Self-Assembling Properties of 11-Ferrocenyl-1-Undecanethiol on Highly Oriented Pyrolitic Graphite Characterized by Scanning Tunneling Microscopy

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Molecular resolution scanning tunneling microscopy images the spontaneous self-assembly of 11-ferrocenyl-1-undecanethiol ((C_5H_5)Fe(C_5H_4)(CH_2)_{11}-SH) forming a large striped-phase on highly oriented pyrolitic graphite (HOPG) at a phenyloctane-HOPG interface. In the image, the alkyl chains lying flat on HOPG appear as bundles in groups of five in the moiré pattern due to lattice mismatch with the underlying HOPG. The ferrocene units appearing as either fuzzy or ring-like structures suggest the random rotation of cyclopentadienyl (Cp) rings sandwiching the central iron ion of the ferrocene moieties with their principal axis either oblique or perpendicular to the HOPG. The ferrocene moieties are more clearly resolved in a mixed film with octanethiol, where the fuzzy or ring-like structures of the ferrocene units are asymmetrically distant from the sulfur head-groups forming alternating rows in the phase segregated image. Both molecules can be clearly distinguished by the length of the molecular rows. [DOI: 10.1380/ejssnt.2008.119]

Keywords: Scanning tunneling microscope; Self-assembly; Ferrocene; Molecular rotation

I. INTRODUCTION

Ferrocene is an organometallic compound consisting of a pair of cyclopentadienyl (Cp) rings sandwiching a central iron atom [1–3]. Each Cp ring carries one extra electron in the orbital and binds itself to the iron by means of d-block electrons. This iron core is then able to exist in both Fe^{2+} or Fe^{3+} making the ferrocene to possess very interesting redox properties. As such, it is routinely used for charge transfer studies [4–6]. It was found for example, that ferrocene moieties deeply buried inside an alkyl chain matrix showed sluggish behavior [7, 8] whereas closely packed ferrocene moieties indicate strong interactions between the redox centers [4, 9].

Despite the role which spatial configuration likely plays in the electronic behaviour of the electroactive moiety [10], the self-assembled structure of thiolated ferrocenes have little been studied before. Thus far, it was not known whether they can self-assemble into ordered arrays despite of the bulky ferrocene moieties, especially with the Cp rings freely spinning along the Cp(centroid)-Fe-Cp(centroid) axis due to the π bonds to the iron d-electrons. NMR measurements [11, 12] on ferrocene compounds in liquid found that both Cp rings in a free ferrocene molecule exhibit very random rotations relative to the iron core at room temperature. Such metalloccenes have since been used in molecular motor assemblies [13] with the rotor comprising a cyclopentadienyl ligand. It was shown that Cp rings of ferrocene cease all rotation at −60°C [11], indicating the rotational energy to be thermal in nature.

Molecular resolution scanning tunneling microscopy (STM) is an ideal tool to characterize the self-assembling of molecules on substrates. Several reports of molecular resolution STM images of ferrocene moieties are available. Vapor deposited native ferrocenes on Au(111) were imaged at liquid helium temperatures by Braun et al. [14]; Wedeking et al. [15] and Zhong et al. [16] synthesized and imaged symmetrical bis-ferrocenes at the ends of oligoethylene chains ((η^5C_5H_4)Fe(η^4C_5H_4)-(CH_2)_5-(η^5C_5H_4)Fe(η^4C_5H_4)) as well as unsymmetrical ferrocenyalkanes on HOPG [17]. Recently, Muller-Meskamp et al. imaged striped phase mercaptoalkylferrocenes on Au(111) [18]. In all experiments, the molecules form striped phase on the substrates by molecular assembly (intermolecular interactions).

We hence attempt STM imaging of 11-ferrocenyl-1-undecanethiol ((η^5C_5H_4)Fe(η^4C_5H_4)-(CH_2)_{11}-SH) (Fig. 1), hereby referred to as ferrocenyl undecanethiol, physisorbed on highly oriented pyrolitic graphite (HOPG) in phenyloctane solution. It is of our interest whether the unsymmetrical ferrocenyl undecanethiol system would self-assemble on HOPG in a similar way as the asymmetrical ferrocenyalkanes [17] or the symmetrical bis-ferrocenes [15] which are stabilized into a 2D crystal by ferrocene-ferrocene interactions. We expect that the van der Waals interactions between HOPG and alkanethiols to which the ferrocene moieties

FIG. 1: Chemical structure of 11-ferrocenyl-1-undecanethiol.

