Chemical Physics Letters 614 (2014) 45–48

Contents lists available at ScienceDirect

Chemical Physics Letters

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

Dynamics of oligo(phenylene-ethynylene) self-assembled monolayers on Au(1 1 1)

Hairong Wu[a,b], Kai Sotthewes[a], Alejandro Méndez-Ardoy[c], Tibor Kudernac[c], Jurriaan Huskens[c], Aufried Lenferink[d], Cees Otto[d], Peter M. Schön[b], G. Julius Vancso[b], Harold J.W. Zandvliet[a,*]

[a] Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
[b] Materials Science and Technology of Polymers, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
[c] Molecular Nanofabrication, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
[d] Medical Cell Biophysics Group, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

ARTICLE INFO

Article history:
Received 26 July 2014
In final form 3 September 2014
Available online 10 September 2014

ABSTRACT

Oligo(phenylene-ethynylene), self-assembled monolayers on Au(1 1 1) have been studied with scanning tunneling microscopy. The oligo(phenylene-ethynylene) molecules are adsorbed in a flat-lying orientation. Time-resolved scanning tunneling microscopy measurements reveal that the molecules continuously switch back and forth between two nearly degenerate configurations. The energy difference between the two configurations is 22 ± 5 meV and the activation barrier for the transition from the low-energy configuration to the high-energy configuration is 0.65 ± 0.03 eV. A statistical analysis of the residence times revealed that the switching process is stochastic. We propose that the two level switching is due to a torsional mode of the central phenyl ring.

1. Introduction

Self-assembled monolayers (SAMs), that are organic assemblies formed by the adsorption of molecular constituents from a solution or gas phase onto the surface of a solid [1], have been extensively studied because of their potential applications in corrosion inhibition [2], surface patterning [3], wetting inhibition, biosensing and molecular electronics [4]. Among the possible applications, molecular electronics, the research field that aims at the use of single molecules as active components in electronic devices, is a research area of increasing interest [5–11]. Design and operation of future molecular electronic devices requires a proper understanding of the electronic properties, dynamics and interactions of the interfaces and molecules utilized.

Alkanethiols consisting of saturated C—C bonds have served as model systems for both experimental and theoretical calculations [5,12–15]. However, alkanethiols have a rather large HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap resulting in a high molecular resistance making them less suited for molecular electronics applications. For electronic devices, conjugated molecules with alternating double and single bonds or delocalized π electrons are much more suitable candidates. Oligo(phenylene-ethynylene) (OPE), rigid and fully conjugated molecules with tunable functionalities, have attracted considerable attention owing to their potential application in molecular electronic devices. OPE molecules have rather small HOMO–LUMO gaps (~3 eV [16]), exhibit synthesis flexibility [17], and some OPE molecules display negative differential resistance (NDR) characteristics [18].

As mentioned before, the design and operation of SAM-based devices requires a fundamental and detailed understanding of the electronic and dynamic properties of the molecules under scrutiny. Using ultra-high vacuum scanning tunneling microscopy (STM), OPE has been investigated extensively regarding their structural, electronic and dynamical properties [18–21]. OPE molecules embedded in a dodecanethiolate monolayer were found to exhibit stochastic conductance switching behavior at room temperature [20]. In an STM study performed by Donhauser et al., spontaneous changes in height of the inserted OPE molecules between subsequent topographic images have been reported [20]. These height fluctuations were interpreted in terms of a stochastic conductance switching, caused by the conformational changes of the inserted OPE molecules [20]. It is argued by Ramachandran et al. that this switching is caused by changes in the thiol bond between the

* Corresponding author.
E-mail address: h.j.w.zandvliet@utwente.nl (H.J.W. Zandvliet).

http://dx.doi.org/10.1016/j.cplett.2014.09.007
0009-2614/

molecules and the gold substrate [21]. The switching behavior was referred by Ramachandran et al. as 'the blinking of a thiol–gold bond' [21]. Hallbäck et al., however, related the 'blinking' effect of the OPE molecules to lateral diffusion and exchange of conjugated molecules, which are embedded as small bundles within the SAM [19]. Despite the fact that the dynamics of OPE molecules embedded in alkanethiols SAMs has been intensively studied, the dynamics of an OPE SAM has, to the best of our knowledge, not been studied yet. In addition to these ultra-high vacuum studies the dynamics of molecular layers have also been extensively studied with scanning probe microscopy at solid–liquid interfaces [22,23].

Despite numerous scanning tunneling and atomic force microscopy studies a proper understanding of the structure and dynamics of OPE SAMs is still lacking. Part of this lack of understanding is due to the limited time resolution of standard scanning probe microscopes (typically seconds to minutes). Because of this limitation in temporal resolution dynamic events are often averaged out. Scanning probe microscopes with a substantially higher temporal resolution are thus required in order to obtain more insight into these processes. A simple, but elegant, method to improve the temporal resolution of an STM is to perform current–time measurements with the feedback loop disabled [24]. In this case the time resolution is only limited by the bandwidth of the current–voltage converter, which can be as high as 500–600 kHz. During the last decade time-resolved STM has experienced a rapid growth in usage, mainly because the time-resolved spectroscopic mode can be implemented for every STM with a sample and hold switch. Time-resolved STM has played, and will continue to play, an important role in understanding the dynamics for a variety of surface systems [24–26].

