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# Tuning the Interfacial Electronic Structure at Organic Heterojunctions by Chemical Design

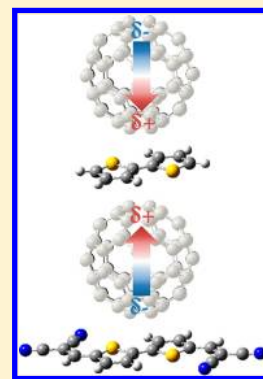
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## S Supporting Information

**ABSTRACT:** Quantum-chemical techniques are applied to assess the electronic structure at donor/acceptor heterojunctions of interest for organic solar cells. We show that electrostatic effects at the interface of model 1D stacks profoundly modify the energy landscape explored by charge carriers in the photoconversion process and that these can be tuned by chemical design. When fullerene C<sub>60</sub> molecules are used as acceptors and unsubstituted oligothiophenes or pentacene are used as donors, the uncompensated quadrupolar electric field at the interface provides the driving force for splitting of the charge-transfer states into free charges. This quadrupolar field can be either enhanced by switching from a C<sub>60</sub> to a perylene-tetracarboxylic-dianhydride (PTCDA) acceptor or suppressed by grafting electron-withdrawing groups on the donor.



**SECTION:** Energy Conversion and Storage; Energy and Charge Transport

In the quest for sources of renewable energy, the design of photovoltaic cells based on organic materials has aroused increasing interest in the past few years.<sup>1</sup> The working principle of solid-state organic photovoltaic devices involves: (i) sun light harvesting and diffusion of the resulting exciton (electron–hole pair) toward interfacial domains between electron-rich (Donor) and electron-poor (Acceptor) materials, (ii) exciton dissociation into free charge carriers at the D/A interface, and (iii) charge transport and collection at electrodes.<sup>2</sup> The photo-induced excitation to produce charge-transfer (CT) states (excitons) requires an energy difference between frontier electronic levels ( $\Delta$ ) that can compensate for the loss in Coulombic exciton binding energy ( $E_b \approx 0.4$  to  $0.6$  eV).<sup>3</sup> Whereas it is possible to engineer the proper combination of donor and acceptor molecules with the requested energy level offsets, this has consequences on the power conversion efficiency ( $\eta$ ) of the cell.  $\eta$  depends on the product of the short circuit current ( $I_{sc}$ ) by the open circuit voltage ( $V_{oc}$ ) of the device. Larger  $\Delta$  promotes exciton dissociation and therefore higher  $I_{sc}$ , yet they result in lower  $V_{oc}$  as this latter essentially follows the energy difference between the HOMO level of the donor and the LUMO level of the acceptor.<sup>4</sup> Therefore, a trade-off is necessary to achieve organic solar cells with maximized power conversion efficiencies. Additional requirements include, among others, a good overlap between the absorption spectrum of the organic materials and the solar emission spectrum for efficient light harvesting and high charge carrier mobilities for efficient charge collection at the electrodes and to reduce nongeminate charge recombination processes.

Although these constraints are known, there is today no clear view on how to circumvent them, mainly due to a poor understanding of the charge photogeneration mechanism in organic photovoltaic cells.<sup>5</sup> Two scenarios are typically invoked to describe the geminate electron–hole pair dissociation at the D/A interface into free charge carriers in the bulk.<sup>4–8</sup> The first scenario, referred to as phonon-assisted mechanism, involves a hot CT state allowing for the delocalization of charge carriers<sup>9</sup> and implies that the full charge separation occurs over a time scale shorter than thermal relaxation. According to the second picture, referred to as the electric-field-assisted mechanism, dissociation of the relaxed CT states is eased by the presence of local electric fields (induced by interfacial dipoles or trapped charges) across the interface. Yet, in most cases, the choice for the donor and acceptor materials used as active components in organic solar cells is driven by their bulk electronic and optical properties, thus neglecting the impact of interfacial electrostatic interactions. Therefore, a comprehensive description of the exciton dissociation or charge recombination mechanisms entails a detailed knowledge of the electronic structure at the heterojunction between the donor and acceptor materials. Here we simulate model D/A interfaces seeking for general strategy rules to bias the electronic structure in favor of exciton dissociation through electrostatic interactions at heterojunctions. In this contribution, we highlight the impact of the

