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Trapping dynamics of diindenoperylene (DIP) in self-assembled monolayers using molecular simulation

Ananth P. Kaushik, Paulette Clancy *

School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY 14853, United States

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ABSTRACT

All-atom Molecular Dynamics simulation methods employing a well-tested intermolecular potential model, MM3 (Molecular Mechanics 3), demonstrate the propensity for diindenoperylene (DIP) molecules to insert between molecules of a self-assembled monolayer (SAM) during a deposition process intended to grow a thin film of this organic semiconductor molecule onto the surface of self-assembled monolayers. The tendency to insert between SAM molecules is fairly prevalent at normal growth temperatures and conditions, but is most strongly dependent on the density and the nature of the SAM. We posit the existence of an optimal density to favor surface adsorption over insertion for this system. DIP is less likely to insert in fluorinated SAMs, like FOTS (fluorooctatrichlorosilane), than its unfluorinated analog, OTS (octatrichlorosilane). It is also less likely to insert between shorter SAMs (*e.g.*, less insertion in OTS than ODTS (octadecyltrichlorosilane)). Very short length, surface-coating molecules, like HDMS (hexamethyldisilazane), are more likely to scatter energetic incoming DIP molecules with little insertion on first impact (depending on the incident energy of the DIP molecule). Grazing angles of incidence of the depositing molecules generally favor surface adsorption, at least in the limit of low coverage, but are shown to be dependent on the nature of the SAM. The validity of these predictions is confirmed by comparison of the predicted sticking coefficients of DIP at a variety of incident energies on OTS, ODTS, and FOTS SAMs with results obtained experimentally by Desai et al. (2010) [23]. The simulation predictions of the tendency of DIP to insert can be explained, in large part, in terms of binding energies between SAM and DIP molecules. However, we note that entropic and stochastic events play a role in the deposition outcomes. Preliminary studies of multiple deposition events, emulating growth, show an unexpected diffusion of DIP molecules inserted within the SAM matrix in a clear attempt of the DIP molecules to aggregate together.

1. Introduction

Self-assembled monolayers (SAMs) consist of a layer of functionalized long-chain molecules tethered to a solid substrate. Their presence as a “coating” on a surface is attractive in a number of applications due to the possibility they provide to tune the properties of the surface by selectively modifying functional groups on the SAM [1,2]. SAMs of organosilane molecules are of particular technological interest in organic electronics because they can be assembled on hydroxylated surfaces such as SiO_2 for applications in areas such as organic electronics, electronic sensors and biosensors [3,4]. Not surprisingly then, they have been the subject of extensive theoretical and experimental research due, for instance, to their ability to improve the mobility of organic thin films for electronic devices, presumably by improving surface order.

There have been several molecular-level computational studies of SAMs, some relevant to the studies in this paper [1,4–10]. Yamamoto et al. studied the influence of hydrogen bond conformations of alkanesilane SAMs using molecular mechanics and Molecular Dynamics simulations [1]. A study of the diffusion of tricresyl phosphate (TCP) molecules on an octadecyltrichlorosilane SAM [4] found that TCP molecules are highly mobile on the surface with a small isotropic diffusion activation barrier of about 0.1 eV (9 kJ/mol). TCP molecules prefer to diffuse over the surface rather than become inserted between the SAM molecules. The structural properties of alkanethiol SAMs have been determined as a function of temperature, lattice spacing (density), and molecular chain length [5]. For instance, chains containing 13 carbons tilt from the surface normal by a collective angle of 25° along the next-nearest-neighbor direction at 300 K. The tilt angle can vary as much as 20° for a temperature increase of 200 K, and change by 30° for a lattice constant increase of 0.6 Å. There have also been studies of hyperthermal deposition of inert gas atoms on SAM surfaces. Simulations of Ar, Xe and Ne on SAMs showed inelastic scattering and trapping dynamics [4,11–14]. Xe, in particular, showed a sort of directed ejection mechanism after insertion into the SAM matrix [15].

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* Corresponding author.
E-mail address: pc@cornell.edu (P. Clancy).

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Experimentally, a variety of preparation methods are available for self-assembled monolayers and multilayers of alkyltrichlorosilanes, including studies that altered the molecule's functional groups in order to get specific desirable properties [16]. There have also been studies aimed at controlling surface properties by varying the alkyl chain lengths of the SAMs to enhance the electrical performance of field-effect transistors (FETs) of different organic molecules [17]. Effects of alkyl chain lengths of SAMs on the film growth of organic molecules like pentacene have been studied. In particular, Bao et al. have observed that the nature of film growth, and hence the performance of transistors, is significantly affected by the alkyl chain of the SAM molecule being odd or even in length and by the density of the SAM [18–20].

Despite these prior computational studies of the characteristics of SAMs in contact with a diffusing surface atom or molecule, there has been no previous study of the *deposition* of organic thin films on SAM surfaces, either at thermal or hyperthermal deposition conditions. Previously studied SAM surfaces have always been well packed; there have been no studies involving low packing densities of SAMs. However, experimental studies, at least on amorphous SiO_2 surfaces, are often performed with a low density of SAM molecules and thus the ability to simulate deposition of molecular species on low density SAM surfaces is of considerable importance. In this study, we considered three molecules that are capable of creating self-assembled monolayers (fluorooctatrichlorosilane (FOTS), octatrichlorosilane (OTS) and octadecyltrichlorosilane (ODTS)) on certain surfaces such as amorphous SiO_2. In addition, we looked at the behavior of hexamethyldisilazane (HMDS), a short-chain, surface-coating, ligand that provides an interesting contrast to the SAMs. These four molecules (OTS, FOTS, ODTS and HMDS) are used as a monolayer-thick "surface" upon which an organic semiconducting molecule, diindenoperylene (DIP), is to be grown as a thin film; see Fig. 1. The SAM molecules have long-chain carbon backbones terminated at one end by a methyl group (a fluorinated methyl group in the case of FOTS) and at the other end by trichlorosilane, $–SiCl_3$. These four molecules vary in chain length: HMDS has a very short (two-carbon) backbone, barely a chain. The FOTS and the OTS molecules have an 8-carbon backbone and the ODTS has an 18-carbon backbone; again, see Fig. 1.

