

Exploring the Energy Landscape of the Charge Transport Levels in Organic Semiconductors at the Molecular Scale

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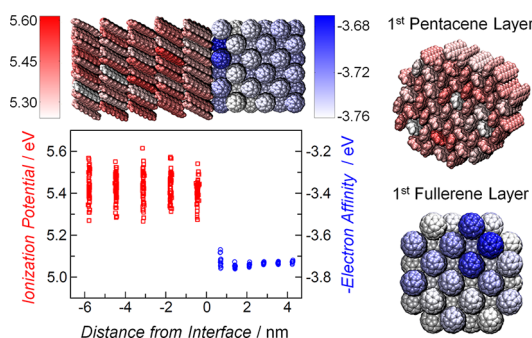
CONSPECTUS

The extraordinary semiconducting properties of conjugated organic materials continue to attract attention across disciplines including materials science, engineering, chemistry, and physics, particularly with application to organic electronics. Such materials are used as active components in light-emitting diodes, field-effect transistors, or photovoltaic cells, as a substitute for (mostly Si-based) inorganic semiconducting materials. Many strategies developed for inorganic semiconductor device building (doping, p–n junctions, etc.) have been attempted, often successfully, with organics, even though the key electronic and photophysical properties of organic thin films are fundamentally different from those of their bulk inorganic counterparts.

In particular, organic materials consist of individual units (molecules or conjugated segments) that are coupled by weak intermolecular forces. The flexibility of organic synthesis has allowed the development of more efficient opto-electronic devices including impressive improvements in quantum yields for charge generation in organic solar cells and in light emission in electroluminescent displays. Nonetheless, a number of fundamental questions regarding the working principles of these devices remain that preclude their full optimization.

For example, the role of intermolecular interactions in driving the geometric and electronic structures of solid-state conjugated materials, though ubiquitous in organic electronic devices, has long been overlooked, especially when it comes to these interfaces with other (in)organic materials or metals. Because they are soft and in most cases disordered, conjugated organic materials support localized electrons or holes associated with local geometric distortions, also known as polarons, as primary charge carriers. The spatial localization of excess charges in organics together with low dielectric constant (ϵ) entails very large electrostatic effects. It is therefore not obvious how these strongly interacting electron–hole pairs can potentially escape from their Coulomb well, a process that is at the heart of photoconversion or molecular doping. Yet they do, with near-quantitative yield in some cases. Limited screening by the low dielectric medium in organic materials leads to subtle static and dynamic electronic polarization effects that strongly impact the energy landscape for charges, which offers a rationale for this apparent inconsistency.

In this Account, we use different theoretical approaches to predict the energy landscape of charge carriers at the molecular level and review a few case studies highlighting the role of electrostatic interactions in conjugated organic molecules. We describe the pros and cons of different theoretical approaches that provide access to the energy landscape defining the motion of charge carriers. We illustrate the applications of these approaches through selected examples involving OFETs, OLEDs, and solar cells. The three selected examples collectively show that energetic disorder governs device performances and highlights the relevance of theoretical tools to probe energy landscapes in molecular assemblies.



1. Introduction

Organic conjugated semiconductors have been widely studied for their opto-electronic properties over the last two decades and are currently exploited in a large range of applications such as light-emitting diodes (OLEDs), field-effect transistors (OFETs), photovoltaic devices, or (bio)sensors. Albeit organic-based devices have already penetrated into the market, especially in the field of displays and integrated circuits, intense research efforts are still carried out at both the academic and industrial level in order to better understand the key electronic processes governing the operation and performance of the devices and provide new guidelines for material design and device architecture. In particular, a ubiquitous process is the transport of electrical charges in organic thin films,¹ which is required in most devices. Theoretical simulations can play a major role by shedding light onto this process at the atomistic scale to complement experimental measurements that probe macroscopically averaged quantities possibly affected by parasitic effects such as the contact resistance for charge injection from metallic electrodes.

When a large amount of disorder is present in thin films, charge transport is often described within a hopping regime. In this weak coupling picture, the charges are localized over individual molecules or polymer segments ("sites") and migrate by successive jumps between sites. Note that a large number of recent theoretical studies further indicate that the charge is also localized in highly organized structures, such as molecular crystals, at room temperature (i.e., in the typical conditions of device operation) due to the dynamic disorder introduced by the thermal activation of lattice vibrations.^{2,3} We will thus consider in this Account that the mobility of charges in organic thin films is primarily governed in first approximation by the rate of a localized charge hopping between individual sites though models accounting for the actual charge delocalization are highly desirable. The rate is typically expressed in most theoretical works via a Miller-Abrahams or Marcus-like expression;¹ note that the molecular parameters (transfer integrals, site energies) fed into transfer rate expressions are also involved in the theoretical description of charge transport in the intermediate and strong coupling (bandlike) regime. Whereas electronic couplings are now calculated on a routine basis via many different approaches, the development of theoretical methods providing a reliable description of the energy landscape for charges in supramolecular architectures is still in its infancy. This has often been treated in a phenomenological way, in

particular via the Gaussian Disorder Model (GDM) assuming that the site energies are randomly distributed within a Gaussian distribution.⁴ The scope of this Account is to describe the pros and cons of different theoretical approaches giving access to the energy landscape defining the motion of charge carriers and to illustrate their applications via selected examples involving OFETs, OLEDs, and solar cells. Note that the success of such approaches relies in part on a reliable description of the molecular packing in noncrystalline materials typically obtained using classical force field simulations.⁵ The three selected examples have in common to illustrate that energetic disorder governs device performances, thus highlighting the relevance of developing theoretical tools to probe energy landscapes in molecular assemblies.