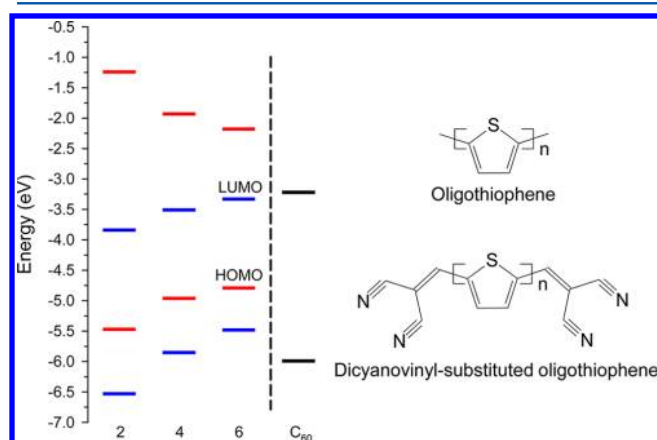
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interfacial electrostatic interactions on the energetic aspect of the photoconversion process; then, we demonstrate that such interactions can be adjusted by chemical design of the donor and acceptor molecules.

As a proof of principle, we have first applied complementary quantum-chemical methods to unravel the electronic structure at oligothiophene/ $C_{60}$  and dicyanovinyl-substituted oligothiophene/ $C_{60}$  interfaces. The ground-state geometry of isolated oligothiophenes (nT), dicyanovinyl-substituted oligothiophenes (DCVnT, with  $n = 2, 4$  and  $6$ ), all imposed planar, and  $C_{60}$  molecules has been optimized at the density functional theory (DFT) level using the B3LYP hybrid functional and the 6-31 g(d) basis set. The corresponding one-electron energy diagram is shown in Figure 1.



**Figure 1.** DFT/B3LYP one-electron energy diagram for isolated nT (red lines) and DCVnT (blue lines) with  $n = 2, 4$ , and  $6$  and  $C_{60}$ .

As expected from their electron-withdrawing character, substitution of the oligothiophenes by dicyanovinyl end groups causes a down shift in the energy of the frontier molecular orbitals, the effect being larger for the LUMO.<sup>10</sup> As a result, whereas the large energy offset between the LUMO of unsubstituted oligothiophenes and the LUMO of  $C_{60}$  is expected to promote efficient exciton dissociation into free charge carriers, the situation is drastically different in DCVnT/ $C_{60}$  pairs where the driving force for free charge generation (related to first approximation to the LUMO energy offset

between the donor and acceptor molecules<sup>11,12</sup>) is close to zero or even negative. Although direct comparison between measured electron affinity and calculated LUMO energies should be considered with caution, we stress that the changes in electronic structure and the reduced LUMO energy offset with respect to  $C_{60}$  in DCVnT compared with nT are consistent with experimental findings:<sup>11</sup> (i) electrochemical data show that the LUMO level is destabilized by  $\sim 0.2$  eV when going from DCV2T to DCV6T, an evolution that is opposite to the corresponding trend for unsubstituted oligothiophenes and results from the weaker electro-active effects induced by the end groups as the oligomers get longer,<sup>13</sup> and (ii) most importantly, the difference in LUMO energies between DCVnT and  $C_{60}$  inferred from these measurements is reduced to  $-0.2$  to  $0$  eV. Despite the small driving force for charge separation, DCVnT molecules have been successfully exploited in solar cells using  $C_{60}$  as acceptor with power conversion efficiencies of 1–3%.<sup>11,14,15</sup> As described below, this apparent inconsistency is lifted when accounting for the readjustment of the electronic levels due to interfacial effects.

Following the strategy developed to model pentacene/ $C_{60}$  interfaces,<sup>16</sup> we have applied a variety of quantum-chemical techniques to assess the electronic structure of nT/ $C_{60}$  and DCVnT/ $C_{60}$  physical dimers (assuming a cofacial configuration with a short interatomic distance of  $3.5$  Å). Table 1 reports the shifts of the frontier electronic levels of the model dimers as well as the Z-component (i.e., along the stacking direction) of the ground-state dipole moment, as calculated at the B3LYP and MP2 levels using the 6-31 g(d) basis set. By comparison with their values in the isolated molecules, both DFT/B3LYP and MP2 calculations show that the HOMO and LUMO levels of unsubstituted oligothiophenes are stabilized in the donor/acceptor dimer, whereas those of the  $C_{60}$  molecule are destabilized. These changes are consistent with the results obtained by using the wB97X-D functional that includes long-range corrections and empirical dispersion. (See the Supporting Information.) The shift in the frontier molecular orbitals at the heterojunction results from the appearance of an interfacial dipole. As the amount of ground-state charge transfer from (DCV)nT to  $C_{60}$  is negligible in all cases, the interfacial dipole is mainly associated with the polarization of the electronic cloud of the  $C_{60}$  molecule, with the positive pole next to the oligothiophene backbone. Similarly to pentacene, this effect is

