the total Mulliken charge on the TTF molecule (filled triangles, dashed curve) as a function of the lateral translation between the molecular centers; the distance between the molecular planes is fixed here at 3.5 Å. Bottom: Shapes of the HOMO and HOMO-1 of TTF and of the LUMO of TCNQ from BHandHLYP/6-31G(d) calculations. The size and color of the orbitals reflect the amplitude and sign of the LCAO coefficients, respectively.

Fig. 6). In order to better rationalize the calculated evolution, we have computed the coupling between the electronic levels using a very convenient approach based on the semi-empirical Hartree-Fock Intermediate Neglect of Differential Overlap (INDO) method.^[41] In this framework, the coupling between two molecular orbitals ϕ_D and ϕ_A (located on the donor D and acceptor A, respectively) can be recast within an atomic orbital basis set as:

$$V_{if} = \langle \phi_D | h | \phi_A \rangle = \sum_{\mu} \sum_{\nu} C_{D\mu} C_{A\nu} \langle \chi_{\mu} | h | \chi_{\nu} \rangle \quad (6)$$

where $C_{D\mu}$ ($C_{A\nu}$) correspond to the LCAO (Linear Combination of Atomic Orbitals) coefficient of the atomic orbital χ_{μ} (χ_{ν}) in the molecular orbital ϕ_D (ϕ_A). The matrix element $\langle \chi_{\mu} | h | \chi_{\nu} \rangle$ is implemented in the INDO method as:

$$\langle \chi_{\mu} | h | \chi_{\nu} \rangle = \frac{1}{2} (\beta_M + \beta_N) \bar{S}_{\mu\nu} \quad (7)$$

where β_M and β_N are two parameters depending on the nature of atoms M and N , $\bar{S}_{\mu\nu}$ is the overlap between the atomic orbitals χ_{μ} and χ_{ν} corrected by empirical factors.^[42] The use of ZINDO is validated by the fact that: i) the electronic coupling is governed by the shape of the orbitals which is similar in ZINDO and DFT

calculations; and ii) ZINDO and DFT are generally found to give similar electronic couplings.^[43]

Intuitively, the largest contribution to the charge transfer should stem from the HOMO (TTF) \rightarrow LUMO (TCNQ) transition due to the fact that the energy separation between them is the smallest. However, the electronic overlap (and hence the electronic coupling) between the HOMO of TTF and the LUMO of TCNQ is equal to zero due to the symmetry of the orbitals when $Y = 0 \text{ \AA}$ since there is an exact compensation between bonding *versus* antibonding interactions in the overlapping region (see Fig. 6, bottom). In this geometry, the largest CT contribution actually arises from HOMO-1 (TTF) \rightarrow LUMO (TCNQ) transition (the electronic coupling between the HOMO of TTF and the LUMO+1 of TCNQ is two orders of magnitude smaller). On the contrary, for a shift of 3 Å along the Y axis, the coupling between the HOMO of TTF and LUMO of TCNQ makes the largest contribution to the charge transfer. The good correlation observed in Figure 6 between the amplitude of the electronic coupling between the HOMO of the donor (TTF) and the LUMO of the acceptor (TCNQ) and the amount of CT character in the ground state demonstrates that the charge transfer is generally mostly governed by the HOMO (D) \rightarrow LUMO (A) transition.

When the TTF and TCNQ molecules are lying flat at the interface (i.e., the molecular planes are lying parallel to the interface), only the Z component of the dipole contributes to the vacuum level shift (see Fig. 7). However, if the planes of

