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Resolving Donor-Acceptor Interfaces and Charge Carrier Energy Levels of Organic Semiconductors with Polar Side Chains

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Abstract

Organic semiconductors consisting of molecules bearing polar side chains have been proposed as potential candidates to overcome the limitations of organic photovoltaics owing to their enhanced dielectric constant. However, introducing such polar molecules in photovoltaic devices has not yet resulted in higher efficiencies. A microscopic un-
derstanding of the impact of polar side chains on electronic and structural properties of organic semiconductors is paramount to rationalize their effect. Here, we investigate the impact of such side chains on bulk heterojunction overall morphology, molecular configurations at donor-acceptor (DA) interfaces, and charge carrier energy levels. The multiscale modeling approach used allows to resolve DA interfaces with atomistic resolution while taking into account the large-scale self-organization process which takes place during the processing of an organic thin film. The polar fullerene-based blends are compared to the well-studied reference system, poly(3-hexyl-thiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM). Introduction of polar side chains on a similar molecular scaffold does not affect molecular orientations at the DA interfaces; such orientations are however found to be affected by processing conditions and polymer molecular weight. Polar side chains, instead, are found to impact considerably the charge carrier energy levels of the organic blend, causing electrostatic-induced broadening of these levels.

Introduction

Functionalization of organic semiconductors with polar ethylene glycol (EG) side chains is recently emerging as a key strategy to boost performance in organic electrochemical transistors\textsuperscript{1,2} and organic thermoelectric devices.\textsuperscript{3-5} In contrast to traditional apolar alkyl side chains, EG side chains have a relatively high degree of polarity due to the permanent dipole moments introduced by substitution of methylene units for oxygen atoms. Replacement of alkyl by EG chains has been found to increase the doping efficiency of organic semiconductors in thermoelectric devices—mostly due to an increased host-dopant miscibility,\textsuperscript{3-5} to allow for mixed ionic-electronic conduction,\textsuperscript{1,6} to decrease the $\pi-\pi$ stacking distance of polymer backbones,\textsuperscript{7} and to increase the dielectric constant.\textsuperscript{8-11} The increase in the dielectric constant of organic semiconductors has been proposed as a strategy to increase the performance of organic photovoltaics (OPVs).\textsuperscript{12} Although EG side chains in particular have found ample
use in achieving organic materials with increased dielectric constants,\textsuperscript{8–11,13–15} this has not yet resulted in OPV devices achieving higher efficiencies.\textsuperscript{14} A microscopic understanding is paramount to rationalize the effect of polar side chains in blends of organic semiconductors. Here, we investigate the impact of introducing polar side chains in bulk heterojunction (BHJ) solar cells by multiscale modeling: we study how their introduction affects phase separation, molecular orientations at the DA interfaces, and charge carrier energy levels.

Despite a growing body of literature comprising modeling studies of organic semiconductors,\textsuperscript{16–19} only few of them have considered the impact of the polarity of the side chains on the functioning of organic devices. For example, by comparing C\textsubscript{60} and C\textsubscript{70} to their well-known soluble derivatives, phenyl-C61-butyric acid methyl ester (PCBM) and the analogous PC\textsubscript{71}BM, it was found that fullerene functionalization leads to increased energetic disorder in neat fullerene morphologies.\textsuperscript{20,21} Fullerene functionalization also decreases the electronic, or high frequency, dielectric constant,\textsuperscript{22} with the increased dielectric constant values recorded for (EG-)functionalized fullerenes\textsuperscript{8} which are thus expected to stem from dipolar contributions. The dipolar origin of such contribution was very recently confirmed by polarizable molecular dynamics (MD) simulations, which also highlighted a synergistic effect between the highly polar EG units and the highly polarizable C\textsubscript{60} which contributes to the increase in dielectric constant.\textsuperscript{23} Such dipolar contributions may positively influence the charge separation process in OPV devices. This scenario is supported by the study of de Gier and co-workers,\textsuperscript{24} where side chains bearing dipole moments have been shown to positively influence the charge separation by stabilizing the charge separated state relative to the lowest charge transfer state.\textsuperscript{24} However, the time scale of the response of such dipoles may not be quick enough to alleviate organic photovoltaics recombination losses.\textsuperscript{23} A definitive picture of the overall positive influence of polar side chains in BHJ solar cells has yet to emerge.

EG-functionalization may also influence molecular configurations at the DA interfaces. Such configurations have been linked to organic solar cell device performance in several studies, both theoretically and experimentally.\textsuperscript{25–30} Experimentally, while some information
regarding molecular configurations at the interfaces can be obtained for planar heterojunctions,\textsuperscript{25,26,30} few studies obtained such information for BHJ interfaces,\textsuperscript{27,28} and there is no wide-spread method to characterize preferential orientation at the DA interfaces in BHJs. Despite the potential of computational modeling to help in this endeavour, previous work was limited either by too low molecular resolution—which makes a direct link to molecular configuration ambiguous,\textsuperscript{31–33} or by timescales—which lead to the modeling of pre-assembled interfaces, thereby hampering the prediction of relative abundance of DA configurations in a given blend.\textsuperscript{29,34,35}

In what follows, we resolve molecular configurations at the DA interface of realistic\textsuperscript{36} BHJ morphologies while taking into account the large-scale self-organization process which takes place during the processing of an organic thin film. A detailed configurational analysis shows how structures at the DA interface are affected by the molecular weight of the polymer—poly(3-hexyl-thiophene) (P3HT)—and processing conditions such as thermal annealing. In the case of the reference P3HT:PCBM blends, while low molecular weight P3HT leads to more end-on DA configurations, higher molecular weight P3HT is found to promote face-on configurations. We then investigate the impact of polar EG-based side chains by replacing the reference fullerene derivative PCBM with a recently synthesized fulleropyrrolidine which showed\textsuperscript{8} an enhanced dielectric constant—PTEG-1. We study how a higher degree of polarity affects 1) the phase separation, 2) the relative orientations of the donor and acceptor molecules at DA interfaces, and 3) the charge carrier energy levels. Functionalization of the fullerene acceptor by EG side chains is found to impact the phase separation to a minimal degree in this case, and it does not impact molecular orientations at the DA interfaces. In contrast, the permanent dipoles of the polar side chains have a large impact on the energetics of the organic blend. Microelectrostatic calculations predict that installing polar side chains leads to considerable broadening of the charge carrier energy levels, due to increased electrostatic disorder.
Results and Discussion

**Molecular Configurations at Donor-Acceptor Interfaces.** We first characterize structurally the DA interfaces in the reference P3HT:PCBM system. We generate realistic BHJ morphologies at the coarse-grain (CG) level (Figure 1a) via large-scale solvent evaporation MD simulations (see Methods). Such simulations mimic the solution-processing step through which organic thin films are produced experimentally, and were previously shown to lead to morphologies in agreement with experimental scanning electron microscopy and scattering data. The use of Martini CG models, which retain a sizable degree of chemical specificity and structural detail (Figure 1b), allows for direct analysis of the DA interfaces of such CG morphologies: we thus retrieve (see Methods) maps of the relative abundance of different DA molecular orientations (Figure 1c).

