

Effect of the Bending Potential on Molecular Arrangement in Alkaneselenolate Self-Assembled Monolayers

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Self-assembled monolayers (SAMs) of hybrid 4,4'-biphenyl-substituted alkaneselenolates, $\text{CH}_3(\text{C}_6\text{H}_4)_2(\text{CH}_2)_n\text{Se}$ (BPnSe) with a variable length of the aliphatic part ($n = 1-6, 10, 11$) have been prepared on (111) gold and silver substrates and characterized by a variety of complementary experimental techniques. The packing density of the SAM constituents and the orientation of the biphenyl moieties were found to exhibit a pronounced "odd-even" variation with the number (n) of methylene units in the aliphatic linker of BPnSe moieties, which was opposite on silver as compared to gold. In particular, a smaller inclination and a corresponding higher packing density of the biphenyl moieties was observed for odd numbers of the methylene units in BPnSe/Au and for even numbers of these units in BPnSe/Ag. The observed odd-even effects were explained by a significant bending potential, favoring definite orientation of the metal-Se-C bond and entering the balance of the structure-building interactions either cooperatively or competitively. The existence of this bending potential is supposed to be closely related to the exact bonding configuration of the headgroup atom, with the optimal substrate-Se-C angles being different for Au and Ag substrates. In view of the analogous behavior of thiolate-based systems, one can assume a common origin of the observed phenomena in chalcogen-based SAMs, in both of which the bonding configuration of the headgroup seems to be an important or even deciding factor in the balance of structure-building interactions.

1. Introduction

During the last two decades, self-assembled monolayers (SAMs), which are 2D polycrystalline films of rodlike molecules that are chemically anchored to a suitable substrate, have attracted considerable attention of both the scientific community and companies working in frontier areas of nanofabrication and bioengineering.¹⁻⁵ The interest in these systems is mostly related to their broad versatility. In particular, they allow the tailoring of different surface properties such as wetting, adhesion, lubrication, corrosion, and biocompatibility, serve as model systems and suitable materials for nanofabrication and lithography, and provide a general platform for future molecular electronics.³⁻⁵ These manifold applications are based on the flexible architecture of the SAM constituents, which generally consist of three essential parts: a headgroup that binds strongly to the substrate, a tail group that constitutes the outer surface of the film defining its chemical and physical properties, and a spacer that separates the head and tail groups.

The exact structure and packing density of a SAM result mostly from a complex interplay of the intermolecular and headgroup-substrate interactions as long as the interaction between the tail groups is weak.^{2,5} Analyzing the impact of the

headgroup-substrate interaction in the balance of the structure-building forces, one may not just consider its strength and the shape of the binding energy hypersurface for a particular SAM as can be frequently found in literature,² but must take into account the precise binding character and exact geometry of the molecular anchoring. The importance of the latter factors has been clearly evidenced for the most popular SAM systems—films of alkanethiolates (ATs) on noble metal substrates. As was shown recently by the example of biphenyl-, terphenyl-, and thiophene-substituted ATs, the spatial orientation of the binding orbitals of sulfur is a determining factor for the orientation of the alkyl chains and consequently the structure of AT SAMs.⁶⁻¹³ In the above films, the intermolecular interaction between the SAM constituents is predominantly mediated by the biphenyl, terphenyl, or thiophene moieties, whereas the relatively short alkyl part does not contribute significantly into this interaction. Under these circumstances, one can expect that the packing density and molecular orientation in these SAMs do not depend on the length of the alkyl part, as long as the substrate-sulfur-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. In contrast, significant changes in the packing density and orientation of the SAM constituents were observed.⁶⁻¹³ These changes had a zigzag-like character, exhibited the opposite directions for the Au and Ag substrates, and could be clearly correlated with the parity of the number of methylene units in the alkyl linker. The above findings disagree with the free joint model and suggest the existence of a significant bending potential for the substrate-sulfur-carbon moiety, with a definite preferable bond angle at the chemisorbed

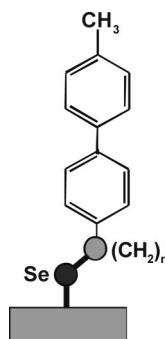
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SCHEME 1: Schematic sketch of the BPnSe molecules ($n = 1-6, 10, 11$)


sulfur headgroup. This potential is believed to be the third major player in the balance of structure-building forces in AT SAMs.⁶⁻¹⁰ Its existence was associated with a definite bonding configuration of the headgroup atom which, in the case of sulfur, was tentatively described as sp^3 and sp hybridization of the S atom on Au(111) and Ag(111), respectively.⁶⁻¹⁰ This hybridization can be associated with the preferable surface-S-C angles of $\sim 104^\circ$ for Au(111) and $\sim 180^\circ$ for Ag(111), which correlated precisely with the experimental data.^{6,7,10}

Recently, we reported that the presence of significant bending potential for the substrate-headgroup-carbon joint is not an exclusive property of thiolate, but characteristic of another headgroup, selenium,¹⁴ which represents a promising alternative to sulfur,¹⁵⁻²⁸ in particular in view of the higher structural quality of selenium-based SAMs²⁶⁻²⁸ and molecular electronic applications, since selenium offers a better electronics match for the metal surface than the usually used sulfur.²⁹⁻³² For SAMs of 4,4'-biphenyl-substituted alkaneselenolates $\text{CH}_3(\text{C}_6\text{H}_4)_2(\text{CH}_2)_n\text{Se}$ (BPnSe) with $n = 2-6$ on (111) Au and Ag substrates, we observed a similar odd-even behavior as for the analogous AT compounds (see above).¹⁴ In this article, we present a detailed study of the BPnSe system (see Scheme 1), complementing a short extract from the X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy data presented in our previous communication¹⁴ by detailed analysis of the respective spectra. Further, we present the results of several other complementary experimental techniques such as high-resolution XPS, infrared spectroscopy, ellipsometry, and contact angle goniometry, which allow a deeper insight into the properties of the BPnSe SAMs. Finally, we complement the results for the BPnSe films with $n = 2-6$ by the data for several further members of the series, viz., BP1Se, BP10Se, and BP11Se layers. The latter two systems are especially important, since the odd-even effects have so far only been observed in the SAMs with a short aliphatic linker ($n \leq 6$). It is open whether these effects persist as well at higher n or, in other words, whether a long aliphatic chain is capable to "transfer" the predominant bonding configuration of the headgroup to the biphenyl or terphenyl tailgroup.

In the following section we describe the experimental procedure and techniques. The results are presented and briefly discussed in section 3. An extended analysis of the data is given in section 4, followed by a summary in section 5.

2. Experimental Section

The target molecules were diselenide compounds, $\text{CH}_3(\text{C}_6\text{H}_4)_2(\text{CH}_2)_n\text{Se}-\text{Se}(\text{CH}_2)_n(\text{C}_6\text{H}_4)_2\text{CH}_3$ ($n = 1-6, 10, \text{ and } 11$) abbreviated below as BPnSe-SeBPn. The synthesis of these compounds is described elsewhere.³³ The gold and silver

substrates were prepared by thermal evaporation of 200 nm of gold or 100 nm of silver (99.99% purity) onto mica or polished single-crystal silicon (100) wafers (Silicon Sense) primed with a 5-nm titanium adhesion layer. The mica substrates were annealed at 320°C for 24 h prior to the metal evaporation, done at the same temperature. The evaporated films were polycrystalline, with a grain size of 20–50 nm for Si or a terrace size of 100–200 nm for mica as observed by atomic force microscopy and scanning tunneling microscopy. The grain surfaces predominantly possess a (111) orientation.^{34,35} The SAMs were formed by immersion of freshly prepared substrates into a 5- μmol solution of the target compounds in absolute ethanol at room temperature for 24 h. Due to the low solubility of BPnSe-SeBPn in ethanol, the substance was preliminary dissolved in toluene to 1-mmol concentration. After immersion, the samples were carefully rinsed with pure ethanol, blown dry with argon, and kept, if necessary, for several days in argon-filled glass containers until the characterization.

For comparison, SAMs of biphenyl selenolate (BP0Se: $\text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{Se}-$) were fabricated from dibiphenyl diselenide ($\text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{Se}-\text{Se}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$) using the same film preparation procedure as for the target compounds of this study.

