Supporting Information

Thiolate *versus* Selenolate: Structure, Stability and Charge Transfer Properties

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Synthesis and analysis of the SAM precursors

General Techniques

All syntheses have been performed in conventional Schlenk apparatus under dried nitrogen to exclude air and humidity. The solvents and reagents were dried according to standard procedures. For chromatography, flash grade silica from Merck (silica 60, 0.040-0.063 mm)

NMR spectra were recorded at 300 K using either an AM250 or an AV300 (Bruker) applying the following frequencies:
AM250: ^{1}H (250.1 MHz), ^{13}C (62.9 MHz).
AV300: ^{1}H (300.1 MHz), ^{13}C (75.5 MHz), ^{77}Se (57.2 MHz).
All the heteronuclear spectra were ^{1}H broadband decoupled. The shifts are given on the δ scale in ppm. The spectra were calibrated to the protonated residuals of the solvents:
^{1}H-NMR ($CDCl_3$: 7.26 ppm; DMSO-D_6: 2.50 ppm).
^{13}C-NMR ($CDCl_3$: 77.16 ppm; DMSO-D_6: 39.52 ppm).

IR spectra were recorded on a Nicolet 6700 FT-IR (Thermo Fisher Scientific). For the bulk spectra, a diamond ATR cell was used. The band intensities were described qualitatively as strong (s), medium (m), or weak (w). For the IRRAS spectra a Smart SAGA unit was employed with p-polarized IR light under an incidence angle of 80°.

GC-MS data were recorded by a combination of a Trace GC 2000 series and a Finnigan TraceMS Instrument (ThermoQuest CE Instruments). For GC, a Macherey Nagel Optimar 210 column was employed using helium as mobile phase.

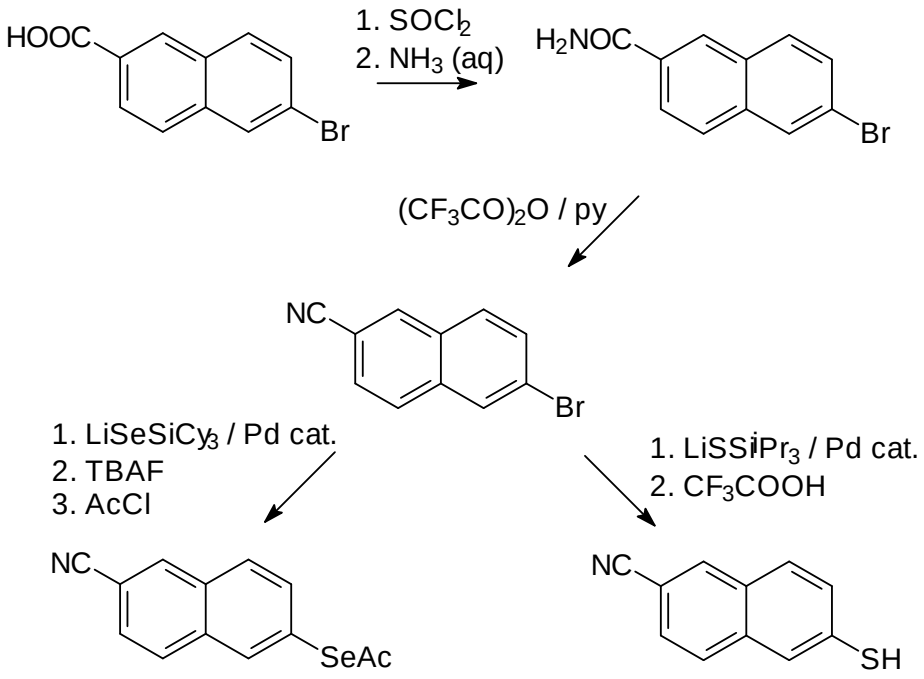
Melting points were recorded on an Optimelt MPA 100 (Stanford Research Systems) typically using a ramp of 5 °C/min. The melting point was determined optically by a three-point detection *via* a CCD camera.

