



Supporting Information

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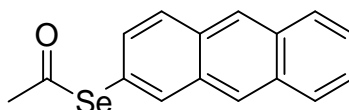
Selenium as a Key Element for Highly Ordered Aromatic Self-Assembled Monolayers

A. Bashir,¹⁾ D. Käfer,¹⁾ J. Müller,²⁾ Ch. Wöll,¹⁾ A. Terfort,²⁾ and G. Witte¹⁾

1) *Physikalische Chemie I, Ruhr-Universität Bochum, 44780 Bochum, Germany and*

2) *Fachbereich Chemie, Philipps-Universität Marburg, D-35032 Marburg, Germany*

Chemical synthesis of selenoacetic acid Se-anthracen-2-yl ester. 2-Bromoanthracene (1.13 g, 4.39 mmol)^[1] was dissolved in THF (80 ml), cooled down to -78°C and *tert.*-butyllithium (5.9 ml, 8.9 mmol) was added to this dropwise. After stirring during warming up to 0°C and cooling back to -78°C, black selenium powder (0.35 g, 4.4 mmol) was added. Again stirring upon warming up was done, following by addition of acetyl chloride (0.35 g, 4.5 mmol) into the cooled solution. Upon further stirring at room temperature, a colorless precipitate was formed. After adding water (100 ml), the aqueous phase was extracted with dichloromethane and the resulting organic phase washed with water (200 ml). After removal of the solvent in vacuum the crude yellow product (1.69 g) was subjected to column chromatography (silica, dichloromethane (5%-100%) / petrol ether, then silica, ethylacetate (5%-100% / petrol ether) and recrystallized from toluene yielding a yellow solid (0.40 g, 1.3 mmol, 30%).



¹H-NMR (400 MHz, CDCl₃) δ[ppm] = 8.42 (d, 2 H, *3J*=12.0 Hz), 8.22 (m, 1 H), 8.03-7.97 (m, 3H), 7.52 (dd, 1H, *J*=1.6Hz, *J*=8.8Hz), 7.51-7.47 (m, 3H), 2.53 (s, 3H). ¹³C-NMR (CDCl₃) δ [ppm] = 197.02, 135.86, 132.23, 131.89, 131.76, 131.30, 130.80, 129.01, 128.25, 128.15, 126.49, 126.32, 125.87, 125.74, 123.74, 34.17. ⁷⁷Se-NMR (CDCl₃) δ[ppm] = 487. Anal. calculated for C₁₆H₁₂OSe: C, 64.22; H, 4.04. Found: C, 64.39; H, 4.10.

Sample preparation. Anthraceneselenolate (AntSe) SAMs have been prepared by immersing Au(111) substrates into ethanolic solution (0.1 μM/l) of selenoacetic acid Se-anthracen-2-yl ester for at least 24h, followed by thoroughly rinsing with ethanol and drying in a nitrogen stream. The gold substrates were prepared by evaporating 140 nm gold (99.995%, Chempur) at 453K under high vacuum conditions (~10⁻⁷ mbar) onto freshly cleaved mica sheets, which had been heated to 590K for 48h before to remove residual crystal water. After deposition, the gold/mica substrates were flame-annealed in a butane/oxygen flame yielding high-quality Au-films with flat terraces of several 100 nm exhibiting a (111) surface orientation.

SAM characterization. The adsorption and formation of AntSe-SAMs were first characterized by means of reflection absorption infrared spectroscopy (RAIRS) and X-ray photoelectronspectroscopy

(XPS). All RAIRS measurements were recorded in grazing incidence reflection mode at a fixed angle of 84° relative to the surface normal using a dry-air purged BioRad Excalibur FTS-3000 FTIR-spectrometer employing *p*-polarized light. The reflected light was detected by a liquid nitrogen cooled MCT narrow band detector using a resolution of 1 cm^{-1} . For background compensation all data were normalized by subtraction of a spectrum which was recorded for a perdeuterated docosanethiol-SAM on gold. This provides a reference sample which is protected against unintentional contaminations by adsorption from the environment as compared to a clean gold surface. The XPS measurements were carried out using a UHV surface analysis apparatus equipped with a X-ray twin-anode (VG) and a hemispheric energy analyzer (Leybold EA200).