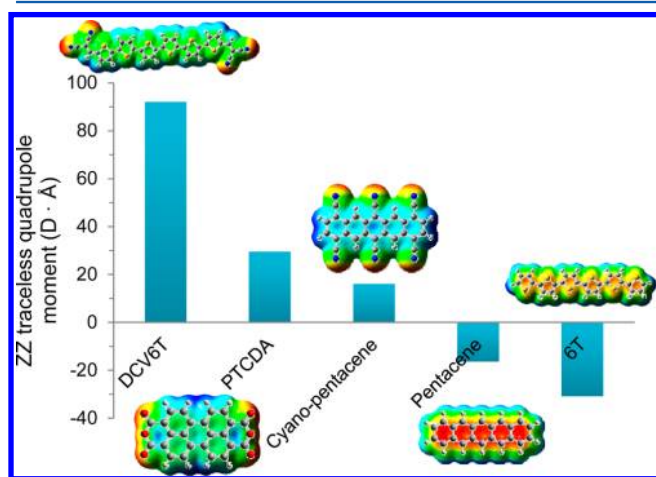
**Table 1.** Shifts (Compared to Isolated Molecules) of the HOMO and LUMO Energy Levels and Values of Interfacial Ground-State Dipole, As Calculated at the B3LYP/6-31g(d) and MP2/6-31g(d) Levels, for (DCV)nT/ $C_{60}$  Interfaces

molecule	DFT (B3LYP/6-31 g(d))			MP2/6-31 g(d)		
	$\Delta E_{\text{HOMO}}$ (eV)	$\Delta E_{\text{LUMO}}$ (eV)	$\mu_z$ (Debye)	$\Delta E_{\text{HOMO}}$ (eV) <sup>a</sup>	$\Delta E_{\text{LUMO}}$ (eV) <sup>a</sup>	$\mu_z$ (Debye)
2T	−0.09	−0.13	−0.975	−0.12	−0.13	−0.929
$C_{60}$	0.13	0.10		0.15	0.10	
4T	−0.06	−0.10	−0.947	−0.05	−0.10	−0.886
$C_{60}$	0.16	0.12		0.17	0.13	
6T	−0.05	−0.06	−0.864	−0.04	−0.06	−0.784
$C_{60}$	0.14	0.12		0.15	0.13	
DCV2T	0.04	0.04	1.142	0.05	0.00	0.898
$C_{60}$	−0.16	−0.18		−0.16	−0.18	
DCV4T	0.02	0.00	0.671	0.02	−0.05	0.335
$C_{60}$	−0.15	−0.17		−0.14	−0.15	
DCV6T	0.00	0.02	0.178	0.00	0.01	−0.131
$C_{60}$	−0.13	−0.14		−0.08	−0.13	

<sup>a</sup>Calculated using the Restricted Hartree–Fock energies.

primarily attributed to the (uncompensated) quadrupolar electric field generated by the oligothiophenes.

In marked contrast, the HOMO and LUMO levels of dicyanovinyl-substituted oligothiophenes are slightly destabilized in the presence of  $C_{60}$ , whereas the corresponding  $C_{60}$  frontier electronic levels are shifted down. Therefore, the strong dicyanovinyl electron-withdrawing moieties perturb the electronic cloud on the oligothiophene backbone and yield an opposite quadrupolar field that in turn swaps the interfacial dipole orientation (now pointing its negative pole toward the oligothiophene backbone within the  $C_{60}$  molecule). This is expected from the opposite sign of the out-of-plane component of the quadrupole moment; compare DCV6T and 6T in Figure 2. Note that, as expected, the overall effect induced by the