For the determination of layer thicknesses, an ellipsometer SE400 (Sentech) was employed, using a laser with 633 nm wavelength and an incidence angle of 70°. Substrates were cleaned by hydrogen plasma for one minute.[1]

Elemental analyses (C, H, N, S) were performed on a Varia Micro CUBE CHN-Analyzer (Elementar).

Single **crystal structure** determinations were performed using IPDS II machines (STOE) with monochromated Mo-K radiation (λ = 0.71073 Å).

Syntheses:



Scheme S1. Overview of the syntheses of NC-NapSH and NC-NapSeAc.

2-Bromo-6-naphthamide[2]

2-Bromo-6-naphthoic acid (8 g, 32 mmol, 1 eq) was treated with thionylchloride (53.2 mL, 733 mmol, 22.5 eq) and DMF (2 mL) at 70 °C for 16 h. The volatiles were removed *in vacuo* and the remaining solid was dissolved in CH_2Cl_2 (50 mL). This soln was added dropwise to a mixture of aqueous ammonia (25%, 28.5 mL) and H_2O (26.1 mL). After stirring for 1 h, the precipitated solid was filtered and washed with a small amount of ethyl acetate.

Yield: 6.77 g (27.1 mmol), 85% of theoretical yield.
mp.: 220 °C.
MS(EI)+: *m/z* (%) = 126.0 (100), 249.0 (44) $[M(^{79}Br)]^+$, 250.9 (48) $[M(^{81}Br)]^+$.
^1H NMR (300.1 MHz, $CDCl_3$): δ 8.32 (s, 1H, H-1), 8.06 (d, $^4J_{HH}$ = 1.5 Hz, 1H, H-5), 7.89

(dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H-4), 7.83 (d, $^3J_{HH}$ = 4.9 Hz, 1H, H-3), 7.80 (d, $^3J_{HH}$ = 5.1 Hz, 1H, H-7), 7.63 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, H-8), 5.95 (s, 2H; NH_2).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 169.0 (C=O), 136.2, 131.2, 131.1, 130.7, 130.6, 130.1, 128.3, 127.8, 125.1, 122.7.

IR: 3321 (w, NH_2), 3129 (w, NH_2), 1698 (w), 1661 (m), 1609 (m, C=O), 1560 (w), 1464 (w), 1410 (m), 1390 (w), 1375 (w), 1347 (w), 1183 (w), 1164 (w), 1113 (w), 1102 (w), 1060 (w), 965 (w), 925 (m), 887 (s), 812 (s), 771 (w), 741 (w), 728 (m).

2-Bromo-6-cyanonaphthalene[3]

To a soln of 2-bromo-6-naphthamide (5 g, 20 mmol, 1 eq) in anhydr. 1,4-dioxane (40 mL) anhydr. pyridine (3.3 mL, 41 mmol, 2 eq.) and trifluoroacetic acid anhydride (3.1 mL, 22 mmol, 1.1 eq) were added at 0 °C. After stirring the mixture for 3 h at room temperature, the reaction was quenched with H_2O (70 mL) and the mixture was extracted with ethyl acetate. The organic phase was washed with H_2O and the solvents were removed *in vacuo*. The remaining solid was recrystallized from methylcyclohexane (500 mL) containing 20 ml of ethylacetate, resulting in the formation of colorless needles.

Yield: 3.21 g (13.8 mmol), 69% of theoretical yield.

mp: 111 °C.

MS(EI)$^+$: *m/z* (%) = 152.2 (100), 231.1 (98) [M(^{79}Br)]$^+$, 233.2 (90) [M(^{81}Br)]$^+$.

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.20 (s, 1H, H-5), 8.07 (d, $^4J_{HH}$ = 1.6 Hz, 1H, H-1), 7.84 (d, $^3J_{HH}$ = 8.6 Hz, 1H, H-8), 7.77 (d, $^3J_{HH}$ = 8.8 Hz, 1H, H-4), 7.69 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, H-3), 7.64 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H-7).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 135.6, 134.2, 131.4, 130.9, 130.4, 130.1, 128.5, 127.7, 123.7, 118.8 (C≡N), 110.1 (*C*–C≡N).