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are attached effectively work for the visualization of dynamically moving ferrocenes in striped phase on HOPG. In this study, the mixed system with octanethiol is also investigated to compare with the assembling property of 11-ferrocenyl-1-undecanethiol in single component system.

II. EXPERIMENTAL

11-ferrocenyl-1-undecanethiol was purchased from Dojindo Laboratories, Japan, and used without further purifications. Phenylotane was used as solvent for STM imaging, by virtue of its properties as isotropic liquid with low vapor pressure and low affinity to HOPG [19]. Solutions of phenylotane containing 11-ferrocenyl-1-undecanethiol at a concentration of 1 mg/ml as well as that containing 1:1 mixtures of 11-ferrocenyl-1-undecanethiol and octanethiol at a total concentration of 1 mg/ml were prepared prior to the experiment. A STM head of Nanoscope II with a Nanoscope IV controller (Veeco, USA) was used for imaging. Commercially available, mechanically cut platinum iridium tips were used as purchased from NIHON Veeco, Japan. A small droplet of the solutions of phenylotane was gently placed onto a freshly cleaved HOPG and the STM tip scanned inside the solution.

III. RESULTS AND DISCUSSION

Figure 2(a) shows a typical STM image of 11-ferrocenyl-1-undecanethiol when spontaneously self-assembled in a striped-phase configuration with the molecular axis of the alkyl chains lying horizontally flat on the HOPG surface. From this figure, the distinct rows of alkyl chains (e.g., Arrow A) are found perpendicular to the double-rows of bright spots (e.g., Arrow B). The bright double-rows, which are quite similar to those in previous STM studies with alkanethiols, are assigned to sulfur head-groups [19–21]. In the image, we also observe other features as ring-like structures (e.g., Arrow C1) or as fuzzy regions (e.g., Arrow C2) adjacent to alkyl chains between the double-rows, which must be the features originating from the ferrocene moieties.

The self-assembly of ferrocenyl undecanethiol on HOPG seems to be largely led by the strong thiol-thiol interactions [22–25] unlike the assemblies of asymmetrical ferrocenyl alkanes [17] and bis-ferrocenes system [15, 16] on HOPG which are governed only by van der Waals interactions between alkyl chains along with ferrocene-ferrocene interactions. The physisorbed patterns of both molecules without thiol functions basically follow the close packing diagrams in three-dimensional crystals as most stable assembled structures. Our STM images with ferrocene moieties equally spaced between sulfur rows are rather in common with the report of ferrocenyl pentanethiol on Au(111) [18].

When the ferrocene moieties appear as ring-like, we observe neighboring sulfur groups and the alkyl chains being well aligned as shown near Arrow C1. The distance of 5 angstroms between sulfur groups are clearly confirmed by the sectional analysis on Arrow B (Fig. 2(b)) in good agreement with the distance of alkyl chains in the commensurate packing on the HOPG substrate. On the other hand, some other regions adjacent to the ring-like structured ferrocene exhibit an intensity fluctuation known as a moiré pattern (see the region of Rectangle σ) [26–32]. This type of contrast fluctuation has been observed in other films such as carboxylic acids [32] and 1-octadecylamine (CH3(CH2)17NH2) on graphite, and been explained by an incommensurate packing of the self-assembled molecules against the underlying graphite lattice [33]. In the region of Rectangle σ, the alkyl chains are found to bundle up together in groups of five or six with 4 angstroms spaces due to van der Waals interactions as shown in sectional analysis in Fig. 2(c), while the sulfur atoms are 5 angstroms distant as shown in Fig. 2(b). The bulky ferrocene moieties attached to the end of undecanethiols seems to contribute the formation of the moiré pattern, since alkanethiols without functional groups are known to form only commensurate packing on HOPG [19, 20]. Such bundling of the alkylchains were not observed in mixed layers with alkanethiols as shown in Fig. 4(a) in this paper, in a similar manner to ferrocenyl-pentanethiol in mixed layers with alkanethiol on Au(111) [18].

