

Polymorphism in Biphenyl-Based Self-Assembled Monolayers of Thiols

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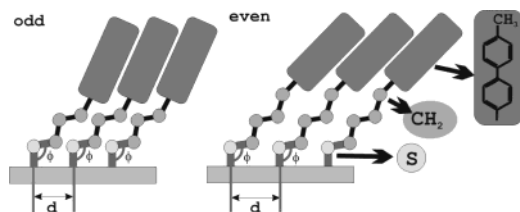
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Toward a rational design of thiol SAMs a number of fundamental studies on alkane thiols have addressed the relationship between molecular structures and the resulting film structure and properties.¹ More recently, activities have been extended to SAMs of aromatic thiols^{2–7} since they are attractive for a number of applications such as control of charge transfer,⁸ organic-based electronic functionality,^{9,10} or patterning on the scale of nanometers.^{11,12} While studies on alkane thiols have described some of the fundamental factors^{1,13} 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 (~ 126 kJ/mol for Au–S¹), 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 S–Au 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 study⁵ of a homologue series of ω -(4'-methyl-biphenyl-4-yl)-alkanethiols ($\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-(\text{CH}_2)_n-\text{SH}$, BP n , $n = 1-6$). The orientation of the aromatic units is crucially influenced by the number of methylene units in the alkane spacer (see Scheme 1), which results from a pronounced

Scheme 1. Illustration of the Odd–Even Effect on Au(111)



directional force originating from the S–Au interface due to an sp^3 -like bonding geometry of the sulfur.^{5,13} Consequently, the film structure, e.g., the intermolecular distance d , alternates between odd and even numbers of CH_2 units. For $n = \text{even}$ a dense molecular packing, i.e., maximization of intermolecular interactions, and an optimum C–S–Au bond angle ϕ 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.^{2,5,14} This picture was fully confirmed by recent studies which demonstrated the odd–even variation in the properties of BP n SAMs. Compared to BP n SAMs with $n = \text{even}$, the ones with $n = \text{odd}$ were found to be electrochemically more stable¹⁵ and more resistant to exchange by other thiols.¹⁶

While the outlined design concept holds for BP n SAMs prepared at room temperature, the even-numbered BP n SAMs exhibit a very

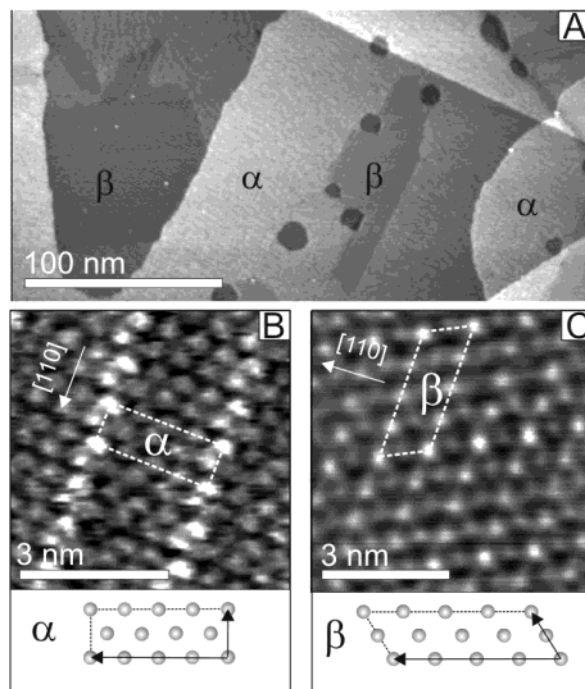


Figure 1. BP4 on Au(111). (A) large scale STM image of a SAM annealed at 373 K showing two structurally different regions labeled α and β . (B,C) High-resolution images of the two phases. Dimensions of unit cells and area per molecule are $(5\sqrt{3} \times 3)$ and 27 \AA^2 (α -phase) and $6\sqrt{3} \times 2\sqrt{3}$ and 32.4 \AA^2 (β -phase). Illustrations of the two unit cells are on the same scale.

unexpected behavior if prepared or annealed at elevated temperatures. In contrast to odd-numbered BP n SAMs which just show the well-known annealing effects of domain growth and Ostwald ripening of vacancy islands¹⁷ but no structural changes, the even-numbered BP n SAMs undergo a pronounced temperature-induced change in structure as demonstrated in Figure 1 for BP4. As described in detail elsewhere,¹⁸ 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 \AA is significantly larger than the 5 \AA of the $\sqrt{3} \times \sqrt{3}$ 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 has substantially increased in size by 20%. Further increase of the temperature to 423 K yields the pure β -phase. As we will discuss in detail in a forthcoming publication, a third phase coexisting with the other two phases also appears intermediately below 423 K.