IR: 2221 (w, C≡N), 1677 (w), 1622 (w), 1581 (w), 1561 (w), 1489 (w), 1459 (w), 1397 (w), 1377 (w), 1330 (w), 1267 (w), 1244 (w), 1187 (w), 1159 (w), 1128 (w), 1059 (m), 957 (w), 889 (s), 875 (s), 804 (m), 792 (m), 765 (w), 700 (w).

6-Cyanonaphthalene-2-selenoacetate

To a soln of 2-bromo-6-cyanonaphthalene (0.232 g, 1.01 mmol, 1 eq) in anhydr. benzene (4 mL) $LiN(SiMe_3)_2$ (1.1 mL, 1 M in THF, 1.1 mmol, 1.1 eq) was added dropwise, followed by addition of a soln of $Pd(OAc)_2$ (11.2 mg, 0.049 mmol, 0.049 eq) and RuPhos[4] (23.2 mg, 0.049 mmol, 0.049 eq) in anhydr. benzene (1 mL). Finally, a soln of tricyclohexylsilaselenole[3]

(0.357 g, 1.01 mol, 1 eq) in of anhydr. benzene (5 mL) was added and the resulting mixture stirred at room temperature for 16 h. Then, acetylchloride (0.35 mL, 4.9 mmol, 4.9 eq) and tetra-n-butylammonium fluoride (1.2 mL, 1 M in THF, 1.2 mmol, 1.2 eq) were added and stirring was continued for 3 h. After dilution with ethyl acetate, the organic phase was washed with H_2O and brine and then concentrated to 2 mL before silica gel (1.9 g) has been added. The slurry was stirred over night and then the solvent was removed completely. Separation of the product by column chromatography (silica, hexane/ethyl acetate gradient 200:1 to 100:1), followed by recrystallisation from methylcyclohexane (100 mL) yielded slightly brownish crystals.

Yield: 0.19 g (0.69 mmol), 69% of theoretical yield.

mp.: 130 °C.

MS(EI)$^+$: *m/z* (%) = 43.2 (100), 274.5 (1) $[M]^+$.

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.24 (s, 1H, H-5), 8.09 (s, 1H, H-1), 7.91 (d, $^3J_{HH}$ = 5.5 Hz, 1H, H-7), 7.88 (d, $^3J_{HH}$ = 5.4 Hz, 1H, H-8), 7.68 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H-3), 7.65 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H-4), 2.54 (s, 3H, CH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 195.6 (C=O), 135.3, 135.1, 134.2, 134.1, 132.1, 129.3, 129.2, 128.4, 127.2, 119.1 (C≡N), 110.5 (*C*–C≡N), 34.5 (CH_3).

^{77}Se NMR (57.2 MHz, $CDCl_3$): δ 672.9.

IR: 3068 (w, CH_3), 2227 (w, C≡N), 1705 (m, C=O), 1622 (w), 1582 (w), 1488 (m), 1457 (w), 1417 (w), 1376 (w), 1349 (m), 1330 (w), 1271 (w), 1249 (w), 1189 (w), 1161 (w), 1100 (m), 1066 (w), 960 (m), 895 (s), 831 (s), 814 (w), 803 (m).

Elemental analysis: Calculated for $C_{13}H_9NOSe$: C, 56.95; H, 3.31; N, 5.11. Found: C, 57.16; H, 3.34; N, 4.95.

