Chemical Physics Letters 678 (2017) 28–34

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Novel surface diffusion characteristics for a robust pentacene derivative on Au(1 1 1) surfaces

Ryan A. Miller *, Amanda Larson [1], Karsten Pohl

Department of Physics and Materials Science Program, University of New Hampshire, 9 Library Way, Durham, NH 03824, United States

ARTICLE INFO

Article history:
Received 4 December 2016
In final form 5 April 2017
Available online 7 April 2017

Keywords:
Molecular dynamics
Surface diffusion
Organic photovoltaics
Pentacene derivatives
Au(1 1 1)

ABSTRACT

Molecular dynamics simulations have been performed in both the *ab initio* and classical mechanics frameworks of 5,6,7-trithiapentacene-13-one (TTPO) molecules on flat Au(1 1 1) surfaces. Results show new surface diffusion characteristics including a strong preference for the molecule to align its long axis parallel to the sixfold Au(1 1 1) symmetry directions and subsequently diffuse along these close-packed directions, and a calculated activation energy for diffusion of 0.142 eV, about four times larger than that for pure pentacene on Au. The temperature-dependent diffusion coefficients were calculated to help quantify the molecular mobility during the experimentally observed process of forming self-assembled monolayers on gold electrodes.

1. Introduction

In the field of tailoring p-n junctions of organic photovoltaic (OPV) devices, pentacene is a well-studied donor molecule [1–7]. Pentacene's assembly and subsequent dynamics as it forms self-assembled monolayers (SAM) on metal surfaces have been studied to a great extent. It is a flat, planar molecule consisting of five adjacent benzene rings, making it symmetric about its long and short axes. This planarity and symmetry leads to a flat adsorption on Au(1 1 1) surfaces with the molecules forming ordered substructures [2]. Furthermore, molecular simulations have shown that pentacene molecules are mobile on Au(1 1 1) surfaces at room temperature due to their relatively low diffusion activation energy of 0.041 eV (calculated), and at low temperatures there is a relatively anisotropic diffusion along the Au(1 1 1) substrate symmetry directions [1].

While pure pentacene itself serves as an effective donor molecule, it has critical drawbacks including photooxidation, which limits its charge-carrying ability. To mitigate these effects, a new class of pentacene derivatives with substituents at the 6 and 13 positions (the top and bottom of the molecule's short axis) have emerged that aim to tailor the base molecule towards more effective electrical and structural properties [8]. Among these derivatives is 5,6,7-trithiapentacene-13-one (TTPO) [9]. As a small-molecule organic semiconductor, TTPO has several beneficial qualities including good solubility, very high thermal stability up to 450 °C, parallel-displaced, head-to-tail crystallization which melts around 350 °C without decomposition, and variable-temperature transistor behavior with increased charge-carrying ability at increased temperature [9]. Scanning Tunneling Microscopy (STM) studies have shown that TTPO can be thermally evaporated to produce very uniform thin films with a unique configuration of individual TTPO molecules on Au(1 1 1) surfaces [10], notably that its assembly on gold is angled, whereas pentacene lies flat [11]. Therefore, studying the unique structure and dynamics of TTPO on gold surfaces will provide new insight and understanding of this class of molecule-substrate systems.

Room temperature STM studies of the self-assembly of TTPO into well-ordered molecular monolayers on Au also revealed a very high mobility of TTPO molecules during the nucleation of the SAM [10], despite the presumed strong interaction of TTPO's thiol bridge with the Au surface. Because scanning probe techniques have time resolution on the order of seconds, molecular dynamics (MD) simulations have been employed to gain a better understanding of the surface diffusion characteristics of this important system. In addition to being able to describe the system down to the atomic level, timescales down to picoseconds and below can be probed to analyze molecular dynamics behavior. By exploring molecular TTPO surface diffusion on Au(1 1 1) via MD simulations, we were able to determine important parameters characteristic to molecular surface diffusion such as activation energy barriers and diffusion coefficients. We found new surface diffusion characteristics includ-

---

* Corresponding author.