The RAIRS spectrum of freshly prepared and well-rinsed AntSe-SAMs on gold reveals a number of distinct peaks in the finger print region between 800 cm^{-1} and 1600 cm^{-1} . Based on the theoretical analysis (see below) they have been identified as C-C stretching and rocking vibrations (at 1611 , 1581 , 1512 and 1462 cm^{-1}), C-H rocking and scissoring modes (at 1369 , 1255 , 1183 , 1091 and 1038 cm^{-1}), and (out-of-plane) C-H wagging modes of the aromatic rings (at 828 and 805 cm^{-1}). Moreover, in addition to the C-H stretching vibration at about 3050 cm^{-1} two further modes at 2930 cm^{-1} (CH_3 vibration) and at 1716 cm^{-1} ($\text{C}=\text{O}$ vibration) were observed which are characteristic for an aromatic acetate and thus indicate the presence of remaining acetate protection groups. This assignment is further corroborated by a distinct oxygen peak observed in the corresponding XP-spectra (see Fig. S1b). Whereas thorough rinsing does not completely remove this acetate-related signal it disappeared completely upon gently heating the film at 330 K under vacuum conditions as demonstrated by the subsequently recorded RAIRS and XPS data shown in the lower curves in Fig. S1 thus providing an important detail in the procedure of preparing pure AntSe-SAMs.

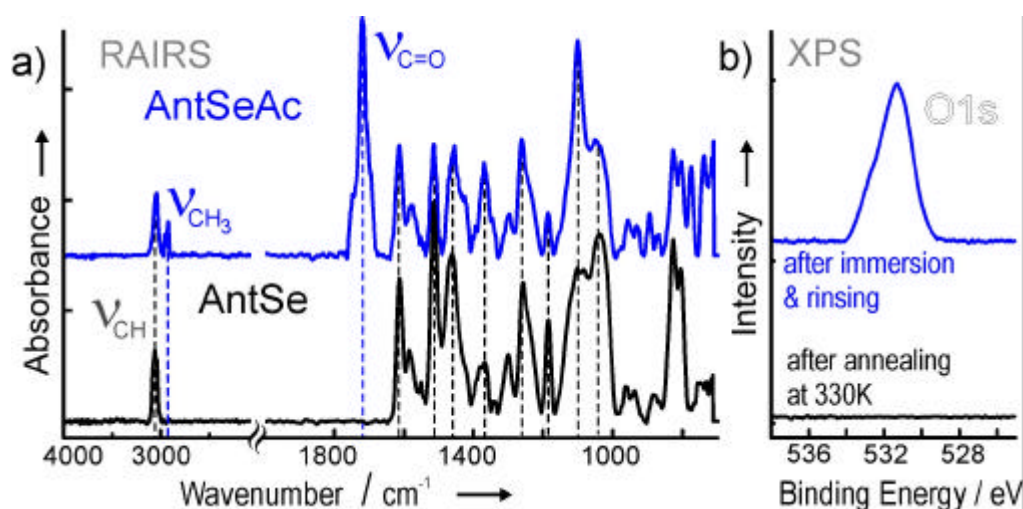


Fig. S1. Comparison of a) RAIRS data and b) XPS data recorded for a freshly prepared AntSe-SAM

curve (blue) and for the same film after brief annealing at 330 K in vacuum (bottom black curve).

STM measurements. The STM data were recorded under ambient conditions with a Jeol JSPM 4210 microscope using tips prepared mechanically by cutting a 0.25mm Pt0.8Ir0.2 wire (Goodfellow). Typically low tunnelling currents of 150pA along with sample bias of -200mV with respect to the sample have been used in the constant-current mode, avoiding any tip-induced changes.

TDS measurements. A quadrupole mass spectrometer (Balzers QMS200, mass range 0-300amu) with a Feulner cup placed in front of the sample surface was used to record thermal desorption spectra (TDS) by employing a computer controlled linear heating ramp of $\beta=0.5\text{K/s}$.^[2] The sample temperature was measured by a chromel/alumel thermocouple mounted directly at the gold surface. In the TD-spectra for AntSe-SAMs (see Fig. S2) only one distinct desorption peak at 478K was observed at the mass of the aromatic anthracene-backbone ($m/z=177\text{amu}$) thus indicating a dissociative desorption. This assignment was confirmed by subsequently recorded XPS data which reveal a distinct selenium signal of the remaining anchoring unit. For comparison additional TD-spectra are also shown for the previously studied anthracenethiol-SAM (AntS)^[3] which exhibit two distinct peaks at 488K and 531K. The former peak was observed for the mass of the molecule ion ($m/z=209\text{amu}$) while the latter was only observed for the aromatic anthracene-backbone ($m/z=177\text{amu}$) thus indicating the presence of different desorption channels which had previously been attributed to different adsorption geometries.^[3]