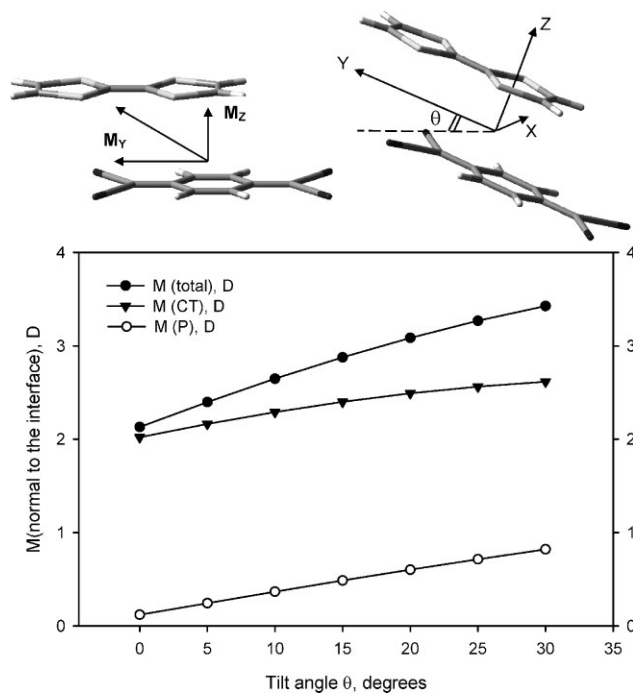


Figure 7. Evolution of the total dipole and its charge-transfer and polarization components in the direction normal to the interface as a function of the tilt angle of the dimer at the interface. The dimer is characterized by a distance between the molecular planes of 3.5 Å and by a lateral shift of 3 Å between the molecular centers. The axes defining the Y and Z components of the dipole are also illustrated. The diagonal arrow on the left graph depicts the direction of the dipole moment.

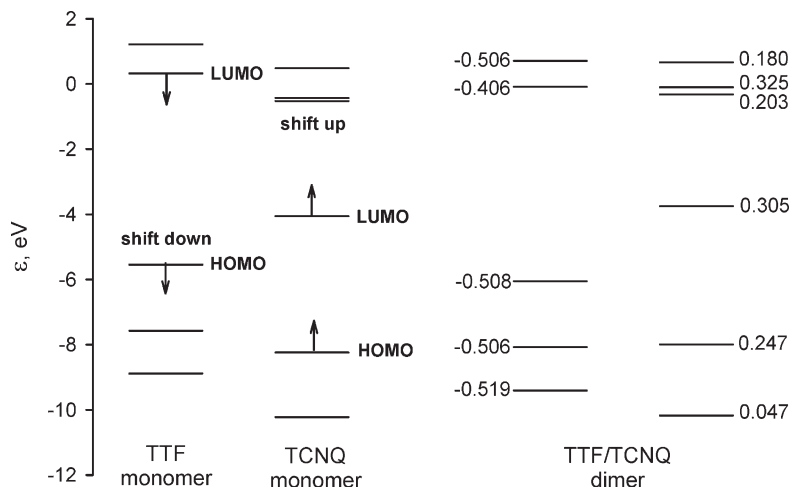


Figure 8. Energy diagram of the frontier electronic levels in the isolated TTF and TCNQ molecules (left) and in the TTF/TCNQ C_{2v} cofacial dimer with an intermolecular distance fixed at 3.5 Å (right). The numbers indicate the shift (in eV) in the energies of the MOs when going from the isolated molecules to the dimer.

the TTF and TCNQ molecules are actually tilted by an angle θ with respect to the normal (Fig. 7), the component of the induced dipole moment along the Y direction will also contribute to the vacuum level shift at the interface. Figure 7 displays the charge-transfer and polarization components of the total dipole normal to the interface when the tilt angle θ is varied from 0 to 30° for a dimer characterized by a shift of the TTF molecule along the Y axis by 3 Å. While it is simple to separate the charge-transfer and polarization contributions for the Z component of the dipole (the polarization component is obtained as the difference between the total dipole and the dipole obtained from the Mulliken charges), this distinction is less obvious for the Y component of the dipole. Due to the symmetry of the TTF and TCNQ molecules, the charge-transfer contribution to the Y component of the dipole moment is given by:

$$M_Y(\text{CT}) = q_m \times R_Y \quad (8)$$

where q_m is the sum of the atomic charges on the individual molecules and R_Y is the projection of the vector connecting the centers of the molecules on the Y axis. The polarization component manifests itself by introducing an asymmetry in the charge distribution within each molecule with respect to the XZ plane passing by the center of each molecule. The polarization contribution to the Y component of the dipole was thus calculated as the difference between the M_Y component taken directly from the SCF calculations and the $M_Y(\text{CT})$ value calculated according to Equation 8. The results show that the total dipole increases with a growing the tilt angle (from ~ 2.1 D for $\theta=0^\circ$ to ~ 3.4 D for $\theta=30^\circ$). This evolution mainly arises from an increased contribution of the polarization component, although the largest contribution to the VLS still originates from the charge transfer whatever the tilt angle.

4.4. Ionization Potential and Electron Affinity at the Interface

The alignment of the frontier electronic levels of the donor and acceptor units is also affected by the creation of the interface dipole when compared to the energy diagram established from the isolated compounds. In the case of the TTF/TCNQ cofacial dimer, both the occupied and unoccupied MOs of TTF experience a decrease in their energy with respect to the MOs of the isolated TTF molecule (Fig. 8); this shift is as high as 0.51 eV for the HOMO level and 0.41 eV for the LUMO. On the contrary, the energies of the frontier MOs of the TCNQ molecule are increased in the TTF/TCNQ dimer (shift of 0.25 eV for the HOMO and of 0.30 eV for the LUMO). The amplitude of the shift varies from orbital to orbital but the direction of the shift is the same for all orbitals of a given compound, including the σ -orbitals.

A very nice correlation is observed between the amplitude of the induced dipole moment in cofacial dimers with various degrees of translation and the corresponding shift in the orbital energies (see Fig. 9). In some cases, the energy shift of a particular orbital is reinforced by a resonant interaction with a deeper orbital of the other molecule; for example, the large shift of the HOMO level of TCNQ for $Y=1$ Å is partially promoted by a resonant interaction with the HOMO-1 level of TTF. The behavior in the interval between 8 and 10 Å is particularly unexpected since we observe there a change in the direction of the dipole moment as well as in the direction of the orbital shifts. In this interval, the sum of the Mulliken charges on TTF or TCNQ is essentially zero and the amount of charge transferred is much too small ($q < 10^{-4} |e|$) to rationalize the calculated induced dipole (~ 0.1 D

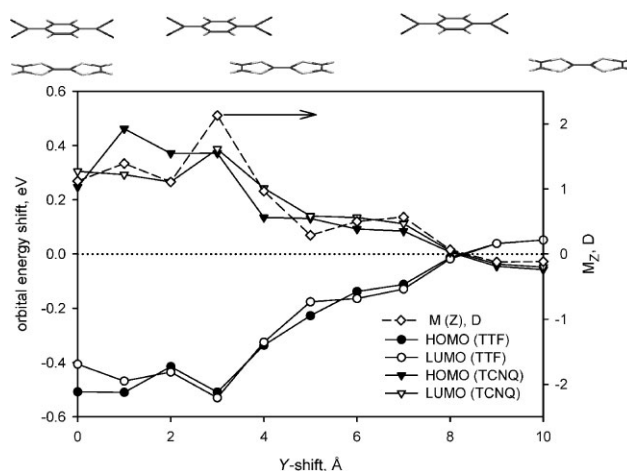


Figure 9. Evolution of the shift of the frontier MOs of TTF (circles) and TCNQ (triangles) versus the amplitude of the dipole moment normal to the molecular planes in a cofacial TTF/TCNQ dimer (diamonds), as a function of the lateral translation along the Y axis. The distance between the molecular planes is fixed here at 3.5 Å.