![Figure 1: Molecular configurations at donor-acceptor interfaces of simulated P3HT:PCBM morphologies. (a) Morphology of a blend of P3HT (24-mer) and PCBM at CG resolution generated via solvent evaporation simulations. (b) All-atom (AA) and CG representations of a P3HT (for clarity, a trimer is shown) and a PCBM molecule. (c) DA configurational space, obtained by partitioning all of the DA pairs at the DA interfaces of a given morphology in the 2D space formed by the distance, \( r_{DA} \), connecting the center of mass of \( C_{60} \) and the center of mass of the thiophene ring, and the angle, \( \theta_{DA} \), between the \( r_{DA} \) vector and the vector normal to the thiophene plane. In this way, regions in the 2D map represent the different DA molecular configurations: face-on, end-on, and edge-on (see insets). In the insets, the reference P3HT monomer and \( C_{60} \) fullerene are highlighted in red and blue, respectively; neighboring P3HT monomers and PCBM side chains are shown in gray. Note that P3HT chains are not rendered in full—only 5 consecutive monomers are shown—for clarity.](image-url)
A representative map for a simulated solution-processed P3HT:PCBM blend (P3HT molecular weight of 2 kDa) is shown in Figure 1c. The map gives a view on the relative abundance of DA configurations found at the heterointerfaces of the blend, which can be classified—according to the relative position and orientation of the donor and acceptor π-systems\textsuperscript{29,39}—in three categories: face-on, end-on, and edge-on. These categories apply in the case of an isotropic shape for one of the two molecules of the blend—this being the case of, for example, fullerene-based organic mixtures. Characteristic snapshots of such configurations are shown as insets in Figure 1c for the P3HT:PCBM blend: in face-on configurations, the P3HT thiophene rings face C\textsubscript{60}; in end-on configurations, the P3HT thiophene rings are in contact with C\textsubscript{60} but the normal to their plane is oriented perpendicularly to the C\textsubscript{60}–thiophene connecting vector (such a configuration can occur with a P3HT thiophene which is at either of the two ends of a P3HT molecule); finally, in edge-on configurations, P3HT side chains separate C\textsubscript{60} and the π-system of P3HT.

The map of Figure 1c shows examples of these three configurations, as three regions can be distinguished. In the bottom-left corner, we can individuate face-on configurations, since such configurations imply the shortest possible \(r_{DA}\) distance and a \(\theta_{DA} \sim 0^\circ\) \((r_{DA} \approx 7.5 \text{ Å}, 0^\circ \leq \theta_{DA} < 25^\circ \Rightarrow \text{face-on})\). In the top-left corner, we can locate end-on configurations, since such configurations imply a slightly larger \(r_{DA}\) distance and a \(\theta_{DA} \sim 90^\circ\) \((r_{DA} \approx 8.5 \text{ Å}, 65^\circ < \theta_{DA} \leq 90^\circ \Rightarrow \text{end-on})\). Finally, around the same angle, but at a larger distance, we can individuate edge-on configurations \((r_{DA} \approx 12 \text{ Å}, 65^\circ < \theta_{DA} \leq 90^\circ, \Rightarrow \text{edge-on})\). The map indicates that, not surprisingly, multiple type of DA interfaces coexist in BHJs. In the next section, we will thoroughly investigate some factors which can affect the relative abundance of molecular configurations at the heterointerfaces.

**Effect of Polymer Molecular Weight and Thermal Annealing on Configurations at Interfaces.** Both P3HT molecular weight (MW) and thermal annealing—a process often employed to post-process solution-processed organic thin films—are known to affect the structural organization of P3HT:PCBM blends on the mesoscale. In particular,
low MW P3HT is known to crystallize more readily,\textsuperscript{40} while in the case of many OPV blends, both fullerene-based\textsuperscript{41} and nonfullerene-based,\textsuperscript{42} annealing the organic film boosts the performance of the device considerably. Annealing is known to increase the crystallinity of (at least) one of the two components of typical organic blends.\textsuperscript{41,42} As a consequence, phase separation also usually increases. However, it is not clear whether and how these two “parameters”—the MW of the polymer phase and thermal annealing—impact the molecular configurations at the DA interfaces. We thus performed the configurational analysis of P3HT:PCBM blends at various P3HT MWs and before and after thermal annealing.

We first discuss the results obtained as a function of P3HT MW. We vary the MW of P3HT from 2 to 8 kDa, corresponding to P3HT chains that are 12 to 48 monomers long. Figure 2a and 2c show typical snapshots of as-cast and annealed (see below) P3HT:PCBM blends for P3HT MW of 2 kDa and 8 kDa, respectively. Their corresponding DA configuration phase spaces are shown in Figure 2b and 2d, respectively. Comparing the DA phase spaces, the first clear feature is the enrichment in end-on configurations of the low MW blend, while the high MW blend is dominated by face-on configurations. This may be understood in terms of the face/end ratio of the two different P3HT chain lengths: low MW P3HT contains more chain-ends than high MW P3HT, thus there is less P3HT “face” available for fullerenes to dock in the low MW case. A second feature is the more marked region at larger $r_{DA}$, corresponding to edge-on configurations, in low MW blends. Results for more blends, including intermediate MWs, are shown in Figure S1 in the Supporting Information and confirm the trends just described: as the P3HT chain length increases, the dominant DA configuration shifts from end-on to face-on.

We anneal the simulated as-cast BHJs (as recently done\textsuperscript{36}—see also Methods) and perform the DA configuration analysis on the resulting morphologies. Comparing the annealed blends and corresponding DA configuration maps of Figure 2 to their as-cast counterparts, we note a few differences between the two extremes of the range of MWs studied here upon thermal annealing. In the low MW case, the crystallinity of the P3HT phase increases dra-
Figure 2: Effect of molecular weight and thermal annealing on the donor-acceptor configurations at the interfaces of P3HT:PCBM blends. Renderings of as-cast and annealed simulated bulk heterojunctions are shown for (a) low MW (2 kDa, corresponding to a 12-mer) and (c) high MW (8 kDa, corresponding to a 48-mer) P3HT blends. Their corresponding DA configuration phase spaces are shown in (b) and (d), respectively. Upon increasing P3HT MW, configurations at DA interfaces shift from end-on enriched to face-on dominated. Upon annealing, the enhanced crystallinity of the P3HT phase leads to an even more drastic shift to end-on configurations for low MW blends (c), while has little effect on the high MW blend (d). In (a) and (c), P3HT side chains are not rendered to highlight the organization of P3HT backbones; plot in (b) and (d) are normalized to the total number of DA pairs.
matically, and this has two consequences on the DA configurations: i) an even more drastic shift towards end-on orientations, and ii) the disappearance of the population at larger distances, due to the formation of contacts between side chains of different P3HT molecules upon P3HT lamella formation. This lamella formation reduces the surface of free P3HT side chains which can be approached by fullerene molecules, hence decreases the DA population on the top-right corner of Figure 2b. However, in the high MW case, the dominant configuration remains face-on, and only a little decrease in the edge-on population is noticeable. This again can be rationalized by considering the different face/end ratio of P3HT chains, this time considering also the effect of annealling, that is enhanced crystallinity. In the low MW annealed case, P3HT backbones readily come together to form polymer crystallites, leaving even fewer backbone “faces” free for interactions with the fullerene. At the same time, the “end” of the crystal grows, effectively increasing the “end-on surface” available for the fullerene derivatives to dock. Hence the further increase of the end-on feature of the 2D map. Also, fewer side chains are free due to the growth of P3HT lamella upon crystallization, thus decreasing the “edge-on surface” as well. In the heaviest MW case, the impact of annealing is relatively reduced with respect to the low MW case—in agreement with earlier results\textsuperscript{36} and experiments which show a higher sensitivity of low MW P3HT to processing conditions\textsuperscript{43}—showing only a minor decrease in the edge-on population. The dominant interface configuration remains face-on.

Given the fact that the heaviest P3HT studied here is still lighter than the ones employed in P3HT-based OPV devices (8 kDa vs 30–60 kDa\textsuperscript{44}), the picture derived in the highest MW case is likely to be more relevant than the low MW one for actual P3HT solar cells and, in general, for polymer-based blends. In contrast, the low MW P3HT picture which emerges is likely to be relevant for small-molecule-based\textsuperscript{45} organic blends.

These findings indicate also that the ratio between the multiple pathways through which charge separation occurs within a BHJ\textsuperscript{29,35} may change depending on the P3HT MW and processing conditions. In particular, Fazzi et al. have recently reported\textsuperscript{46} that end-on con-
figurations allow for “cold-splitting” of excitons, where intermediate charge-transfer states first thermalize and then split into free charges; in contrast, face-on configurations are more suited to a “hot” charge separation mechanism, where the excess vibrational energy of the higher lying intermediate charge-transfer state is used to overcome the Coulomb attraction between the hole and the electron. In view of the present work, high MW P3HT:PCBM blends are expected to allow for cold exciton splitting to a lesser degree than low MW ones, given the dominance of face-on configurations at the heterointerfaces. In the present case, shifts on the DA configuration populations at the heterointerfaces are driven by the chain length and degree of crystallization of the polymer. However, other factors such as steric accessibility of molecular moieties may also play a role. The current protocol allows to explore whether and to which extent factors such as processing conditions and molecular features impact the relative orientations of molecules at the DA interfaces. This constitutes a necessary step in the direction of an increased rational approach to the design of high performance OPVs.