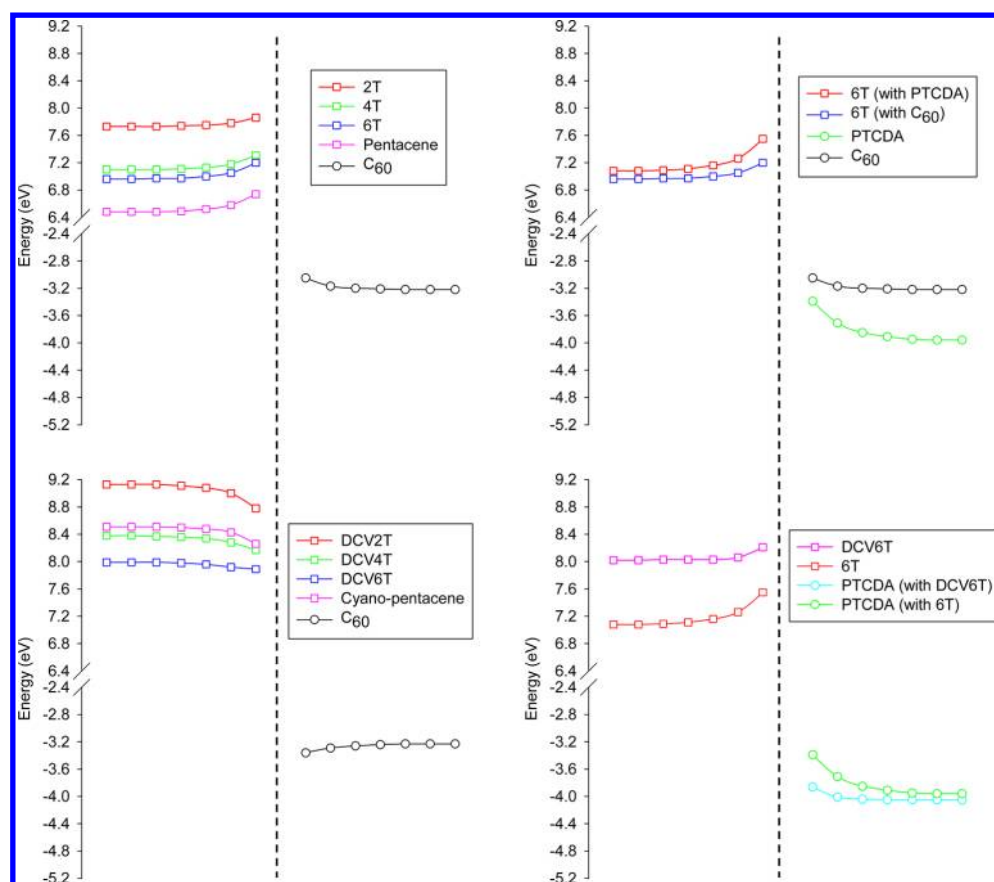
**Figure 2.** Out-of-plane traceless quadrupole moment for isolated molecules, as calculated at the DFT (B3LYP/6-31 g(d)) level. Electrostatic surface potential (ESP) contour maps are also shown.

terminal groups decreases as the thiophene oligomer increases in size and the end-group effects die away for long oligomers. (We have checked that the interfacial dipole in the cofacial dimer approaches the value computed for the corresponding  $nT$  for  $n \approx 15$ .) Very interestingly, unlike the  $nT/C_{60}$  case, the electrostatic effects computed at the DCVnT/ $C_{60}$  interface are found: (i) to increase (by 0.1 to 0.2 eV) the energy offset between the LUMO levels of DCVnT and  $C_{60}$  (which should affect the driving force for charge separation,  $\Delta_{LUMO}$ ) and (ii) to reduce the energy difference between the HOMO level of the donor and the LUMO level of the acceptor (which might affect the open-circuit voltage,  $V_{oc}$ ). Although we are aware that the simplicity of the dimer model used here does not allow pulling out a quantitative estimate for  $\Delta$  and  $V_{oc}$ , it nicely demonstrates how the electronic structure at donor/acceptor interfaces can be controlled by tuning the chemical structure of the interacting molecules (here through grafting electro-active moieties on the donor molecules) and how discontinuity at organic interfaces can dramatically renormalize the energy levels compared with the corresponding bulk values. Besides, the interfacial dipoles were also calculated in the various systems in the presence of a continuum solvation model with an increasing dielectric constant (varying from 5 to 20) to account for environment effects (Supporting Information). As expected, the electrostatic screening due to the continuum reduces the intermolecular interactions and in turn the magnitude of the interfacial dipoles, without changing the general conclusions.

We have previously shown that the uncompensated quadrupolar field at pentacene/ $C_{60}$  interfaces reshuffles the energy landscape explored by charges as they move from the interface to the bulk.<sup>17</sup> To study these effects in (un)substituted oligothiophenes, we have built model 1D stacks comprising 15 donor and 15 acceptor molecules in a cofacial arrangement (with a 3.5 Å separation). Changes in the ionization potential of dicyanovinyl-substituted and unsubstituted oligothiophenes as well as in the electronic affinity of  $C_{60}$  have been computed as a function of distance to the interface using the valence bond/Hartree–Fock (VB/HF) scheme<sup>18</sup> at the AM1 level. This method uses molecular orbitals localized on a molecular fragment to describe the electronic properties of the entire cluster, thereby allowing the assignment of a net charge to each individual molecule. Here an excess positive or negative charge is brought onto a single molecule while allowing its neighbors to electronically relax fully to account for both electrostatic and dynamic polarization effects. The ionization potential or electron affinity of a particular molecule within the aggregate is then calculated by taking the difference in the total energy of the charged and neutral systems. To seek for general trends, we have extended these calculations to other donors and acceptors, where the out-of-plane component of the quadrupole moment can be either enhanced or decreased with respect to pentacene; see Figure 2.