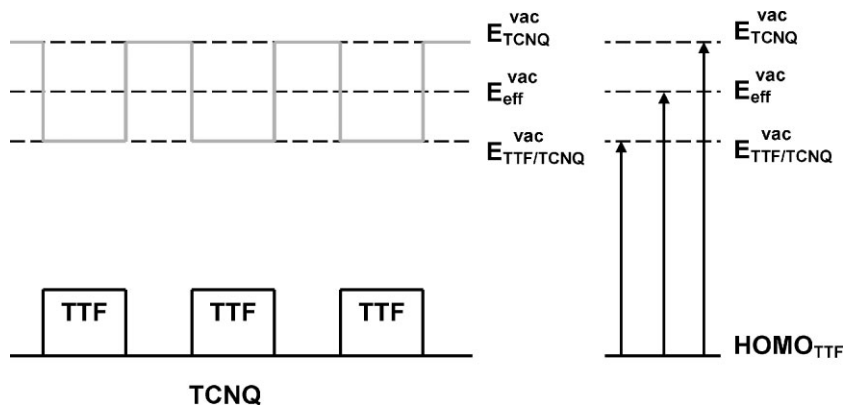


Figure 10. Schematic evolution of the position of the vacuum level over a TCNQ substrate covered by small islands of TTF (left, solid grey curve). In such a case, the HOMO energy of TTF is measured against the position of an effective vacuum level and is thus larger than the actual HOMO energy at the TTF/TCNQ interface.

vs. $M(CT) \sim 10^{-3} D$). This change in the sign of the dipole is thus driven by polarization effects and shows that the direction of the dipole can be sometimes opposite to that predicted by simply considering the difference in electronegativities between the two molecules, as it was evidenced for some organic-organic interfaces.^[44] Of course, the geometries generated here for large Y shifts are not realistic for bimolecular complexes; the results point to the complex behavior of long-range intermolecular interactions in dense arrays of molecules at interfaces whose detailed consideration is beyond the scope of the present paper.

These theoretical findings are consistent with recent UPS studies performed on the TTF/TCNQ interface.^[45] At the lowest degree of coverage of TTF over TCNQ, the energy of the HOMO of TTF decreases down to ~ -5.9 eV compared to -5.6 eV in a solid thin film of TTF. At the same time, no change in the HOMO value was observed for TCNQ molecules deposited on TTF. However, these experimental results should be interpreted with much caution since the actual film morphology is not known. If the interface at small coverage is actually made of small clusters of TTF over the bare TCNQ surface, the HOMO energy of TTF is actually measured against an effective vacuum level, which is higher than the local vacuum level over the TTF clusters; this yields in turn an overestimation of the energy of the HOMO level of TTF molecules deposited on a TCNQ substrate (see Fig. 10); a similar picture holds for TCNQ molecules deposited on TTF. Note also that the values obtained for the solid thin film are also affected by solid-state effects, thus preventing a fully direct comparison with the calculations. These results have strong implications for organic solar cells since they demonstrate that the actual offset between the frontier electronic levels of the donor and acceptor components in the device might be significantly different from the value inferred from measurements performed on the isolated compounds.

5. Summary and Conclusions

In this work, we have performed quantum-chemical calculations on a donor/acceptor complex in various molecular arrangements in order to distinguish and quantify the electronic effects leading

to the formation of an interface dipole layer. We have shown that the dipole is governed not only by the difference in electronegativities of the two materials but more essentially by the electronic coupling between the frontier electronic levels of the donor and acceptor units. In the case of a TTF/TCNQ dimer, the dipole mostly originates from a partial charge transfer from the donor to the acceptor molecules though polarization effects also contribute in a significant way. Our work further indicates that the values of ionization potential and electron affinity of both donor and acceptor molecules may experience shifts as large as several tenths of eV at the interface with respect to the redox properties of the bulk materials. This has strong implications for organic solar cells where the offset between the electronic levels at the interface between donor

and acceptor units plays a key role in defining the efficiency of light conversion into charges. We have also discussed the conditions favoring a partial versus integer charge transfer at organic/organic interfaces and rationalized on that basis the apparent contradictions between the experimental results reported so far. We believe that this work opens new perspectives aimed at a more rational design of interfaces in organic-based opto-electronic devices; in future we plan to investigate other materials and to address explicitly the impact of long-range interactions, which will be the next step towards a unified picture of electronic processes at organic/organic interfaces.

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