6-Cyanonaphthalene-2-thiol

To a soln of 2-bromo-6-cyanonaphthalene (1.16 g, 5.01 mmol, 1 eq) in anhydr. benzene (25 mL) $LiN(SiMe_3)_2$ (5.5 mL, 1 M in THF, 5.5 mmol, 1.1 eq) were added, followed by addition of a soln of $Pd(OAc)_2$ (56 mg, 0.25 mmol, 0.05 eq) and RuPhos[5] (111 mg, 0.248 mmol, 0.05 eq) in anhydr. benzene (5 mL). After dropwise addition of a soln of $^iPr_3SiSH$ (0.936 g, 4.98 mol, 1 eq) in anhydr. benzene (20 mL) the mixture was heated to 70 °C for 16 h. After cooling, the mixture was taken up in ethyl acetate, washed with H_2O and brine, and evaporated to dryness. The remaining solid was dissolved in CH_2Cl_2 (10 mL) and treated with trifluoroacetic acid (1.9 mL, 25 mmol, 4.9 eq) for several hours. Then the volatiles were

removed again *in vacuo* and sublimed in a gradient sublimation apparatus at 120 °C/10^{-3} mbar to yield a colorless solid.

Yield: 0.339 g (1.83 mmol), 37% of the theoretical yield.

mp.: 129 °C.

MS(EI)$^+$: *m/z* (%) = 185.4 (80) $[M]^+$, 233.1 (100).

^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.15 (d, $^4J_{HH}$ = 1.0 Hz, 1H, H-5), 7.75 (m, 3H, H-1, H-3, H-8), 7.59 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.6 Hz, 1H, H-4), 7.44 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H-7), 3.71 (s, 1H, SH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ 135.1, 134.1, 133.8, 130.2, 129.2, 128.0, 127.5, 126.3, 119.3 (C≡N), 109.0 (*C*–C≡N).

IR: 2546 (w, S-H), 2222 (w, C≡N), 1619 (w), 1585 (w), 1490 (w), 1466 (w), 1402 (w), 1378 (w), 1336 (w), 1273 (w), 1249 (w), 1163 (w), 1136 (w), 1081 (m), 959 (w), 932 (w), 907 (s), 900 (m), 876 (s), 819 (s), 808 (s), 759 (w), 715 (w).

Elemental analysis: Calculated for $C_{11}H_7NOS$: C, 71.32; H, 3.81; N, 7.56; S, 17.31. Found: C, 69.55; H, 4.18; N, 7.20; S, 17.19.

Crystal structure of 2-bromo-6-naphthamide

A single crystal was obtained by evaporation of a solution of 2-bromo-6-naphthamide (5 mg) in dichloromethane (1 ml). The compound crystallizes in the space group *P*21/c with four molecules in the elementary cell. The aromatic system is completely planar with C-C-C bond angles of consistently 120°. Also the angles N1–C11–C7, O1–C11–C7, C1–C2–Br1, and C3–C2–Br1 are about 120°. The only torsional angles deviating from 0° or 180° are C8–C7–C11–O1 and C6–C7–C11–N1, which amount to 160.9° and 163.3°, respectively (Figure S1). In benzamide, the latter angle amounts to 155.8°.[6]

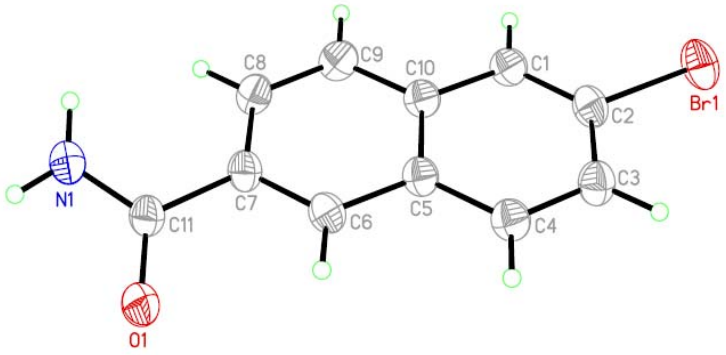


Figure S1. Molecular structure of 2-bromo-6-naphthamide in the solid.

Due to the formation of an extended hydrogen bond network between the amide groups, the aromatic systems do not adopt a simple herringbone structure. Coplanarity is achieved in a pairwise manner (see Figure S2).

