Different interface orientations of pentacene and PTCDA induce different degrees of disorder

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Abstract
Organic polymers or crystals are commonly used in manufacturing of today's electronically functional devices (OLEDs, organic solar cells, etc). Understanding their morphology in general and at the interface in particular is of paramount importance. Proper knowledge of molecular orientation at interfaces is essential for predicting optoelectronic properties such as exciton diffusion length, charge carrier mobility, and molecular quadrupole moments. Two promising candidates are pentacene and 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA). Different orientations of pentacene on PTCDA have been investigated using an atomistic molecular dynamics approach. Here, we show that the degree of disorder at the interface depends largely on the crystal orientation and that more ordered interfaces generally suffer from large vacancy formation.

Keywords: Organic interfaces, Organic electronic devices, Interface disorder, Molecular dynamics, PTCDA, Pentacene

Background
Organic light emitting diodes (OLEDs), organic solar cells, organic thin films transistors, etc. are made of organic polymers or crystals [1-3]. The effect of the disorder in organic devices on optoelectronic properties was analyzed by Rim et al. [4]. They showed an increased photocurrent generation with improved molecular order. It occurs due to the influence of the stacking on the exciton diffusion length. Hu et al. measured a strong dependence of the conductance across highly oriented pentacene nanocrystals on the packing orientation [5]. The influence of packing on charge transport in organic solids was also analyzed using Monte Carlo methods [6]. Kwiatkowski et al. [6] were able to predict the mobilities of electron and holes for ordered and disordered Alq3. Different functional organic materials were reviewed by Ishii et al. [7]. They highlighted the energy level alignment and electronic structures at organic/inorganic and organic/organic interfaces of, for example, Alq3, 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and 1,4,5,8-tetrafulvalene (TTF).

In our work, the morphology of interfaces between pentacene [8] and PTCDA [9] was analyzed (Figure 1a). Both molecules form different crystal modifications. Pentacene is known to have a high temperature (HT) and a low temperature (LT) polymorph. Yoneya et al.[8] showed that the LT polymorph is destabilized by substrates and transforms into HT polymorph. Therefore, the HT polymorph was used as the base for simulations. For PTCDA, the α polymorph [9] was used.

Molecular orientation at interfaces is decisive for predicting optoelectronic properties such as exciton diffusion length [10], charge carrier mobility [11], and molecular quadrupole moments [12]. Verlaak et al. analyzed the impact of the molecular quadrupole moments, influenced by e. g., material and crystal orientation on the interface energetics. An insight on models of electronic processes across organic interfaces is given by Beljonne et al. [13], while a review of the corresponding theoretical approaches is presented by Brédas [14].
Our study of organic-organic pentacene/PDCDA interfaces is organized as follows: after a brief introduction presented above, we proceed with the presentation of the methods followed by the results and some conclusive remarks.

Methods

The molecular dynamic (MD) simulations of the interfaces between PTCDA and pentacene have been performed with the atomistic molecular dynamics package GROMACS (Stockholm Center for Biomembrane Research, Stockholm, Sweden and Biomedical Centre, Uppsala, Sweden) [15] using the generalized amber force field (GAFF) parameterization [16] for organic molecules, having Yoneya et al.’s work [8] in mind, and ESP charges [17] calculated with the semi-empirical quantum chemistry package MOPAC (Stewart Computational Chemistry, Colorado Springs, CO, USA) [18]. The parameter conversion from amber to GROMACS was done with the help of Antechamber python parser interface (ACPYPE) [19], the recommended tool for using GAFF with GROMACS, cf [8,20-22]. After simulation, a check of basic molecule parameters was done and the results for the example of pentacene are presented in Table 1. A more detailed report on relative errors in energy, dehridals, etc can be found in the ACPYPE wiki [23].

The systems were simulated with a step size of 0.5 fs for more than 3 ns at a temperature of 300 K using a Berendsen thermostat [26] for temperature control. The van der Waals cut-off was set to 1.2 nm, the Coulomb cut-off to 5 nm and the relative permittivity was set to four which was taken from Wang et al. [27]. No periodic boundary conditions were used owing to the different crystal lattices.