In the case of the oligothiophene/ $C_{60}$  interfaces, our results are consistent with previous findings on cofacial pentacene/ $C_{60}$  heterojunctions in the sense that the interfacial electrostatic effects provide an improved driving force for electron–hole pair separation. Indeed, both the positive charged state of oligothiophenes and the negative charged state of  $C_{60}$  get destabilized at the vicinity of the interface and lead to a band bending (Figure 3, top left). Interfacial electrostatic effects thus push the charges into opposite directions, from the interface into the bulk, which might at least partially compensate for the loss in Coulomb binding energy. A band bending effect in the opposite direction is predicted in the case of the dicyanovinyl-substituted oligothiophene and cyano-pentacene as a result of the opposite quadrupole-induced interfacial dipole (Figure 3, bottom left). Therefore, in this case, we expect that the interfacial electronic interactions will add to the Coulomb attraction to stabilize further the electron–hole pair across the heterojunction. In the case of the hexathienyl/perylene-tetracarboxylic-dianhydride (PTCDA) interface, a larger reshuffling in the electronic structure at the interface is predicted compared with the 6T/ $C_{60}$  heterojunction (Figure 3, top right). Unlike  $C_{60}$ , the PTCDA acceptor molecule indeed generates a quadrupolar electric field that, because of the opposite polarization of its electronic cloud (as evidenced by the out-of-plane quadrupole moment, Figure 2), adds constructively to the corresponding field generated by the 6T donor, hence the larger band bending. Comparing the DCV6T/PTCDA and 6T/PTCDA interfaces (Figure 3 bottom right), much smaller changes in the energetic positions of the positively and negatively charged states is predicted close to the heterojunction with respect to the bulk in the former case, owing to a partial cancellation of the quadrupolar fields sourced by the two partners. As a rule of thumb, imparting a quadrupolar moment polarized in opposite directions for the donor (with local dipoles having their positive poles lying outward with respect to the center of the molecule, e.g., C–H in pentacene) and the acceptor (with local dipoles having their positive poles lying inward with respect to the center of the





**Figure 3.** (Left) Ionization potentials of dicyanovinyl-substituted oligothiophenes and cyano-pentacene (bottom), oligothiophenes and pentacene (top), and electronic affinities of  $C_{60}$  molecules in model 1D stacks, as a function of distance to the interface. (Right) Ionization potentials of dicyanovinyl-substituted hexathieryl (bottom) and hexathieryl (top), and electronic affinities of perylene-tetracarboxylic-dianhydride (PTCDA) and  $C_{60}$  molecules in model 1D stacks, as a function of distance to the interface. The dashed line indicates the interface.

molecule, e.g.,  $C=O$  in PTCDA) appears as an attractive strategy to bias the energy landscape in favor of full separation of the electron–hole pairs generated at the interface, yet we would like to stress that a complete picture of the exciton dissociation process requires addressing the influence of the relative positions of the molecules on the calculated interfacial dipole<sup>16,19</sup> and the role of solid-state polarization effects when the charges separate, both issues being beyond the scope of the present work.

In conclusion, electrostatic effects at organic heterojunctions are ubiquitous phenomena resulting from the polarizability difference of the two molecules.<sup>20</sup> These effects can change the energy landscape explored by charges in the photoconversion process in multiple and subtle ways. We have shown that interfacial electronic interactions in model 1D aggregates can facilitate the conversion from charge transfer into fully charge-separated states by creating a favorable energy profile or provide the necessary driving force for the formation of charge-transfer states by tuning the energy level alignment. Our work thus highlights the importance of accounting for interfacial electronic interactions in designing new materials for organic photovoltaic devices.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Shifts (compared with isolated molecules) of the HOMO and LUMO energy levels and values of interfacial dipoles of (DCV)nT/ $C_{60}$  dimers calculated at the DFT (wB97X-D/6-31

g(d)) level. Interfacial dipoles of (DCV)nT/ $C_{60}$  dimers calculated at the wB97X-D/6-31 g(d) level using a continuum solvation model with different dielectric constants. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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