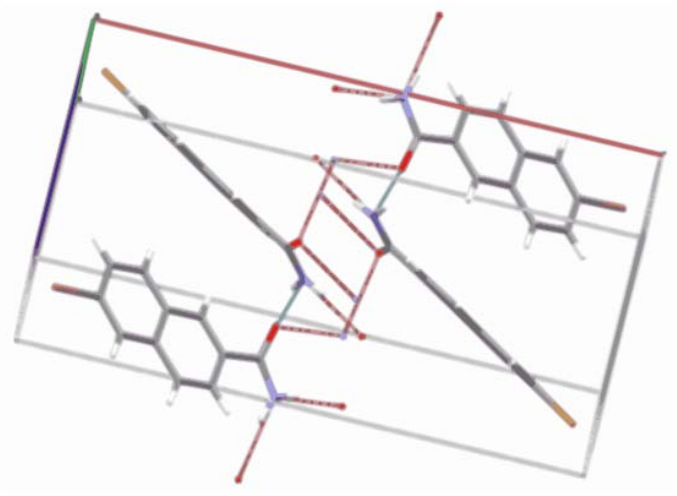


Figure S2. Elemental cell of 2-bromo-6-naphthamide. Hydrogen bonds are indicated as red, dashed lines.

Crystal structure of 2-bromo-6-cyanonaphthalene

A single crystal of 2-bromo-6-cyanonaphthalene was obtained by slow evaporation of a saturated solution in dichloromethane. The compound crystallizes in the space group *P* 1 with only one molecule in the cell.

As has been observed in the series of the 4-halobenzonitriles,[7]

significant orientational disorder can be found in the crystal due to electronic and steric similarity of the cyano group with the bromine atom. This increases residual electron densities and thus the r value of the structure. In addition, the disorder results in a virtual center of inversion between C1 and C1a. Nevertheless some observations can be made:

The aromatic ring again is completely planar with bond angles of 120° (Figure S3). The C-C≡N bond angle is 177° and thus deviates only slightly from the expected 180°. The C≡N bond length amounts to 1.122 Å and is therefore somewhat longer than in 4-halobenzonitriles (1.085 Å).[8]

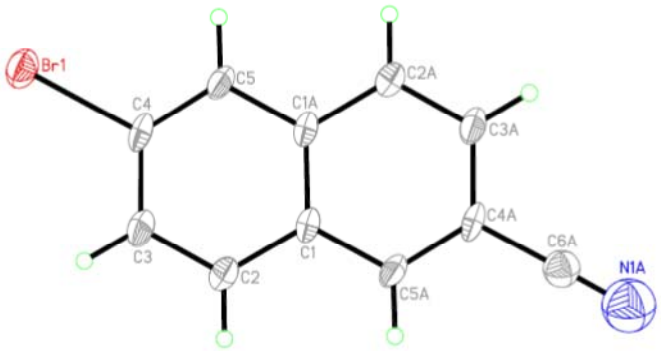


Figure S3. Molecular structure of 2-bromo-6-cyanonaphthalene in the crystal. The structural disorder has been lifted for clarity.

As a result of only one molecule per elemental cell, all the molecules within the crystal have to be aligned in parallel (Figure S4). This is a significant difference compared to most other aromatic structures, which typically crystallize in herringbone patterns due to H···π interactions. It has to be assumed that this parallel alignment is a result of the Br···NC interactions,[8] which force the molecules into a linear arrangement.

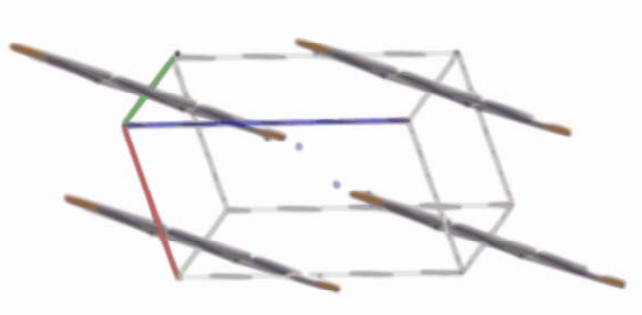


Figure S4. Packing of 2-bromo-6-cyanonaphthalene. To make the arrangement of the molecules clearer, the content of four elemental cells is depicted.

