Journal of Electroanalytical Chemistry 781 (2016) 20–23

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Self-assembly of a sulfur-bridged annulene: Substrate effect and donor-acceptor complex

Zhen-Feng Cai [a,b], Jie-Yu Yue [a,b], Jing Li [a,b], Dong Wang [a,*], Wei Xu [c,*], Li-Jun Wan [a,*]

[a] CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, People's Republic of China
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[c] CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, People's Republic of China

ARTICLE INFO

Article history:
Received 9 August 2016
Accepted 6 September 2016
Available online 8 September 2016

Keywords:
Scanning tunneling microscopy
Substrate effect
Sulfur-bridged annulene
Self-assembly

ABSTRACT

We have studied the self-assembly structure of meso-diphenyltetrathia [22]-annulene [2,1,2,1] (DPTTA) on highly oriented pyrolytic graphite (HOPG), Au(111), and single-layer graphene (SLG) modified Au(111) substrates. High resolution scanning tunneling microscopy (STM) reveals that DPTTA molecules pack into one dimensionally ordered row structure on graphene and HOPG surfaces, while assemble into two dimensional close-packed structure on Au(111) surface. We ascribe this difference to the effect of the substrate. The addition of C_{60} molecules on these DPTTA modified substrates further reveals that the structural difference in DPTTA adlayer can affect its ability to form donor-acceptor (D-A) hierarchical structure with C_{60} molecules. The results provide an example of substrate effect in self-assemblies of functional molecules, which is significant for the design of molecular based devices.

1. Introduction

Cyclic π-conjugated compounds have attracted a great deal of attention and have been widely investigated in materials science and supramolecular chemistry because of their interesting optical and electronic properties [1–4]. In recent years, sulfur-bridged annulenes have been recognized as promising materials for organic field effect transistors (OFETs) [5–7]. As an important derivative of sulfur-bridged annulene, meso-diphenyltetrathia [22]-annulene [2,1,2,1] (DPTTA) displays superior hole-transport properties compared with porphyrins [4], which can be attributed to their extended π-conjugated systems. The chemical structure and optimized model of DPTTA is shown in Fig. 1. In addition, it has been reported that DPTTA can formed self-assembled co-crystal of alternatively stacked donor-acceptor (D–A) complexes with n-type semiconductor materials [6,7] like C_{60}, C_{70}, tetracyanoquinodimethane (TCNQ), *etc.* However, comparatively little is known about the two dimensional (2D) self-assembly behaviors and the properties of DPTTA molecules on solid surfaces.

Understanding the interfacial structures and properties of functional molecules on different substrates is significant to the design of molecular materials based field-effect transistors (FETs) [8,9]. A variety of advanced characterization techniques can be applied to study the 2D interfacial structures on solid surfaces, such as X-ray photoelectron spectroscopy (XPS) [10,11], atomic force microscopy (AFM) [12,13], scanning tunneling microscopy (STM) [14,15] et al. Among these techniques, STM has been demonstrated to be a powerful tool to image and investigate the structural information about 2D molecular assemblies on different substrates [16–18]. For example, the self-assembly of cobalt phthalocyanines on graphene transferred onto silicon dioxide (SiO_2) and hexagonal boron nitride (h-BN) substrates has been investigated by STM and it is shown that the single domain size extends larger on h-BN than on SiO_2 substrate [18]. Different self-assembly behaviors of the 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (TBPT) molecules have been found and studied by STM on reconstructed Au(111) surface and highly oriented pyrolytic graphite (HOPG) substrate [17]. As has been well-demonstrated, the interfacial structure of the first few layers between the active functional molecules and electrodes has a significant impact on their performance [8]. Thus, understanding the assembly structures of DPTTA molecules on different substrates can shed light on the structural optimization and the performance improvement of the sulfur–bridged annulenes based OFETs device.

In the present study, the self-assembly behaviors of DPTTA (Fig. 1) on HOPG, Au(111), and single layer graphene (SLG) modified Au(111) substrates is selected as a model system to understand the assembly structures of functional annulene derivatives. We find that the substrate exerts a much stronger effect than the intermolecular interactions of the DPTTA molecules in the self-assembly. DPTTA molecules self-organize into one dimensionally (1D) ordered row structure on both SLG and

* Corresponding authors.
E-mail addresses: wangd@iccas.ac.cn (D. Wang), wxu@iccas.ac.cn (W. Xu), wanlijun@iccas.ac.cn (L.-J. Wan).

http://dx.doi.org/10.1016/j.jelechem.2016.09.010
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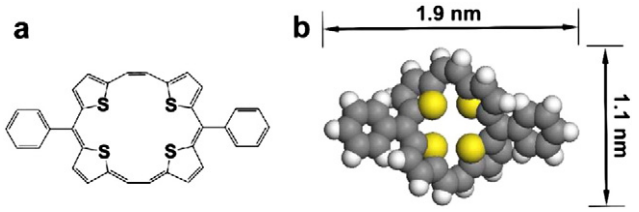

Fig. 1. Chemical structure (a) and optimized model (b) of DPTTA.

HOPG substrates, while assemble into two dimensionally ordered closed-packed domains on Au(111) substrate. C_{60} molecules, which have strong intermolecular interaction with DPTTA and can form 1:1 complex with DPTTA in bulk crystal [6], are selected as acceptor molecules to construct D-A bilayer on DPTTA modified surfaces. It is shown that C_{60} molecules can be better dispersed and assemble on DPTTA modified Au(111) surface while aggregate on DPTTA modified HOPG substrate. The results provide an example to understand the substrate effect on supramolecular assembly behaviors of functional molecules, which is important for the design of sulfur–bridged annulenes based OFETs.

