Surface Science 603 (2009) 716–722

Contents lists available at ScienceDirect

Surface Science

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

Structural ordering of ω-ferrocenylalkanethiol monolayers on Au(1 1 1) studied by scanning tunneling microscopy

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ARTICLE INFO

Article history:
Received 1 October 2008
Accepted for publication 13 January 2009
Available online 20 January 2009

Keywords:
Scanning tunneling microscopy
X-ray diffraction
Molecular electronics
Self-assembly
Ferrocenes
Monolayer structure

ABSTRACT

The self-assembly of ω-ferrocenylalkanethiols (FcCnSH) with different alkyl-spacer lengths on Au(1 1 1) substrates has been studied by scanning tunneling microscopy (STM). Upon deposition at room temperature FcCnSH molecules tend to form multilayers, while by thermal treatment monolayer formation, a rearrangement of the molecules and the formation of ordered domains is achieved. The surface structure of the resulting full coverage self-assembled monolayers is resolved with molecular resolution by STM. The ordered monolayer structure of ω-ferrocenylpropanethiol is discussed in comparison with its bulk crystal structure, derived from single crystal X-ray analysis. Based on these results a monolayer structure of ω-ferrocenylalkanethiols with longer alkyl chains closely related to the bulk crystal structure of the shorter alkyl-spacer derivates is suggested. Our results provide detailed insight into the self-assembly of FcCnSH on gold substrates.

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1. Introduction

Electronic circuits based on organic thin films became increasingly interesting over the last years. As a first step towards a successful integration of molecular building blocks into electronic circuits, the investigation and characterization of structural and electronical properties of molecular thin films is necessary. In this work, ω-ferrocenylalkanethiol monolayers are studied, which combine the structural backbone alkanethiol, known for the formation of highly ordered self-assembled monolayers, with the redox-active organometallic ferrocene moiety.

Ferrocenes are known to be redox-active molecules in electrochemical surrounding [1] and therefore are promising candidates as active elements in nanoelectronic circuits. Furthermore, the low energy barrier between the different charged states admits the use of ferrocenes in donor/acceptor charge transfer systems with, as envisioned by Aviram and Ratner [2]. Ferrocene derivatives are well applicable due to their stability at ambient conditions and easy derivatization with common aromatic synthesis techniques. Their properties were studied in detail by Chidsey et al. starting with the electrochemical investigations, regarding the chemisorption of ω-ferrocenylalkanethiols on gold surfaces and the electrochemical characterization of the formed self-assembled monolayers [1]. Especially the concentration effects in mixed layers consisting of ferrocene derivatives and alkanethiols [3–5] and the charge transfer behavior of the spacer layer and the redox moiety were examined [6,7]. For pure ω-ferrocenylalkanethiol monolayers a redox state dependent thickness change and a tendency for multilayer formation has been observed by ellipsometry [8,9], with the thickness change probably being due to a tilt of the ferrocene endgroup upon oxidation/reduction [10]. Full-coverage, self-assembled monolayers of pure ω-ferrocenylalkanethiols were also studied by scanning probe microscopy (SPM) and show interesting electronical properties [11–14]. However, little is known about their structural properties. The only real space images revealing the structure of physisorbed monolayers of alkyl-ferrocenes and alkane-bridged diferrocenes on Ag and HOPG were presented by Wedeking et al. [15,16]. In earlier studies we characterized mixed monolayers of chemisorbed ω-ferrocenylalkanethiols and alkanethiols on Au(1 1 1) surfaces [17–19], showing islands and mixed structures which are resolved with molecular resolution. Similar structures were examined by Hara et al. in an electrochemical environment [13]. In this paper we report on STM investigations of the surface structure of ω-ferrocenylalkanethiol self-assembled monolayers (Fc-$(CH_2)_n$-SH, abbreviated as FcCnSH with $n = 3$, 5 and 11 in the following) chemisorbed on Au(1 1 1) compared to single crystal X-ray measurements.

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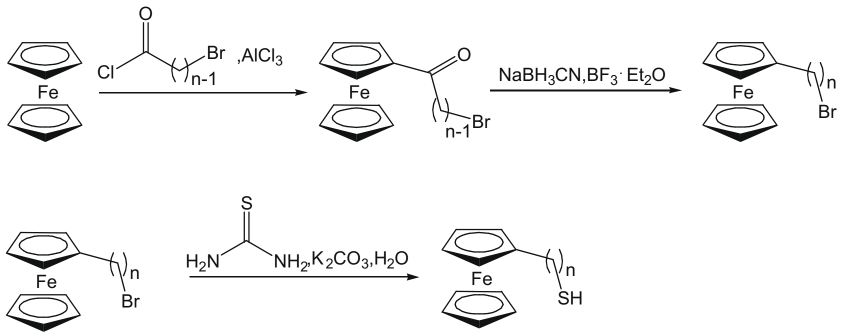
doi:10.1016/j.susc.2009.01.013



Scheme 1.