Table S1. Wavenumbers, given in cm^{-1}, of bands* in the ATR (neat), IRRA (SAM) and calculated (calc) infrared spectra of NC-NapS and NC-NapSe species, together with assignments to vibrational modes** and, where applicable, with the directions*** of the respective transition dipole moments (TDMs) within the molecular frames.

			NC-NapS			NC-NapSe		
	Vibrational mode	TDM	neat	SAM	calc	neat	SAM	calc
1	ν CN	||	2222 m	2229 vs	2256	2227 m	2229 s	2259
2	ν CO acetyl					1706 s		1793
3	δ CH ν CC arom.	||	1618 m	1618 m	1625	1622 m	1620 m	1622
4	δ CH ν CC arom.	||	1585 m	1580 w	1592	1582 m	1577 m	1583
5	ν CSe ρ CH_3 acetyl					1100 m		1073
6	δ CCC	||	877 vs	898 m	891	895 vs	889 m	882
7	ω CH	oop	820 vs	829 vw	796	831 s	833 vw	814
8	ω CH	oop	809 vs		785	804 s	814 w	807

*) vs: very strong, s: strong, m: medium, w: weak, vw: very weak

**) ν: stretch mode, δ: in-plane bending, ω: out of plane bending, ρ: rocking mode, arom.: aromatic

***) ||: parallel or almost parallel to the CN bond direction, oop: perpendicular to the aromatic plane

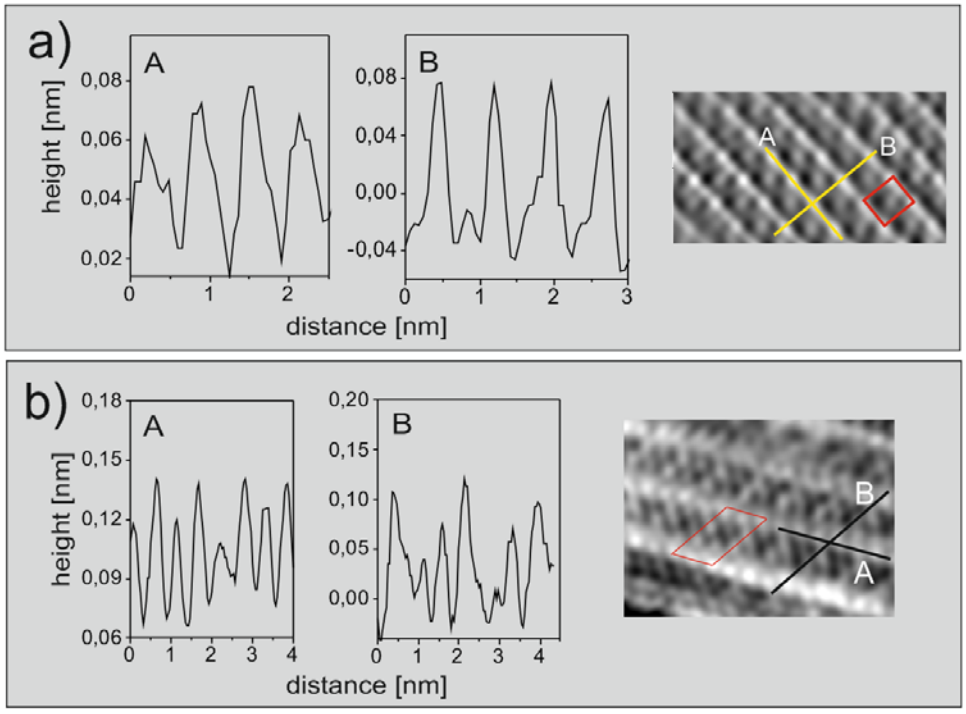


Figure S5: Scaled height profiles for the high resolution STM images obtained for NC-NapS/Au(111) (panel a) and NC-NapSe/Au(111) (panel b).