Impact of Polar Side Chains on the Phase Separation and DA Configurations.

We now investigate the impact of polar side chains in bulk heterojunctions, firstly from a structural point of view. To this end, we replace the reference fullerene derivative, PCBM, with a recently synthesized fulleropyrrolidine, PTEG-1 (Figure 3e). PTEG-1 has a longer and EG-based side chain and showed a dielectric constant of 5.7 ± 0.2, considerably higher than the one of the reference compound PCBM (3.9 ± 0.1).

Figure 3 collects a structural comparison between P3HT-based blends of the two fullerene derivatives, PCBM and PTEG-1 (see Figure 3a and 3e for the atomistic structures and CG representations of the two fullerene derivatives). We first analyze the impact of the EG-based side of PTEG-1 on the overall phase separation. We do so by looking at the number of donor-acceptor contacts throughout the simulated BHJ: a higher number of such contacts indicates higher likelihood to find a P3HT molecule close to a fullerene one, i.e., a more intimately mixed morphology. The numbers of contacts in the planar heterojunction and completely
Figure 3: Structural impact of polar side chains. (a)-(d) P3HT-based blends of the reference fullerene derivative PCBM are compared to (e)-(h) P3HT-based blends of PTEG-1, a fullerene derivative bearing an EG-based polar side chain (see (e) for a rendering of its atomistic structure overlaid with its CG representation). Snapshots of as-cast (b) P3HT:PCBM and (f) P3HT:PTEG-1 simulated BHJs are shown for the 8 kDa P3HT case. In this case, polar side chains tend to increase the miscibility between the donor and acceptor molecules, as quantified by the number of DA contacts for the (c) P3HT:PCBM and (g) P3HT:PTEG-1 blends. DA configurations at the interfaces—shown in (d) and (h) for 8 kDa P3HT-based blends—show, however, no major difference.
intermixed extremes, respectively, have been used as references to normalize the computed fraction of P3HT-fullerene contacts (see also Ref. 36). While low P3HT MW blends show slightly decreased mixing upon EG-functionalization of the fullerene (Figure 3c and 3g, 2 kDa), high P3HT MW blends show no significant difference in mixing (Figure 3c and 3g, 8 kDa), as quantified by the number of P3HT-fullerene contacts in the two cases. A larger difference in polarity between P3HT and PTEG-1 may explain the decreased mixing in the low MW blends. However, overall the predicted effect on the morphology phase separation is minimal.

Turning to the DA interfaces, representative 2D maps of the DA configuration spaces are shown in Figure 3d and Figure 3h. They show no major difference between P3HT:PCBM and P3HT:PTEG-1 blends (see also Figure S2 in the Supporting Information). Accordingly, we conclude that the overall geometry of the molecules, that is C_{60}-like in the case of both PCBM and PTEG-1, drives molecular orientations at the DA interfaces, and dominates over side chain functionalization with ethylene glycol. Sizable differences are expected in the case of going from fullerene to non-fullerene acceptors, given the anisotropic shape of the latter. This is currently being investigated and will be part of future work.

**Effect of Polar Side Chains on the Charge Carrier Energy Levels.** We now turn to explore the impact of polar side chains on the charge carrier energy levels of bulk hetero-junctions. The CG morphologies are thus backmapped—using a published protocol\(^{50}\) (see Methods)—to retrieve full atomistic resolution. Subsequently, we compute hole and electron energy levels, ionization potentials (IPs) and electron affinities (EAs), for the simulated BHJs. We employ Tight-binding Density Functional Theory (DFTB)—see also Methods—to compute the gas-phase energy levels. In condensed phases, charge carrier energy levels are largely affected by intermolecular interactions. These shift the gas-phase IP and EA values,\(^{51}\) and stabilize charges with respect to the gas-phase. Such shifts are called polarization energies and are usually indicated as \(P^+\) for a hole, and \(P^-\) for an electron. Two main contributions determine \(P^\pm\):\(^{51}\)\( I\) the contribution of the electrostatic field experienced
by the charge carrier in the condensed phase—the *electrostatic* contribution, $S^{\pm}$; and 2) the contribution of the induced dipoles between the charge carrier and its surrounding—the *induction* contribution, $I^{\pm}$. We evaluate these two contributions and hence the polarization energies by microelectrostatic, or induced dipoles, calculations using the classical polarizable Direct Reaction Field (DRF) force field as implemented in the DRF90 software.\textsuperscript{52} We consider a central molecule—either neutral or charged—and a surrounding of 2 nm around such molecule taken from the simulated large-scale morphology (for details, see Methods).

P3HT-based BHJs containing PTEG-1 lead to broader charge carrier energy level distributions, as shown in Figure 4. The standard deviation ($\sigma$) of these distributions quantifies the energetic disorder. Both the HOMO and LUMO energy distributions are considerably broader in blends containing PTEG-1. In particular, $\sigma$ increases on average by 30% when going from P3HT:PCBM to P3HT:PTEG-1 blends, indicating increased energetic disorder. It is instructive to first compare the electron energy levels in neat fullerene morphologies of PCBM and PTEG-1, as shown in Figure 5. While the gas-phase LUMO levels almost coincide (Figure 5a), once the electrostatic and induction effects of the surrounding molecules are taken into account, the LUMO distributions broaden considerably, and this is more so in the case of PTEG-1. For PCBM, $\sigma = 0.22$ eV, a value somewhat higher than the ones reported in previous computational works (0.13 eV\textsuperscript{20} and 0.16 eV\textsuperscript{21}), which is due to a difference in the magnitude of the induction contribution when comparing to Ref. 21 (see below). As compared to PCBM, PTEG-1 shows a markedly broader distribution, with $\sigma = 0.30$ eV.

Analyzing the contributions to the broadening of the energy levels, Figure 5b shows that: 1) the energetic disorder is mostly due to the electrostatic contribution, in agreement with previous findings;\textsuperscript{21} the $\sigma_{S-} = 0.28$ obtained for PCBM agrees well with the value obtained by D’Avino et al.;\textsuperscript{21} 2) the induction contribution is the same in both cases: this is not surprising, as the polarizability of PCBM and PTEG-1 are expected to be very similar given the fact that they are dominated by C\textsubscript{60}; we note also that the induction contribution is about half in magnitude than what computed by D’Avino et al.,\textsuperscript{21} which explains the discrepancy.
in the total $\sigma$ for PCBM between this work and Ref. 21; 3) the induction contribution is anti-correlated with the electrostatic one: as a consequence, the final energetic disorder is smaller when considering the induction than what it would be in a purely electrostatic picture—in agreement with previous findings; 4) the electrostatic contribution is centered around zero for PCBM but has an overall stabilizing effect in the case of PTEG-1: this indicates that the combination of the arrangements of PTEG-1 molecules and its dipoles, along with

![Normalized Occurrence](energy_distribution.png)

**Figure 4:** Impact of polar side chains on the charge carrier energy levels of simulated bulk heterojunctions. (top) Charge carrier energy levels in (a) P3HT:PCBM and (b) P3HT:PTEG-1 blends. The introduction of polar side chains broadens the hole and electron energy levels in the BHJ, with standard deviations ($\sigma$) which increase from 0.18 and 0.19 eV for the hole and electron energy levels in P3HT:PCBM blends to 0.23 and 0.25 eV in P3HT:PTEG-1 ones. (bottom) The decomposition of the energy distributions in electrostatic, $S^\pm$, and induction, $I^\pm$, contributions, highlights that the increased broadening is due to increased electrostatic disorder caused by the presence of the dipole-loaded EG side chains.

the localization of the excess charge, gives rise to favorable interactions. The same effects observed for the neat fullerene blends can be observed for the blends (Figure 4); however,
this time not only on the electron but also on the hole energy levels. In conclusion, the longer and dipole-loaded side chain of PTEG-1 gives rise to considerably more electrostatic disorder, which broadens both charge carrier energy levels.