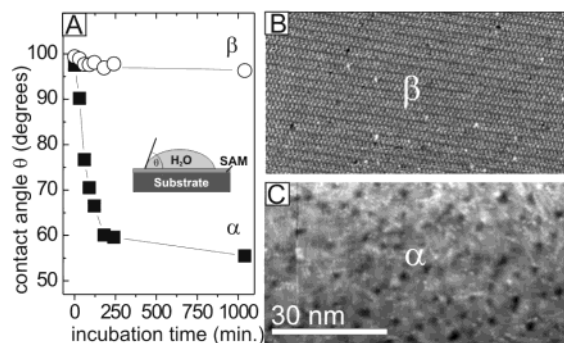


Figure 2. Stability of different phases of BP4 SAMs on Au(111) against displacement by mercaptohexadecanoic acid (MHA), which forms a hydrophilic SAM. (A) Contact angle of water vs time of immersion into a 1 mM solution of MHA in ethanol. Open circles and solid squares represent data for samples prepared 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).

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.^{1,19,20} It is irreversibly formed as reimmersion into BP4 solutions leaves the SAM unchanged. We note at this point that analysis with X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption spectroscopy (NEXAFS) excludes that this structure arises from a chemical change of the layer. Second, the transition from the structure prepared at room temperature to the β -phase also yields a fundamental change in stability against exchange by other thiols. Prolonged exposure to, for example, alkane thiols leaves the β -phase unchanged. This is demonstrated by exchange experiments where BP4 SAMs were immersed into a solution of ω -mercaptohexadecanoic acid (MHA) for different periods of time. The degree of exchange was monitored by measuring the contact angle θ (Figure 2A). In agreement with earlier experiments,¹⁶ the contact angle for a BP4 layer prepared at room temperature changes quickly from the value of the native BP4 monolayer toward the one of an MHA SAM. However, the change in structure of the initial BP4 SAM (Figure 2C) to the one exhibiting the β -phase (Figure 2B) results in a dramatic change in stability 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° over an immersion period of more than 30 days. This switch in stability is in striking contrast to alkane thiols and the odd-numbered biphenyl thiols such as hexadecane thiol and BP3, respectively, where no significant influence of the preparation temperature is observed. We would like to point out that formation of the β -phase is paralleled by a remarkable improvement in the structural perfection of the SAM. Domains exceeding 10^5 nm² are routinely observed, i.e., they are well beyond what we have ever observed for other SAMs. Wherever one zooms in to molecular resolution the lattice is as perfect as that shown in Figure 2B. Notably, steps in the gold substrate do not introduce major distortions such as differently oriented domains.

Since polymorphism is not observed for odd-numbered BP n SAMs where the various factors entering the energy balance act cooperatively, it appears to be the competition between different factors, e.g., sulfur bonding geometry vs intermolecular interactions,

which gives rise to the phenomenon reported here. A consequence of this competitive effect is that the energy hypersurface is characterized by a number of pronounced local minima. This, in turn, gives rise to a fundamentally different relationship between stability and molecular density compared to other thiol systems with unstable low-density phases.^{1,20} Experiments with other even-numbered biphenyl thiols where phase transitions are also seen suggest that a competition-based structural variety is a more general phenomenon rather than a special case limited to a single molecular structure such as BP4.

While further studies will have to unravel the molecular and mechanistic details, in particular, structural changes at the Au–S interface which we believe to occur, the experiments presented here show that competitive effects can give rise to polymorphism and, thus, to an additional dimension in tailoring thiols SAMs.

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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>.

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