

ADVANCED ELECTRONIC MATERIALS

Supporting Information

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Thermally Stable and Highly Conductive SAMs on Ag
Substrate—The Impact of the Anchoring Group

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Thermally Stable and Highly Conductive SAMs on Ag Substrate – the Combined Impact of the Backbone and Anchoring Group

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2. Experimental Methods

SAM Preparation. The absolute ethanol (99.8%), used as a solvent in all experiments, was purchased from POCH (Poland) and used after degassing (usually 5 cycles of freeze-pump-thaw procedure). The synthesis of 6-cyanonaphthalene-2-thiol (NC-NapSH) and 6-cyanonaphthalene-2-selenoacetate NC-NapSeAc used for the respective SAMs formation is described in the previous publication.^[1] 6-Cyano-2-naphthoic acid (NC-NapCOOH) was purchased from Enamine Ltd and used without further purification.

Several sample series were fabricated for the different experiments. For the XPS, NEXAFS spectroscopy, static SIMS, and WCA measurements, the Ag(111) substrates were prepared by evaporation of approx. 100 nm of silver (rate = 0.7 nm/s, room temp.) onto polished single-crystal silicon (100) wafers (ITME, Warsaw) primed with 4 nm of chromium to improve the adhesion of the silver layer. For the temperature-programmed SIMS (TP-SIMS) analysis, the Ag(111) substrates were prepared by evaporation of ~100 nm of silver (rate = 0.7 nm/s, temp. ~260°C) on mica substrates. For the EGaIn measurements, the Ag^{TS} substrates were prepared using the template stripping method described by Whitesides et al.^[2]

For the SAM formation, the Ag(111) substrates were immersed at room temperature into 1 mM ethanolic solution of the respective compound for either 24 hours in the case of NC-NapS/Ag and NC-NapSe/Ag or 5 min in the case of NC-NapCOO/Ag, as this deposition time turned out to be optimal^[3] in this type of SAM system. After incubation all samples were removed from the solution, rinsed with pure solvent, and dried under nitrogen. The characterization was performed immediately after the sample preparation except for the experiments at the synchrotron (see below), which were carried out after a few days of storage.

XPS. The measurements were performed with a monochromatized Al K_α source (E = 1486.6 eV, MX-650 VG Scienta) and VG SCIENTA R3000 hemispherical analyzer. The spectra were recorded at the normal emission geometry; the energy step was 0.15 eV; and the base pressure in the analytical chamber was 5×10⁻⁹ mbar. The overall energy resolution of the spectra was estimated at ca. 1.15 eV, based on the full width at half maximum (fwhm) of the Ag 3d_{5/2} peak (the natural fwhm of this peak is ~0.4 eV)^[4]. The inelastic background was subtracted using the Shirley method, and the photoemission peaks were fitted using the convolution of the Gaussian and Lorentzian functions with adjustable weights. The binding energy (BE) scale was referenced to the Ag 3d_{5/2} peak at 368.2 eV.^[4] To fit the S 2p_{3/2,1/2} and Se 3p_{3/2,1/2} doublets we used a pair of peaks with a branching ratio of 2:1 (p_{3/2}/p_{1/2}), and spin-orbit splittings (verified by fit) of ~1.18 eV (S 2p_{3/2}/2p_{1/2}) and ~5.8 eV (Se 3p_{3/2}/3p_{1/2}).

In addition to the laboratory XPS measurements, analogous experiments at the synchrotron radiation facility BESSY II in Berlin, Germany were performed, prior to the NEXAFS analysis (see below). The parameters of the beamline, experimental station, and the spectrometer can be found in literature.^[1] The respective data agree well with the laboratory ones and are only presented in the Supporting Information (Figure S1), to avoid repetitive discussion of the same characteristics and parameters.