E-mail addresses: rmiller1291@gmail.com (R.A. Miller), ami3.phys@gmail.com (A. Larson), karsten.pohl@unh.edu (K. Pohl).

[1] Current address: Tufts University, Department of Chemistry, Medford, MA, United States.

http://dx.doi.org/10.1016/j.cplett.2017.04.018

ing a strong preference for the molecule to align its long axis parallel to the sixfold Au(1 1 1) symmetry directions and subsequently diffuse along these close-packed directions, and an activation energy for diffusion of 0.142 eV.

2. Methodology

2.1. Simulation details

To study for the first time the surface diffusion characteristics of TTPO, MD simulations were performed in two frameworks. Quantum-mechanical based (*ab initio*) simulations fully relax the coupled electronic wavefunctions self-consistently at each timestep while evolving the atomic configurations in the molecules and are therefore considered to be the most accurate form of molecular simulation. However, these are extremely time consuming and only very small timescales can be sampled for a reasonably large system. In contrast, molecular mechanics (MM) simulations approximate each pairwise atomic interaction with a closed-form analytic expression and therefore run orders of magnitude faster. Though they introduce approximation into the simulation, MM simulations can be used to successfully model large-scale molecular behavior that would otherwise be computationally infeasible with *ab initio* approaches [6,7,12–15].

The *ab initio* simulations were run with the Quantum ESPRESSO (QE) package [16]. Specifically, the Car-Parrinello (CP) [17] technique was employed within QE along with Vanderbilt Ultrasoft Pseudopotentials to simulate core electron behavior. Periodic boundary conditions were employed in the *x*, *y*, and *z* directions. Kinetic energy cutoffs of 30.0 Ry and 400.0 Ry were used for the wavefunctions and charge densities, respectively.

The MM simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software package [18]. The gold substrate was simulated with the embedded-atom model (EAM) [19]. The TTPO molecules were constructed using an all-atom method with the following energy terms: harmonic bonds, harmonic angular energy, and dihedral torsional energy. A Lennard-Jones potential was used to simulate long-range molecular interaction, and a Morse potential to represent the Au-S, Au-C, and Au-H interactions. The Au-S interaction requires particular attention since it is a partially covalent, partially ionic bond, and the pairwise potential must be tailored to take this into account. The Morse potential has modeled this behavior successfully before [20,12,21,22] and was used in this study with the form shown in Eq. (1):

$$E_{morse} = D_0[e^{-2\alpha(\vec{x}-\vec{x}_0)} - 2e^{-\alpha(\vec{x}-\vec{x}_0)}] \tag{1}$$

Table 1 displays all non-Coulombic parameters of the pairwise and bonded/non-bonded parameters used in this study. The AMBER94 [23] and GAFF [24] force field databases were used to find interaction parameters for many common atomic interactions, indicated in Table 1. All LAMMPS simulations were performed with periodic boundary conditions in the *x*, *y* directions and a fixed boundary in the *z* direction.

TTPO is an inherently dipolar molecule, with a dipole moment extending from the central sulfur atom (positively charged) to the oxygen atom (negatively charged). To capture the effect of atomic charges on the molecular trajectories, a Coulombic potential of the form

$$E_C = \frac{Cq_iq_j}{\epsilon r}$$

was used, where C is an energy conversion constant (set to 1 here), and ϵ is the dielectric constant (set to 1.0). The partial charges on the TTPO molecule were assigned based on the Natural Bond Order population analysis performed in [26] and are shown in Fig. 1.

Table 1
Interaction parameters for LAMMPS simulations.