2. Methods

2.1. Chemicals

DPTTA was synthesized as reported in the literatures [5]. The molecules were dissolved in dimethyl formamide (Sigma-Aldrich Co.) to form a 1×10^{-4} M solution. Fullerenes-C_{60} (97%) was purchased from Suzhou Dade Carbon nanotechnology Corporation and used without further purification. The electrolyte solution (0.1 M $HClO_4$) was prepared with ultrapure $HClO_4$ (Kanto Chemical Co.) and Milli-Q water (18.2 MΩ · cm, total organic carbon <5 ppb).

2.2. STM

STM measurements on Au(111) and SLG modified Au(111) substrates were performed in constant-current mode using a Nanoscope E STM instrument (Bruker) and the tips were electrochemically etched from W wires in 0.6 M KOH and sealed with transparent nail polish to minimize Faradic currents. STM experiments on HOPG substrate were performed by using a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, *CA*) in constant-current mode under ambient air condition at room temperature and the tips were prepared by mechanically cutting a Pt/Ir wire (90:10). The Au(111) single-crystal electrode was prepared by the Clavilier method [19] and used as a substrate. The adlayer of DPTTA was formed by immersing an Au(111) electrode into a DPTTA saturated solution for 1 min after annealing it in a hydrogen-oxygen flame and cooling down in an ultrapure N_2 atmosphere. The DPTTA-adsorbed Au(111) electrode was then mounted in an electrochemical cell for STM measurements. The DPTTA adlayer on HOPG substrate were prepared by depositing a droplet (~5 μL) of THF solution containing ~10^{-5} M DPTTA on freshly cleaved HOPG surface and allow them to dry before STM measurements.

3. Results and discussion

3.1. HOPG substrate

The self-assembly of DPTTA molecules from a solution (1×10^{-4} M) in tetrahydrofuran (THF) at a highly oriented pyrolytic graphite (HOPG) surface leads to a 1D ordered linear structure (Fig. 2). Fig. 2a shows the large-scale STM image of DPTTA monolayer on HOPG substrate. It can be observed that the DPTTA molecules adsorb on atomically flat HOPG surface and self-organize into well-ordered adlayer extended over 100 nm with few point defects. The DPTTA adlayer is ordered in one dimension while disordered in two dimension. Fig. 2b displays the high-resolution STM image of DPTTA adlayer. DPTTA molecules pack side by side in adjacent rows and the width of each row is measured to be between 1.2 nm and 5.0 nm. On the basis of the above analysis, a tentative structural model is proposed in Fig. 2c.

3.2. Au(111) surface

When the substrate was changed from HOPG to Au(111), different self-assembly architecture of DPTTA molecules can be obtained. Fig. 3a shows the large-scale STM image of DPTTA on Au(111) surface. It is evident that the atomically flat terrace is covered by ordered monolayer of DPTTA molecules which appear as bright spots. The DPTTA molecules self-assemble into 2D close-packed ordered domains and the domain size can extend over 70 × 70 nm^2 (Fig. S1). The underlying reconstruction lines of the Au(111) surface can be distinguished in the STM image, which indicates the relative week interaction between DPTTA molecules and Au(111) surface [20,21]. More details about the internal structure and orientation of DPTTA adlayer are revealed in the high-resolution STM image (Fig. 3b). Each bright spot is seen as a parallelogram with a large bright at the center and two additional spots at opposite corners, corresponding to the sulfur-bridged annulene framework and the benzene rings in the DPTTA molecule, respectively. A single unit is outlined by a white box and the parameters of the unit cell are measured to be a = 1.37 ± 0.1 nm, b = 1.46 ± 0.1 nm, γ = 105° ± 2°. On the basis of the above analysis, a structural model is proposed in Fig. 3c.

3.3. Graphene substrate

To further demonstrate the substrate effect, we investigate the DPTTA self-assembly on single-layer graphene (SLG) on Au(111) substrate. The single-layer graphene was grew through chemical vapor deposition (CVD) method and was transferred onto the Au(111) surface by the polymethyl mechacrylate (PMMA) assisted transfer method as

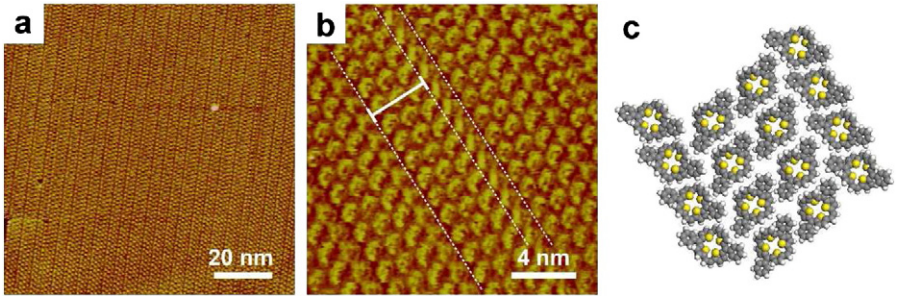

Fig. 2. Large–scale (a) and high–resolution (b) STM images of DPTTA adlayer on the HOPG surface. (c) Proposed structural model for the DPTTA adlayer on HOPG surface. Imaging conditions: (a) $V_{bias} = -500$ mV, $I_t = 0.605$ nA; (b) $V_{bias} = 805$ mV, $I_t = 0.413$ nA.