NEXAFS Spectroscopy. The measurements were performed at the HE-SGM beamline (bending magnet) of the synchrotron radiation facility BESSY II in Berlin, Germany. This beamline provides linearly polarized synchrotron light with a polarization factor of ~90 %. The spectra were collected at the carbon and nitrogen K-edges in the partial electron yield (PEY) mode with retarding voltages of -150 V and -300 V, respectively. The incidence angle of the X-rays was varied between the normal (90°) and grazing (20°) incidence geometry to monitor the linear dichroism effects, which are representative of molecular orientation in the SAM samples.^[5] The energy resolution was ~0.3 eV at the C K-edge and ~0.45 eV at the N K-edge. The photon energy scale was referenced to the pronounced π^* resonance of HOPG at 285.38 eV.^[5] The C K-edge spectra were corrected for the PE dependence of the incident photon flux and reduced to the standard form with zero intensity in the pre-edge region and the unity jump in the far post-edge region. The N K-edge spectra are shown as measured.

WCA Measurements. The advancing WCA measurements were conducted with the Rame-Hart goniometer, model 200, using ultrapure water (~18 M Ω). The experiments were performed under ambient conditions (temperature = 21 °C, humidity = 25%), with the needle tip in contact with the drop. Averaged values of at least 50 measurements at different locations on each sample are reported.

SIMS and TP-SIMS Measurements. The SIMS and TP-SIMS experiments were performed using a time-of-flight (TOF) SIMS V system (IONTOF GmbH, Germany) with pressure in the analytical chamber at the level of 5×10^{-10} mbar. During data acquisition, the primary beam of the 30 keV Bi⁺ ions was scanned over a 500 $\mu\text{m} \times 500 \mu\text{m}$ area (256 \times 256 data points) of the sample. Both positive and negative secondary ions were detected by a multichannel plate (MCP) detector after passing the reflectron TOF mass spectrometer. Before the analysis, all spectra were normalized to the respective total number of counts. For the TP-SIMS measurements, the temperature of the samples was linearly ramped at a rate (β) of 3.75 K/min from room temperature up to 700 K. The SIMS measurements were performed simultaneously with the sample heating, with a one-minute delay between individual scans. For the thermal

desorption analysis, the emission intensities of the respective secondary ions were normalized to the intensity measured at room temperature.

DFT. All calculations were performed using spin-polarized density functional theory (DFT) with the projector augmented waves (PAW)^[6] and van der Waals corrected functional (vdW-DF)^[7] available in VASP (Vienna ab-initio simulation package).^[8] The optPBE-vdW implementation of the vdW-DF method was used.^[9] To model the system, periodic boundary conditions and the repeated slab approach were employed representing the substrate by four (111) layers of Ag. Periodic replicas of the slab were separated by a vacuum gap of 25 Å in order to avoid the interaction between the replicas. All the atomic positions, except the bottom layer, were relaxed by a conjugate gradient method until the largest force in any direction was below 0.01 eV/Å. During the geometry optimization the Ag atoms in the bottom layer were fixed in their bulk positions. The calculations were performed in the rectangular ($3\times\sqrt{3}$) surface unit cell with the bulk Ag lattice constant of 4.149 Å. The plane-wave energy cutoff for all calculations was set to 700 eV. The Brillouin zone was sampled by a $4\times 8\times 1$ Monkhorst-Pack k-point grid including the Γ point.^[10] The convergence criterion for the total energy in the self-consistency cycle was set to 10^{-6} eV.

The ($3\times\sqrt{3}$) unit cell for the NC-NapS(Se)/Ag monolayers, which was analyzed here, contains 6 Ag atoms per layer and two molecules arranged in herringbone fashion. Two models of the Ag(111) surface were considered: (i) bare surface with no adatoms and (ii) surface decorated with Ag adatoms (two adatoms per unit cell, which gives an adatom coverage of 1/3 monolayer). More than twenty initial geometries for each molecule type were checked starting either from bare or adatom-decorated relaxed surfaces and placing the docking groups in fcc-hollow sites with the molecules exhibiting slight tilt to the surface normal (about 10°) and rotation by $\pm 30^\circ$ and $\pm 210^\circ$ along their long axis. The rotation angles were chosen to maintain the 60° angle between the molecules to give their herringbone arrangement. To verify that the final geometries are the lowest energy structures, the relaxed geometries were crosschecked against the replacement of docking atoms. This means that relaxed geometries of NC-NapS/Ag(111) served as initial guess for NC-NapSe/Ag(111), and *vice versa*. We also checked the structural models of the molecules on Au(111) surface found in ref^[11].