In previous studies, Pertaya et al. [34] has reported the STM images with cyclopentadienyl rings left on Ag(110) surfaces after the decomposition of ferrocene. Braun et al. [14] has also imaged ferrocene moieties with their Cp rings immobilized on Au(111) at 5K. The ring-like structures in our images at room temperature are in excellent agreement with the size of Cp rings in their reports. There is one report concerning STM image of rotating molecules by Gmiezewski et al. [35]. He found that the six lobes of hexa-tert-butyl decacyclenes (HB-DC) were clearly resolved when they were surrounded by adjacent molecules on the surface. However, HB-DC exhibit doughnuts or inner tube like structures by rotation when they were free from steric hindrance by surrounding molecules. In a similar manner to HB-DC molecules, we believe that the ring-like structures we obtained are the ferrocene moieties rotating with their Cp(centroid)-Fe-Cp(centroid) vector perpendicular to the HOPG surface (right in Fig. 3).

Density functional theory (DFT) calculations have determined physisorbed bis-ferrocenes on graphite to have the lowest binding energy (−18.9 kcal mol⁻¹) when assembled in an orthogonal configuration with one of the Cp(centroid)-Fe-Cp(centroid) vectors vertical to the HOPG and the second ferrocene having its vector horizontal to the surface [15]. The single rows of ring-like structures (e.g., Arrow C1) imaged between sulfur double rows in Fig. 2(a) can be explained by this alternate packing (one parallel and the other perpendicular) of ferrocenes.

The origin of fuzzy regions (e.g., Arrow C2) between the sulfur double rows is not as clear as the ring-like structures. However, the clearly resolved images of the sulfur double rows and alkyl chains proves that the locally confined fuzzy regions did not result from simple failure of STM imaging but suggests some phenomena occurring at the interface. We consider the local motion of ferrocenes, which was equivalent to the STM scan speed, to have constituted the fuzzy regions. According to DFT calculation of bis-ferrocenes [15], ferrocene moieties having both the Cp(centroid)-Fe-Cp(centroid) axes par-
FIG. 2: (a) STM image of 11-ferrocenyl-1-undecanethiol self-assembled monolayer (SAM) at phenyloctane–HOPG interface in constant height mode at 150 pA and 550 mV. A: alkyl chains. B: double row of sulfur head groups. C1: ring-like structure. C2: fuzzy regions. The molecular structures with the ČP(centroid)-Fe-ČP(centroid) axes parallel (green) and perpendicular (blue) to the surface are superposed in the image to indicate the fuzzy and ring-like structures respectively. (b) Sectional view taken along arrow B in Fig. 2(a) showing commensurate packing of the alkyl chains on HOPG with the distance between alkyl chains being 5 angstroms. (c) Sectional analysis taken along the sulfur rows from Rectangle σ in Fig. 2(a), showing moiré pattern and bundles of 5-6 alkyl chains with incommensurate packing and spaced at 4 angstroms.

FIG. 3: Schematic model of 11-ferrocenyl-1-undecanethiol lying flat on surface with the principal axis of ferrocene moiety perpendicular (blue) and parallel (green) to the surface.

Bistable rotaxane molecules have a molecular structure in which a cycolbis(paraquat-para-phenylene) (CBPQT4+) ring rotates along a central axis containing a redox-active tetrathiafulvalene (TTF) unit and a naphthalene ring system. This system has been studied extensively as linear artificial molecular muscles [36, 37], however, to the best of our knowledge, the molecular resolution STM images of the rotaxane have never been reported by any groups yet. The plane of rotation of these molecules is along the scanning direction when the molecules are lying flat on the substrates, similarly to the ferrocene with the ČP(centroid)-Fe-ČP(centroid) axes parallel to the surface. Here we would also like to point out that the rotating HB-DC molecules were visualized only with the rotation axis perpendicular to the surface [35]. Thus we presume that rotation of ferrocene with the ČP-Fe-ČP axes perpendicular to the surface is more stable against STM scanning compared with that with the ČP-Fe-ČP axes parallel to the surface. Further studies are required to elucidate the detailed mechanism.

The following coadsorption study of ferrocenyl undecanethiol with octanethiol justified our assignment of the images described above. Figure 4(a) shows a STM image on HOPG surface comprised of a mixture of ferrocenyl-undecanethiol and octanethiol in a phenyl-octane solution. The molecules in a mixed system were phase segregated into defect-free, alternate molecular rows with head to head assembly, mimicking β-sheet bilayers in biological systems which adopt similar perpendicular packing [38–40]. Here the bright double rows of sulfur head group (e.g., Arrow S) and fully stretched alkyl chains (e.g., Arrows F and G) were clearly observed by molecular resolution. In the image, the fuzzy regions (e.g., Arrow D) appeared again between the bright double rows and alkyl chains of clear molecular resolution. The ring-like structures simi-
lar to Arrow C\textsubscript{1} of Fig. 2(a) were detected in only a few positions (Arrow E) as exceptions. It is again to be noted that, since the bright double rows as well as the alkyl chains are clearly resolved in the same STM scanning, the fuzzy regions are not resulted from poor STM resolution but suggest the essential property of ferrocene moieties, i.e., their dynamic movement on the surface.

