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Controlling Growth to One Dimension in Nanoislands of Ferrocene-Sugar Derivatives

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Supporting Information

ABSTRACT: Ferrocenyl-Alkyl-Protected Sugar (Fc-Sug) and Ferrocenyl-Oxo-Alkyl-Protected Sugar (Fc-Oxo-Sug) were deposited on the basal plane of Highly Oriented Pyrolytic Graphite (HOPG) using a drop-casting method. Ultrathin films of these molecules were investigated using Atomic Force Microscopy to understand the growth at low coverage. Both molecules are forming highly ordered one-dimensional molecular islands, which are growing from a dimer building block. The *dimer* and *interdimer* interactions (along the length of islands) are stabilized by $-C_2O\cdots H-C$ hydrogen bonding. Unlike for Fc-Sug, the islands of Fc-Oxo-Sug are extended to tens of micrometers, and the growth is only limited by terrace edges or other islands on the surface. This exceptional growth of islands is understood in terms of an additional $-C{=}O\cdots H-C-$ hydrogen bonding leading to stronger interdimer interactions along the length of the islands compared to Fc-Sug.

INTRODUCTION

Right from its discovery, ferrocene (Fc) and its derivatives are well-known for their catalytic applications.[1] Recently, derivatives of Fc have attracted interest in molecular thin-film-based electronic applications due to the redox activities of Fc.[2−5] The electrochemical potential of Fc is highly sensitive to the group attached to cyclopentadienyl (Cp) rings.[6] Thin-film transistors based on Fc derivatives have been realized recently.[6,7] Adsorption-induced modifications in the electronic structures of few Fc derivatives have been investigated, and the electronic properties are showing their potential applicability in molecular electronics.[8−10]

The quality (defect-free) and structure of such molecular two-dimensional adlayers on surface are decisive in their applications. The adlayer patterns, which in turn are controlled by intermolecular interactions, influence their electronic structure.[11−13] Molecules with electronic functions (i.e., diodes, switches) show strong dependency between molecular adlayer patterns and their electronic functions.[6,14−16] Several Fc derivatives have been studied on surface and show excellent two-dimensional patterns.[17−21] The stability and symmetry of these patterns are controlled by the chemical nature of groups attached to Fc.

Here, we present one-dimensional growth of a Fc derivative—controlled by selective hydrogen bonding—over the expected 2D growth. Ultrathin films of Ferrocenyl-Alkyl-Protected Sugar (Fc-Sug) and Ferrocenyl-Oxo-Alkyl-Protected Sugar (Fc-Oxo-Sug) molecules (cf. Figures 1a and 2a) on the basal plane of highly oriented pyrolytic graphite (HOPG) were investigated using an Atomic Force Microscopy (AFM). Due to high diffusion rate, metallocenes (Mc) form ordered patterns on the surface only at low temperatures.[9,17] To reduce the diffusion, anchoring groups are attached to Mc, and these derivatives show an ordered adlayer at room temperature.[14,22] Ferrocenyl Alkyl-Protected Sugar molecules are chosen here due to their long-term chemical inertness at ambient conditions over molecules with unprotected sugar and the protected sugar group is offering reasonable number of oxygen atoms for hydrogen bonding. Fc-Sug molecules grow into very regular islands with well-defined growth facets at submonolayer coverage. The growth is unidirectional and forms long nanoscale islands aligned along a lattice direction of graphite. Fc-Oxo-Sug shows similar unidirectional growth as Fc-Sug. Strikingly, the islands are growing exceptionally long, and the growth is limited only by terrace edges and other islands. Typical scan areas of 10 μm are revealing islands whose length extends to tens of micrometers. The width of islands (typically 200 nm) increases only with high surface coverage of molecules suggesting a high preference for the growth along the length of islands. Using density functional theory (DFT) calculations and high-resolution images, a microscopic structural model is proposed. A $-C{=}O\cdots H-C-$ interdimer interaction seems to be at the origin of the unexceptional length of Fc-Oxo-Sug islands.

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