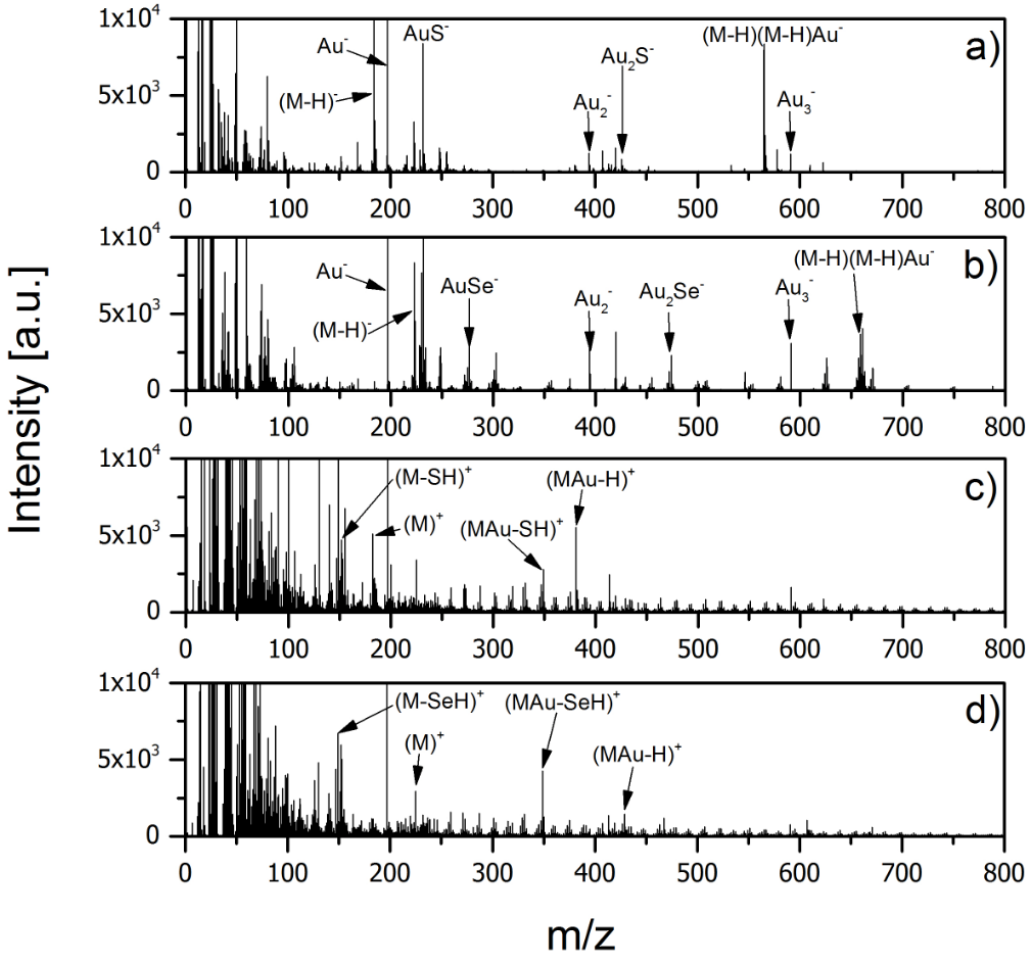


Figure S6. Examples of the S-SIMS data. In (a) and (b) negative spectra for NC-NapS/Au(111) and NC-NapSe/Au(111) are depicted, respectively. Panels (c) and (d) show positive spectra for NC-NapS/Au(111) and NC-NapSe/Au(111), respectively. Different types of characteristic secondary ions are assigned by arrows.

References

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