2. Theoretical Considerations

The evolution of the site energies (i.e., HOMO/LUMO energy levels in a one-electron picture) on a given molecule/polymeric segment going from the gas phase to the solid state is primarily driven by the electrostatic interactions with the permanent atomic charges of the neighboring molecules and the induced dipoles resulting from the polarization of their π -electronic cloud. Computing this energy thus requires calculations to be performed on a charged molecule surrounded by a polarizable medium. A simple quantum-chemical approach would be to rely on continuum models in which the molecule is located in a cavity surrounded by a dielectric medium.⁶ Such continuum models have been developed to model the impact of a solvent on the geometric, electronic, and optical properties of solutes. In thin films, however, one would obtain identical site energies for every molecule of an amorphous film, since the standard continuum methods do not account for the anisotropy of the medium and certainly not for the dynamic and spatial heterogeneities responsible for the distribution of the site energies. On the other hand, the most sophisticated theoretical approach would be to treat at a quantum-chemical level a large cluster made of a central charged unit surrounded by neutral molecules. Doing so, a first constraint to model the hopping transport is to force the charge to be localized over a single molecule in the cluster, which is not always guaranteed with standard quantum-chemical calculations due to the neglect of dynamic disorder induced by the thermal activation of intermolecular vibrational modes (except if the central molecule has a very different nature compared to the neighboring molecules); the latter thus reduces the charge

delocalization triggered by the electronic coupling between the individual molecules. A solution to circumvent that issue is to use a fragment approach in which the molecular orbitals are imposed to be localized on a single unit to describe the electronic properties of the entire cluster.^{7,8} It is possible with fragment orbitals to assign the charging of each individual unit and hence to compute the ionization potential of a given molecule within the cluster as the difference between the energy of the neutral cluster and that of the cluster with the charged molecule. Repeating the procedure for each molecule surrounded by a cluster of similar size would then yield the energy landscape explored by the charge in the full system. Although very attractive, this approach is very time-consuming and suffers from the small size of the clusters that can be treated⁸ in comparison to the long-range character of Coulomb interactions. However, this is not a major issue when the relative energy difference between site energies is of prime concern, as it is the case in charge transport simulations. The localization of a charge over a single molecule can also be achieved with the Constrained Density Functional Theory (C-DFT) method,⁹ which optimizes the external potential to constrain the density arbitrarily within the self-consistent resolution of the Kohn–Sham equations.

Another alternative receiving growing attention is to call for hybrid approaches mixing quantum-mechanical and molecular mechanics (QM/MM) calculations. The two levels of theory can be combined in a single run treating the core shell at a QM level and the outer shell (neighboring molecules) with a *polarizable* force field accounting in a self-consistent way for the formation of induced dipoles.^{10,11} The latter technique has been nicely reviewed by Van Voorhis and co-workers in a recent Account.¹² Hybrid QM/classical approaches are appealing because they allow for obtaining the wave function of the target molecules while taking into account explicitly the electrostatic effects of the surrounding medium, and to evaluate the time dependence of electronic properties through QM/MM dynamics simulations. However, at least in the case of a polarizable MM shell, this comes at a higher computational cost with respect to a pure QM calculation on the core shell, because self-consistency is required between the QM and MM parts: this aspect limits the size and the sampling of the systems to be studied.

A different framework for the evaluation of electrostatic interactions and electronic polarization effects in molecular crystals was developed by Tsiper and Soos.^{13,14} In this

method, molecules are treated as nonoverlapping quantum systems (using the INDO/S semiempirical Hamiltonian to evaluate the relevant parameters) interacting through electrostatic forces between atomic charges and induced dipoles. The molecular linear response to external and internal electric fields results from two contributions: (i) a non-local redistribution of point atomic charges with respect to the gas phase (via atom–atom polarizabilities reflecting the polarization of valence electrons) and (ii) a local classical contribution in terms of induced atomic dipoles (atom-centered polarizabilities reflecting the deformation of the electronic cloud). This offers a clear physical picture of the polarization mechanism in organic materials and proved successful in the evaluation of site energy, electron–hole binding energy, and dielectric tensor in molecular crystals and thin films.