![Figure 5: Electron energy levels in neat fullerene morphologies: PCBM vs PTEG-1.](image)

According to the present findings, PTEG-1 is predicted to decrease the open-circuit voltage ($V_{OC}$), given the same blend, due to increased electrostatic disorder. Such a decrease in $V_{OC}$ was previously reported upon EG-functionalization of polymers\textsuperscript{7} and nonfullerene acceptors\textsuperscript{53} and upon cyano-functionalization\textsuperscript{54} of polymers, the latter being another way of introducing permanent dipole moments in organic semiconductors.\textsuperscript{14} Broadening of charge carrier energy levels can also lead to lower mobilities.\textsuperscript{54} A decrease in $V_{OC}$ and lower charge carrier mobilities are detrimental to the efficiency of OPVs. However, polar side chains may counterbalance this detrimental effect by stabilizing charge separated states,\textsuperscript{24} thereby making the charge dissociation more enthalpically favorable, or by suppressing bimolecular
recombination. Moreover, other factors, notably morphology, can further influence the charge carrier energy levels, which may explain why PTEG-1 was found to have a larger $V_{OC}$ when blended with the polymer PTB7 than PCBM.\textsuperscript{55}

**Conclusion**

We investigated the effect that functionalization of an organic semiconductor with polar side chains has on the structural and energetic landscape of organic blends. The multiscale modeling approach used allows for the investigation of molecular orientations at the heterointerfaces as a function of processing conditions and molecular features. In general, low molecular weight P3HT is found to lead to more end-on donor-acceptor configurations, while higher molecular weight P3HT is found to promote face-on configurations. The impact of a polar fullerene derivative on phase separation and donor-acceptor configurations is only limited. However, the dipole-loaded side chains of the polar fullerene impact considerably the charge carrier energy levels. They induce broadening of the latter by electrostatic disorder. This may be undesirable, as it leads to charge carrier relaxation, which in turn can lead to lower charge mobilities and voltage losses.

The polar side chain-induced broadening of charge carrier energy levels is not restricted to fullerene-based organic solar cells but is expected to be relevant for all molecular semiconductors and thus is anticipated to play a similar role also in nonfullerene-based or all-polymer organic solar cells.
Methods

Coarse-Grain and Atomistic Models. We use CG models based on the Martini force field.\textsuperscript{37,38} The models for P3HT and PCBM were taken from Ref. 36, while the model for PTEG-1 from Ref. 56. The PTEG-1 model uses the latest EG Martini parameters\textsuperscript{57} which are the most transferable EG parameters within the current version of the Martini force field (EG notably making for a difficult modeling case in Martini partly because it requires a three-to-one atoms-to-bead mapping\textsuperscript{58}). The Martini C\textsubscript{60} model was developed in Ref. 59. We refer to these publications for a thorough description of the models and their validation. Atomistic models were built upon the models we developed in Refs. 36 and 56. Nonbonded parameters are taken from the GROMOS 53A6 force field.\textsuperscript{60} Bonded parameters, however, were derived from quantum chemical (QC) calculations using the Q-Force toolkit (see Supporting Information). Compared to general atomistic molecular mechanics force fields which use libraries of bonded parameters to enhance transferability, the Q-Force approach derives molecule-specific bonded parameters, and has thus the benefit of having an MD potential energy landscape matching the QC one. This is highly beneficial for later performing QC calculations on geometries obtained from MD simulations, as the use of general force field geometries for QC calculations may lead to systematic and/or uncontrolled errors.\textsuperscript{17,61} The Q-Force procedure used in this work consists of two steps: (i) fitting of the stiff bonded force field terms (bonds, angles, stiff dihedrals and improper dihedrals) to the QC Hessian and (ii) fitting of the flexible EG dihedral potentials to the $\omega$B97X-D\textsuperscript{62}/6-311G(d,p) dihedral scans. These two steps are further explained in the Supporting Information. There, we also compare the effect of using GROMOS and Q-Force bonded parameters on QC energies (see also Figure S5 and associated discussion in the Supporting Information). A script to generate arbitrarily long all-atom P3HT chains and their corresponding GROMACS topology files has been developed and can be downloaded from Figshare.\textsuperscript{63} Details on the script are given in the Supporting Information.

Simulated Solvent Evaporation and Thermal Annealing. Morphologies were gen-
erated by solvent (the solvent being chlorobenzene, CB) evaporation MD simulations as in Ref. 36, following the method introduced by Lee and Pao. More specifically, starting from a simulation box (30 × 30 × 88 nm$^3$) containing a ternary mixture P3HT:fullerene:CB (with fullerene being either PCBM of PTEG-1) in a 1:0.8 weight ratio (corresponding to concentrations of ∼39 mg mL$^{-1}$ in P3HT and ∼31 mg mL$^{-1}$ in PCBM), 1.25% of CB is removed every 15 ns until a dried blend is obtained (30 × 30 × 5 nm$^3$). This leads to a total drying time of 11 µs, which was found to lead to morphologies in agreement with experimental scanning electron microscopy data. For further details, we refer to Ref. 36. The code used for the evaporation is available at https://github.com/ricalessandri/evaporate. Run parameters in the CG simulations follow the “new” Martini set of run parameters and are available on the Martini portal http://cgmartini.nl. Simulated thermal annealing was carried out according to Ref. 36. Briefly, the final configuration of a solvent evaporation simulation is annealed by running MD simulations at a higher temperature, as follows: 20 ns at 398 K, 20 ns at 498 K, 160 ns at 598 K, and 1.8 µs at 698 K, totaling to 2 µs of annealing time. The blend was then cooled down by performing 400 ns of MD simulation at 298 K. Note that, while the employed annealing temperature is higher than the experimental one (∼420 K), annealing time scales are also different (blends are commonly annealed for 5–10 min); this makes a direct comparison between CG and experimental conditions not trivial. The GROMACS package version 2016.x (or later) was employed to run the simulations. The (CG and backmapped) morphologies can be downloaded from Figshare.

**Backmapping.** The procedure developed by Wassenaar et al. has been used for converting the CG morphologies back to full atomistic detail. We refer to the publication for all the details. Briefly, after the initial projection made by the program backward.py through which atoms are placed according to the CG particles-space definitions contained in mapping files, a series of energy minimizations and MD simulations is carried out until a relaxed atomistic morphology is obtained. Further details, including the creation of mapping files, are given in the Supporting Information.
Definition of Donor-Acceptor Pairs and DA Configuration Analysis. The determination of the configuration phase space spanned by DA complexes at the interfaces was done at the CG level. No essential information is left out as compared to using the backmapped morphologies, as we perform the analysis using the centers of mass of molecular moieties, such as the center of mass of C$_{60}$. The implemented procedure consists of the following 4 steps – illustrated here for the P3HT:PCBM case, but valid also for P3HT:PTEG-1 blends:

i) Selection of molecules at the DA interface. The CG morphology (typical sizes of $300 \times 300 \times \approx 50 \text{ Å}^3$) is divided, in the $x$ and $y$ dimensions, in overlapping voxels of dimensions $20 \times 20 \times z \text{ Å}^3$; this is done so that no interfaces are missed. Within each voxel, P3HT (PCBM) atoms are then selected if they are found to be within 6 Å of PCBM (P3HT) atoms. These lists are then corrected for double-counting of atoms and complemented with the atoms which were not found to be within the 6 Å but which belong to molecules which had some atoms within the 6 Å.

ii) Reduction of coordinates. The position of the centers of mass of P3HT thiophene rings, PCBM C$_{60}$s, P3HT side chains, and PCBM side chains are then stored in matrices. Distance matrices between each of these groups are then computed, giving rise to a set of distances which can be used to characterize the DA pairs.

iii) Definition of DA pairs. Iterating over the PCBM molecules at the interfaces, 3HT monomers are considered to form a DA pair if $r_{DA}$, i.e., the C$_{60}$-thiophene distance, is within a cutoff of 16 Å. For each DA pair, the angle ($\theta_{DA}$) between the vector normal to the thiophene plane ($\vec{r}_{THIO}$) and the vector connecting the center of mass of the C$_{60}$ and the center of mass of the thiophene ring ($\vec{r}_{DA}$) is computed, another geometrical feature characterizing the DA pair along with the distances computed in step ii).

iv) Projecting the DA phase space on selected coordinates. The DA pair phase space was then projected onto the 2D space formed by the $r_{DA}$ distance and the $\theta_{DA}$
angle by binning each DA pair according to their \((r_{DA}, \theta_{DA})\) values. Such 2D projection allows to distinguish between face-on, edge-on, and end-on DA arrangements. For more details, see Figure S3 in the Supporting Information.

