J|A|C|S
COMMUNICATIONS

Balance of Structure−Building Forces in Selenium-Based Self-Assembled Monolayers

Andrey Shaporenko,† Jan Müller,‡ Tobias Weidner,† Andreas Terfort,‡ and Michael Zharnikov*,†

Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany, and Anorganische und Angewandte Chemie, Universität Hamburg, 20146 Hamburg, Germany

Received December 13, 2006; E-mail: michael.zharnikov@urz.uni-heidelberg.de

Although covalently bound self-assembled monolayers (SAMs) have been known for more than two decades and are now integrated in a number of technical applications,[1,2] efforts in understanding the factors determining their structure started only recently. While most work focused on the influence of the structure of the carbon backbone, it became apparent lately that the binding geometry around the first surface-bound atom (the so-called anchoring group) is of outstanding importance. By using suitable hybrid systems, it could be shown for the most popular SAM system of thiolates on coinage metals that the substrate-dependent binding geometry—which might be formulated as the hybridization of the sulfur atom—is the determining factor for the orientation of the alkyl chains and consequently the structure of alkanethiol (AT) SAMs.[3−6] For this particular system, the experimental data implied an sp^3 bonding configuration of the chemisorbed sulfur head group on Au(111) and sp bonding on Ag(111) associated with surface−S−C angles of ~104 and ~180°, respectively.[3−6]

Theoretical calculations predicted that the substitution of the sulfur anchoring atom by selenium would result in a more flexible binding geometry[7] and thus permit a higher influence of the molecular backbone on the orientation of the molecules in the respective SAMs. Here we wish to report that the substrate−Se bond is of much higher directional character than previously anticipated,[8−11] which has direct implications for the basic understanding of the structure−building interactions in SAMs and the design of Se-based SAMs, in particular. The latter SAMs can be of special interest for molecular electronics since selenium offers a better electronic match for the metal surface than usually used sulfur.[12−14] As was shown recently, contact resistance of the anchor group is of crucial importance for the electronic transport in molecular junctions.[15]

The systems used in this study are SAMs of hybrid 4,4′-biphenyl-substituted alkaneselenolates, $CH_3(C_6H_4)_2(CH_2)_nSe^-$ (BPnSe, $n = 2-6$), on gold and silver substrates. In the BPnSe films, the intermolecular interaction between the SAM constituents is predominately mediated by the biphenyl moieties, whereas the relatively short alkyl part does not contribute significantly to this interaction. Under these circumstances, one can expect that the packing density and molecular orientation in the BPnSe SAMs do not depend on the length of the alkyl part if the substrate−selenium−carbon linkage behaves as a free joint or the aliphatic linker adapts an arbitrary conformation to suit the arrangement of the biphenyl moieties, determined by their interaction. However, the exactly opposite behavior is observed; see Figure 1. As follows from the quantitative evaluation of the X-ray photoemission data, the effective thickness of the BPnSe SAMs on both Au and Ag does not exhibit a continuous increase with increasing length of the aliphatic linkage, expected within the above assumptions, but shows a systematic zigzag variation overimposed onto the general increase trend.

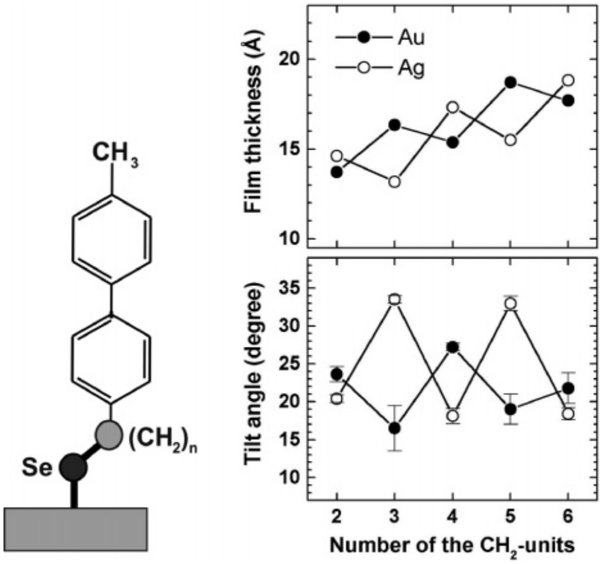

Figure 1. Left: a scheme of the BPnSe molecules. Right: effective thickness of the BPnSe SAMs (top panel) and the average tilt angle of the biphenyl moieties (bottom panel) in these films as functions of the number (n) of the methylene units in the alkyl part of the molecules. The plots exhibit a systematic zigzag-like variation of the packing density and molecular inclination in the BPnSe SAMs with varying n.