Another simpler but robust approach to compute ionization potentials in the solid state is to use microelectrostatic (ME) models where classical expressions are used to depict the interaction of the charge with poles of increasing order in the adjacent molecules (generally limited to dipoles and quadrupoles);^{15,16} these interactions are then subtracted from the gas-phase ionization potential of the molecule to yield the site energies in the solid-state medium. In this approach, the key interactions to be computed are those between (i) the charge and the permanent atomic charges, dipoles, and quadrupoles of the surrounding molecules; (ii) the charge and the induced dipoles on the neighboring molecules that are estimated via the consideration of a polarizability tensor (this should be done preferentially in a self-consistent way in order to account for mutual polarization effects). In practice, all quantities are casted down artificially into subgroup contributions (for instance, a positive charge is distributed equally over the 22 carbon atoms of a pentacene molecule or over the centers of the 5 aromatic rings) in order to account for the molecular topology. The number of subgroups is chosen as a compromise to reproduce results obtained experimentally or with atomic expansions and limit the computational time. The main limitations originate from the fact that (i) all key quantities for the model parametrization must be previously obtained independently via experimental measurements or quantum-chemical calculations; (ii) the method cannot grasp subtle electronic effects such as the hybridization of the molecular orbitals of adjacent molecules.¹⁷ Moreover, a limitation of the ME and Tsiper/Soos methodologies is the neglect of the nuclear displacements of the molecules surrounding the

central charged unit. However, the main advantage of these approaches is clearly the extended size of the medium that can be treated (over 500 pentacene molecules¹⁶). The ME approach has been shown to provide a very satisfactory estimation of the polarization energies in the bulk of organic semiconductors.¹⁶

3. Applications

Influence of the Polymer Dielectric Layer in OFETs.

Several experimental studies have reported a drop in the hole OFET mobility of pentacene when changing the nature of the saturated polymer used as gate dielectric from polystyrene (PS) to polymethylmethacrylate (PMMA) incorporating polar carbonyl groups. This evolution might be attributed both to changes in the morphology of the organic layer on different polymer dielectric layers (especially in the size of the crystalline grains) or to an enhanced energetic dispersion of the site energies induced by electrostatic interactions with the substrate.¹⁸ We assess here to which extent the electrostatic effects can affect the charge mobilities. Tackling this issue thus requires realistic morphologies of the interface between pentacene layers and the polymer dielectrics at the atomistic scale and determining the actual energy landscape experienced by the charge carriers in the layers.¹⁹ To do so, we have first modeled via a molecular dynamics (MD) approach based on the AMBER94 force field the morphology of the amorphous polymer layer before depositing four layers of 80 pentacene molecules; see ref 19 for theoretical details. On the basis of the fully equilibrated structure (see Figure 1), the energy difference ΔE_{if} associated to a charge hopping from an initial site i to a final site f , as induced by the electrostatic interactions with the polymer substrate, has been estimated as

$$\Delta E_{if} = E_i^0 + E_f^+ - (E_i^+ + E_f^0) \quad (1)$$

with E_i^0 representing for instance the interaction between the charge distribution of the initial site in the neutral state and the dielectric layer. Since we are primarily interested in relative energies, we do not consider here the interactions between the charge and the permanent quadrupoles/induced dipoles of the adjacent pentacene molecules, which are expected to be similar for each molecule in a given layer of the crystal; we have also neglected the polarization effects in the saturated polymer chains. The calculated histogram of ΔE_{if} for all pairs localized in the first layer yields a Gaussian distribution with a standard deviation of 0.07 and 0.03 eV in the presence of

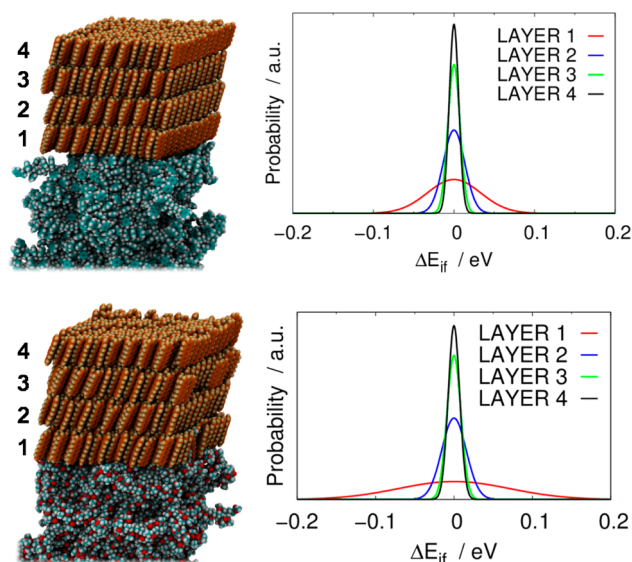


FIGURE 1. (Left) Snapshots extracted from two molecular dynamics simulations of the periodic pentacene/polystyrene (top) and pentacene/polymethylmethacrylate (bottom) systems. (Right) Distributions of ΔE_{if} for all pairs lying in a given layer, as extracted from a MD snapshot.

PMMA versus PS chains, respectively. The results thus nicely demonstrate that an energetic disorder is indeed created in the first pentacene layer where the majority of charge carriers get accumulated in the OFET and that the disorder is more pronounced in presence of polar groups along the polymer chains. The standard deviation of the Gaussian distribution is found to evolve as the inverse of the distance when moving to the upper pentacene layers.