The fabricated films were characterized by XPS (the spectra are not shown, since HRXPS is superior), high-resolution XPS (HRXPS), infrared reflection absorption spectroscopy (IRRAS), angle-resolved NEXAFS spectroscopy, ellipsometry, and contact angle goniometry. All experiments were performed at room temperature. The XPS, HRXPS, and NEXAFS measurements were carried out under UHV conditions at a base pressure better than 1.5×10^{-9} mbar. The spectra acquisition time was selected in such a way that no noticeable damage by the primary X-rays occurred during the measurements.³⁶⁻³⁹

HRXPS experiments were performed at the bending magnet beamline D1011 at the MAX II storage ring of the MAX-lab synchrotron radiation facility in Lund, Sweden. For these measurements, only the films on mica were used. The spectra were collected in normal emission geometry at photon energies of 150 eV for the Se 3d range and 350 and 580 eV for the C 1s range. In addition, Au 4f and Ag 3d spectra were acquired and the O 1s range was monitored. The binding energy (BE) scale of every spectrum was individually calibrated using the Au 4f_{7/2} emission line of AT-covered Au substrate at 83.95 eV. The latter value is given by the latest ISO standard.⁴⁰ It is very close to a value of 83.93 eV, observed by us for Au 4f_{7/2} using a separate calibration to the Fermi edge of a clean Pt foil.³⁵ The energy resolution was better than 100 meV, which is noticeably smaller than the full widths at half-maximum (fwhm) of the photoemission peaks addressed in this study.

HRXPS spectra were fitted by symmetric Voigt functions and either a Shirley-type or linear background. To fit the Se 3d_{5/2,3/2} doublet, we used a pair of such peaks with the same fwhms, a branching ratio of 3:2 (3d_{5/2}/3d_{3/2}) and a spin-orbit splitting (verified by fit) of ~ 0.86 eV (3d_{5/2}/3d_{3/2}).⁴¹ The fits were carried out self-consistently: the same peak parameters were used for identical spectral regions. The accuracy of the resulting BE/fwhm values in the case of HRXPS is 0.02–0.03 eV.

XPS measurements were performed using a Mg K α X-ray source and a LHS 11 analyzer. The spectra acquisition was carried out in normal emission geometry with an energy resolution of ~ 0.9 eV. The X-ray source was operated at a power of 260 W and positioned ~ 1.5 cm away from the samples. The fitting of the XPS spectra was performed in a similar way as for the HRXPS ones. Since the spectral quality

of the latter technique was superior, XPS data were only used to determine the effective thickness of the BPnSe SAMs. The thickness was determined on the basis of the $I_{\text{C1s}}/I_{\text{Au4f}}$ and $I_{\text{C1s}}/I_{\text{Ag3d}}$ intensity ratios, assuming a standard exponential attenuation of the photoelectron signal and using the attenuation lengths reported in ref 42 (the procedure has been verified for several reference samples).

NEXAFS spectroscopy measurements were performed at the HE-SGM beamline of the synchrotron storage ring BESSY II in Berlin, Germany. The spectra acquisition was carried out at the C K-edge in the partial electron yield mode with a retarding voltage of -150 V. Linear polarized synchrotron light with a polarization factor of $\sim 82\%$ was used. The energy resolution was ~ 0.40 eV. The incidence angle of the light was varied from 90° (E -vector in surface plane) to 20° (E -vector near surface normal) in steps of 10 – 20° to determine the orientational order in the SAMs. This approach is based on the dependence of the cross section of the resonant photoexcitation process on the orientation of the electric field vector of the synchrotron light with respect to the molecular orbital of interest (so-called linear dichroism in X-ray absorption).⁴³ Raw NEXAFS spectra were normalized to the incident photon flux by division through a spectrum of a clean, freshly sputtered gold sample. In the case of Ag substrate, a spectrum of clean silver was subtracted from the raw spectrum of a SAM sample before the normalization. Note that this procedure did not affect the resonance structure of the spectra, but just corrected for the difference in the electron yield between gold and silver in the given photon energy range, which made the comparison of the spectra for the samples on Au and Ag more straightforward.^{44,45} The photon energy scale was referenced to the pronounced π_1^* resonance of highly oriented pyrolytic graphite at 285.38 eV.⁴⁶

IRRAS measurements were performed with a dry-air-purged Bio-Rad FTIR spectrometer model FTS 175C equipped with a liquid nitrogen-cooled MCT detector. All spectra were taken using p-polarized light incident at a fixed angle of 80° with respect to the surface normal. The spectra were measured at a resolution of 2 cm^{-1} and are reported in absorbance units $A = -\log R/R_0$, where R is the reflectivity of the substrate with the monolayer and R_0 is the reflectivity of the reference. Substrates covered with a perdeuterated hexadecanethiolate SAM were used as a reference.

The ellipsometry measurements were carried out using an ellipsometer SE 400 (Sentech Instruments GmbH) under an incidence angle of 70° at a wavelength of 633 nm . A refractive index $n = 1.5$ was assumed for all films in the calculation of their thickness as an average between the refractive index for aromatic compounds (1.55) and the one typical for aliphatic compounds (1.45).⁴⁷

Advancing contact angles of Millipore water were measured on freshly prepared samples with a Krüss goniometer model G1. The measurements were performed under ambient conditions with the needle tip in contact with the drop. At least three measurements at different locations on each sample were made. The averaged values are reported. Deviations from the average were less than $\pm 1^\circ$.

3. Results

3.1. HRXPS. Normalized Se 3d HRXPS spectra of BPnSe/Au and BPnSe/Ag ($n = 2$ – 6) are presented in Figure 1 along with the corresponding fits (we will use the abbreviation BPnSe for the films formed from BPnSe–SeBPn). These spectra are representative for the entire data set, except for BP1Se/Au, which is a poor-quality film, and BP1Se/Ag (see below). The

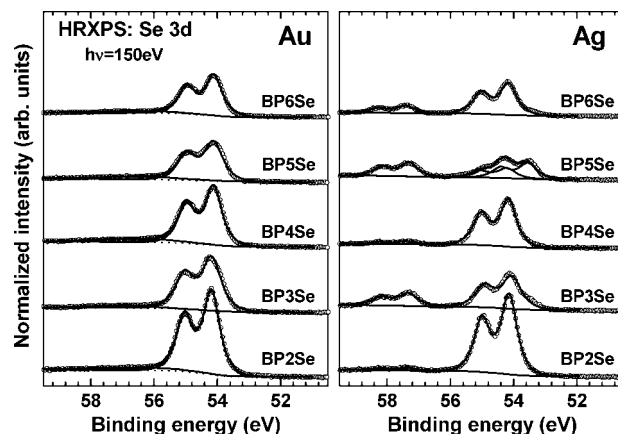


Figure 1. Normalized Se 3d HRXPS spectra of BPnSe/Au (left panel) and BPnSe/Ag (right panel) acquired at a photon energy of 150 eV , along with the corresponding fits (solid lines) by several individual Se $3d_{5/2,3/2}$ doublets and a background (see text for details).

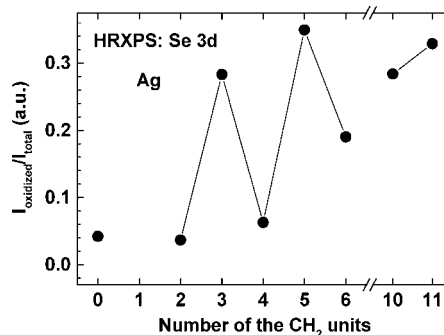


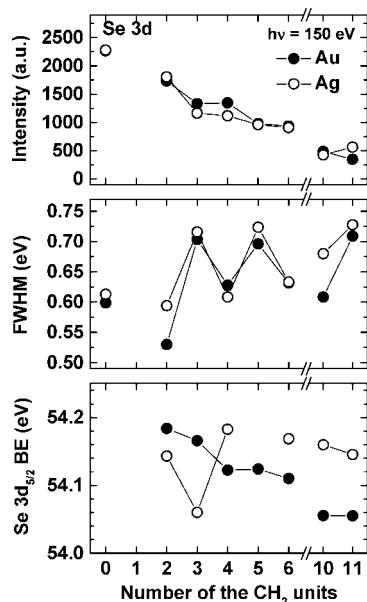
Figure 2. Relative weight of the Se 3d signal related to the oxidized headgroups in BPnSe/Ag.