2. Experimental

2.1. Synthesis

All solvents were purified by standard methods. The following chemicals were used as purchased without further purification: $AlCl_3$, ferrocene, 3-bromopropionic acid, 5-bromovaleric acid, 11-bromoundecanoic acid, $BF_3 \cdot Et_2O$, $NaBH_3CN$, Na_2SO_4, K_2CO_3, and thiourea. The ω-ferrocenylalkanethiols are prepared in similar ways as described in literature for analoguous compounds, via Friedel–Crafts acylation of ferrocene [20,21], reduction of the respective ω-alkanoylferrocenes with $NaBH_3CN$ and final conversion of the bromide moiety to SH via reaction with thiourea [22] (Scheme 1). As byproducts, the correlating disubstituted derivatives and the respective disulfides are identified. Purification of the ω-ferrocenylalkanethiols is achieved by crystallization or by preparative HPLC. In the case of the FcC3SH derivative single crystals suitable for X-ray analysis were obtained from hexane at +6 °C.

2.2. X-Ray analysis

The single crystal X-ray structure determination was performed with a Bruker SMART APEX CCD detector on a D8 goniometer using Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator) on a crystal of approximate dimensions 0.41 × 0.11 × 0.05 mm. Crystal data at $T = 130(2)$ K: $C_{13}H_{16}FeS$, $fw = 260.17$, monoclinic space group $P2_1/c$, $a = 12.1605(12)$, $b = 7.6702(8)$, $c = 12.9191(13)$ Å, $\beta = 108.3610(10)°$, $V = 1143.7(2)$ Å^3, $Z = 4$, $d_{calc} = 1.511$ g cm^{-3}, $\mu = 1.462$ mm^{-1}, and $F_{000} = 544$. About 12,331 reflections with $3.1 \leqslant \theta \leqslant 30.8°$ were collected and corrected for absorption ($T_{min} = 0.585$, $T_{max} = 0.931$) [23]. The structure was solved by direct methods [24] and refined with full-matrix least-squares on F^2 [25]. Convergence was reached for 3362 reflections and 137 variables at agreement factors of $wR_2 = 0.1184$ (all data), $R_1 = 0.0459$ [2855 observations with $I > 2\sigma(I)$]. Maximum and minimum from final difference Fourier map 0.69 and −0.71 eÅ^{-3}.

Characterized FcC3SH crystals from the same run were used for the SAM formation on gold substrates described in this paper.

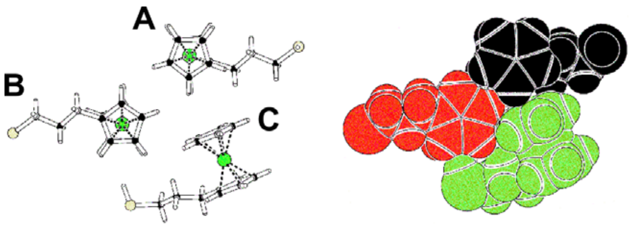


Fig. 1. Ball-and-stick (left) and space-filling representations (right) of three neighbouring molecules of FcC3SH. Molecules B (red in the space-filling model) and C (green) are related to A (black) by the symmetry operations 1 − x, 1 − y, −z and 1 − x, 1/2 + y, 1/2 − z, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

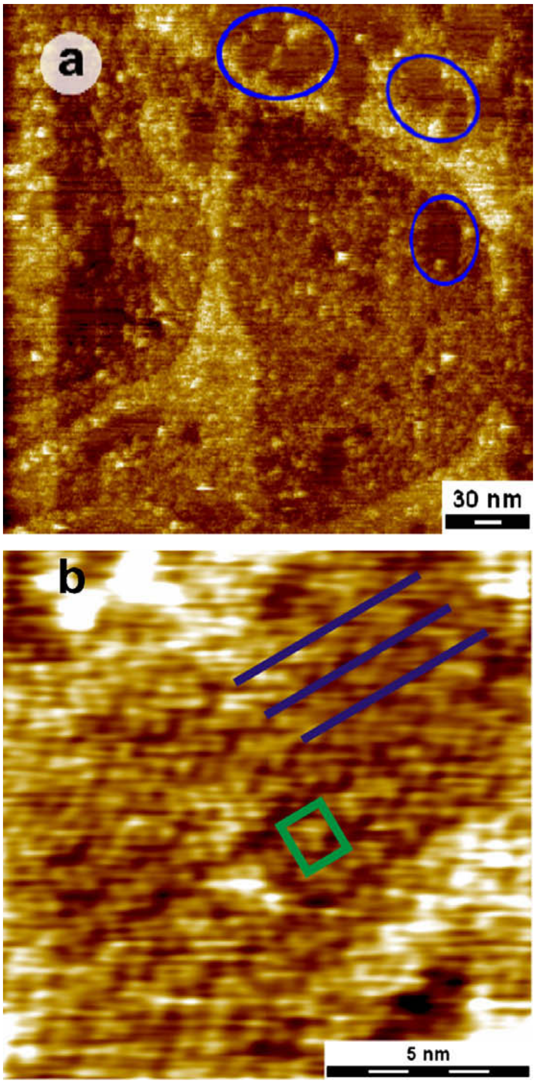


Fig. 2. Topography of a chemisorbed FcC5SH monolayer. A disordered monolayer with substrate features (steps, etch pits) and embedded, ordered domains of darker and flatter texture (marked in blue) is observed (a). In (b) the surface texture of an ordered island is imaged, showing a characteristic striped pattern marked in blue. The unit cell of the FcC5SH molecules is marked in green.

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