An elegant way to assess the influence of the energetic disorder on the charge mobility and establish a direct link with experiments is to inject the calculated ΔE_{if} values into a rate expression and compute separately the other two key ingredients that are the electronic coupling V_{if} between the HOMO levels of the interacting molecules and the internal reorganization energy λ_i (97 meV in the case of pentacene for holes¹). We have used here a Marcus–Levich–Jortner rate expression that accounts for possible tunneling across the potential energy barrier and writes, when neglecting entropy contributions:²⁰

$$k_{\text{hop}} = \frac{2\pi}{\hbar} V_{if}^2 \sqrt{\frac{1}{4\pi\lambda_S k_B T}} \sum_{n=0}^{\infty} \exp(-S) \frac{S^n}{n!} \exp\left[-\frac{(\Delta E_{if} + \lambda_S + n\hbar\omega)^2}{4\lambda_S k_B T}\right] \quad (2)$$

with $\hbar\omega$ being the energy of an effective vibrational mode assisting the charge transfer (set equal to a typical stretching value of 0.2 eV), S the Huang–Rhys factor directly related to the internal reorganization energy ($S = \lambda_i/\hbar\omega$), and λ_S the external reorganization energy of

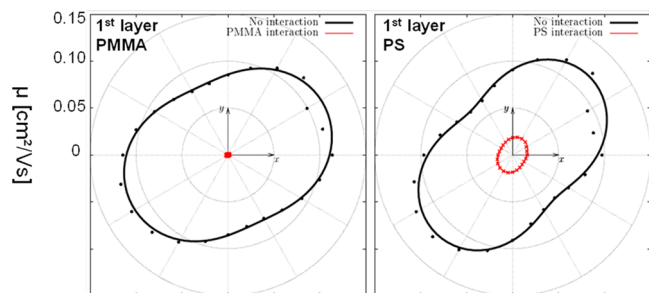


FIGURE 2. Polar plots of the mobility calculated in the first pentacene layer in contact with PMMA (left) and PS (right). In each plot, the radius corresponds to the mobility value and the angle to the electric-field orientation. This plot is obtained by averaging for each direction of the electric field the mobility calculated for 100 different snapshots.

the medium set to a rather arbitrary value of 0.2 eV. Note that the ΔE_{if} value in eq 1 is supplemented by an additional term reflecting the application of an external electric field:

$$\Delta E_{\text{field}} = e\vec{F}\vec{d} \quad (3)$$

with \vec{d} and \vec{F} vectors representing the separation between the centers of mass of the two molecules and the electric field, respectively. In turn, all rates can be injected into kinetic Monte Carlo simulations to propagate a single charge carrier into the energy landscape and estimate the mobility μ as²¹

$$\mu = d/(tF) \quad (4)$$

with d being the total distance traveled by the charge during the simulation, t the total time of the simulation, and F the strength of the electric field. Figure 2 depicts the mobility anisotropy plot in the first pentacene layer with and without the presence of the dielectric layer. Note that time-averaged values of ΔE_{if} have been used in eq 2, in order to take into account that a pair of molecules can explore a large conformational space before the charge hopping occurs, as suggested by the fast saturation in time of the width of the Gaussian distributions.¹⁹ All together, the results suggest that the hole mobility in the first pentacene layer is reduced by a factor of 60 in the presence of PMMA chains and only 5 with PS chains, thus demonstrating how critical is the choice of the insulating layer in OFETs. The theoretical ratio of 12 is in qualitatively good agreement with the experimental trends but overestimates the experimental ratio of 4^{22,23} which might be further affected by morphological differences

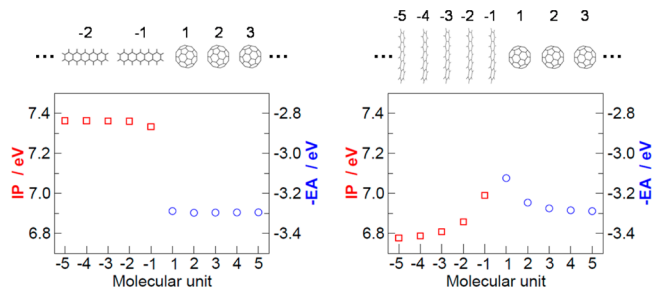


FIGURE 3. Ionization potential of pentacene and electronic affinity of C_{60} in one-dimensional stacks in which the pentacene molecules are stacked parallel (right) or perpendicular (left) to the interface.

at the macroscopic scale that cannot be grasped with our atomistic simulations. The present calculations thus point to the key role played by energetic disorder and open the way to the search of new morphologies or chemical structures for dielectric layers perturbing less the transport properties. Coarse-grained approaches are also highly desirable to integrate in the modeling the influence of macroscopic parameters such as the surface roughness.