Se 3d spectra of BPnSe/Au exhibit a single Se $3d_{5/2,3/2}$ doublet, accompanied by a weak Au $5p_{3/2}$ emission at higher BE. The BE position of this doublet (54.1 – 54.2 eV for Se $3d_{5/2}$) is distinctly different from that for the bulk diselenides, e.g., didodecyl diselenide (55.3 eV for Se $3d_{5/2}$),²² which suggests the expected^{25–27} cleavage of the covalent Se–Se bond and building of a selenolate–metal bond upon the adsorption of BPnSe–SeBPn on Au. The analogous doublet dominates the Se 3d spectra of BPnSe/Ag, suggesting that the adsorption of BPnSe–SeBPn occurs in a dissociative way on Ag substrate as well. However, for $n = \text{odd}$ and $n = 6$, this doublet is accompanied by an additional feature at a BE of 57.4 – 57.5 eV , which can be tentatively assigned to the oxidized selenolate (RSeO_3) in analogy to sulfonate species for thiolate-derived SAMs;⁴⁸ the relative intensity of the respective doublet is presented in Figure 2. Further, for $n = 5$, there is one more doublet at 53.55 eV , which is presumably related to differently bound selenolate species. Analogous features are frequently observed in the HRXPS spectra of thiolate-derived SAMs.¹¹

An overview of the selenium-derived species observed in the spectra of the BPnSe films on Au and Ag is presented in Table 1. As was mentioned above, Se 3d spectra of these films are exclusively composed of or dominated by the selenolate-related doublet with only exception of the BP1Se layers. The Se 3d spectrum of BP1Se/Au (not shown) exhibits a superposition of the doublets related to selenolate, differently bound selenolate, SeO_2 , and SeO_3 species, with the approximately equal intensities of the two former and two latter features. The Se 3d spectrum of BP1Se/Ag (not shown) exhibits, in addition to the selenolate-related doublets, a noticeable intensity stemming from diselenide

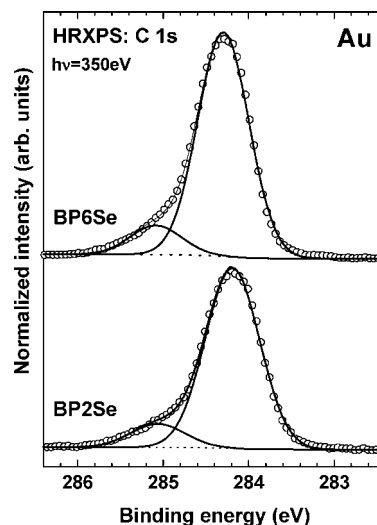
TABLE 1: Binding Energies of Selenium-Derived Species Observed in the HRXPS Spectra of BP n Se Films on Au and Ag

| species | differently bound selenolate | selenolate | diselenide or unbound selenium | RSeO ₂ | RSeO ₃ |
|-----------------------------|------------------------------|------------|--------------------------------|-------------------|-------------------|
| Se 3d _{5/2} BE, eV | 53.5–53.6 | 54.1–54.2 | 55.3 ^a | 57.0 | 57.4–57.5 |

^a Reference 22.**Figure 3.** Total intensity of the Se 3d signal (top panel), fwhm of the Se 3d_{5/2,3/2} components (middle panel), and BE (Se 3d_{5/2}) of the selenolate-related doublet (bottom panel) for BP n Se/Au (●) and BP n Se/Ag (○). In the bottom panel, the data for BP5Se/Ag are excluded because of the large spectral weight of the differently bound selenolate species.

or unbound selenol. Both BP1Se/Au and BP1Se/Ag spectra have been reproduced several times with different, individually prepared samples, so that we consider them representative of these particular films and assume that there is a specific chemistry going between the BP1Se–SeBP1 species and the Au and Ag substrates. This chemistry is obviously different from that for all other BP n Se–SeBP n compounds of this study, which show a consistent behavior independent of the n value. In view of the specific properties of the BP1Se–SeBP1-derived films, we will mostly exclude them from consideration below in the paper.

Total intensity of the Se 3d signal, fwhm of the Se 3d_{5/2,3/2} components, and BE position of the selenolate-related doublet (except for $n = 1$) are presented in Figure 3. The total Se 3d intensity exhibits the expected continuous decrease with increasing length of the aliphatic linker, due to the increasing attenuation of the respective signal by a thicker film. This decrease is accompanied by a weak zigzag-like intensity variation, which is systematic for the films on Au and less systematic for the films on Ag. Similar effects were observed previously in the films formed from CH₃(C₆H₄)₂(CH₂) $_n$ SH (BP n S)⁴⁹ and C₆H₅(C₆H₄)₂(CH₂) $_n$ SH (TP n S)¹¹ on (111) Au and Ag and were related to the odd–even variation of the effective thickness of the above films. Also, the fwhm of the Se 3d_{5/2,3/2} components in the BP n Se SAMs exhibit pronounced and systematic odd–even variation with increasing length of the aliphatic linker. Similar behavior was previously observed in the BP n S⁴⁹ and TP n S¹¹ SAMs and ascribed to the variable heterogeneity of the adsorption sites of the headgroups at changing molecular arrangement at going from an odd to even n . Also the BE position of the selenolate-related doublet in the

**Figure 4.** C 1s HRXPS spectra of BP6Se/Au and BP2Se/Au (○) acquired at a photon energy of 350 eV, along with the corresponding fits (solid lines) by the main emission and high BE shoulder (solid lines). Background is shown by a dotted line.

BP n Se films exhibits a odd–even behavior, even though the respective effect is very weak and lies within the accuracy of the HRXPS measurements. A similar, but stronger effect has been previously observed in the BP n S SAMs⁴⁹ and associated with the odd–even straining of the headgroup–substrate bond at the variation of the packing density in the film.

In contrast to the common total intensity, fwhm, and BE behavior, oxidation of the headgroups occurs neither in the BP n S or in TP n S films.^{11,49} In the BP n Se SAMs, it takes place for Ag substrate only and exhibits a pronounced odd–even behavior, being extensive for the films with an odd n (see Figure 2).

C 1s HRXPS spectra of BP2Se/Au and BP6Se/Au are shown in Figure 4, representative of the entire data set. The spectra of all BP n Se SAMs except for BP1Se/Au (poor quality of the film) exhibit a main emission at 284.1–284.15 eV and a high BE shoulder at ~285.1 eV; the fwhm of both features is ~0.7 eV. Whereas the BE positions of both features vary in a nonsystematic way with increasing length of the aliphatic chain in the BP n Se films, the relative BE position of the shoulder exhibits a systematic odd–even variation, which on Ag is inverse to that on Au as shown in Figure 5. Also, the relative intensity of the high BE shoulder exhibits pronounced odd–even behavior with the opposite directions of changes on Au and Ag as shown in Figure 6. Note that, at a given photon energy of 350 eV, the C1s HRXPS spectra are mostly representative of the topmost part of the BP n Se films, since the attenuation of photoelectrons (a BE of ~284.1 eV) is maximal at a kinetic energy of 60–80 eV.⁵⁰ Thus, the high BE shoulder can be related either to the terminal CH₃ groups or the whole aromatic matrix, in which case it presumably represents a low-energy shakeup excitation.^{11,49} Note that we favor the latter assignment, since this shoulder is also observed for SAMs of nonsubstituted biphenyl thiolates and selenolates.^{26,51}

Due to the relatively low primary photon energy, HRXPS data are less suitable for determining effective thickness of the

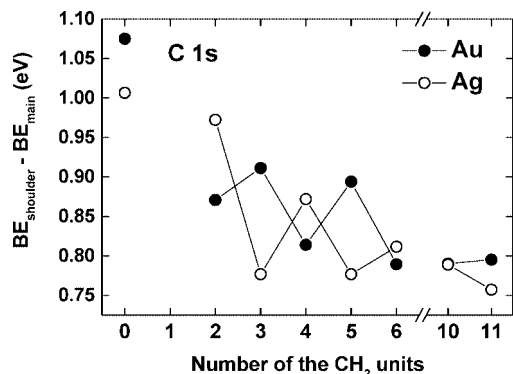


Figure 5. Relative BE position of the high BE shoulder with respect to the main emission in the C 1s HRXPS spectra of BPnSe/Au (●) and BPnSe/Ag (○).

