Polymorphism in Biphenyl-Based Self-Assembled Monolayers of Thiols

Piotr Cyganik* and Manfred Buck*

School of Chemistry, University of St. Andrews, St. Andrews KY16 9ST, U.K.

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Toward a rational design of thiol SAMs a number of fundamental studies on alkane thiols have addressed the relationship between molecular structures and the resulting film structure and properties. More recently, activities have been extended to SAMs of aromatic thiols since they are attractive for a number of applications such as control of charge transfer, organic-based electronic functionality, or patterning on the scale of nanometers. While studies on alkane thiols have described some of the fundamental factors it is not clear to what extent design concepts derived from alkane thiols can be applied to aromatic SAMs which differ significantly from aliphatic ones in geometry, conformational degrees of freedom, and intermolecular interactions.

Among a number of factors which contribute to the energetics of thiol SAMs such as intralayer interactions and interactions of the SAM with the environment, the SAM–substrate interface is of particular importance since substrate–sulfur bonding, adsorption site, and bonding geometry are mutually dependent parameters which enter into the energy balance in a crucial way. Even though the details of the SAM–interface are still far from being understood, some essential points have been unravelled. One is the crucial role of the C–S–Au bending potential as pinpointed in a recent experimental study of a homologue series of -(4′-methyl-biphenyl-4-yl)-alkanethiols (H₂C=CH₂₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋╭) which results from a pronounced directional force originating from the S–Au interface due to an sp³-like bonding geometry of the sulfur. Consequently, the film structure, e.g., the intermolecular distance, alternates between odd and even numbers of CH₂ units. For n = even a dense molecular packing, i.e., maximization of intermolecular interactions, and an optimum C–S–Au bond angle cannot be simultaneously realized. For this reason, insertion of one methylene unit or, more general, an odd number of them between the aromatic unit and the sulfur appears preferable to optimize quality and stability of the monolayers. This picture was fully confirmed by recent studies which demonstrated the odd–even variation in the properties of BPn SAMs. Compared to BPn SAMs with n = even, the ones with n = odd were found to be electrochemically more stable and more resistant to exchange by other thiols.

While the outlined design concept holds for BPn SAMs prepared at room temperature, the even-numbered BPn SAMs exhibit a very unexpected behavior if prepared or annealed at elevated temperatures. In contrast to odd-numbered BPn SAMs which just show the well-known annealing effects of domain growth and Ostwald ripening of vacancy islands but no structural changes, the even-numbered BPn SAMs undergo a pronounced temperature-induced change in structure as demonstrated in Figure 1 for BP4. As described in detail elsewhere, the initial structure observed for preparation temperatures below 343 K is described by a unit cell containing eight molecules (see Figure 1B). In this so-called α-phase, which is described by a rectangular unit cell, the intermolecular spacing of more than 6 Å is significantly larger than the 5 Å of the √3 x √3 gold matching lattice. If the samples are annealed at higher temperatures, fundamental changes occur. After annealing at 373 K, large-scale STM images show extended areas which differ in contrast (Figure 1A). A close look reveals that the brighter areas are the α-phase, whereas the darker areas represent a new phase. This β-phase, which is shown at molecular resolution in Figure 1C, differs substantially from the α-phase. The shape of the unit cell with again eight molecules is changed to oblique and contains intermediately below 423 K.

Figure 1. BP4 on Au(111). (A) large scale STM image of a SAM annealed at 373 K showing two structurally different regions labeled α and β. (B,C) High-resolution images of the two phases. Dimensions of unit cells and area per molecule are 5√3 x 3 Å (α-phase) and 6√3 x 2√3 and 32.4 Å² (β-phase). Illustrations of the two unit cells are on the same scale.
Two aspects of the phase transition are striking. First, the β-phase is in marked contrast to lower density phases observed for other thiol SAMs.\textsuperscript{1,19,20} It is irreversibly formed as reimmersion into BP4 is in marked contrast to lower density phases observed for other SAMs. Wherever one zooms in to molecular resolution the lattice is as perfect as that shown in (B) (β-phase) and (C) (α-phase).

Figures 2. Stability of different phases of BP4 SAMs on Au(111) against displacement by mercaptohexadecanoic acid (MHA), which forms a hydrophilic SAM. (A) Contact angle of water vs time of immersion into a 1 mM solution of MHA in ethanol. Open circles and solid squares represent data for samples prepared by annealing at 423 K (β-phase) and room temperature (α-phase), respectively. Corresponding STM images shown in (B) (β-phase) and (C) (α-phase).

The mechanical stability of a β-phase is indicated by the high contact angle for a BP4 layer prepared at room temperature against exchange. The contact angle remains virtually unchanged. Beyond the period of time displayed in Figure 2A, the contact angle changes by less than 2° after prolonged exposure to, for example, alkane thiols.

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Supporting Information Available: Film preparation and characterization (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


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