In this paper, we will study the mechanistic processes which lead to the inadvertent trapping of deposited molecules between SAM molecules on the surface, (Fig. 2 (a–c)) which we will call "trapping dynamics," as opposed to surface adsorption events which are the usual intent of a deposition process (Fig. 2 (d–f)). As shown in Fig. 2 (g–i), depositing molecules can also be "scattered", that is, they hit the surface, or are inserted into the SAM, but ultimately are expelled from the vicinity of the SAM without inclusion either on the surface or between SAM molecules. Whether "trapping" of molecules between SAM molecules is disadvantageous or not is not clear: At first glance, the unintended trapping process seems likely to lead to problems with the creation of an ordered surface (depending, perhaps, on the length of the deposited molecules in relation to that of the SAM molecule). It could also be speculated that the insertion process could lead to an effectively higher density SAM monolayer, perhaps one that enhances surface deposition, and hence be essentially a benign process in terms of the quality of film growth that can occur subsequently. We will investigate some of these issues here.

In this study, we have performed (MD) simulations to characterize the trapping dynamics of diindenoperylene (DIP) on some commonly studied SAM surfaces and to identify the major factors that affect the growth of DIP thin films on SAMs. The motivation for performing a molecular simulation study is that it allows an elucidation of the mechanisms of trapping in greater detail than is possible from experiments alone. In addition to studies that replicate the conditions of energetic deposition experiments by the Engstrom-led group at Cornell, molecular simulations also afford the chance to investigate trapping dynamics in regimes that are difficult or impossible to study experimentally: the effect of packing density, orientation of the incident DIP molecule and, to some extent, temperature on deposition outcomes fall into this category. In this paper, we will identify several key parameters which affect the trapping of DIP and which could be tuned to increase the efficiency with which SAMs are able to affect the ordered growth of DIP molecules (and, by extension, other small organic semiconductor molecules).

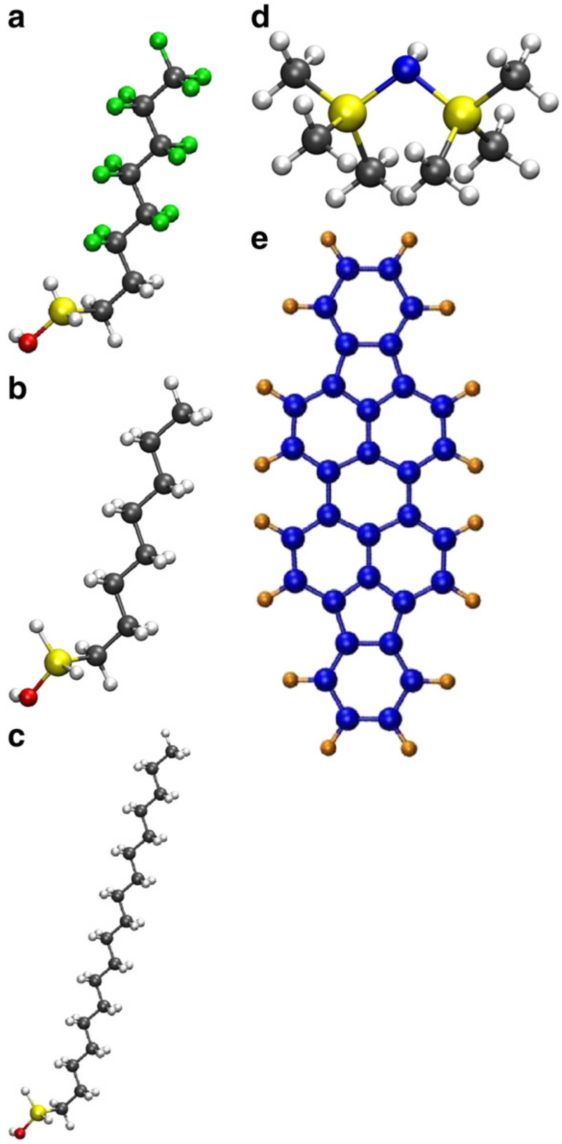

Fig. 1. Molecular models of the molecules: (a) FOTS, (b) OTS, (c) ODTS, (d) HMDS and (e) DIP.

One of the advantages of a computational study of this kind is the ability to observe deposition events at a molecular scale. This gives us an opportunity to calculate the outcome of a single deposition event without having to perform a post-mortem analysis once the bulk film has been deposited. In experiments, it is possible to calculate the fraction of DIP molecules that are not scattered from the SAM surface, but it is essentially impossible for experiments to differentiate between the fraction that becomes inserted into the surface and the fraction adsorbed on the surface. Such knowledge is potentially important since the fate of depositing molecules governs both the nature and quality of the bulk film grown. This study is intended to capture details of deposition events, some of which may not be accessible experimentally, in order to explain a few key aspects that affect the observed bulk properties of the deposited film.