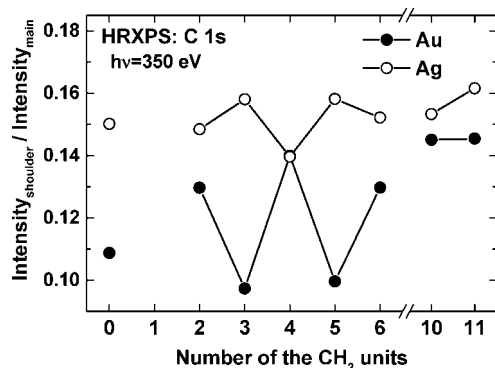


Figure 6. Ratio of the intensities of the high BE shoulder and main emission in the C 1s HRXPS spectra of BPnSe/Au (●) and BPnSe/Ag (○).

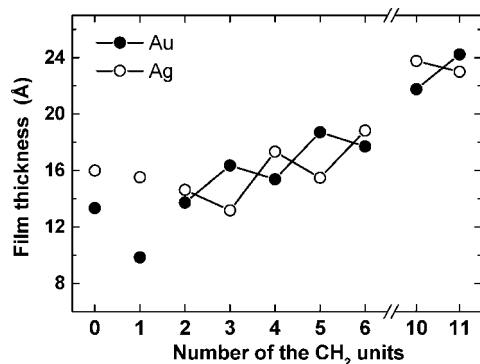


Figure 7. Effective thickness of BPnSe/Au (●) and BPnSe/Ag (○) derived from the XPS data (C1s/Au4f and C1s/Ag3d intensity ratios).

BPnSe films. For this purpose, XPS data suit better, since they were acquired with an Mg Ka X-ray source (1253.6 eV) and are, thus, more representative for the entire film.

3.2. XPS. The effective thicknesses of the BPnSe films derived from the XPS data are presented in Figure 7. With the only exception of the BP1Se films (poor film quality on Au and a “special” behavior on Ag), the effective thickness exhibits an expected continuous increase with increasing length of the aliphatic linkage. This general increase trend is, however, accompanied by a systematic zigzag intensity variation, which 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

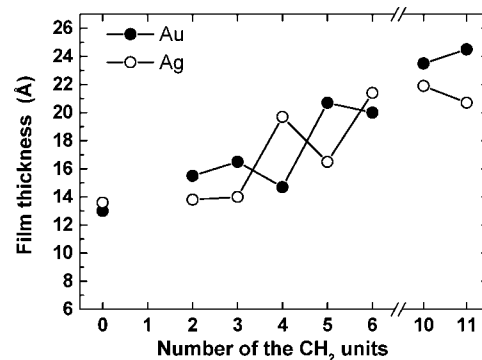


Figure 8. Effective thickness of BPnSe/Au (●) and BPnSe/Ag (○) derived from the ellipsometry data.

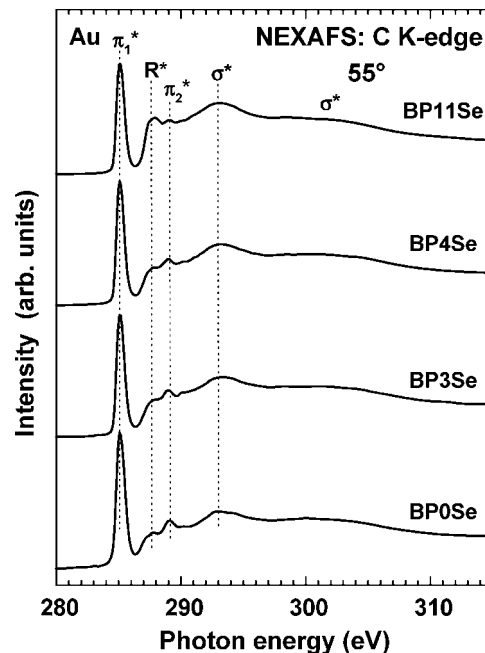


Figure 9. Carbon K-edge NEXAFS spectra of BPnSe/Au ($n = 0, 3, 4, 11$) acquired at an X-ray incident angle of 55°. Most pronounced absorption resonances are marked. Dotted lines are guides for eye.

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. Interestingly, the odd–even changes in the packing density occur not only at moderate lengths of the aliphatic linker ($n = 2–6$) but for large n ($n = 11, 12$) as well.

3.3. Ellipsometry. Complementary to XPS, the thickness of the BPnSe films was also probed by ellipsometry. The results are presented in Figure 8. Even though there is a difference in the absolute values of the thickness as compared to the XPS-derived ones for some of the films, the odd–even variation of the packing density exhibited in Figure 7 is reproduced well, supporting the conclusions of section 3.2.

3.4. NEXAFS Spectroscopy. Carbon K-edge NEXAFS spectra of some selected BPnSe SAMs acquired at an X-ray incident angle of 55° are presented in Figure 9, representative of the entire data set (except for BP1Se/Au). Note that the spectra acquired at a “magic” angle of 55° are not affected by the molecular orientation in the SAMs and are therefore exclusively representative of the electronic structure of the investigated films.⁴³ The spectra in Figure 9 exhibit characteristic absorption resonances of the phenyl rings^{43,52–56} and are

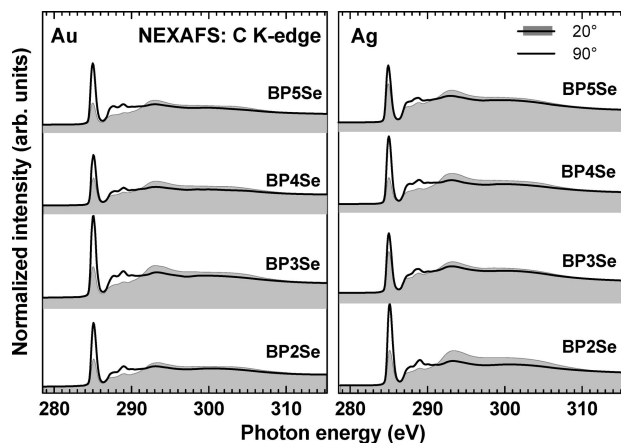


Figure 10. Carbon K-edge NEXAFS spectra of BP n Se/Au (left panel) and BP n Se/Ag (right panel) acquired at X-ray incident angles of 90° (thick line) and 20° (shadowed), respectively.

dominated by the intense π_1^* resonance at ~ 285.0 eV, which is accompanied by the weaker π_2^* resonance at ~ 288.9 eV and several broad σ^* resonances at higher photon energies. These resonances overlap with characteristic features of the aliphatic linker, most pronounced of which is so-called Rydberg resonance (R^*) at 287.7 eV.^{57–60} In accordance with the molecular composition of BP n Se, the intensity of this resonance increases with increasing length of the aliphatic linker as clearly seen in Figure 9.

Carbon K-edge NEXAFS spectra of some selected BP n Se SAMs acquired at X-ray incident angles of 90° and 20° are presented in Figure 10, representative of the entire data set (at least 5 spectra at different X-ray incident angles for every sample). The spectra exhibit a pronounced linear dichroism, i.e., a dependence of the absorption resonance intensity on the X-ray's incidence angle. Such a dependence is a fingerprint of the orientational order and is related to the fact that the cross section of the resonant photoexcitation process depends on the orientation of the electric field vector of the synchrotron light with respect to the molecular orbital of interest.⁴³ Considering that the transition dipole moment (TDM) of the π^* resonances is oriented perpendicular to the plane of the phenyl rings in the BP n Se molecules, a higher intensity of these resonances at an X-ray incident angle of 90° suggests that the biphenyl moieties in the BP n Se SAMs have an upright orientation (the opposite intensity relation occurs for the σ^* resonances, whose TDMs are oriented within the ring's plane). Further, the larger difference between the 90° and 20° resonance intensity observed for odd n on Au and even n on Ag (as compared to even n on Au and odd n on Ag) implies the odd–even variation of the molecular inclination in both BP n Se/Au and BP n Se/Ag. This effect was also numerically evaluated using the entire set of the NEXAFS spectra and a standard evaluation procedure.⁴³ For this purpose, the intensity of absorption resonances I was monitored as a function of the X-ray incidence angle θ and the resulting dependence evaluated according to the theoretical expression (for a vector-type orbital)⁴³

$$I(\alpha, \theta) = A \left\{ P \times \frac{1}{3} \left[1 + \frac{1}{2} (3 \cos^2 \theta - 1) (3 \cos^2 \alpha - 1) \right] + (1 - P) \frac{1}{2} \sin^2 \alpha \right\} \quad (1)$$

where A is a constant, P is a polarization factor of the X-rays, and α is the average tilt angle of the molecular orbital. To avoid an ambiguity related to decomposition of the spectra, the most