Following former studies^[11] the energies (E_{X-Y}) for the bond-breaking between the docking atoms S or Se (X) and either the Ag surface or adjacent C atom (Y) were calculated as the differences in total energy between the isolated molecular fragments ($E_{\text{mol-fragment},X-Y}$) plus the energy of the Au(111) surface ($E_{\text{surf},X-Y}$) eventually containing adsorbed S or Se atoms and the energy of the system with adsorbed molecules ($E_{\text{SAM-bonded}}$):

$$E_{X-Y} = E_{\text{mol-fragment},X-Y} + (E_{\text{surf},X-Y} - E_{\text{SAM-bonded}})/2. \quad (1)$$

In general, $E_{\text{surf},X-Y}$ contains also contribution from the Ag adatoms, if present. The factor of 1/2 gives the average energies per molecule since each unit cell contains two molecules. Note that all above energies require fully relaxed geometries of the corresponding subsystems, which have been obtained in a periodic boundary fashion with the $(3 \times \sqrt{3})$ unit cell, except for the $E_{\text{mol-fragment},X-Y}$, for which the rectangular cell of $12 \times 16 \times 20 \text{ \AA}^3$ was used.

EGaIn Measurements: The EGaIn setup for the conductivity measurement was similar to that described by Whitesides et al.^[12] For every new junction a fresh EGaIn tip was prepared, and only tips without any irregularities (controlled by optical microscopy) were used to form junctions. Following analysis performed by Whitesides et al.,^[13] the contact area between the tip and the samples exceeded $1500 \mu\text{m}^2$ for all junctions.