The whole procedure is implemented in Python and makes extensive use of the MDAnalysis library.\(^\text{67,68}\)

**Tight-Binding Density Functional Theory Calculations.** To compute gas-phase energy levels, we employ self-consistent charge density functional tight binding (SCC-DFTB)\(^\text{69}\)—here referred to simply as DFTB. Calculations were performed using the ADF 2016,\(^\text{70,71}\) suite of programs, employing the QUASINANO 2015 parameter set.\(^\text{72}\) We compute the HOMO and LUMO energy levels of neutral species. Note that, within DFTB, the IP (computed as \(U^+ - U^0\) where \(U^+\) and \(U^0\) are the energies of the cationic and uncharged species, respectively) equals the negative of the HOMO energy, while the EA (computed as \(U^0 - U^-\), where \(U^0\) and \(U^-\) are the energies of the uncharged and anionic species, respectively) equals the negative of the LUMO energy. Moreover, Mulliken charges computed at the DFTB level are employed to capture the conformation-dependent hole (de)localization of P3HT chains (see below). Being about 3 orders of magnitude faster than DFT, the method allows for the computation of the gas-phase energy levels for all the molecules of the simulated BHJs (typically between \(\sim 1800\) and \(\sim 2400\) molecules, totaling \(\sim 0.5 \cdot 10^6\) atoms) in about 15 minutes. A detailed description of the computational cost of the whole methodology is available in the Supporting Information.

**Microelectrostatic Calculations.** We compute the polarization energies on the charge carrier energy levels by a *induced dipole* (or *microelectrostatic*) scheme (see Refs. 73 and 51 for recent reviews). We here briefly summarize the general framework and the key points and parameters of the approach. The polarization energy for a positive or negative charge carrier in a molecular condensed phase is defined as the difference between the values of the ionization potential or electron affinity in the condensed (IP or EA) and gas (\(\text{IP}_{\text{gas}}\) or \(\text{EA}_{\text{gas}}\))
phase:\textsuperscript{51,74}

\[ P^+ = IP - IP_{gas} \] \hspace{1cm} (1)

\[ P^- = EA_{gas} - EA \] \hspace{1cm} (2)

Note that a negative \( P^\pm \) value stabilizes the charge carrier in the crystal. Note that the historical\textsuperscript{51} name of \( P^\pm \), \textit{i.e.}, polarization energies, may be misleading. Indeed, the \( P^\pm \) which shift \( IP_{gas} \) and \( EA_{gas} \) of Equations 2 and 1 have at least \textit{two} main contributions due to intermolecular interactions: 1) the electrostatic contribution, \( S^\pm \); and 2) the induction, \( I^\pm \). Charge delocalization and an intramolecular contribution due to the geometrical relaxation upon ionization do impact \( P^\pm \) to a lower extent.\textsuperscript{51} Thus, we have \( P^\pm = S^\pm + I^\pm \).\textsuperscript{51,73}

Here, we compute \( S^\pm \) and \( I^\pm \) using the classical polarizable Direct Reaction Field (DRF) force field as implemented in the DRF90 software.\textsuperscript{52} The molecules are thus described classically with point charges and atomic polarizabilities. Within DRF, polarizabilities are described according to Thole’s method for interacting polarizabilities,\textsuperscript{75,76} which avoid numerical instabilities by employing a distance-dependent damping function. The induction contribution has to be evaluated self-consistently.\textsuperscript{51,52} In practice, the polarization energy (for a spherical cluster of \( N \) molecules) can be obtained with the following expression:\textsuperscript{73,77}

\[ P^\pm_N = U^\pm_N - U^0_N \] \hspace{1cm} (3)

where \( U^0_N \), \( U^+_N \), and \( U^-_N \) are the energies of a cluster of \( N \) molecules where the central molecule is either neutral, positively, or negatively charged, respectively. The method was first applied to the anthracene crystal—a system widely studied in the literature—and found to give results in line with previous experimental and theoretical data, as shown in Figure S8 and Table S3 in the Supporting Information.

The input of DRF90 requires atomic polarizabilities and atomic charges for each (neutral and charged) molecule. In the case of fullerenes, molecular geometries of the neutral and negatively charged fragments were first optimized at the B3LYP/6-311G(d,p) level of DFT.
For both the neutral and anionic fullerene molecules, we computed charge distributions at their respective optimized geometry via the CM5\textsuperscript{78} scheme, which is based on Hirshfeld partitioning\textsuperscript{79} of the electron density, as implemented in Gaussian 16.\textsuperscript{80} Charges were computed with a few basis sets and DFT functionals, among which ωB97XD, and were found to be very robust (see also the Supporting Information), in line with previous reports.\textsuperscript{78} In the case of P3HT, molecular geometries of neutral P3HT chains with 6, 8, 10, and 12 monomers were first optimized at the ωB97XD/6-311G(d,p) level. CM5 charges for the neutral fragments were then computed as done in the case of the fullerenes. By comparing the charges of these four chains, charges for arbitrarily long neutral P3HT chains were derived. We distinguished two types of monomers: termini (the two termini 3HT residues) and central (all the monomers but the two termini). For details, we refer to the Supporting Information. The charges for the positively charged P3HT chains, however, cannot be computed for a single chain conformation, as the flexibility of P3HT chains affects the localization of the hole.\textsuperscript{35,81} In order to take into account this dependence of the hole localization on conformational disorder, we follow the approach of D’Avino et al.\textsuperscript{35} we compute Mulliken atomic distributions of excess positive charge for each P3HT geometry at the DFTB level. These are then summed to the CM5 atomic charges of the neutral P3HT, obtaining distributions for charged P3HT chains. The procedure is described in detail in the Supporting Information.

For the polarizabilities, we employed the standard set of polarizabilities of the DRF force field. These have been parametrized on the basis of a large set of experimental molecular polarizabilities.\textsuperscript{52,76}

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Supporting Information Available

Results on additional P3HT:PCBM and P3HT:PTEG-1 blends; details on the constructions of the 2D DA maps, the atomistic models, and the backmapping procedure; impact of the atomistic force field on the energy levels; details on the microelectrostatic calculations; detailed description of the computational cost of the whole protocol; CG and backmapped BHJ morphologies, CG and AA topologies (in GROMACS format), and mapping files can be downloaded from https://doi.org/10.6084/m9.figshare.12338633.

This material is available free of charge via the Internet at http://pubs.acs.org/.