This systematic variation suggests that the packing density of the BPnSe SAMs depends on the length of the alkyl part of the BPnSe molecules in a specific, "odd−even" way. For Au, a higher packing density is observed for an odd n, whereas a lower packing density occurs at an even n. For Ag, the exactly opposite relation between the packing density and n takes place. The relative change in the packing density at going from odd to even n or from even to odd n is approximately 15 and 20% for the BPnSe SAMs on Au and Ag, respectively.

The odd−even variation of the packing density should be accompanied by the corresponding variation in the inclination of the SAM constituents. The respective information can be derived from near-edge X-ray absorption fine structure (NEXAFS) experiments. The NEXAFS spectra of all BPnSe SAMs (not shown) exhibited pronounced absorption resonances of the phenyl rings, with the dominance of the characteristic π_1^* resonance at 285.1 eV. The observed linear dichroism of the above resonances, that is, dependence of their intensity on the incidence angle of linear polarized X-ray light, suggests that the biphenyl moieties in the BPnSe SAMs have an upright orientation. The derived values of the average tilt angle of these moieties (with respect to the surface normal) could be obtained from the numerical analysis of the NEXAFS data (see refs 6 and 11 for the procedure description).

---

† Universität Heidelberg.
‡ Universität Hamburg.

10.1021/ja068916e CCC: $37.00

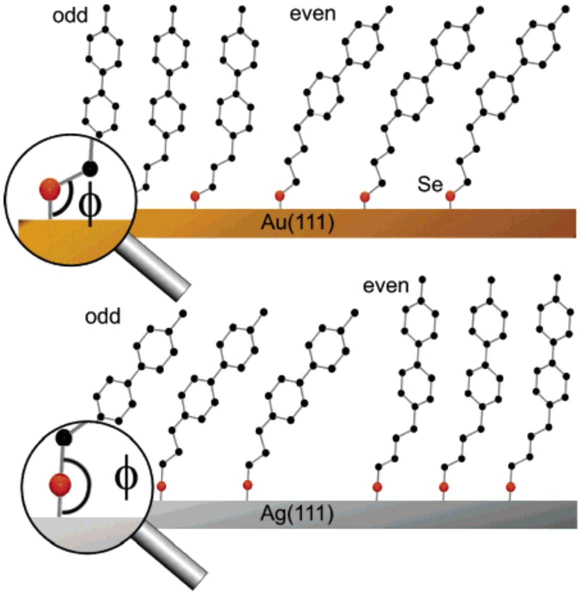

Figure 2. Schematic drawings of the orientation and packing of the BPnSe molecules in the respective SAMs on Au(111) (top) and Ag(111) (bottom) for an odd and an even number of methylene entities in the alkyl part. There is a significant energy contribution from the hybridization of the selenium atom, associated with the definite substrate−Se−C bonding angle ϕ, which is different on Au and Ag.

The results are presented in Figure 1 (bottom panel). As shown in this figure, the average tilt angle of the biphenyl moieties exhibits a systematic zigzag variation with the varying number of CH_2 units in the alkyl part of the BPnSe molecules. For Au, smaller molecular inclination is observed for odd *n*, whereas larger molecular inclination occurs at even *n*. For Ag, the relation between the molecular inclination and *n* is exactly opposite. The change of the average tilt angle of the biphenyl moieties going from odd to even *n* or from even to odd *n* is approximately 6−9 and 14° for the BPnSe SAMs on Au and Ag, respectively.

The odd−even changes in the packing density and inclination of the biphenyl moieties in the BPnSe SAMs correlate with each other. A smaller molecular inclination, as it, for example, occurs for an odd *n* on Au, corresponds to a larger packing density, and vice versa, as it, for example, takes place for an even *n* on Au. The film thicknesses calculated by the multiplication of the molecular length by the cosine of the respective tilt angle correlate well with the XPS-derived values. It can then be reasonably assumed that the zigzag changes in the packing density of the biphenyl moieties result from the respective variation of molecular inclination since strongly inclined molecules require more space that less inclined ones.[1]