2. Synchrotron-based XPS data

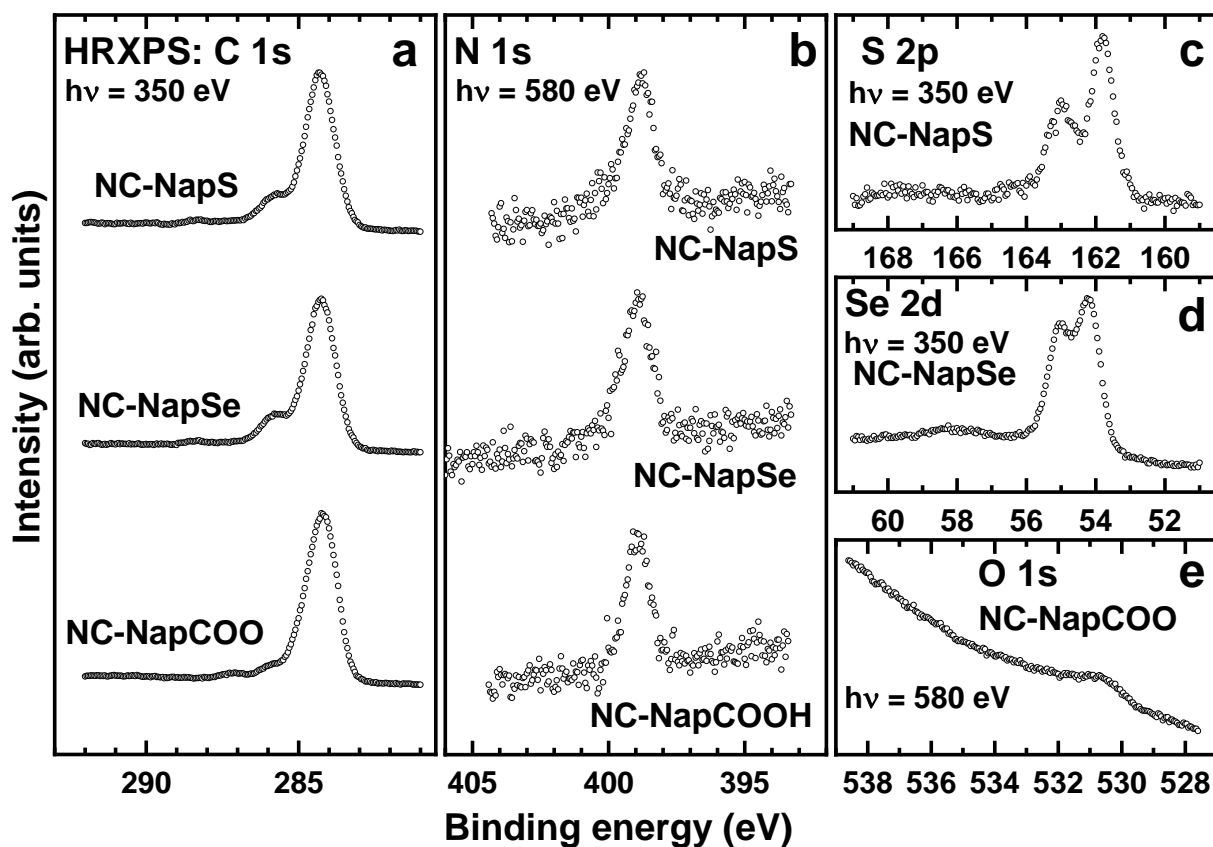


Figure S1. C 1s (a), N 1s (b), S 2p (c), Se 2d (d) and O 1s (e) XP spectra of NC-NapS/Ag, NC-NapSe/Ag, and NC-NapCOO/Ag. The spectra were acquired at the synchrotron; the primary photon energy is given in the panels. The C 1s and N 1s spectra are characteristic of the molecular backbone and terminal nitrile group, respectively, underlining the proper organization and similar packing density in the monolayers. The S 2p, Se 3p, and O 1s spectra are characteristic of the anchoring groups in NC-NapS/Ag, NC-NapSe/Ag, and NC-NapCOO/Ag, respectively. They only exhibit the signals of the properly bound docking groups, with no other features perceptible.