Charge Separation at Organic/Organic Interfaces. Another hot issue in the field of organic electronics is to understand how free charges can be generated in organic solar cells, as reviewed recently.²⁴ Such devices are typically built by blending electron-donating and electron-accepting compounds. The light absorbed by the organic layer is initially converted into a polaron pair with a positive charge on the donor and a negative charge on the adjacent acceptor, in close similarity to the operation of a p–n inorganic junction. The two charges of opposite sign are strongly bound coulombically so that charge recombination processes are likely to be very efficient. We will illustrate here that theoretical calculations can prove very useful to shed light on the mechanism of free carrier generation from the lowest charge-transfer state, especially when considering that such interfacial phenomena cannot be easily probed experimentally; note that we will not discuss here other mechanisms based on the dissociation of excited charge-transfer states. In this context, it is instructive to have first a look at Figure 3 where we have reported the evolution of the ionization potential of pentacene molecules and of the electron affinity of C_{60} molecules in two model one-dimensional systems mimicking different interface morphologies, with either a cofacial or edge-to-edge arrangement of the pentacene molecules, as calculated at the AM1 level with a fragment orbital approach. The results show that the

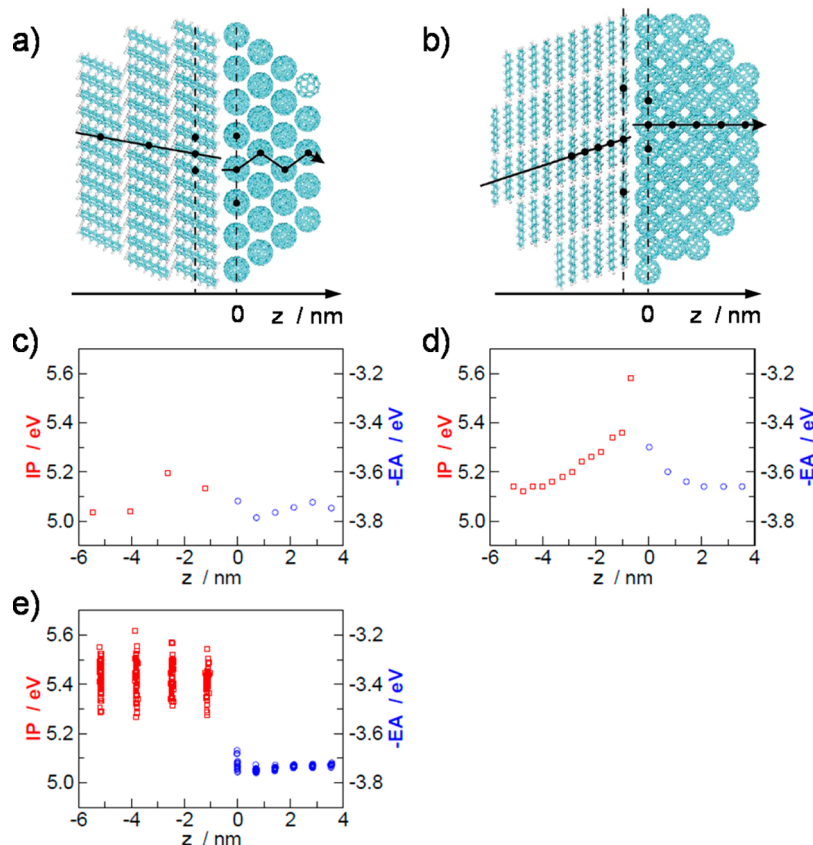


FIGURE 4. (a) Pentacene(001)/C₆₀(001) interface and (b) pentacene(01–1)/C₆₀(001) interface. Dots denote the molecules for which simulation results are shown. Computed energy diagrams of (c) pentacene(001)/C₆₀ interface and (d) pentacene(01–1)/C₆₀ interface. (e) Energy diagram obtained for a large number of snapshots extracted from a MD simulation of the growth of pentacene layers on top of C₆₀ molecules.

ionization potential (IP) of the pentacene units in the cofacial array is reduced while the electron affinity (EA) of the C₆₀ balls increases when going away from the interface. In contrast, the IP and EA show much weaker deviations from their bulk values in the edge-to-edge arrangement, owing to the weak overlap between the electronic clouds of neighboring molecules. These different evolutions are rationalized by the fact that the total electrostatic potential felt by the molecules changes as a function of their position in the stack. The asymmetry of the electrostatic potential at the interface actually translates into the appearance of induced dipoles over both the C₆₀ and pentacene molecules, whose amplitudes are damped when moving away from the interface. These calculations on model systems thus teach us on a qualitative basis that an intrinsic energetic bending can be settled at organic/organic interfaces and might help in the charge separation process provided a favorable interface morphology is generated. Dealing quantitatively with long-range effects such as electrostatic interactions and electronic polarizations requires the consideration of systems much larger than those affordable

at a quantum-chemical level. This has motivated the use of a ME model to address the full charge separation process by analyzing the balance between the energy required to break the Coulomb attraction and the energy gained by polarization effects.