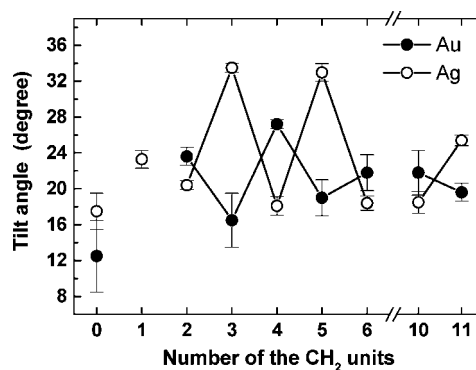


Figure 11. Average tilt angle of the biphenyl moieties in BP n Se/Au (●) and BP n Se/Ag (○) derived from the NEXAFS data. The error bars represent the accuracy of the theoretical fit and are not representative of the accuracy of the NEXAFS experiment, which is usually believed to be ± 3 –5°.

intense and well-separated π_1^* resonance has been selected for the evaluation. Equation 1 was slightly modified to take into account the twist of the biphenyl backbones.^{61,62} A herringbone packing of these backbones with a twist angle of 32°, which is close to that for bulk aromatic compounds,⁶³ was assumed.^{8,47,64,65} Note that a herringbone arrangement of the aromatic moieties optimizes the intermolecular interaction in the densely packed 2D-layers and is assumed to occur in aromatic SAMs.^{8,9,65} Note also that a significant twist angle in aromatic SAMs was evidenced by the analysis of Fourier transform infrared spectra for a variety of 4'-substituted biphenylthiolate SAMs on Au^{66,67} and direct evaluation of NEXAFS spectra for a series of nitrile-substituted aromatic SAMs on Au.⁶⁸

The resulting values of the average tilt angles of the biphenyl moieties in the BP n Se films are presented in Figure 11. The accuracy of these values is ± 3 –5°, which is just a general accuracy of the NEXAFS experiment and data evaluation. However, most of these values were reproduced in the control experiments with a significantly higher accuracy. According to Figure 11, the average tilt angle of the biphenyl moieties exhibits a systematic zigzag variation with the varying length of the aliphatic linker in the BP n Se 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 changes of the average tilt angle of the biphenyl moieties at going from odd to even n or from even to odd n are approximately 6–9° and 14° for the BP n Se SAMs on Au and Ag, respectively. Interestingly, and in accordance with the XPS and ellipsometry data (see Figures 7 and 8), the odd–even variation of the average tilt angle occurs not only for moderate n ($n = 2$ –6) but also for large n ($n = 10, 11$) as well.

Note that the C K-edge NEXAFS spectra of BP1Se/Au (not shown) are distinctly different from the spectra of all other BP n Se films. The characteristic absorption features of the BP n Se molecules are quite weak in these spectra, and almost no linear dichroism is observed. This result correlates with the Se 3d HRXPS spectra of these films (see section 3.1) and suggests that the BP1Se–SeBP1 precursor does not form a well-defined BP1Se SAM but rather a low-density, poor-quality film. In contrast to BP1Se/Au, the NEXAFS spectra of BP1Se/Ag look very similar to the spectra of all other BP n Se films, and a pronounced linear dichroism, similar to all other BP n Se films, is exhibited. In view of these results and the Se 3d HRXPS data (see section 3.1) we can assume that densely packed and ordered BP1Se SAMs are formed upon the adsorption of the

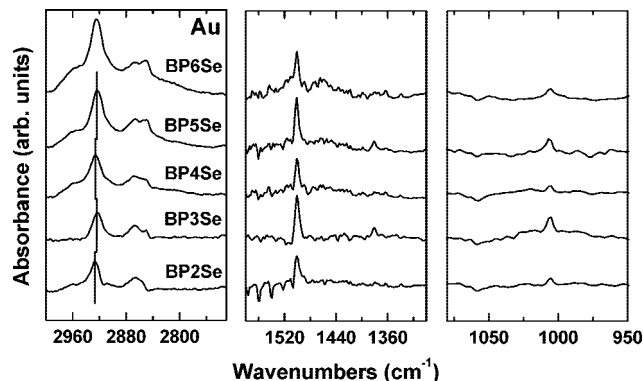


Figure 12. IRRAS spectra of BP n Se/Au ($n = 2-6$) for three characteristic regions (see text for details).

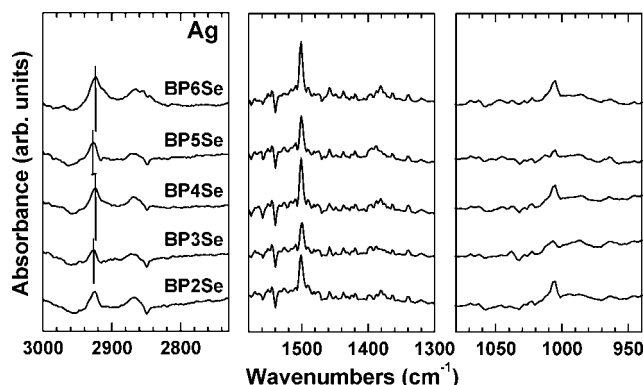


Figure 13. IRRAS spectra of BP n Se/Ag ($n = 2-6$) for three characteristic regions (see text for details).

BP1SeSeBP1 precursor onto the Ag(111) substrate, but these SAMs contain some amount of physisorbed BP1Se–SeBP1 species located, presumably, at the SAM–ambient interface.

3.5. IRRAS. The IRRAS spectra of BP n Se/Au and BP n Se/Ag ($n = 2-6$) for three selected regions are presented in Figures 12 and 13, respectively. These spectra exhibit characteristic absorption bands of the building blocks of the BP n Se molecules. First, there are the characteristic bands of the biphenyl moiety, namely, the C=C ring stretching mode at ~ 1475 cm^{-1} and the C–H bending mode at ~ 1004 cm^{-1} (the above and below mode assignment was performed in accordance with refs 7, 69 and 70). Second, there are bands related to the aliphatic linker, namely, asymmetric (ν_a) and symmetric (ν_s) C–H stretching bands of methylene at ~ 2920 and ~ 2852 cm^{-1} , respectively. Third, there is a weak band assigned to the tail group, namely, the C–CH₃ symmetric deformation band at ~ 1381 cm^{-1} . The results of the quantitative evaluation of the IRRAS spectra are presented in Figures 14–16.

In Figure 14, the intensities of the characteristic absorption bands of the biphenyl moiety are depicted. These intensities exhibit pronounced zigzag-like odd–even behavior with varying length of the aliphatic linker. For Au, higher intensity of these modes is observed for odd n , whereas smaller intensity is exhibited at even n . For Ag, the relation between the absorbance and n is exactly opposite. Considering that the TDMs of both C=C stretching and C–H bending modes are oriented along the 4–4' axis of the biphenyl moieties, the observed behavior can be explained by the odd–even variation of the molecular inclination in the BP n Se films. Taking into account the TDM orientation and selection rules for IRRAS (only modes with the TDM parallel to the substrate normal are visible),⁶⁹ higher absorbance of the C=C stretching and C–H bending modes corresponds to a smaller molecular inclination, whereas the

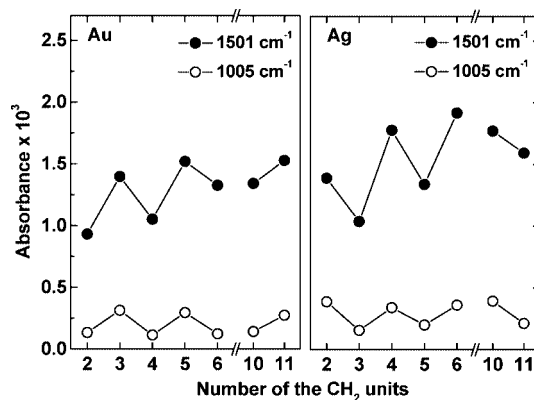


Figure 14. Intensities of the characteristic absorption bands for the C–H stretching modes (full squares) and C=C ring modes (hollow squares) in BP n Se/Au (left panels) and BP n Se/Ag (right panels) derived from the spectra in Figures 12 and 13.