3. SIMS data

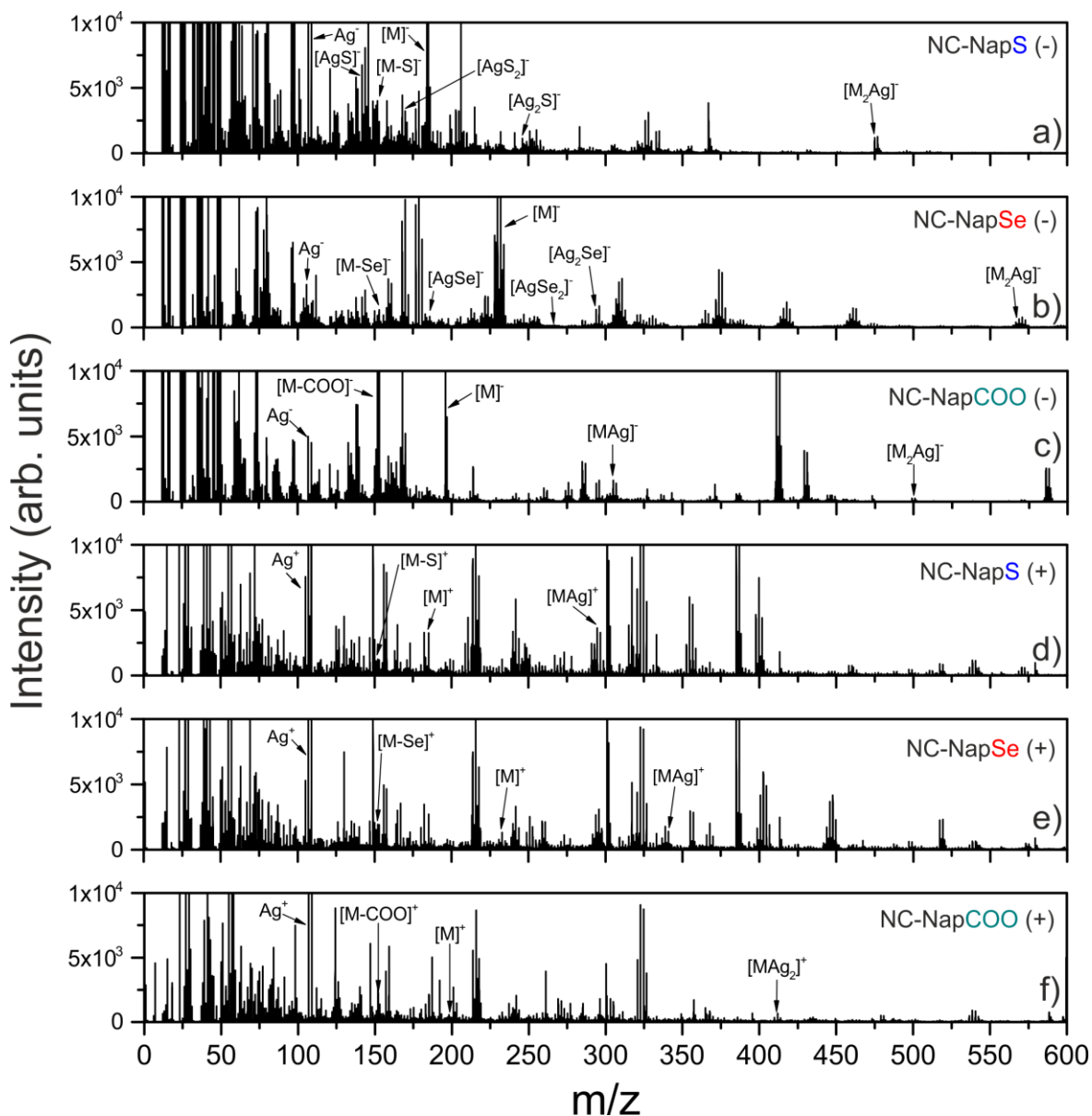


Figure S2. The S-SIMS spectra. In (a), (b), and (c) the negative spectra for NC-NapS/Ag, NC-NapSe/Ag, and NC-NapCOO/Ag are presented, respectively. In (d), (e), (f) the positive spectra for NC-NapS/Ag, NC-NapSe/Ag, and NC-NapCOO/Ag are presented, respectively. Characteristic secondary ions for analyzed SAMs are indicated by arrows.