Accordingly, we have estimated the energy landscape for charge separation at the C₆₀/pentacene interface by gluing the (001) or (0–11) facets of the pentacene molecular crystal with the (011) crystalline facet of C₆₀ and by only relaxing the relative orientation and distance between the two facets with the help of the MM3 force field (see Figure 4). The individual site energies have then been computed by accounting for the interaction between the charge and induced dipoles, between the charge and permanent quadrupoles, and between the charge and the dipole induced by the asymmetry of the interface, as discussed above; the detailed procedure is described in ref 25. The profile of the hole and electron energy landscape in the vicinity of the two interfaces is reported in Figure 4, showing that an energetic bending favorable for charge separation occurs at the (01–1)/C₆₀ interface whereas no significant

bending is observed for the other interface. When accounting for the Coulomb attraction between the charges, the total energy of the geminate polaron-pair at the (001)/C₆₀ interface is estimated at the ME level to be -2.69 eV while the sum of the energy of a positive charge in pentacene and of a negative charge in C₆₀ far away from the interface amounts to -2.25 eV. This translates into a huge energy barrier of 0.44 eV to be overcome for the generation of free carriers. Strikingly, the corresponding energies are calculated to be -2.09 and -2.06 eV, respectively, at the (01-1)/C₆₀ interface, thus making the separation process quasi barrierless. A higher degree of sophistication can be reached by generating more realistic structures of the interface with MD simulations of the growth of pentacene molecules on top of the C₆₀ surface.²⁶ This introduces a certain amount of structural (positional/orientational) disorder that can give rise to a dispersion of the site energies by several hundreds of meV, as shown in Figure 4e. This broadening of the energy levels at the interface creates new pathways for the geminate pair recombination/dissociation and further affects the dynamics of these processes. All together, the present results offer a nice explanation for the high performance typically obtained in solar cells including C₆₀ derivatives and motivates further work on the molecular engineering of the energy landscape at organic/organic interfaces. Our model could be further improved by integrating the role of lattice dynamics on the charge separation process.

Mechanism of Molecular Doping. In this last example, we will illustrate that determining the energy profile of charge carriers at the molecular level can provide hints to unravel the mechanism of molecular doping in organic semiconductors. Besides the body of knowledge accumulated on conducting polymers (*chemical doping*), many recent experimental studies on *molecular doping* have demonstrated that introducing only a few percent of electron-donating or electron-accepting molecular dopants in an organic layer can also increase by several orders of magnitude its electrical conductivity and lower the resistance associated to charge injection from metallic electrodes.²⁷ This concept is now widely exploited in light-emitting diodes or solar cells under the name of p-i-n architectures, where p- and n- represent the layers doped with electron-accepting and electron-donating units, respectively, and i- is the central intrinsic, that is, undoped, region. Since any electron transfer between the organic layer and a molecular dopant yields a strongly bound polaron pair as it is the case in solar cells, a detailed understanding of the significant increase in the

number of free carriers generated (and hence in the electrical conductivity) upon light doping based on a robust theoretical approach is highly desirable.

In this context, we have recently developed a model of doping induced charge donation that accounts for the electronic and structural features of the host and doping molecules to clarify in a quantitative way the doping mechanism.²⁸ In order to ensure its validity, we applied this model to a canonical host-guest system of pentacene doped with electron-accepting tetrafluorotetracyanoquinodimethane molecules (F₄TCNQ) and compared theoretical findings to corresponding experimental data. In our approach, the doping of a spherical host crystal (containing 330 pentacene molecules) is realized by first introducing individual dopant molecules in artificially created host vacancies and then allowing them to geometrically relax using the MM3 force field. This simple procedure yields structures in relatively good agreement with low-doping concentration STM measurements pointing to a good insertion of F₄TCNQ in the pentacene matrix.²⁹ This provides us the unique opportunity to clarify the doping mechanism quantitatively in a well-defined supramolecular architecture. The methodology to compute site energies is very similar to that used for the study of C₆₀/pentacene interfaces.²⁵ Figure 5 illustrates the energy profile for holes and electrons on the pentacene molecules lying around a single dopant positioned in the center of the spherical aggregate; this profile has been plotted along the directions A and B featuring the closest contacts though with different geometries between molecules; see Figure 5. The ME results indicate that when a strongly accepting F₄TCNQ molecule is introduced in the pentacene matrix, its electron affinity is larger than the ionization potential of the adjacent pentacene unit only along the B direction ($\Delta E = 0.43$ eV), pointing to a thermodynamically favorable electron transfer to the dopant. The electron transfer leaves the adjacent pentacene molecule positively charged, thus creating a geminate pair between the negatively charged dopant and positively charged host, which is strongly stabilized by the mutual Coulomb attraction (Figure 5). This leads to an energy barrier for charge recombination of 2.62 eV, ensuring that the charge transfer state persists for a very long time in the doped layer. Note that the ME model cannot account for an initial hybridization of the electronic levels of the host and guest molecules, as suggested by a recent study.¹⁷ However, a thermal excitation between the split levels would generate the same charge-transfer state as the one depicted in the ME approach. In order to contribute to the electrical conductivity, a positive