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Graphical TOC Entry

DA interface
configuration
analysis
CG morphology
backmapping
end-on edge-on
face-on
Energy levels
HOMO LUMO
AA morphology
QC + ME
DA configuration space
Energy (eV)
Normalized Occurrence
(a) (b)
DA interface configuration analysis

end-on

edge-on

CG morphology

backmapping

AA morphology

QC + ME

Energy levels

Normalized Occurrence

(a) (b)

Energy (eV)

DA configuration space

θ_{DA} (deg)

r_{DA} (Å)

CG morphology

HOMO LUMO
Supporting information for:

Resolving Donor-Acceptor Interfaces and Charge Carrier Energy Levels of Organic Semiconductors with Polar Side Chains

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1 P3HT:PCBM Blends: Additional Results

Figure S1: Effect of MW and thermal annealing on morphologies and DA configurations. PCBM blended to P3HT (a)-(b) 12-mers (2 kDa), (c)-(d) and (e)-(f) 24-mers (4 kDa) (two replicas), and (g)-(h) 48-mers (8 kDa) (replica of simulation shown in Figure 2c-2d in the main text).
Figure S2: Donor-acceptor pairs at the interfaces of P3HT:PCBM (left) and P3HT:PTEG-1 (right) blends span very similar configuration spaces. Results for blends with P3HT 12-mers (2 kDa, top), 24-mers (4 kDa, center), and 48-mers (8 kDa, bottom) are shown.
Classifying Donor-Acceptor Complexes: Normalization

Figure S3: Construction of the 2D maps representing a projection of the DA configuration space. Binning of the DA pairs according to their \((r_{DA}, \theta_{DA})\) values results in the (a) raw plot. This needs to be normalized to account for the increasing considered volume with increasing \(r_{DA}\) distances, and hence the higher chances of finding a neighbor with increasing \(r_{DA}\) distances. For three dimensions, this normalization is the volume of the spherical shell, which symbolically can be expressed as \(\rho \int 4\pi r^2 dr\), and the resulting map is shown in (b). Finally, in order to compare 2D maps obtained from different simulated BHJs, which can contain different amounts of DA pairs, we normalize by the total number of DA pairs (c).
4 Atomistic Models

**P3HT.** The starting atomistic model for P3HT is taken from Ref. S1 (dubbed “GROMOS”). Two more versions of the P3HT model were developed. A “GROMOS stiff” version, where backbone dihedral potentials were stiffened to better preserve the planarity of the thiophene rings. The polythiophene backbone was otherwise too flexible with the GROMOS standard force constant for the improper dihedrals. In particular, two dihedral terms have been modified with respect to the GROMOS model, as shown in Table S1. The third version of the P3HT atomistic model is the “Q-Force” version, where bonded parameters were matched to quantum chemical calculations. The Q-Force procedure is explained further at the end of this Section. Note that all three P3HT models share the same nonbonded GROMOS 53A6 parameters. The effect of the use of these three different sets of bonded parameters is shown in Figure S5.

**PolyP3HT.** The script to generate arbitrarily long P3HT atomistic chains and topologies (in Gromacs format), dubbed “PolyP3HT”, makes use of the Gromacs tool `gmx pdb2gmx`, so a residue database (.rtp) file has been created for P3HT. In the GROMOS force field, the third (or 1–4) covalently bound neighbor atoms that are part of or bound to aromatic rings are excluded from the nonbonded interactions, while all the other 1–4 interactions are included. This requires the presence of the section `[pairs]` in the Gromacs `itp` file, a section which lists all the 1–4 pairs for which nonbonded interactions exist. This list should thus contain all the 1–4 but the ones that should be excluded, i.e., the 1–4 between non-H atoms which are part of or bound to rings (note that there is no need for the presence of a `[exclusions]` section in the final topology file, since if the 1–4 interactions are not in the `[pairs]` list, they will not be computed). The correct `[pairs]` section can be achieved by defining `[exclusions]` in the `rtp` file use by the `gmx pdb2gmx` tool (which would otherwise automatically generate all the 1–4 pairs). Termini database files (extensions `.n.tdb` and `.c.tdb`) are also needed in order to cap the dangling bonds at the termini with hydrogen atoms.
Table S1: P3HT atomistic bonded parameters. The indices \( i, j \) and \( k \) indicate that the bonded term is defined between subsequent thiophene units. If the bonded parameters are standard GROMOS 53A6, the corresponding GROMOS labeling is shown in parenthesis next to the bond (angle) equilibrium value and/or force constant. The non-standard GROMOS parameters (refined to better describe the thiophene rings) are indicated with a *.

\(^a\) Fitted to QM data. The bonded terms which are present only on the “standard” (std)\(^1\) or on the “stiff” (stiff) version are indicated by the corresponding labels.

| Atoms                  | \( b_0 \) (nm) | \( \kappa_b \) (kJ mol\(^{-1}\) nm\(^{-2}\)) |
|------------------------|----------------|---------------------------------------------|
| S-C                    | 0.1730 (gb,53*)| 5.94 \( \cdot \) 10\(^6\) (gb,31)          |
| HC-C                   | 0.1090 (gb,3)  | 1.23 \( \cdot \) 10\(^7\) (gb,3)           |
| C-C (CT2-CT3, CT4-CT5) | 0.1360 (gb,13) | 1.02 \( \cdot \) 10\(^7\) (gb,13)          |
| C-C (CT3-CT4)          | 0.1430 (gb,19) | 9.21 \( \cdot \) 10\(^6\) (gb,19)          |
| C-C (CT3-C6)           | 0.1520 (gb,26) | 5.43 \( \cdot \) 10\(^6\) (gb,26)          |
| C-C (hexyl chain)      | 0.1530 (gb,27) | 7.15 \( \cdot \) 10\(^6\) (gb,27)          |
| C\(_i\)-C\(_j\) (CT2\(_i\)-CT5\(_j\)) | 0.1430 (gb,19) | 9.21 \( \cdot \) 10\(^6\) (gb,19)          |

| Atoms                  | \( \theta_0 \) (deg) | \( \kappa_\theta \) (kJ mol\(^{-1}\)) |
|------------------------|-----------------------|----------------------------------------|
| C-S-C                  | 92.80 (gb,55*)        | 420.00 (ga,2)                          |
| S-C-HC                 | 119.00 (gb,56*)       | 575.00 (ga,36)                         |
| S-C                    | 110.00 (gb,57*)       | 530.00 (ga,15)                         |
| HC-C-C (thiophene)     | 126.00 (ga,36)        | 575.00 (ga,36)                         |
| C-C-C                  | 111.00 (ga,15)        | 530.00 (ga,15)                         |
| C-C-C (CT-CT-C)        | 126.00 (ga,37)        | 640.00 (ga,37)                         |
| HC-C-C,HC (hexyl chain)| 109.50 (ga,11)        | 425.00 (ga,11)                         |
| C\(_i\)-C\(_i\)-C\(_j\) (thiophene) | 130.00 (ga,58*) | 760.00 (ga,39)                      |
| S\(_i\)-C\(_i\)-C\(_j\) (thiophene) | 120.00 (ga,29) | 760.00 (ga,29)                      |

| \( \phi_0 \) (deg) | \( \kappa_\phi \) (kJ mol\(^{-1}\)) | \( n \) |
|--------------------|--------------------------------------|--------|
| thiophene impropers | 0.00 (gi,1) | 167.36 (gi,1) | n/a std |
| thiophene impropers | 0.00 (gi,4*) | 1339.38 (gi,4*) | n/a stiff |
| thiophene propers  | 1.00 (gd,39) | 180.00 (gd,39) | 6 std  |
| thiophene propers  | 1.00 (gd,44*) | 180.00 (gd,44*) | 1 stiff |
| C-C-C-C (CT-CT-C-C) | 0.00 (gd,40) | 1.00 (gd,40) | 6      |
| C-C-C-C (hexyl chain)| 0.00 (gd,34) | 5.92 (gd,34) | 3      |
| \( S_i-C_i-C_j-S_j \) | 0.00 (gd,42*) | 1.80 (gd,42*) | 1      |
| \( S_i-C_i-C_j-S_j \) | 0.00 (gd,43*) | -9.50 (gd,43*) | 2      |
The script can be downloaded from Figshare\textsuperscript{S5} or https://github.com/ricalessandri/PolyP3HT. The script can be run by typing:

```
./PolyP3HT.sh 12
```

where 12 is the desired number of monomers. Make sure the files `shift-resnr.py`, `header`, `residuetypes.dat`, `p3ht_dimer_repeat_unit_50atoms.gro`, and `top2itp.sh` are in the folder where the script is executed, along with the directory `p3ht_gromos_v_2017RA-JACS.ff/` which contains the force field. The output files are in Gromacs format (`itp` and `gro` for the topology and geometry, respectively). The force field directory will contain:

| File Name          | Description                                                      |
|--------------------|------------------------------------------------------------------|
| forcefield.doc     | ff description file (incl. references and notes)                 |
| forcefield.itp     | the GROMOS 53A6 one                                             |
| atomtypes.atp      | the GROMOS 53A6 one                                             |
| ffnonbonded.itp    | the GROMOS 53A6 one                                             |
| ffbonded.itp       | the GROMOS 53A6 one containing also the P3HT bonded              |
| dimer.rtp          | the (dimer-based) residue database file for P3HT                 |
| dimer.c.tdb        | the n-termini database file for P3HT                              |
| dimer.c.tdb        | the c-termini database file for P3HT                              |

**Fullerene Derivatives.** PCBM and PTEG-1 starting models are taken from Refs. S1 and S6. Analogously to P3HT, “stiff” and “Q-Force” versions have also been developed – see Figure S5 and associated discussion for their impact on the QM energies.