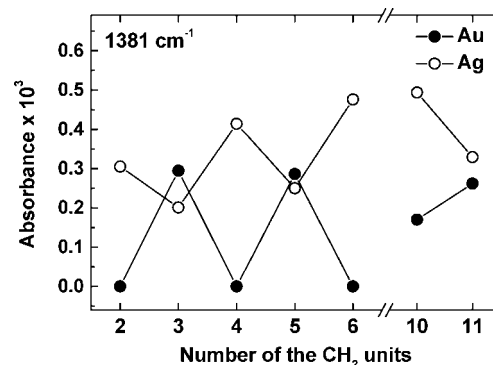


Figure 15. Intensities of the characteristic absorption bands for the C–CH₃ symmetric deformation in BP n Se/Au (●) and BP n Se/Ag (○) derived from the spectra in Figures 12 and 13.

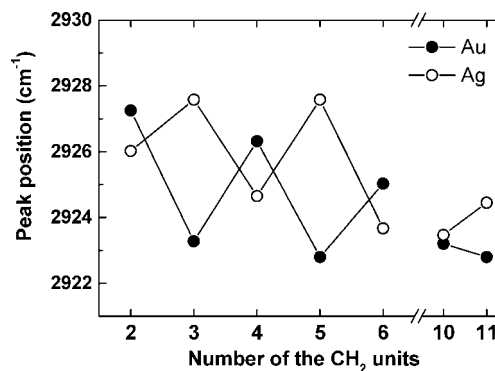


Figure 16. Positions of the asymmetric C–H stretching mode in BP n Se/Au (●) and BP n Se/Ag (○) derived from the spectra in Figures 12 and 13.

lower absorbance is associated with a larger tilt. Thus, according to the data in Figure 14, BP n Se moieties are less inclined for odd than for even n on Au, and for even than for odd n on Ag, in full agreement with the NEXAFS data (see Figure 11). This statement is additionally supported by Figure 15, where the intensities of the characteristic absorption bands for the C–CH₃ symmetric deformation in the BP n Se films are presented. The behavior of these intensities mimics those for the C=C stretching and C–H bending modes of the biphenyl moiety, which is understandable considering that, due to the rigidity of the BP n Se molecule, the TDM of the C–CH₃ symmetric deformation is also oriented along the 4–4' axis of these moieties.

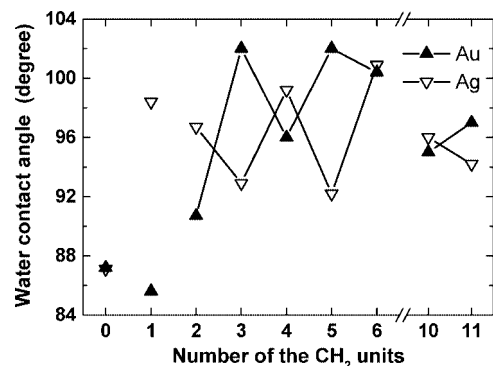


Figure 17. Advancing water contact angles for BPnSe/Au (up filled triangles) and BPnSe/Ag (down open triangles).

The odd–even variation of the packing density and inclination of the biphenyl moieties in the BPnSe SAMs is accompanied by the changes in the aliphatic part of these films. In Figure 16, positions of the characteristic C–H stretching modes in the BPnSe SAMs are presented. These positions exhibit pronounced zigzag-like behavior depending on the parity of n . The modes are shifted to lower wavenumbers for odd n in BPnSe/Au and for even n in BPnSe/Ag. This shift can be associated with a better crystallinity of the aliphatic part in the BPnSe films at these particular n . In fact, the positions of the methylene stretching bands are generally considered as a fingerprint of the molecular conformation in aliphatic systems. In particular, the corresponding values for the asymmetric and symmetric bands in well ordered AT SAMs with all-trans molecular conformation are ~ 2920 and ~ 2852 cm^{-1} , respectively.^{71,72} Each gauche bond shifts the vibrational frequencies of the adjoining methylene groups by 10–20 wavenumbers. A liquid alkane at room temperature has $\sim 40\%$ C–C gauche conformations and peak maximums at 2928 and 2856 cm^{-1} .⁷¹ Thus, on the basis of the data presented in Figure 16, we can conclude that the aliphatic linkers in BPnSe/Au with odd n and BPnSe/Ag with even n have predominantly all-trans conformation with a low concentration of gauche defects, whereas the aliphatic part of BPnSe/Au with even n and BPnSe/Ag with odd n is noticeably disordered and contains a significant amount of gauche defects. An additional trend, visible in Figure 16 and overimposed onto the general zigzag-like behavior, is a continuous shift of the positions of the asymmetric C–H stretching mode to lower wavenumbers with increasing length of the aliphatic linker. This tendency is understandable considering that an aliphatic film composed of longer chains usually exhibits a higher crystallinity than one consisting of shorter chains.⁷³

3.6. Wetting Properties. The odd–even variation of the packing density, the orientational order in the BPnSe SAMs, and, in particular, the resulting odd–even changes in the inclination of the terminal methyl groups (see Figure 15) should result in a variation of the wetting properties of these films. Indeed, such a variation occurs as demonstrated by Figure 17, in which the advancing water contact angles (θ_a) for BPnSe SAMs are presented. BPnSe/Au with odd n and BPnSe/Ag with even n exhibit higher θ_a values as compared to BPnSe/Au with even n and BPnSe/Ag with odd n , respectively. This is understandable taking into account that BPnSe/Au with odd n and BPnSe/Ag with even n are densely packed (see above) and the terminal methyl groups in these films have more upright orientation as compared to their counterparts (see Figure 15). Apart from the odd–even behavior, θ_a values for all BPnSe SAMs are noticeably higher than those for the BP0Se films, which is explained by the difference in the CH₃ (BPnSe) and

H (BP0Se) terminations. As for the films with the CH₃ tailgroup, θ_a values for all BPnSe films are noticeably larger than that for the SAMs formed from CH₃–(C₆H₄)₂–SH on Au, which is 85°⁶⁷ (regretfully, no θ_a data for the respective SAMs with the selenolate headgroup are available), but comparable to the analogous values for the BPnS films.⁷

4. Discussion

The results of all experimental techniques used in this study consistently evidence that high-quality selenolate SAMs can be formed on both (111) Au and Ag substrates from the BPnSe–SeBPn precursors with a large variety of the alkyl linker lengths. The only exception in the series ($n = 1–11$) are BP1Se films, which exhibited a poor quality and a large amount of different selenide-derived species on Au and revealed a chemical inhomogeneity (a noticeable amount of the physisorbed molecules) on Ag, even though the orientational order in the latter films was quite high. Other BPnSe SAMs did not exhibit any contamination or inhomogeneity, except for the films with odd n on Ag, where a noticeable part of the selenolate headgroups was oxidized (see Figure 1 and discussion below).

The BPnSe SAMs exhibit a pronounced zigzag-like variation of the packing density and inclination of the biphenyl moieties with the varying length of the alkyl linkage situated between the selenolate headgroup and biphenyl spacer. The packing density changes were clearly observed by XPS, HRXPS, and ellipsometry, while the variation of the biphenyl inclination, which clearly correlated with the packing density changes, was independently evidenced by NEXAFS spectroscopy and IRRAS. Also, contact angle goniometry showed pronounced changes of the wetting properties, related to the combining effect of the orientation and packing density of the terminal methyl groups. In view of the zigzag character of the observed changes, the occurrence of either high or low packing density (or, respectively, small or large inclination of the biphenyl moieties) can be unequivocally correlated with the parity of the number of methylene units in the alkyl part of the BPnSe molecules. For Au, higher packing density and smaller inclination of the biphenyl moieties are observed for odd n , whereas lower packing density and larger biphenyl inclination are characteristic of even n . For Ag, the relation between the packing density and biphenyl inclination on one side and n (either odd or even) on the other side is exactly opposite.

