



A computational study of surface diffusion of C₆₀ on pentacene

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ABSTRACT

The morphology of the C₆₀/pentacene heterojunction is of interest for organic photovoltaic applications, yet is not well characterized. With that in mind, all-atom molecular dynamics simulation techniques were used to elucidate the diffusional behavior of small numbers of C₆₀ molecules on the surface of crystalline pentacene as a probe of the molecular-level interactions between C₆₀ and pentacene. The ultimate molecular probe of the pentacene surface, a single C₆₀ ad molecule, exhibited an anisotropic diffusion pattern that lingered in energetically preferred sites in the [110] direction, intercepting the (0, 1/2, 0) point in the unit cell. An Arrhenian analysis of this diffusion data gave estimates for the prefactor, D_0 , and energy barrier, E_a , of 2×10^{-3} cm²/s and 0.1 eV, respectively. Surface diffusion of one C₆₀ molecule on pentacene is significantly more rapid (by about 1–2 orders of magnitude) than if even one additional C₆₀ ad molecule is present, implying that the C₆₀–C₆₀ cohesion interaction is stronger than the C₆₀–pentacene adhesion interaction. Simulations with up to four C₆₀ molecules, the practical limit of an all-atom approach, reinforced the suggestion that C₆₀ likes to dewet a pentacene surface and will show a preference for forming small 3D nuclei.

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1. Introduction

Organic semiconductor materials are a key component in the growing field of organic electronics, covering electronic devices such as organic light-emitting diodes (OLEDs), organic thin film transistors (OTFTs), and organic photovoltaic cells (OPVs). This paper focuses on materials for OPVs, which are of increasing interest in solar cell applications [1]. Although photovoltaics provided only 0.04% of the world's primary energy supply in 2004, their market segment has grown every year since then [2], spurred by their low cost and flexibility [3].

Simple organic solar cells can be fabricated by layering thin films of organic semiconductors between electrodes with different work functions causing electrons to flow until the Fermi levels are equal. Unfortunately, the performance of current OPVs is often hampered by poor charge transport, structural instabilities, and the low red absorption of organic materials. High photocurrent quantum efficiencies are achieved in heterojunction systems that include both electron-donating and electron-accepting layers, akin to a p–n junction in a conventional device [4]. One of the most studied of these heterojunctions for an organic/organic system involves an interface between the fullerene, C₆₀, and the small crystalline organic molecule, pentacene, with relatively large charge carrier mobilities [5].

Understanding the interfacial properties of this heterojunction and acquiring the ability to grow ordered thin films is important

for improving the performance of OPVs. Even small changes in film morphology can affect charge separation at the donor/acceptor interface, hole and electron mobility, and hence overall device performance. Interactions at the buried heterojunction depend sensitively on the atomic-level structure of the materials, and are difficult to probe experimentally. This provides the motivation for a molecular-scale computational study of the properties of organic heterojunctions.

In this paper, molecular simulation is used to explore the nature of the intermolecular interactions between C₆₀ and pentacene. Specifically, molecular dynamics (MD) techniques, in concert with semi-empirical interatomic potential models, are used to obtain information about surface diffusion coefficients and energy barriers. These properties are difficult to measure either experimentally or through continuum approaches.

1.1. Experimental C₆₀ growth and surface diffusion simulations

There have been a number of experimental papers describing C₆₀ thin film growth. Two recent papers, by Kobayashi et al. [6] and Itaka et al. [7], led to important conclusions about the order present in the C₆₀ thin films. Kobayashi et al. grew C₆₀ thin films on a typical dielectric layer, SiO₂, to study the influence of temperature and grain size on field-effect mobility (for OTFT applications). The C₆₀ grain sizes were found to be small – at most, around 50 nm – and lacking notable orientation, which resulted in low film crystallinity. Itaka et al. improved the C₆₀ crystallinity by placing an atomically flat “buffer” layer of pentacene between the C₆₀ and a sapphire substrate. They claimed that the presence of the

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pentacene layer increased the C_{60} wettability, thus improving the C_{60} film crystallinity. They observed that the C_{60} grains tend to take on a hexagonal structure. These papers show that the nature of the substrate beneath the C_{60} layer strongly influences the crystallinity of the C_{60} overlayer.

Wang et al. [8] compared the C_{60} /pentacene heterojunction to the reversed heterojunction, pentacene on C_{60} , finding much lower charge carrier mobilities in the C_{60} /pentacene case than for pentacene/ C_{60} . They speculated that this is due to the difference in geometry of the two molecules, reaffirming that details of adlayer-substrate interactions play an important role in the performance of small organic molecule devices. However, there is a clear lack of fundamental understanding of the behavior of C_{60} when it interacts with the surface of pentacene. Molecular simulation is an appropriate way to begin to redress this need, showing how and why the presence of pentacene molecules affects the crystallinity of adsorbed C_{60} layers.

There are a growing number of experimental publications on the electronic properties of organic materials (e.g., charge carrier mobilities), but there has been relatively little simulation work on organic electronic materials compared to inorganic ones. There are some recent publications that use computational means to study organic electronic materials, some of which involve *ab initio* studies of idealized crystal structures of a handful of molecules (often only two molecules) reflecting interest in the electronic structure of these materials [9–11]. However, resource utilization effectively prohibits *ab initio* simulations from predicting the dynamics of surface diffusion and the structures attainable during film growth. Since film structure plays a large role in determining electronic properties, there is clearly a need to coordinate *ab initio* calculations of very small systems with semi-empirical modeling of much larger systems for which simulation of thin film growth provides a good guess at the structure of the thin film.