**Q-Force Bonded Parameters.** All stiff bonded force field terms (bonds, angles, stiff dihedrals and improper dihedrals) are expressed as harmonic potentials:

\[
V_{\text{bonded}} = \sum_{\text{terms}} \frac{1}{2} k_t (t - t_0)^2
\]  

(1)

where \(k_t\) is the force constant of each term and \((t - t_0)\) corresponds to the difference to the equilibrium distance or angle for that term.

The second derivative of the energy terms with respect to \(x\), \(y\), and \(z\) in Equation 1 are taken to compute the MD Hessian. The QM Hessian is also calculated using Gaussian 16\textsuperscript{S7}.
with DFT using the ωB97X-D functional and the 6-311G(d,p) basis set in the case of P3HT and the PM7\textsuperscript{88} semi-empirical method for the fullerenes. Then, the squared differences between QM and MD Hessians are minimized with the force constants $k_i$ given as fitting parameters. As the result, bonded MD force field parameters that produce the best match between MD and QM Hessians are obtained.

Force field parameters for flexible dihedrals with multiple minima cannot be obtained from the Hessian, since the Hessian only contains information about the minimum energy structure. For each of such dihedrals, a QM and MD dihedral scan can be performed. Then, the energy difference between the QM and MD profiles can be fitted to a function of choice. We have chosen in this work to use Ryckaert-Bellemans (RB) type dihedral function whose form is given in Equation 2.

$$V_{RB} = \sum_{n=0}^{5} C_n (\cos(\phi))^n$$ (2)

### 5 Backmapping

**General details.** The method developed by Wassenaar et al. is used,\textsuperscript{89} and we refer to the publication for all the details. The *initram.sh* script calls *backward.py* (which performs the actual backmapping) and then runs a series of minimization and equilibration simulations to get the final backmapped structure. The following files are needed in order to run the script: 1) the CG structure to backmap (e.g., *cg.gro*); 2) a complete fine-grained force field including all the CG molecules to be backmapped; 3) a .map file in the Mapping directory for all residues and molecules to be backmapped. Further, *initram.sh* requires Gromacs to be installed. The script is then executed using the following command:

```bash
./initram.sh -f cg.gro -o aa.gro -to gromos -p AA.top -em 1500
```

which tells *initram.sh* to backmap the *cg.gro* file to GROMOS using the AA topology specified in *aa.top* and assuming that mapping files for the residues involved are present in the Mapping directory. Additionally, usually a number of steps between 1500 and 2000
was necessary for the initial bonded-only energy minimization (EM) for typical morphologies of $30 \times 30 \times 5 - 10$ nm$^3$. Instead, neat P3HT films usually require 500 steps of bonded-only EM, and 4000 of full EM (the latter can be passed to initram.sh with -nb). A too long EM without nonbonded interactions can lead to too many hydrogen-hydrogen overlaps.

Mapping files are required by the program for the initial positioning of the atoms. These will contain (i) mapping definitions (position of an atom with respect to one or more CG sites – e.g. Figure S4c) and, (ii) geometrical modifiers (note that these are optional). After the initial projection based on the mapping definitions the (eventual) geometrical modifiers are executed following the order in which they appear in the mapping file. All the type of modifiers implemented in backward.py are thoroughly described in Ref. S9.

**P3HT mapping file.** A mapping file for a P3HT monomer is the only file required for backmapping P3HT chains. There’s also no need for “special” termini mapping files, as the hydrogen(s) missing from the mapping file in the case of the P3HT termini (there will be one hydrogen atom more at the beginning and at the end of the P3HT chain as compared to a core monomer) will be added automatically by backward.py, as long as they are present in the atomistic P3HT topology file. The definitions used in the P3HT mapping files are shown in Figure S4c. Given the large size of the morphologies studied ($\sim 400000$ atoms), the use of geometrical modifiers to better define the projections of the position of the hydrogens was found critical to the successful backmapping (allowing a projection which was much closer to the local atomistic minimum).

**PCBM mapping file.** Generating the mapping file for the buckyball was done by superimposing the CG and AA structures and then defining a unique mapping for each carbon atom of the C$_{60}$ in terms of the F$_{16}$ CG beads. Note also that in the backmapping step it was found more convenient have a unique residue number for PCBM.

**Relaxation.** The volume of the backmapped AA system is appreciably less than its CG version: the lower CG density turns out to facilitate the backmapping step (in terms
6 Impact of the Atomistic Force Field on the Energy Levels

Figure S5 shows the impact of the force field used for the backmapping step on the energy levels computed by DFTB calculations. Going from the “GROMOS”, to the “GROMOS stiff” and “Q-Force” version, the P3HT HOMO distribution shifts to lower energies, indicating an increased stability for Q-Force structures. Moreover, both GROMOS versions lead to much broader energy distributions, while the Q-Force P3HT model provides structures on average much closer to the QM potential energy surface, hence leading to a narrower
HOMO distribution. The same plot produced for the LUMO levels of PCBM (Fig S5b) highlights the smaller impact of the bonded parameters of the force field on the QM energies – especially in terms of the width of the distributions. However, a systematic shift of the LUMO levels is observed when going from the GROMOS to the Q-Force parameters, again hinting at an increased stability of the Q-Force structures.

In addition, Fig S5c shows that performing a force field energy minimization or simply taking a snapshot from an MD simulation leads to a virtually identical HOMO distribution when using the Q-Force models. The Q-Force models are thus recommended for use in combination with subsequent quantum mechanical calculations on the P3HT geometries.

Figure S5: Effect of atomistic force field on the gas-phase (a) HOMO and (b) LUMO energies of (a) P3HT and (b) PCBM molecules at the interfaces of a simulated bulk heterojunction. Distributions are obtained by computing the energies with DFTB after backmapping a morphology consisting of 422 (24-mer) P3HT chains and 1480 PCBM molecules with three different atomistic force fields: the GROMOS version developed in Ref. S1, its “stiff” version, and a version employing Q-Force derived bonded parameters (these latter two versions were developed in this work and are described in the text). Note that in (b) the distributions for “GROMOS” and “GROMOS stiff” overlap. (c) P3HT HOMO distribution for a neat P3HT morphology containing 624 P3HT (24-mer) chains: the DFTB energies obtained directly on a snapshot from an MD simulation (using the Q-Force force field) and the same snapshot energy minimized (with the molecular mechanics force field) show no significant difference.
7 Microelectrostatic Calculations

Calculations were performed with the DRF90 software, the classical implementation of the DRF method\textsuperscript{10}—available from http://www.marcelswart.eu/drf90/index.html. The program is used to employ the complete classical DRF expressions for single point energies.

**P3HT Charges: Neutral Chains.** DFT CM5 charges for the neutral P3HT chain are reported in Table S2 (for brevity, only non-hydrogen atoms are shown with the charges of the hydrogens summed on them; however, the performed DRF90 calculations take into account all atomic charges). Charges are well defined among different monomers, with standard deviations of at most 0.001. Charges are also virtually the same among different oligomers; it is thus reasonable to assume that they can approximate well charge distributions in arbitrarily long P3HT chains. Charges obtained from the 12-mer are used as charges for the neutral P3HT chains and as base (see below) for the positively charged P3HT chains in the DRF90 calculations.