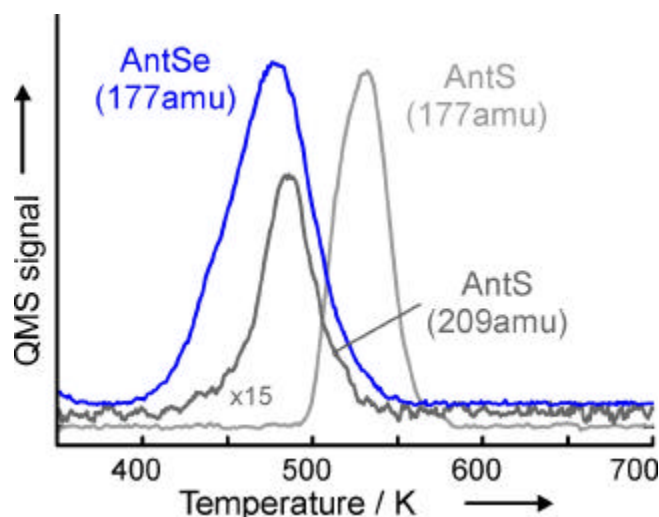


Fig. S2. Comparison of TD-spectra of AntSe-SAMS (blue) and AntS-SAMS (grey) on Au(111) recorded at a constant heating rate of $\beta = 0.5\text{K/s}$.

NEXAFS measurements. The NEXAFS measurements were performed at the synchrotron storage ring BESSY II in Berlin (Germany) at the dipole beamline HE-SGM using an end-station described in

details elsewhere.^[4] All NEXAFS measurements were carried out with linear polarized light ($P \approx 85\%$) with an energy resolution of 100 meV at the C K-edge. The NEXAFS spectra were recorded in a partial electron yield mode using a homemade electron detector based on a channel plate and a retarding field of -150 V. The energy calibration of all NEXAFS spectra is carried out by recording simultaneously with each spectrum the photocurrent of a carbon contaminated gold grid in the incident beam. This signal reveals a characteristic absorption peak at a photon energy of 284.9 eV^[5] which had been cross-calibrated by means of a graphite sample. The NEXAFS raw data have been normalized in a multi step procedure by considering the incident photon flux, which was monitored by the photocurrent on the gold grid, and using the background signal of the clean substrate (for details see Ref. [4]). To determine the molecular orientation from the linear dichroism spectra have been recorded for at least 4 different angles of incidence of the synchrotron light ($\theta=30^\circ, 55^\circ, 70^\circ, 90^\circ$; not all shown).

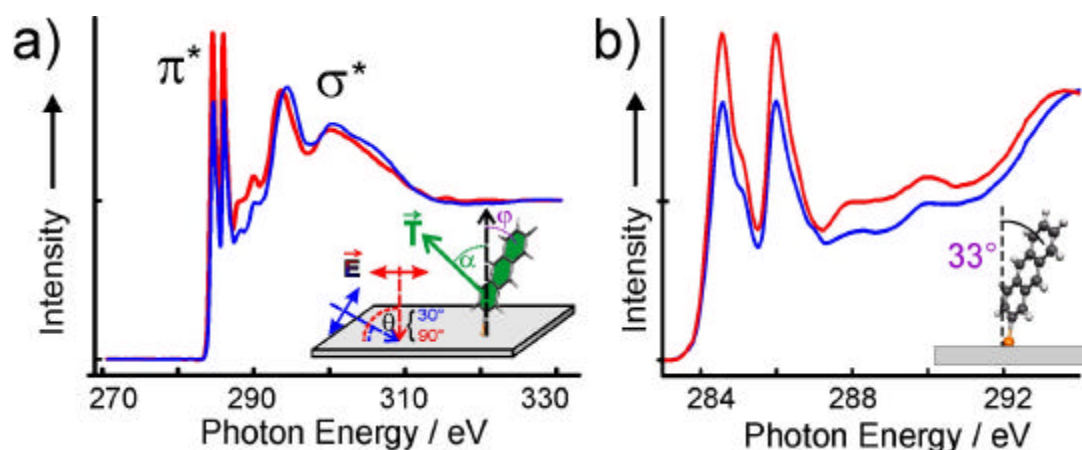


Fig. S3. A typical NEXAFS spectrum for a AntSe-SAM on Au(111) recorded at room temperature is shown in a)

together with the measuring geometry (inset). A magnification of the π^* -region along with the molecular

tilt angle derived from the dichroism is displayed in panel b).