In that regard, there has been some recent computational effort using molecular dynamics (MD) techniques to predict surface phenomena of organic materials for a variety of applications [12–16]. Wang et al. [15] used MD to study self-diffusion mechanisms of pentaerythritol tetranitrate (PETN) on the (1 1 0) surface of crystalline PETN. They showed that PETN was stable at off-lattice sites, that it diffused along specific directions of the crystal, and that the site-to-site energy barrier was roughly 0.1 eV. As will be seen in Section 1.2, these observations of off-lattice site stability and anisotropic diffusion will also be seen in the results for the C_{60} /pentacene system studied here. A recent paper by Liu et al. [17] is one of the few dynamic simulation studies of growth processes of organic electronic materials. They combined STM experiments, coarse-grained MD, and kinetic Monte Carlo (kMC) simulations to investigate the fractal growth process of C_{60} on C_{60} . In contrast, Itaka et al. observed a hexagonal growth pattern of C_{60} on pentacene (a non-fractal growth pattern), clearly showing the effect of substrate topography on the growth pattern of C_{60} . Liu et al. found that there is a large Ehrlich–Schwöbel barrier for downward jumps of C_{60} onto C_{60} , which will help explain an observation here that will be discussed later.

1.2. Known C_{60} and pentacene structures

The equilibrium crystal structure of both pentacene and C_{60} are well known. In its bulk crystalline phase, the triclinic pentacene unit cell contains two molecules arranged in a herringbone configuration [18], with the (001) orientation as its lowest energy surface [19]. The intermolecular bonding of the pentacene molecules is a result of dipole–dipole and weak van der Waals interactions [19,20]. Pentacene is a planar molecule that is about 14 Å long and 5 Å wide. The lattice parameters of the bulk phase pentacene unit cell are $a = 7.90$ Å, $b = 6.06$ Å, and $c = 16.01$ Å, and the triclinic

angles are $\alpha = 101.9^\circ$, $\beta = 112.6^\circ$, and $\gamma = 85.8^\circ$; these values are reported by Northrup et al. [19] based on X-ray diffraction results from Campbell and Monteath Robertson [21] and were used in this paper to set up the thin films.

C_{60} is an organic molecule with 60 carbon atoms arranged in an interlocked series of 20 hexagons and 12 pentagons. At room temperature and ambient pressure, single-crystal X-ray diffraction experiments have shown that bulk C_{60} molecules prefer a rotationally disordered face-centered cubic crystal structure bound by weak van der Waals forces and having a lattice constant of 14.2 Å [22–24]. The molecular diameter of C_{60} is 7.1 Å and equilibrium center-to-center intermolecular distance is 10.0 Å [22]. C_{60} thin film lattice parameters do not vary with the lattice parameters of the substrate, in contrast to the epitaxial growth habit of most van der Waals crystals [25–28].

2. Methods

All simulations performed and reported in this paper were carried out using the freeware software package TINKER which is an atomic-scale (all-atom) modeling package with molecular dynamics (MD) capabilities for a choice of semi-empirical potentials [29]. For the MD simulations, the Beeman integration method was used to obtain positions, velocities, accelerations, and relevant system energies at each integration step (a time step of 0.5 fs). For each simulation, a short thermalization run of 5 ps was performed using a canonical ensemble in which a specified equilibrium temperature is achieved and maintained using a Berendsen thermostat [29]. Once the system reached the desired temperature without significant fluctuations (± 3 K), the simulation was continued using a microcanonical ensemble which maintains constant energy.

In order to improve the statistics of the results, simulations of all the systems reported here were repeated three times, each simulation followed for 1.5 ns with an integration step of 0.5 fs (i.e., 3,000,000 time steps). The average local pressure in the system was 10 ± 210 atm, exhibiting the typical large pressure fluctuations seen in NVE simulations. Each system of three runs was carried out at eight different temperatures between 225 and 400 K, designed to cover a range of temperatures similar to that used in experimental studies of C_{60} on the surface of pentacene [30].

Since little is known about the molecular-scale characteristics of this two-component system, we initially carried out MD simulations for all possible C_{60} –pentacene combinations of adsorbed molecules and substrate: C_{60} on the surface of pentacene (Fig. 1a), pentacene on the surface of pentacene (Fig. 1b), C_{60} on the surface of C_{60} (Fig. 1c), and pentacene on the surface of C_{60} (Fig. 1d). We began by considering the diffusion of just one adsorbent molecule on a given surface, in essence, using this adsorbed molecule as a single molecular probe of the interactions between depositing molecules and substrate. In subsequent simulations, the diffusion of up to four C_{60} molecules on a pentacene surface would be studied as a means to observe the tendency of C_{60} molecules to prefer to bind to one another rather than to pentacene.

In each case, the computational system consisted of two substrate layers with the bottom layer fixed and the top layer free to move. For the C_{60} /pentacene system, system sizes of 3×3 and 4×4 surface unit cells (in the x – y direction) were considered in order to test the effects of finite system size. A 3×3 system size involves 1356 total atoms, whereas a 4×4 system has 2364 atoms – corresponding to a large increase in computational cost. The resulting mean-squared displacements of C_{60} on pentacene showed a negligible difference between the two system sizes, implying that the 3×3 system is sufficient to properly capture the dynamics. For each of these runs, the coordinates of the center of mass of the adsorbed molecule were tracked to allow us to calculate sur-

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