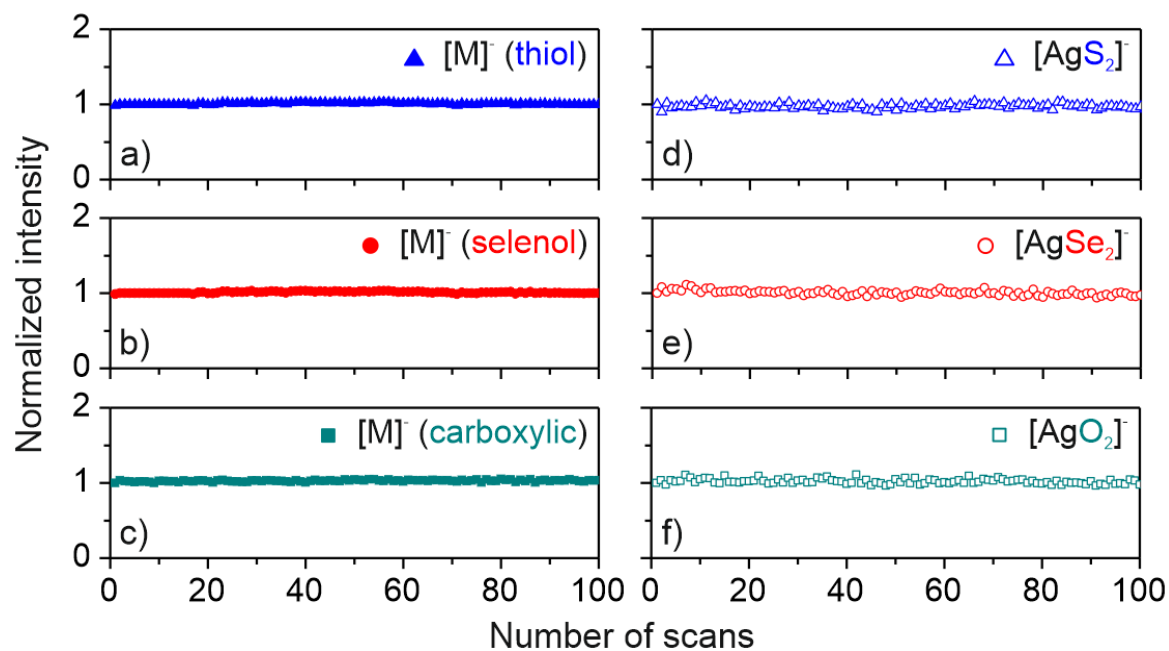


Figure S3. SIMS control measurements. In (a), (b) and (c) normalized signal of complete molecule $[M]^-$ as a function of number of scans for NC-NapS/Ag, NC-NapSe/Ag, and NC-NapCOO/Ag, respectively. In (d), (e) and (f) normalized signal of $[AgX_2]^-$ ($X = S, Se, O$) metal-anchoring group cluster for NC-NapS/Ag, NC-NapSe/Ag, and NC-NapCOO/Ag, respectively. Measurements were performed without heating program at room temperature for the total number of scans (100) which is larger than used for complete thermal analysis of the respective samples.