Considering that a high packing density, as observed in BPnSe SAMs with an odd n on Au and an even n on Ag, is energetically more preferable than a low packing density, as observed in BPnSe SAMs with an even n on Au and an odd n on Ag, one can assume that there is an additional, powerful factor, which hinders the efficient molecular packing in the latter films. Taking into account the odd–even character of the observed changes and a negligible difference in the molecular composition between the odd and even counterparts, this factor can only be a strong bending potential of the substrate–headgroup–carbon joint. Such a potential gives a predefined orientation to the alkyl linkage, which, as far as this linkage has the all-trans conformation or, at least, a sufficient rigidity, “transfers” this orientation to the biphenyl moiety. If the geometry of the substrate–headgroup–carbon joint and the parity of the alkyl linkage fit to the energetically preferred, small inclination of the biphenyl moiety, high-density SAMs are formed, as it happens in the case of BPnSe SAMs with an odd n on Au and an even n on Ag. If the combination of this geometry and the linkage parity does not fit to the small inclination of the biphenyl moiety, the bending potential works

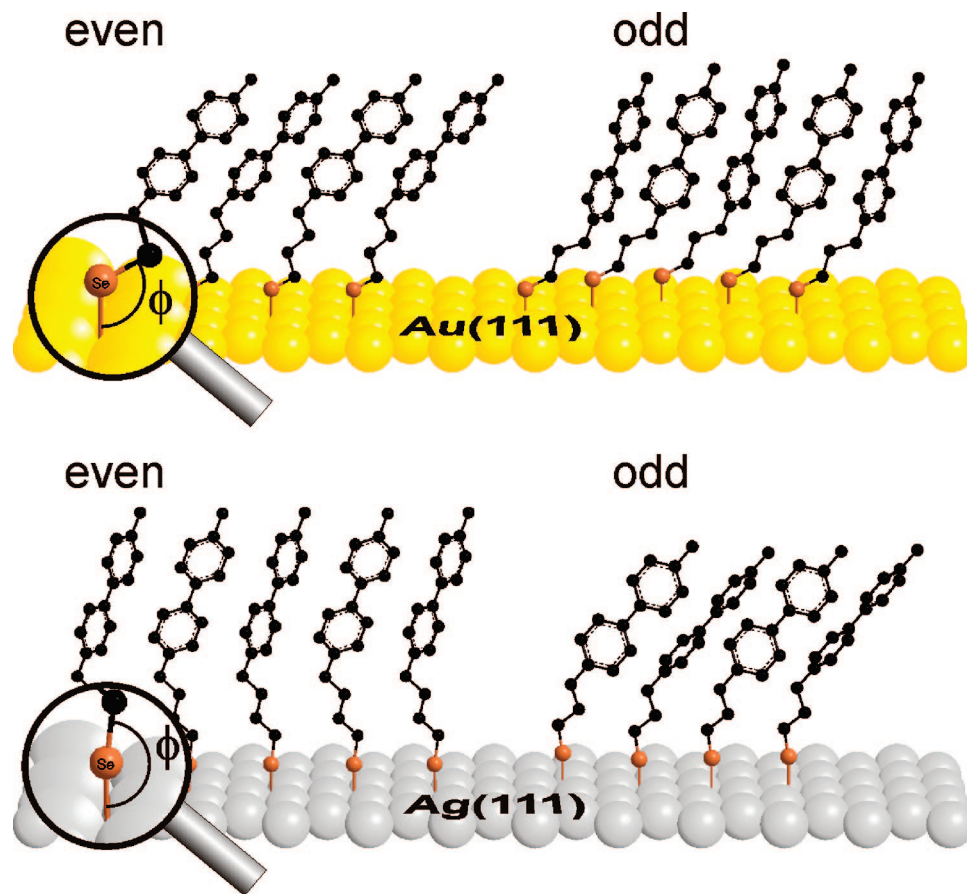


Figure 18. Schematic drawing of the orientation and packing of the BPnSe molecules in the respective SAMs on Au and Ag. The preferable values of the substrate–Se–C angles, ϕ are taken in analogy to the S case ($\phi_{\text{Au}} \sim 104^\circ$ and $\phi_{\text{Ag}} \sim 180^\circ$), even though one cannot probably associate these angles with the definite hybridization of Se atom as it has been done for S (see text for details).

against the intermolecular forces, and as the result, a compromise structure with a low-density packing will be achieved. The fact that we observe the relatively large inclination of the biphenyl moieties and low packing density in BPnSe SAMs with an even n on Au and an odd n on Ag suggests that the bending potential in these systems is an important factor, determining, to a large extent, the entire structure of the films.

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, 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 than less inclined ones.

The existence of the strong bending potential can be associated with a definite bonding configuration of the headgroup selenium atom. As mentioned above, in the case of thiolate, which shows the similar behavior, this configuration was tentatively described as sp^3 and sp hybridization of the S atom on Au(111) and Ag(111), respectively.^{6–10} However, this description is not directly applicable to the case of selenium, since the energy separation of the s and p orbitals is larger and the space overlap of these orbitals is much smaller for this element, so that the extent of sp hybridization is small as well, and neither sp^3 nor sp hybridization is in principle possible.^{74–78}

Thus, the presented results cast some doubt on our previous explanation for the origin of the bending potential in alkanethiolate SAMs on Au and Ag (see refs 6–10). Considering the striking similarity of the odd–even effects in the thiolate- and selenolate-based systems, this origin should be common. It is clear that, for both alkanethiolate and alkaneselenolate SAMs, the bending potential can be associated with the definite preferable substrate–headgroup–carbon angle, which is different for Au and Ag substrates, as schematically shown in Figure 18. If these angles are not related to a definite hybridization of the headgroup (sp^3 versus sp), they can be probably associated with different preferable local bonding geometries of the chalcogen headgroups on Au(111) and Ag(111). Whereas this geometry is not precisely known and remain a subject of ongoing vivid discussions (see, e.g., refs 79–84), there are indications that this geometry is distinctly different for Au(111) and Ag(111).^{81,83} Regrettably, there is not much theoretical work on odd–even effects in SAMs, but mostly experimental results (see, e.g., a recent review by Tao and Bernasek).⁸⁵ Available computer simulations reproduce general details of the odd–even behavior of BPnS SAMs, but relate this effect to the odd–even variation of the torsion angle between the adjacent phenyl rings comprising the biphenyl moiety.⁸⁶ This model, however, disagrees with recent results suggesting the planar conformation of the oligophenyl backbones in the respective SAMs.⁸⁷ Further, no significant change in the twist of the biphenyl moiety is observed upon the odd–even variation of the alkyl linker length in SAMs of nitrile-substituted biphenyl alkanethiols on Au(111).⁶⁷

Apart from the bending potential, the essential factor behind the observed odd–even effects is a certain rigidity of the aliphatic linker, which, as mentioned above, transfers the orientational “information” given by the bending potential to the biphenyl moiety. Would this linker be absolutely flexible, as one might assume for aliphatic chains, the substrate–headgroup–carbon joint and the biphenyl moieties would be fully decoupled, enabling a dense packing of the latter, independently of the length of the aliphatic linker. As shown for the first time in this study, such a rigidity is not only characteristic for short ($n \leq 6$) aliphatic linkers but for long ($n \geq 10$) linkers as well, since clear odd–even variation of the packing density and molecular inclination was observed for BP10Se and BP11Se SAMs. As far as the length (in terms of the parity of n) of the aliphatic linker, at the given bending potential, fits to the optimal, dense packing of the biphenyl moieties, the linker is not disturbed and can take the preferable, all-trans conformation with a low percentage of gauche defects. In fact, as shown in Figure 16, the positions of the asymmetric C–H stretching mode in densely packed BP n Se/Au ($n = \text{odd}$) and BP n Se/Ag ($n = \text{even}$) are 2923.3–2922.8 and 2926.0–2923.4 cm^{-1} , respectively, which is close (especially for Au) to the value for crystalline n -alkanes and high-quality alkanethiolate SAMs (2920 cm^{-1}).^{71,72,88} In contrast, the positions of the asymmetric C–H stretching mode in more loosely packed BP n Se/Au ($n = \text{even}$) and BP n Se/Ag ($n = \text{odd}$) are 2927.3–2925.0 and 2927.6–2924.5 cm^{-1} , respectively, which is close to the value for liquid n -alkanes (2928 cm^{-1}).⁸⁸ Note that the latter systems have $\sim 40\%$ C–C gauche conformations at room temperature.⁷¹ Thus, the aliphatic linker in the loosely packed BP n Se SAMs is mostly disordered but still rigid enough to transfer the predominant orientation given by the substrate–Se–C bending potential to the biphenyl units. The reason for this disordering is a competitive way, by which the intermolecular interaction, forcing a dense packing, and the bending potential, forcing a large inclination and consequently a loose packing of the biphenyl moieties, enter the energy balance. The resulting SAM structure represents then a compromise between these two factors, leading to a significant reduction of the observed odd–even effects as compared to the values one would obtain by pure geometrical analysis assuming a definite, most preferable bonding angle and the absolutely rigid, all-trans aliphatic linker.