Interaction	Interaction type	Value	Reference
Au—Au	EAM	N/A	N/A
Au—S	Morse	$D_0 = 0.138, \alpha = 1.38, r_0 = 2.903$	[12]
Au—C	Morse	$D_0 = 0.0096, \alpha = 1.013, r_0 = 4.104$	[13]
Au—H	Morse	$D_0 = 0.0031, \alpha = 1.166, r_0 = 4.006$	[13]
Au—O	LJ	$\epsilon = 0.00392, \sigma = 2.946$	[25][a]
C—C	LJ	$\epsilon = 0.00372, \sigma = 3.399$	[23]
H—H	LJ	$\epsilon = 0.00065, \sigma = 2.599$	[23]
O—O	LJ	$\epsilon = 0.00910, \sigma = 2.959$	[23]
S—S	LJ	$\epsilon = 0.0108, \sigma = 3.563$	[23]
C=O	Bond	$K_{bond} = 24.72, r_0 = 1.229$	[23]
C—C	Bond	$K_{bond} = 12.579, r_0 = 1.55$	[24]
C—H	Bond	$K_{bond} = 15.914, r_0 = 1.08$	[23]
C=S	Bond	$K_{bond} = 10.563, r_0 = 1.79$	[23]
S—S	Bond	$K_{bond} = 7.198, r_0 = 2.038$	[24]
C=C	Bond	$K_{bond} = 20.340, r_0 = 1.400$	[23]
C—S	Bond	$K_{bond} = 14.262, r_0 = 1.675$	[24]
H—C—C	Angle	$K_\theta = 1.51, \theta_0 = 120$	[23]
C—C—C	Angle	$K_\theta = 2.73, \theta_0 = 120$	[23]
S—C—C	Angle	$K_\theta = 2.69, \theta_0 = 120$	[24]
O—C—C	Angle	$K_\theta = 3.11, \theta_0 = 120$	[24]
H—C—C—C	Dihedral	$K_D = 0.157, d = -1, n = 2$	[23]
H—C—C—H	Dihedral	$K_D = 0.157, d = -1, n = 2$	[23]
C—C—C—C	Dihedral	$K_D = 0.157, d = -1, n = 2$	[23]
O—C—C—C	Dihedral	$K_D = 0.130, d = -1, n = 2$	[24]
S—C—C—C	Dihedral	$K_D = 0.157, d = -1, n = 2$	[24]

[a] Computed manually from Au-Au and O-O parameters from mixing rules. All energies are in eV, angles in degrees, and distances in Å.

For all simulations a Nosé-Hoover (NH) [27,28] thermostat was used to control the temperature of the substrate and diffusing TTPO molecules. This method essentially couples the system to a fictitious heat bath (through an extra degree of freedom in the system's Hamiltonian) that will act as a friction term to either dampen or accelerate atomic motion in a way that simulates the user-defined ambient temperature.

2.2. Physical model

STM images in Ref. [10] suggest low-coverage TTPO molecules to be highly mobile on a flat, pristine surface, and there to be little to no organization in assembled substructures. To overcome the poor time resolution of STM we employed simulations to study the diffusion of thermally-deposited TTPO molecules and their cluster nucleation on Au(1 1 1). *Ab initio* calculations were employed to study the diffusion along close-packed directions, indicated by the red lines in Fig. 5(b). The Density Functional Theory (DFT) simulations consisted of a one-layer slab of 60 fixed gold substrate atoms and two TTPO molecules deposited on top. The cell was equilibrated to a temperature of 300 K via the NH thermostat and ran for 5 ps with a timestep of 0.25 fs. The TTPO molecules were placed at a non-equilibrium position close to the surface initially to ensure they would stay adsorbed to the surface.

As stated previously, classical simulations allow for much larger unit cells to be explored. Thus, the majority of the simulations in this study were run in this framework, with the *ab initio* simulations providing additional support. Simulations to investigate close-packed direction diffusion were run with five-layer gold slabs, with the top three layers now allowed to move in the three Cartesian directions. Four TTPO molecules were placed far from each other to minimize intermolecular interaction. The unit cell contained 10,512 atoms and ran for over 400 ps. The simulations to calculate diffusion coefficients and activation energies were run with a three-layer gold slab, where the top layer was allowed