The NEXAFS spectra of anthraceneselenol show at least three distinct peaks in the π^* -region at 284.52, 285.14 and 286.06 eV with a typical FWHM of 0.74 eV followed by several σ^* resonances. A quantitative analysis of the dichroism of the π^* -resonances yields an average angle of the transition dipole moment \mathbf{T} of such excitations relative to the surface normal of $\alpha = 59^\circ$. With knowledge of the herringbone angle $\vartheta = 48^\circ$ (see STM data) this can be transformed into a tilt angle $\varphi = 33^\circ$ of the molecular backbone with respect to the surface normal.^[3]

Quantum chemical calculations. To identify the characteristic signatures obtained in the RAIR spectra the normal modes of AntSe have been analyzed theoretically on the basis of *ab initio*

calculations by using the DFT-B3LYP algorithm in the Gaussian98 program package with a 6-311+G(2d,2p) basis set.^[6] Moreover, the ZINDO algorithm^[7,8] was used to also determine the electronic band gap by calculating the highest occupied orbitals as well as the lowest (unoccupied) virtual orbitals. The results of these calculations which were also carried out for other aromatic molecules are summarized in Fig. S4.

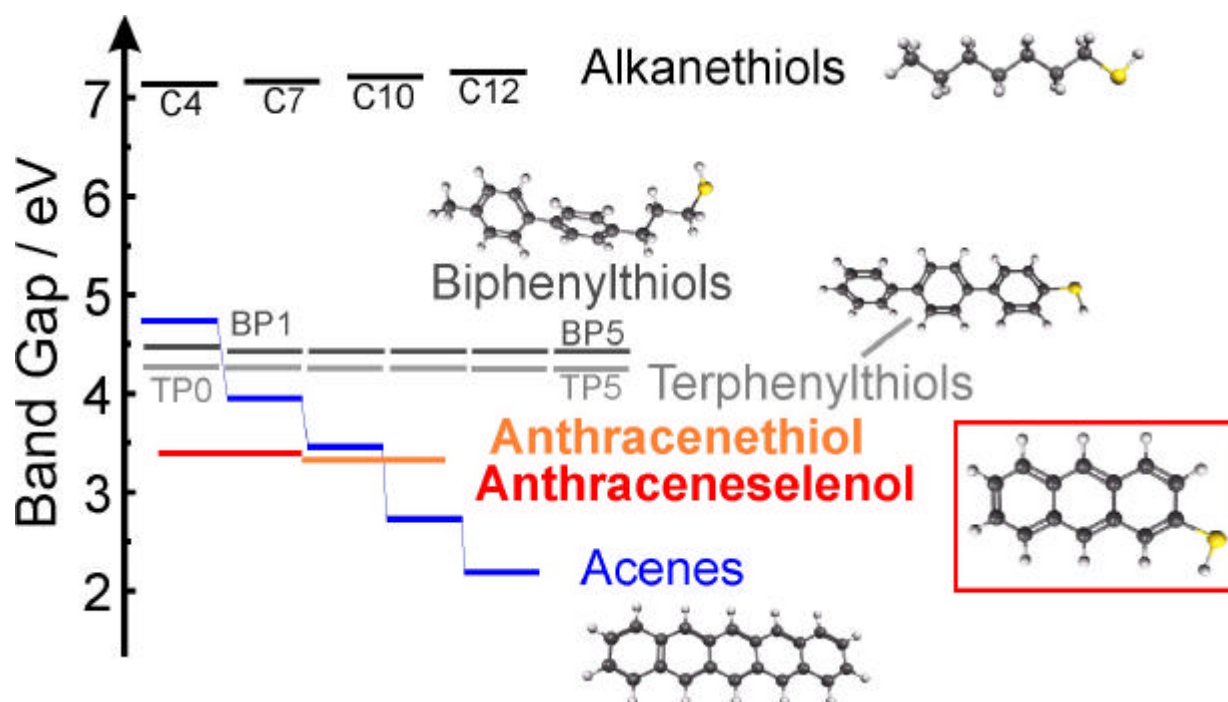


Fig. S4. Comparison of calculated band gaps of various aromatic molecules used for the preparation of aromatic SAMs

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