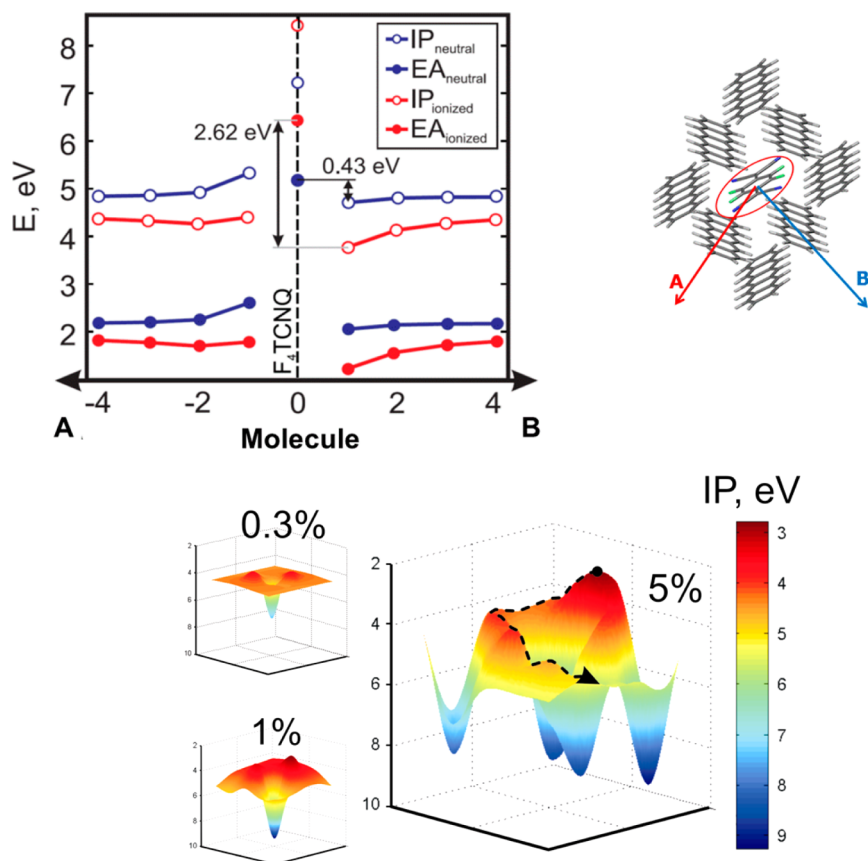


FIGURE 5. (Top left) Ionization potential (IP) and electron affinity (EA) profiles around a neutral (blue) and ionized (red) dopant molecule; the distances are in Å. (Top right) Cross section view showing the position of F_4TCNQ molecules in the pentacene matrix and the A/B directions: in direction A, the face of the nearest pentacene is exposed to the fluorine atoms of the dopant, while in direction B the edge of the nearest pentacene is exposed to the π -orbitals of the dopant. (Bottom) IP landscapes of pentacene films doped with 0.3%, 1%, and 5% F_4TCNQ . A possible percolation pathway for charge pair dissociation by the energetic disorder created at high doping concentration is illustrated by the dashed arrow. The central dopant is located in the center of the (x,y) square.

hole generated on a pentacene molecule has to escape from the Coulomb attraction of the parental dopant; this process is inefficient at low doping ratio in view of the unfavorable energetic bending reported in Figure 5 along the B direction. When the doping concentration increases, charge pairs start interacting and promote a growing energetic disorder of the HOMO levels of the pentacene molecules (the standard deviation doubles when going from 1 to 5%); see Figure 5. This disorder is expected to create new dissociation pathways and increase the probability of the charge pair dissociation, in close similarity to the charge transport properties of conducting polymers where charges are pinned to inorganic counterions.³⁰ This has been demonstrated by solving Master equations based on Marcus–Levich–Jortner rates. On the basis of the charge distribution at equilibrium, the results show that the probability for a hole to leave a site next to the associated dopant increases linearly with the doping rate and is equal to $\sim 0, 6, 14,$ and 23% for a dopant

concentration of $<0.3, 1, 3,$ and 5% , respectively. A linear increase in the dopant concentration accompanied by a linear increase in the dissociation probability thus leads to a quadratic evolution of the total charge density (when neglecting dopant clustering), in agreement with experimental measurements.³¹ Even though the doping efficiency in the studied canonical system is rather limited (compared to 100% doping efficiencies in inorganic semiconductors), our model can now be exploited for selection of promising host-dopant combinations toward improved doping efficiencies.

4. Conclusions

Multiscale modeling aims at bridging the gap between molecular and material properties. In the field of organic electronics, the ultimate goal is to go all the way from atomistic design principles of the individual components (molecules or polymer chains) to predictions of device

quantum efficiencies. A quantitative assessment of the optoelectronic processes taking place in the actual device architectures represents a formidable challenge and multiscale modeling as applied to organic electronics is still in its infancy. Part of the complexity arises from the need to combine in a single theoretical framework multiple and diverse ingredients: (i) of course, a high level quantum-mechanical treatment, preferably from first principles, should be reserved at the molecular scale; (ii) as such treatments can only be handled for limited size systems, a proper embedding scheme is needed, where the surrounding of the active molecular components is treated for instance using classical electrostatic laws; and (iii) last but not least, efficient sampling methods should be applied as the elementary processes at play in organic based devices, such as charge separation and transport, are usually heterogeneous in space (due to the presence of structural disorder) and span multiple time scales (from subps exciton dissociation at organic interfaces to charge scattering by low-frequency lattice modes in the bulk).