In the mixed system, the ring-like or fuzzy features were asymmetrically distant from the sulfur double-rows. One unit cell is shown as Rectangle R in Fig. 4(b). The center of the ring-like structures was found to be at distances 2.1 nm and 1.5 nm from the adjacent double rows. This distance accurately corresponds to the alkyl chain length of head to head and tail to tail aligned ferrocenyl undecanethiol (11 carbon atoms) and octanethiol (8 carbon atoms). We found that these two molecules never form symmetry rows such as 2.1 nm–2.1 nm or 1.5 nm–1.5 nm adjacent to each other but always form alternate asymmetry rows (2.1 nm–1.5 nm). In addition, the molecules of the mixed system were much better ordered compared to those of single component ferrocenyl undecanethiol which contained misaligned and bundled alkyl chains as was shown in Fig. 2(a). The intermolecular spacing of alkyl chains in the mixed system, that is 5 angstroms, is equal to the commensurate packing of the alkanethiols on HOPG.

The difference in packing between single and mixed systems could be due to steric effects [19, 20]. It seems that the alternate rows with octanethiol better stabilize the commensurate assembly of ferrocenyl undecanethiol with the bulky ferrocene moieties on HOPG. In other words, the incommensurate packing of ferrocenyl undecanethiol on HOPG may originate from the strong interactions between ferrocene moieties facing each other by head to head alignment.

Here we would like to add one note concerning the bias voltage of STM imaging. Since no clear STM image could be obtained at low bias voltage, we have to increase it to 1500 mV for the mixed system, which is the optimized condition to visualize clear sulfur double rows from alkanethiol monolayers on HOPG as reported before [41, 42]. On the other hand, Gorman et al. has mentioned that the ferrocene derivatives become unstable under high bias voltage (>1000 mV) for STM imaging [43]. We cannot deny the influence of applied voltage on ferrocene completely, however, since the fuzzy structures are obtained even at the bias voltage of 550 mV as shown in Fig. 2(a), we believe that they are not the simple product of high bias voltage but attributed to essential characteristics of ferrocene moieties.

IV. CONCLUSION

The self-assembly of 11-ferrocenyl-1-undecanethiol ([(η\textsuperscript{5}C\textsubscript{5}H\textsubscript{5})\text{Fe}(η\textsuperscript{5}C\textsubscript{5}H\textsubscript{4})(CH\textsubscript{2})\textsubscript{11}SH]) was successfully imaged by molecular resolution STM in a striped phase configuration at a phenyloctane-HOPG interface. The ferrocene moieties were observed to be undergoing rotations and appeared as ring-like or fuzzy structures corresponding to their principal axis being perpendicular or oblique to the HOPG surface. The mixed film with octanethiol at a 1:1 mixing ratio provides alternate rows composed of each molecule. The ferrocene moieties in the mixed system again exhibited fuzzy or ring like structures asymmetrically distant from the sulfur double rows due to the lengths of the alkyl chains of both molecules. Our results suggest the possibility to control the density and orientation of ferrocene redox center on the surface by the molecular assembly.

FIG. 4: (a) 15 nm × 15 nm STM image of 11-ferrocenyl-1-undecanethiol and octanethiol mixed SAM at phenyloctane–HOPG interface in constant current mode at 150 pA and 1500 mV. S: double row of sulfur head group; D: Ferrocene moieties imaged as fuzzy; E: Ferrocene moiety imaged as ring-like structure; F: CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{7} alkyl chain; G: (CH\textsubscript{2})\textsubscript{11} alkyl chain. (b) Cartoon depicting the self-assembly pattern of the mixture of 11-ferrocenyl-1-undecanethiol and octanethiol. The turquoise rectangle spanning over two pairs of both thiols represents one unit cell denoted by Rectangle R of Fig. 4(a). Full height scale: 0.1 nm.
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