Three surfaces were chosen and combined. For pentacene the surfaces (100), (010), and (001) were used and for PTCDA the surfaces used are (102), (-221), and (212) as defined by Miller indices. The combination of these surfaces led to nine different interface facets, e.g., (212) on (010) and (-221) on (001), as depicted in Figure 1b,c showing their relaxed structures, leaving rotation and translation as degrees of freedom. An optimal relative orientation within each of these nine facets was found by

Table 1 Comparison of calculated and experimental relevant parameters

| Bonds in pentacene | C1-C2 | C2-C3 | C3-C4 | C4-C5 | C5-C6 | C6-C7 | C4-C21 | C6-C19 | C-H |
|--------------------|-------|-------|-------|-------|-------|-------|-------|-------|-----|
| Ab initio          | 1.43  | 1.38  | 1.44  | 1.4   | 1.42  | 1.43  | 1.46   | 1.46   | 1.1 |
| Exp                | 1.441 | 1.358 | 1.428 | 1.381 | 1.409 | 1.396 | 1.453  | 1.464  | na  |
| MD                 | 1.397 | 1.394 | 1.395 | 1.399 | 1.395 | 1.395 | 1.403  | 1.403  | 1.088 |

| Angles in pentacene | C-C-C | C-C-C | C-C-C | C-C-C | C-C-C | C-C-C | C-C-C | C-C-C | C-C-C | C-C-C | C-C-C |
|---------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Exp                 | 121   | 123   | 124   | 124   | 123   | 119   | 119   | 118   | 118   | 118   | 118   |
| MD                  | 120.2 | 120.1 | 120.1 | 120.3 | 120.2 | 119.8 | 119.8 | 119.8 | 119.8 | 119.8 | 119.8 |

A representative selection of bonds and angles of pentacene is presented. A comparison of measured [24] and ab initio [25] parameters with results from the MD calculations is displayed showing a generally good agreement between the methods.
performing four simulations each with relative orientations from being twisted against each other. After a total energy comparison, the structure with the lowest mean energy per molecule of the fully relaxed systems was chosen. As an example, the energy-evolution for the interface facet (-221)/(100) is shown in Figure 2. The set of simulations were done on systems arranged to fill a 10 × 10 × 10 nm³ cube with each crystal type, filling half the space.

Results and discussion
In order to quantify the disorder at the pentacene/PTCDA interface, we used distribution of \( \phi \), defined as the angle between the molecular and the interface plane (or rather their respective normals) as shown in Figure 3. Owing to the fact that the molecules will start to relax, they will start to deviate from the bulk values. The more molecules have different \( \phi \), the more disordered is the structure.

In the histograms of Figure 4, the y-axis was defined as distance in Å from the (ideal) interface in z-direction, while the x-axis shows the angle distribution. Light blue regions mark the disordered regions. Two clear patterns can be observed: 1) size of the disordered region can vary from 2 to 16 Å, and 2) the disorder seems to spread asymmetrically from the ideal interface, clearly preferring pentacene-rich regions. The first pattern can be explained as having two competing effects at the interface, one being the optimization of the intermolecular distance/interaction and the other being the conservation of bulk properties. The second pattern can be understood in the light of much stronger \( \pi - \pi \) stacking of the PTCDA molecules, leading to a stronger intermolecular interactions, and greater energies are required to disrupt these molecules from their bulk positions when compared to pentacene bulk.

Conclusions
Analysis of PTCDA/pentacene interfaces was performed with two emerging messages: there seems to be two competing effects, one coming from intermolecular interaction, which leads to disordered interfaces, while the other coming from the preservation of bulk properties results in large interfacial vacancies. Both of the effects would lead to dramatically diminished transport properties. Namely, increased disorder would cause greater energy disorder of the interfacial hopping sites, while interfacial vacancies would lead to diminished intermolecular overlaps,
or hopping matrix elements. Whether which of the competing effects is influencing more the hopping transport properties is the focus of our ongoing research. Our second observation is that pentacene seems to be, in general, a more flexible material, which can be observed from the fact that the disordered regions are predominantly pentacene-rich.

**Competing interests**
The authors declare that they have no competing interests.

**Author's contributions**
AP carried out the molecular dynamics calculations, the setup of the initial system and helped in drafting of the manuscript, and revisions. VM helped in analysis and interpretation of data, and drafted the manuscript and revisions. RM provided the calculation of the partial charges. WW participated in the design of the study, formulated the original scientific question and helped in analysis and interpretation of data. All authors read and approved the final manuscript.

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