In this Account, we described a few attempts to simultaneously deal with the different components listed above when modeling the energy landscape for charge dissociation and transport in bulk materials and at interfaces. Interestingly, the examples showed that energetic disorder can be detrimental for charge transport by creating traps in thin films or favorable by detrapping charges in host–guest systems created by molecular doping. With the risk of being too optimistic, it is reassuring to see that one can now reasonably cope with the various elementary optoelectronic processes using reliable computational schemes. There is, however, a caveat. On the practical side, the overall formalism is fragmented as it combines information provided by multiple codes of very different nature (quantum chemistry, force fields, and transport models) and would have to be unified into a single computational protocol to be useful to the community of organic electronics on a broader scale. On the fundamental side, the results of the simulations discussed here are strictly valid in the limit of the approximations used to derive the models. Referring to the doping example, one can legitimately raise questions about the validity of assuming complete charge localization over individual molecules, neglecting quantum-chemical interactions between dopant and host molecules or propagating charges in an incoherent hopping regime within a frozen lattice. Thus, there is a clear need for a general theoretical formalism that would integrate in a self-consistent and modular way the various aspects involved in the multiscale

modeling of organic electronic devices. To the best of our knowledge, such a modeling toolkit is not available yet.

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Note Added after ASAP Publication. This manuscript was published on November 9, 2012 with an error in the Conspectus graphic. The corrected version was reposted on November 21, 2012.

BIOGRAPHICAL INFORMATION

Jérôme Cornil is a Senior Research Associate of the Belgian National Fund for Scientific Research (FNRS) in Mons and holds a Visiting Principal Research Scientist position at the Georgia Institute of Technology since 2005. His main research interests deal with the quantum-chemical characterization of the electronic and optical properties of organic conjugated materials in the bulk and at interfaces, in relation to their use in optoelectronic devices.

Stijn Verlaak was a senior researcher and later consultant at imec between 2004 and 2008 in the field of small molecule organic film growth and semiconductor physics. His activities focused on a combined molecular mechanics and microelectrostatic description of clusters of small organic molecules.

Nicolas Martinelli got his Ph.D. from the University of Mons in 2011. His work aimed at developing Kinetic Monte Carlo approaches to propagate charge carriers in supramolecular assemblies and assess the influence of lattice dynamics and Coulomb interactions.

Alexander Mityashin is a member of the Large Area Electronics department at imec and a PhD candidate at the Electrical Engineering department of K.U. Leuven. His research focuses on the fundamental principles of organic electronic devices, their technology and real-life applications.

Yoann Olivier is a post-doctoral fellow of the Belgian National Fund for Scientific Research since 2009 in Mons. His research interests deal with the theoretical understanding of electronic processes in organic conjugated materials, especially the relationship between their chemical structure, assembly and charge transport properties.

Tanguy Van Regemorter is a post-doctoral researcher at the University of Mons (Belgium) since 2009 and holds a Ph.D. in Materials Chemistry from Uppsala University (Sweden). His main research interests deal with quantum-chemical calculations of the structural and electronic properties at interfaces in organic electronic devices.

Gabriele D'Avino obtained his Ph.D. at the University of Parma and is currently working at the University of Bologna as a postdoc. His research mainly focuses on the theoretical modeling of multi-stable molecular crystals and materials for organic electronics.

Luca Muccioli works as postdoctoral researcher at the University of Bologna. His scientific activity is aimed at the prediction of the self-assembly and physical properties of organic materials (liquid crystals, crystals, polymers) by molecular modeling and simulation techniques.

Claudio Zannoni is Professor of Physical Chemistry at the University of Bologna. His main research interests are in studying the molecular organization of bulk and nano soft materials, particularly liquid crystals, organic semiconductors, elastomers, and their interfaces using computer simulations, theory, and spectroscopic techniques.

Frédéric Castet is Assistant Professor in the Chemistry Department of the University Bordeaux 1 (France) since 2000. His main research activities focus on the characterization of the electronic structure of supramolecular organic assemblies by using fragment orbital-based quantum-chemical methods, as well as on the modeling of the nonlinear optical properties of molecular systems and materials with promising characteristics for exploitation in optoelectronics and photonic devices.

David Beljonne is a FNRS research director at the University of Mons and also holds a visiting principal research position at the Georgia Institute of Technology. His expertise deals with the multi-scale modeling of light harvesting, excitation transport, and dissociation in the bulk phase of organic materials and at interfaces.

Paul Heremans is a Fellow at imec and Professor in Electronic Engineering at the K.U.Leuven. He is also heading imec's Large Area Electronics department, where he directs the research on organic and oxide semiconductor technology, devices, and applications, in particular organic solar cells and flexible OLED displays.

FOOTNOTES

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The authors declare no competing financial interest.

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