In the current Letter, we report a time-resolved scanning tunneling microscopy study of OPE SAMs on Au(1 1 1) surfaces. Current–time spectroscopy with a time resolution down to 10 μs is utilized to explore the dynamic events of OPE SAMs. We found that the OPE molecules switches back and forth between two well-defined levels, which we ascribe to a torsional mode of the central phenyl ring.

2. Experimental

Au substrates (11 mm × 11 mm, 250 nm Au on 2 nm Cr on borosilicate glass) were purchased from Arrandee (Werther, Germany). Au(1 1 1) samples were obtained by annealing these substrates in a high purity H_2 flame for 5 min. After flame annealing the Au substrates were cleaned in a piranha solution (7:3 H_2SO_4:H_2O_2 (30%) by volume), followed by rinsing with Milli-Q water and ethanol and dried in a nitrogen stream. 2,5-Bis(4′-mercapto-phenylethynyl)benzene (OPE-Ac) was purchased from Sigma–Aldrich and further purified by preparative thin-layer chromatography in dichloromethane–hexane (1:1). The chemical structure of the OPE molecule used in this study is shown in Figure 1A. Self-assembled monolayers (SAMs) were prepared by incubating freshly annealed Au(1 1 1) for 3–24 h in a 1 mM solution of the OPE-Ac molecules in freshly distilled, deoxygenated tetrahydrofuran (THF) to which a 5–10 μL of a 25% aqueous solution of ammonium hydroxide was added [19,27]. In this solution the thiolate groups are deprotected. The sample preparation was performed under oxygen-poor conditions to prevent disulfide formation of the OPE molecule. After preparation the samples were quickly loaded in the ultra-high vacuum system.

All STM measurements were performed with an ultra-high vacuum (UHV) STM (RHK Technology, Inc.) with a base pressure of 1×10^{-10} mbar at room temperature. STM tips were prepared from tungsten wire using electrochemical etching [28]. For current–time spectroscopy measurements, the tunneling current was recorded

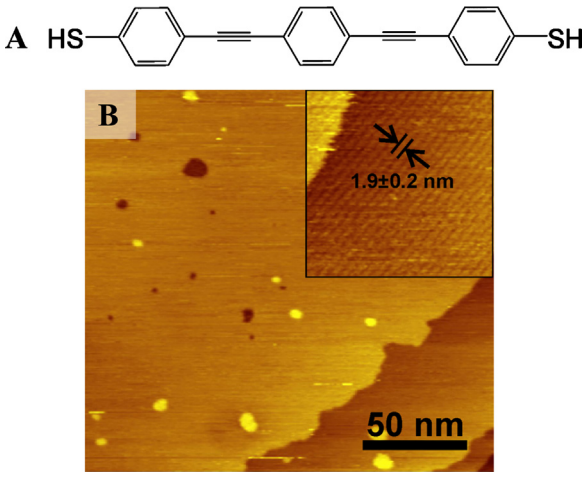

Figure 1. (A) Chemical structure of 2,5-bis(4′-mercapto-phenylethynyl)benzene (OPE). (B) STM image of OPE SAM on Au(1 1 1). Image size 196 nm × 180 nm. The tunneling parameters are 188 pA and 1.20 V. The stripes have a width of 1.9 ± 0.2 nm (inset).

as a function of time (*I*–*t* traces), while the feedback loop was switched off. Sampling frequencies in the range of 1–100 kHz were used. Each *I*–*t* trace was acquired for 10–20 s. In total we have recorded more than 3000 *I*–*t* traces on the OPE SAMs.

3. Results and discussion

STM measurements of 2,5-bis(4′-mercapto-phenylethynyl)benzene (Figure 1B) SAMs on Au (1 1 1) were performed in ultra-high vacuum at room temperature. As seen in Figure 1B, the surface exhibits several characteristic defects, such as substrate steps and vacancy islands [14,25,29]. The depth of the vacancy islands [30] is exactly one atomic Au layer, i.e. 2.5 Å, revealing that the vacancy islands are actually vacancies in the Au(1 1 1) substrate rather than defects in the SAM. Islands with a diameter of several nanometers show up as bright spots on top of the SAM. The height of these islands is the same as the height of Au(1 1 1) monoatomic steps, i.e. 2.5 Å, indicating that the islands are Au islands covered with an OPE SAM. The SAM appears as a flat and structure-less layer [19,27]. The resolution of our STM images is in the vast majority of cases rather poor. We believe this is due to the fact that the apex of the STM tip is decorated with some OPE molecules. An OPE molecule that diffuses underneath the STM tip can easily be picked up by the STM tip [27]. However, STM images with a high spatial resolution are obtained, as well. A striped phase with a well-defined width of 1.9 ± 0.2 nm is observed frequently (inset Figure 1B). We propose that for the striped phase the OPE molecules are lying flat down on the Au(1 1 1) surface. The observed stripe width is somewhat smaller than the length of the OPE molecular and therefore we propose that either the end groups of the OPE molecules are interlaced or that the long axis of the OPE molecules is not exactly orthogonal to the stripes. We suggest that an attractive intermolecular interaction between the OPE molecules make them line up in stripes [31]. We have found three rotational domains, indicating that the adsorbed OPE monolayers adapt themselves to the threefold symmetry of the underlying Au(1 1 1) substrate.

Current–time (*I*–*t*) spectroscopy measurements were carried out at different locations on the surface to obtain more information on the various dynamic processes that take place within the OPE SAM [24,25]. The *I*–*t* traces are recorded with the feedback loop of the STM electronics disabled resulting in a temporal resolution of 10 μs. This spectroscopic mode allowed us to investigate relatively