Table S2: $\omega$B97X-D/6-311G(d,p) CM5 charges for P3HT chains with 6 to 12 3HT monomers (6- to 12-mer). For each chain, the charges on non-hydrogen atoms (compare to Figure S4 for the atom labels) averaged over the central 3HT monomers (all but the two termini) are shown. Standard deviations are at most 0.001 in all cases.

| Atom label | 6-mer | 8-mer | 10-mer | 12-mer |
|------------|-------|-------|--------|--------|
| ST1        | 0.0576| 0.0577| 0.0577 | 0.0576 |
| CT2        | -0.0267| -0.0266| -0.0265| -0.0265|
| CT3        | -0.0264| -0.0263| -0.0262| -0.0262|
| CT4        | -0.1161| -0.1160| -0.1159| -0.1157|
| CT5        | -0.0212| -0.0213| -0.0213| -0.0213|
| C06        | -0.1532| -0.1532| -0.1532| -0.1532|
| C07        | -0.1606| -0.1606| -0.1606| -0.1606|
| C08        | -0.1605| -0.1605| -0.1605| -0.1605|
| C09        | -0.1602| -0.1602| -0.1602| -0.1602|
| C10        | -0.1610| -0.1610| -0.1610| -0.1610|
| C11        | -0.2394| -0.2394| -0.2393| -0.2393|

**P3HT Charges: Charged Chains.** In order to take into account the dependence of the hole localization on conformational disorder of P3HT chains, we follow the approach of D’Avino and co-workers.\textsuperscript{11} Namely, we compute atomic distributions of *excess* positive
charge for each P3HT geometry at the DFTB level, and then sum such a distribution to the CM5 atomic charges just derived. Thus, for each atom of the charged molecular fragment a \( \delta q_i \) was obtained as the difference between the DFTB Mulliken charge in the cationic and in the neutral polymer chain. Note that \( \sum_i \delta q_i = 1 \). Each set of \( \delta q_i \) is summed to the CM5 atomic charges of the neutral P3HT, obtaining distributions for charged P3HT chains.

Hole distributions are shown for two randomly picked P3HT chains in Figure S7. For these chains, DFT CM5 excess charges (Figure S7a and S7c) have been computed and are shown (Figure S7a and S7c) along with the DFTB charges (Figure S7b and S7d). The localization of the hole charge distribution is qualitatively the same at both DFT and DFTB levels; the hole charge distribution is slightly more delocalized (and individual charges are slightly larger in magnitude) in the DFTB case than in the DFT one.

**Fullerene Charges.** CM5 charges for the neutral and anionic fullerene derivatives were computed at their respective B3LYP/6-311G(d,p) optimized geometries. Their difference, the excess electron charge distribution, is shown in Figure S6 for both PCBM and PTEG-1. Note that CM5 charges were found to be robust not only with respect to the basis set and DFT functional but also to the chosen geometry, with a fullerene taken from a MD trajectory giving charges practically identical to the ones obtained at the B3LYP-optimized geometries.
Figure S6: Rendering of the excess electron charge distribution for (a) PCBM and (b) PTEG-1 computed via the CM5 scheme. For each atom, an excess charge $\delta q_i$ was obtained as the difference between the CM5 charge in the anionic and in the neutral states. The distributions for the two molecules are very similar: as expected, the excess negative charge is distributed over the fullerene cage.

**Anthracene Crystal.** To test the approach, we performed calculations on the anthracene crystal, a widely studied case in the literature$^{S12,S13}$ for which experimental polarization energies both for a positive and a negative charge carrier are available.$^{S14,S15}$ As explained in the Methods section of the main text, the polarization energy (for a spherical cluster of $N$ molecules) can be obtained by computing $U_N^0$, $U_N^+$, and $U_N^-$, i.e., the energies of a cluster of $N$ molecules where the central molecule is either neutral, positively, or negatively charged, respectively. The polarization energy for infinite crystals is obtained by extrapolation (see Figure S8), as it scales linearly with the reciprocal of the radius of the cluster.$^{S13}$

Figure S8 shows the results for anthracence, while Table S3 reports the extrapolated $P^+$ and $P^-$, which agree well with experimental data. For comparison, results of other computational approaches from the literature are also shown. The hole-electron asymmetry is due to the electrostatic—namely, charge-quadrupole—contribution to the polarization energy.$^{S13,S16}$
Figure S7: Rendering of the excess hole charge distribution for P3HT. Two conformations
taken from a backmapped dried blend are taken: (a) hole charge distribution for conformation
1 computed at the DFT level via the CM5 scheme, and (b) the same charge distribution
for the same conformation computed at the DFTB level (Mulliken charges). (c) Hole charge
distribution for conformation 2 computed at the DFT level via the CM5 scheme, and (d) the
same charge distribution for the same conformation computed at the DFTB level (Mulliken
charges). For each atom, an excess charge $\delta q_i$ was obtained as the difference between the
charge in the cationic and in the neutral states.
Figure S8: Computed polarization energy for charge carriers for the anthracene crystal (a) computed by the classical polarizable Direct Reaction Field (DRF) force field as implemented in the DRF90 software. Holes (red circles) and electrons (blue circles) polarization energies are plotted as a function of $N^{-1/3}$, where $N$ is the number of molecules in the cluster considered. Solid lines are linear regressions; the intercept represent the extrapolated value corresponding to the infinite crystal limit (see also Table S3). The experimental values are indicated on the horizontal axis with filled points.

Table S3: Computed and experimental polarization energies for charge carriers in the anthracene crystal. Values extrapolated in the infinite crystal limit (see also Figure S8.) The methods shown are the microelectrostatic scheme used by D’Avino and co-workers where induced dipoles of atoms on the same molecule are allowed to interact (ME$_a$) or not (ME$_0$); charge redistribution (CR) schemes; and the approach of Ryno et al. which use the polarizable AMOEBA force field.

| Method          | $P^+$ | $P^-$ | $\Delta P$ |
|-----------------|-------|-------|------------|
| DRF90 (this work) | -1.27 | -0.76 | 0.51       |
| AMOeba$^{12}$   | -1.11 | -0.85 | 0.26       |
| ME$_0$$^{13}$   | -1.26 | -1.07 | 0.16       |
| ME$_2$$^{13}$   | -1.23 | -1.08 | 0.18       |
| CR$^{13}$       | -1.18 | -0.95 | 0.23       |
| CR$^{17}$       | -1.38 | -0.82 | 0.56       |
| exp$^{14,15}$   | -1.51 | -0.89 | 0.62       |
8  **Workflow: Summary, Timings, and Computational Cost**

Table S4 breaks down the workflow in (sub)steps with associated software used and timings (wall and CPU times).

Table S4: Workflow for a typical P3HT:PCBM blend evaporated (drying time 11 µs) and annealed. It contains 844 P3HT 12-mer chains and 1480 PCBM molecules, leading to a total of 2324 molecules. † GPU time in this case.

| Step | Substeps     | Software, Resources | Wall time (hours) | CPU hours |
|------|--------------|---------------------|-------------------|-----------|
| 0    | CG morphology | Evaporation         | Gromacs, 384 CPUs | 70        | 27000     |
|      |              | Annealing           | Gromacs, 128 CPUs | 22        | 2800      |
|      |              | **Subtotal:**       |                   | **92**    | **29800** |
| 1    | Backmapping  | Backmapping         | Python, 1 CPU     | 0.3       | 0.3       |
|      |              | Relaxation          | Gromacs, 216 CPUs | 13        | 2800      |
|      |              | Relaxation          | Gromacs, 16 GPUs  | 9.5       | (152) †   |
|      |              | **Subtotal:**       |                   | **13.3**  | **2800**  |
| 2    | DA configurations | Analysis      | Python, 1 CPU     | 0.08      | 0.08      |
|      |              | **Subtotal:**       |                   | **0.08**  | **0.08**  |
| 3    | QC calculations | Input making   | Python, 1 CPU     | 0.25      | 0.25      |
|      | DFTB run     | ADF, 1 CPU (x 4648) |                  | 0.003     | 6.5       |
|      |              | **Subtotal:**       |                   | **0.253** | **6.75**  |
| 4    | ME calculations | Input making | Python, 1 CPU     | 0.5       | 16        |
|      | ME run       | DRF90, 1 CPU (x 1688) |              | 0.05      | 84        |
|      | ME run       | DRF90, 1 CPU (x 2960) |              | 0.003     | 9         |
|      |              | **Subtotal:**       |                   | **0.553** | **109**   |
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