Along with the definite rigidity discussed in details above, a longer aliphatic linker has more flexibility to disentangle the competitive forces associated with the bending potential and optimal (i.e., dense) molecular packing as compared to a short one, which results in a decreasing extent of the odd–even effects with increasing length of this linker as follows from all the experimental data.

Comparing the extent of the odd–even effects in biphenyl-substituted alkaneselenolate and alkanethiolate SAMs (i.e., in BP n Se and BP n S SAMs), we found that most of the characteristic parameters are comparable, even though the observed odd–even changes of the packing density and molecular inclination are slightly larger in case of the latter systems. In particular, 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 6–10° and 14° for the BP n Se SAMs on Au and Ag, respectively. For the BP n S SAMs on Au and Ag ($n = 3–6$), the analogous values are 12–14° and 16–17°, respectively.⁶ It is, however, difficult to make a meaningful conclusion on possible differences in the energetics of the Se–Au/Ag and S–Au/Ag bonds on the basis of these findings. Another prominent effect, observed exclusively for BP n Se SAMs (and

not for BP n S films), is the oxidation of the selenolate groups occurring only for the films on Ag with $n = \text{odd}$. This effect has been reproduced several times and is presumably related to the higher reactivity of Se as compared to S. We propose that this oxidation occurred after the formation of the above SAMs and can be explained by the poor quality (in terms of the orientational order) and low packing density of the hydrocarbon matrix in these particular films, so that chemically active oxygen-derived species could penetrate to the Se–substrate interface and oxidize the headgroups. Generally it is well-known that SAMs on Ag can be oxidized much easier than those on Au, as has been in particular shown by the example of biphenyl telluride films.⁸⁹

The odd–even variation of the molecular inclination and packing density in BP n Se SAMs should be accompanied by the respective changes in the exact molecular arrangement, similar to that occurring in BP n S^{8,9} and TP n S¹² films on Au(111) (there are regrettably no STM data for Ag). In these systems, a high-symmetry $(2\sqrt{3} \times \sqrt{3})R30^\circ$ lattice was observed for $n = \text{odd}$, whereas a less dense $c(5\sqrt{3} \times 3)$ arrangement, with different symmetry was recorded for $n = \text{even}$.^{8,9,12} Note that even though the $(2\sqrt{3} \times \sqrt{3})R30^\circ$ lattice mimics the symmetry of the substrate, it can be incommensurate due to a small mismatch between the optimal packing of the oligophenyl backbones and the exact template provided by the substrate. A fingerprint of the incommensurate lattice is the higher fwhm values for the S 2p emission from BP n S/Au⁴⁹ and TP n S/Au¹¹ with $n = \text{odd}$ as compared to $n = \text{even}$. The analogous relation is also observed for the Se 3d emission in BP n Se SAMs of this study (see Figure 3), which allows us to suggest its generality for both oligophenyl-substituted alkanethiolate and alkaneselenolate SAMs. The reason for the incommensurate lattice can be a strong interaction between the oligophenyl backbones, occurring at the dense molecular packing. Under this condition, the molecular lattice can be decoupled to some extent from the template provided by the substrate. It would be interesting to look at the exact molecular arrangement in BP n Se SAMs by STM or AFM, which we intend to do in the near future.

The molecular arrangement in BP n Se SAMs with loose packing (BP n Se/Au at $n = \text{even}$ and BP n Se/Ag at $n = \text{odd}$) can be unstable similar as it occurs in BP n S^{90–93} and TP n S SAMs,¹² where distinctly different structures were observed when the films were prepared at room (as in this study) and elevated temperatures. The reason for this effect is the compromise character of the molecular structure in these films, resulting from the interplay of the competitive interactions. Under these conditions, the balance can be easily shifted by the change of such an important thermodynamic parameter as temperature, so that a new molecular arrangement emerges. For BP n Se SAMs, we are planning to look into this phenomenon in the near future.

5. Summary

The packing density, structure, and orientational and conformational order in biphenyl-substituted alkanethiolate (BP n Se) SAMs with variable length of the aliphatic part ($n = 1–6, 10$, and 11) on polycrystalline (111) gold and silver substrates were studied by several complementary experimental techniques, including XPS, HRXPS, ellipsometry, NEXAFS spectroscopy, IRRAS, and contact angle goniometry. All the above techniques gave consistent results: the packing density and orientation of the biphenyl moieties in BP n Se SAMs (except for $n = 1$: low quality) were found to exhibit a pronounced zigzag-like variation depending on the parity of the number of methylene units in

the aliphatic part (linker) of the BPnSe moieties, which was opposite on silver than on gold. A higher packing density and a smaller inclination of the biphenyl moieties was observed for an odd number of methylene units in the aliphatic linker in BPnSe/Au and an even number of these units in BPnSe/Ag. Vice versa, a lower packing density and a larger inclination of the biphenyl moieties was found for an even number of the methylene units in the aliphatic linker in BPnSe/Au and an odd number of these units in BPnSe/Ag. Interestingly, the above effects were observed not only at small n ($n \leq 6$) as recorded before for the analogous thiol-based systems^{6–10} but also for relatively large n ($n = 10, 11$) as well. Another novel feature characteristic of BPnSe SAMs only is a partial oxidation of the selenolate headgroups in the loosely packed SAMs on Ag (i.e., at $n = \text{odd}$), which is presumably related to a higher reactivity of Se as compared to S.

The observed odd–even effects can only be explained by assuming that there is a significant bending potential related to the anchoring of the BPnSe moieties to the substrate. This quite “rigid” bending potential, favoring a definite substrate–Se–C bonding angle, which is different for Au(111) and Ag(111) substrates, enters into the balance of the structure-building interactions and defines to a high extent the entire structure of the films. Depending on the substrate and the parity of n , the bending potential enters either cooperatively or competitively into the balance of the structure-building interactions in BPnSe SAMs, resulting in respectively dense or loose molecular packing. The structure of the films in the latter case represents a compromise between the competitive interactions and can be associated with the presence of significant stress, which is released to some extent through a partial deviation from the optimal value of the substrate–Se–C angle and partial disordering of the aliphatic part of the BPnSe moieties. However, in spite of this disordering, the aliphatic linkers are rigid enough to “transfer” the predominate orientation given by the bending potential to the biphenyl moiety.

The odd–even effects in the BPnSe films are very similar to those observed previously in analogous thiol-based SAMs, viz. biphenyl- and terphenyl-substituted alkanethiols on Au and Ag,^{6–10,12} both in their dependence on the n parity and in their extent (even though the effects appear to be somewhat weaker compared to the BPnS films). This suggests a common origin of the observed phenomena in alkaneselenolate and alkanethiolate SAMs, in both of which the bonding configuration of the chalcogen headgroup seems to be an important or even deciding factor in the balance of structure-building interactions. 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) molecular packing. Significantly, the observation of the odd–even effects in the selenolate-based systems cast a doubt on the previous explanation of this effect by the preference of either sp^3 or sp hybridization for the headgroup.^{6–10} Since the extent of sp hybridization is expected to be much smaller for Se, but a common explanation should exist for both S and Se in view of the similar odd–even effects in the related systems, one can rather think that the preferable geometry of the adsorption site can be the reason for the existence of the strong bending potential. This geometry is assumed to be different on Au(111) and Ag(111),^{81,83} which explains the opposite directions of the odd–even changes on these two substrates.

An exact knowledge of all factors affecting the structure in monomolecular films is a valuable prerequisite for molecular engineering of SAMs, applications of these systems, and SAM-

based nanofabrication and lithography. As for the oligophenyl-substituted alkanethiolate and -selenolate films, the quality of the oligophenyl matrix is superior to that in pure aromatic systems (i.e., without the aliphatic linker between the oligophenyl part and headgroup).^{6–12} In particular, these molecules can be used for the fabrication of thiol-terminated surfaces.^{55,94} Further, the radiation sensitivity and electrochemical stability of the former systems can be precisely tailored by the variation in the packing density of their molecular constituents.^{85,95,96} Finally, a combination of high structural quality and radiation sensitivity of terphenyl-substituted alkanethiolates has been successively used in the fabrication of SAM-based monomolecular resists.^{97–99}

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