The changes in molecular inclination of the biphenyl moieties can only be caused by the changes in the orientation of the adjacent CH_2-CH_2 segment of the alkaneselenolate anchor. The latter can, in turn, only be explained by dropping the “free joint” model for the substrate−selenium−carbon linkage and assuming the persisting all-trans conformation for the alkyl part. The free joint description should be exchanged for a model suggesting a predominant surface−Se−C angle, associated with a definite hybridization of the selenium atom in the alkaneselenolate SAMs. Assuming an sp^3 bonding configuration of the chemisorbed selenium headgroup on Au(111) and sp bonding on Ag(111), analogous to the sulfur headgroup in AT SAMs,[3−6,16] one gets the predominant substrate−Se−C angles of ∼104 and ∼180°, respectively. Mediated by the all-trans oriented alkyl chain, this yields a more tilted orientation for the last CH_2-CH_2 segment of this chain for an odd *n* on Au and an even *n* on Ag, as schematically shown in Figure 2. This orientation allows for a more upright orientation of the adjacent biphenyl moieties (a smaller tilt angle) and, consequently, for a denser molecular packing, exactly as observed in our experiment (see Figure 1). Similarly, for an even number of the CH_2 units in the BPnSe SAMs on Au or for an odd number of these entities for the films on Ag, a less tilted orientation of the last segment of the alkane chain is predicted, resulting in a larger tilt of the adjacent biphenyl moieties and, thus, in a reduced density.

The most important finding of the present study is that the bonding configuration of the selenium headgroup is the deciding factor in the balance of structure−building interactions in the alkaneselenolate SAMs. The energy associated with the persistence of this configuration is high enough to prevail over the energy gain associated with the optimal (i.e., dense) packing of the biphenyl moieties in the BPnSe SAMs. Considering that the similar effects have been observed in AT SAMs as well,[3−6] we can conclude on the generality of this phenomenon, stating that the exact bonding configuration of the headgroup is an important or even deciding factor in the balance of different contributions responsible for the molecular packing and structure of aliphatic self-assembled monolayers. Note that different bonding configurations of S and Se on Au and Ag substrates can be related to different coordinations on these two substrates.[17,18]

Acknowledgment. We thank M. Grunze for the support, Ch. Wöll for technical cooperation at BESSY, and the BESSY II staff for their assistance. This work has been supported by DFG (ZH 63/9-2) and the German BMBF (05 KS4VHA/4).

Supporting Information Available: Information on the sample preparation and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533−1554.
(2) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103−1169.
(3) Zharnikov, M.; Frey, S.; Rong, H.; Yang, Y. J.; Heister, K.; Buck, M.; Grunze, M. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3359−3362.
(4) Rong, H. T.; Frey, S.; Yang, Y. J.; Zharnikov, M.; Buck, M.; Wühn, M.; Wöll, C.; Helmchen, G. *Langmuir* **2001**, *17*, 1582−1593.
(5) Cyganik, P.; Buck, M.; Azzam, W.; Wöll, C. *J. Phys. Chem. B* **2004**, *108*, 4989−4969.
(6) Shaporenko, A.; Brunnbauer, M.; Terfort, A.; Grunze, M.; Zharnikov, M. *J. Phys. Chem. B* **2004**, *108*, 14462−14469.
(7) Mankfors, S.; Grigoriev, A.; Wendin, G. *Nanotechnology* **2003**, *14*, 849−858.
(8) Yee, C. K.; Ulman, A.; Ruiz, J. D.; Parikh, A.; White, H.; Rafailovich, M. *Langmuir* **2003**, *19*, 9450−9458.
(9) Monnell, J. D.; Stapleton, J. J.; Jackiw, J. J.; Dunbar, T.; Reinerth, W. A.; Dirk, S. M.; Tour, J. M.; Allara, D. L.; Weiss, P. S. *J. Phys. Chem. B* **2004**, *108*, 9834−9841.
(10) Shaporenko, A.; Ulman, A.; Terfort, A.; Zharnikov, M. *J. Phys. Chem. B* **2005**, *109*, 3898−3906.
(11) Shaporenko, A.; Cyganik, P.; Buck, M.; Terfort, A.; Zharnikov, M. *J. Phys. Chem. B* **2005**, *109*, 13630−13638.
(12) Yaliraki, S. N.; Kemp, M.; Ratner, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 3428−3434.
(13) Di Ventra, M.; Lang, N. D. *Phys. Rev. B* **2002**, *65*, 045402−045409.
(14) Patrone, L.; Palacin, S.; Charlier, J.; Armand, F.; Bourgoin, J. P.; Tang, H.; Gauthier, S. *Phys. Rev. Lett.* **2003**, *91*, 096802/1−4.
(15) Engelkes, V. B.; Beebe, J. M.; Frisbie, C. D. *J. Am. Chem. Soc.* **2004**, *126*, 14287−14296.
(16) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152−7167.
(17) Yu, M.; Driver, S. M.; Woodruff, D. P. *Langmuir* **2005**, *21*, 7285−7291.
(18) Yu, M.; Bovet, N.; Satterley, C. J.; Bengio, S.; Lovelock, K. R. J.; Milligan, P. K.; Jones, R. G.; Woodruff, D. P.; Dhanak, V. *Phys. Rev. Lett.* **2006**, *97*, 166102/1−4.

JA068916E