4. TP-SIMS data

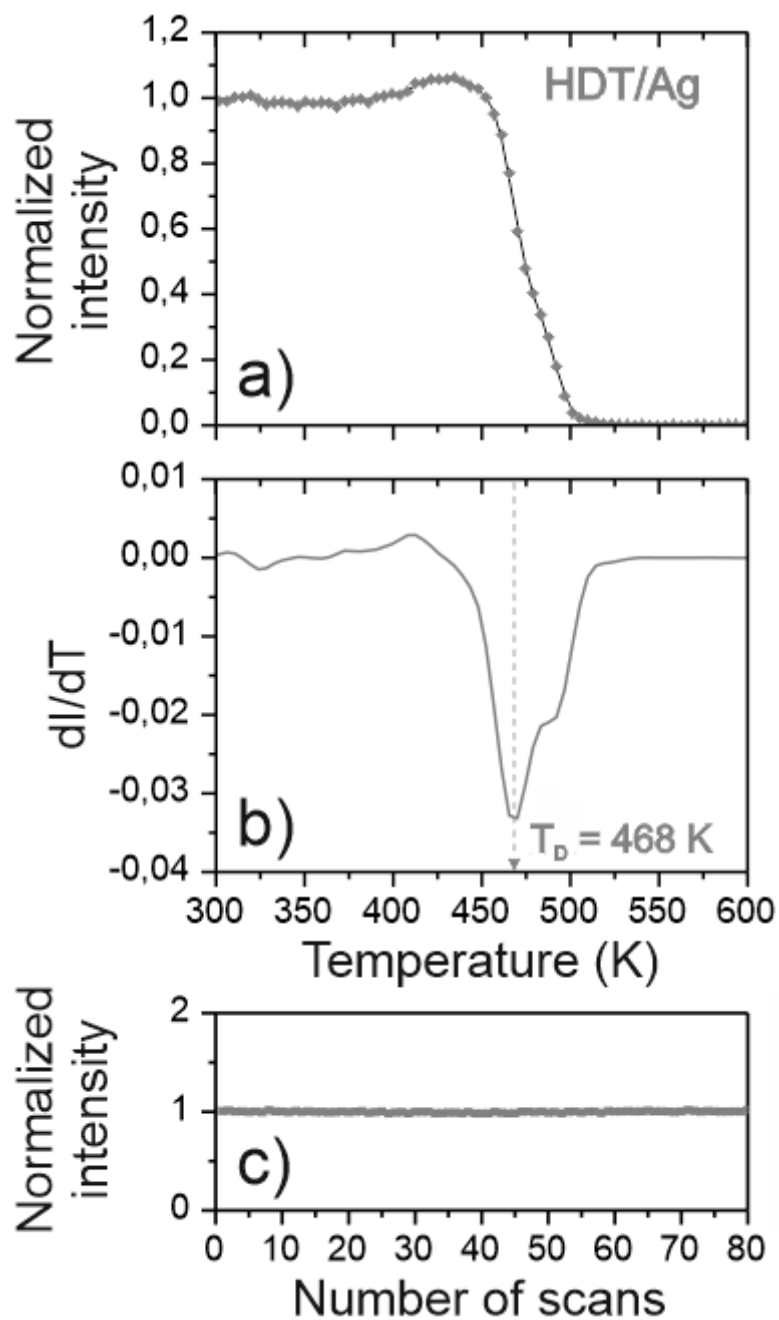


Figure S4. Thermal stability analysis for reference system – hexadecanethiol (HDT) on silver substrate. In (a) the normalized signal of complete molecule ($[M]^+$, $M = C_{16}H_{33}S$) as a function of temperature for HDT SAMs on silver. Black line is the spline function fitted to the data points in order to process them. In (b) derivative of the aforementioned spline functions. The characteristic desorption temperature (T_D) is indicated. In (c) control measurements without heating program (collected at room temperature).

5. DFT calculations

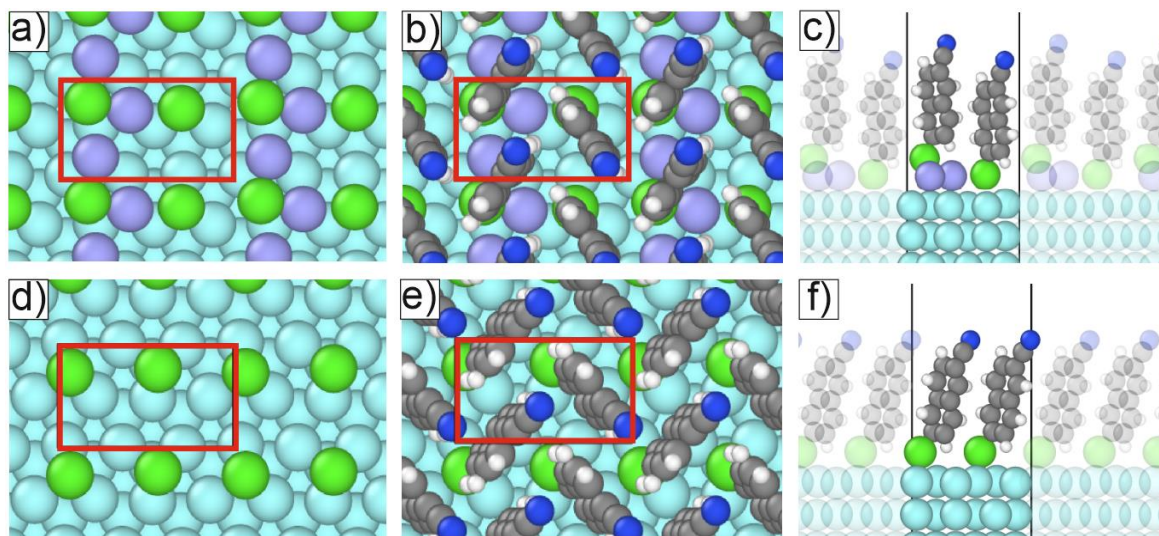


Figure S5. DFT simulations for NC-NapSe. Top and side views of the NC-NapSe adsorbed on adatom-decorated (a-c) and adatom-free (d-f) Ag(111) surface after geometry optimization. The rectangular ($3\times\sqrt{3}$) unit cells contain two molecules in herringbone arrangement and two (a-c) or none (d-f) Ag adatoms. In panels (a) and (d) only the docking groups and the Ag adatoms are displayed in order to show their relative positions. Different chemical species are marked by different colors: Ag – silver, Ag adatoms – purple, Se – green, C – gray, H – white, and N – blue.

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