

Electronic Supplementary Information for "Controllable hierarchical self-assembly: Systematic study forming metallocupramolecular frameworks on the basis of helical beta-oligoamides."

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Oligoamide synthesis

3H was synthesized on a 100 μ mol scale using standard Fmoc chemistry on Wang resin (0.9 mmol/g loading, GL Biochem, Shanghai, China). The resin was washed (3 x 30 s) with DMF and the Fmoc-protected β -amino acid (3.1

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eq. to resin loading) was dissolved in DMF along with HBTU (3 equivalents (eq.) to resin loading), HOBt (3 eq. to resin loading) and DIPEA (4.5 eq. to resin loading). 4-Dimethylaminopyridine (0.1 eq. to resin loading) in DMF was added dropwise and the reaction proceeded overnight. At this stage of oligoamide synthesis proceeded as normal. Following the overnight coupling, the resin was washed with DMF (5 x 30 s) and DCM (5 x 30 s) and oligoamide synthesis was continued. One cycle of oligoamide elongation consisted of the following steps. The loaded resin was first washed with DMF (3 x 30 sec) and the terminal Fmoc protecting group was removed with 20% piperidine/DMF (2 x 15 min). The deprotected resin was then washed with DMF (5 x 30 s) and treated for 90 min with a solution containing 3.1 eq. of the appropriate β -amino acid, 3 eq. HBTU, and 4.5 eq. DIPEA. The resin was then washed three times with DMF (3 x 30 s), unreacted amino groups were acetylated upon treatment with 10% v/v acetic anhydride and 1% v/v DIPEA in DMF (2 x 20 min), and the capped resin washed with DMF (3 x 30 s). These steps were repeated until the β -oligoamide sequence was complete. Once the final Fmoc-protecting group had been removed, the resin was treated with 10% v/v acetic anhydride and 1% v/v DIPEA in DMF (2 x 20 min) to afford an acetyl-capped N-terminus. The resin was subsequently washed with DMF (5 x 30 s) and DCM (5 x 30 s), dried for 20 min under vacuum, and then treated for 90 min with a cleavage solution containing 2.5% v/v water and 2.5% v/v triisopropylsilane in TFA. The cleaved resin was washed twice with

the cleavage solution (2 x 30 s) and the cleaved β -oligoamide in TFA was collected. The TFA was evaporated under a stream of N_2 and the oligoamide was precipitated by the addition of diethyl ether. The precipitate was filtered through a sintered glass funnel and reconstituted in H_2O /acetonitrile (1:1) for lyophilization. Oligoamides were then purified to homogeneity by reverse-phase HPLC.

X-Ray Photoelectron Spectroscopy (XPS)

This section contains the spectra corresponding to the Wagner plots presented in the main text, in order of ascending atomic number.

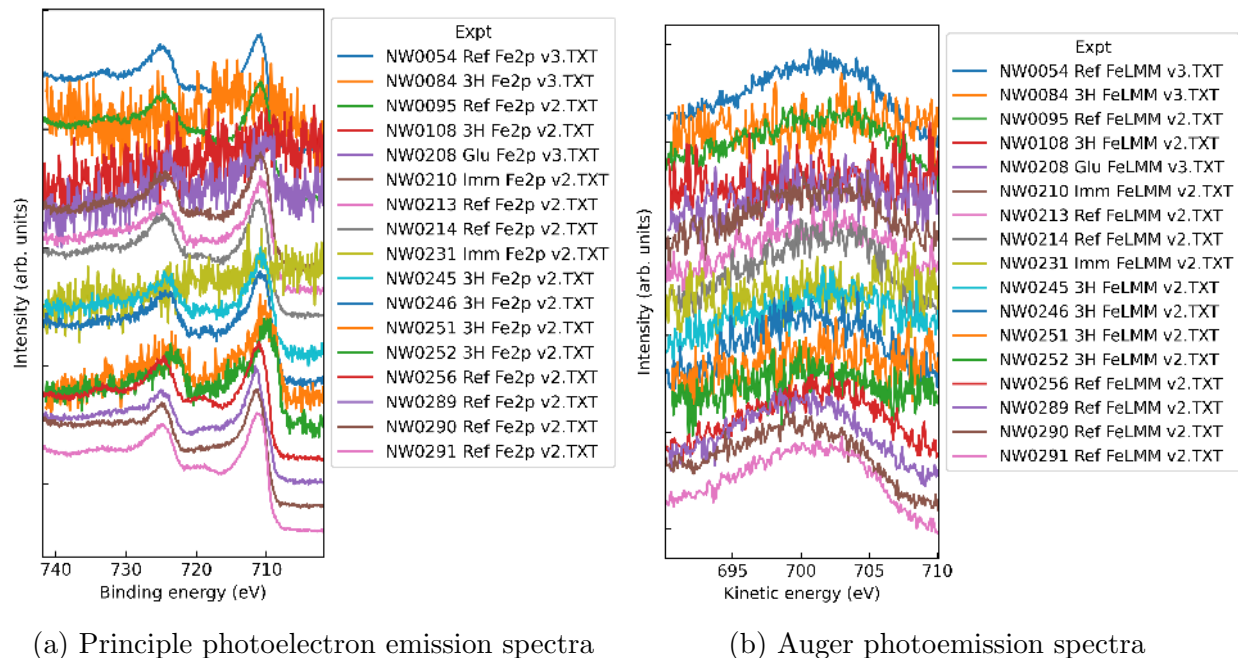
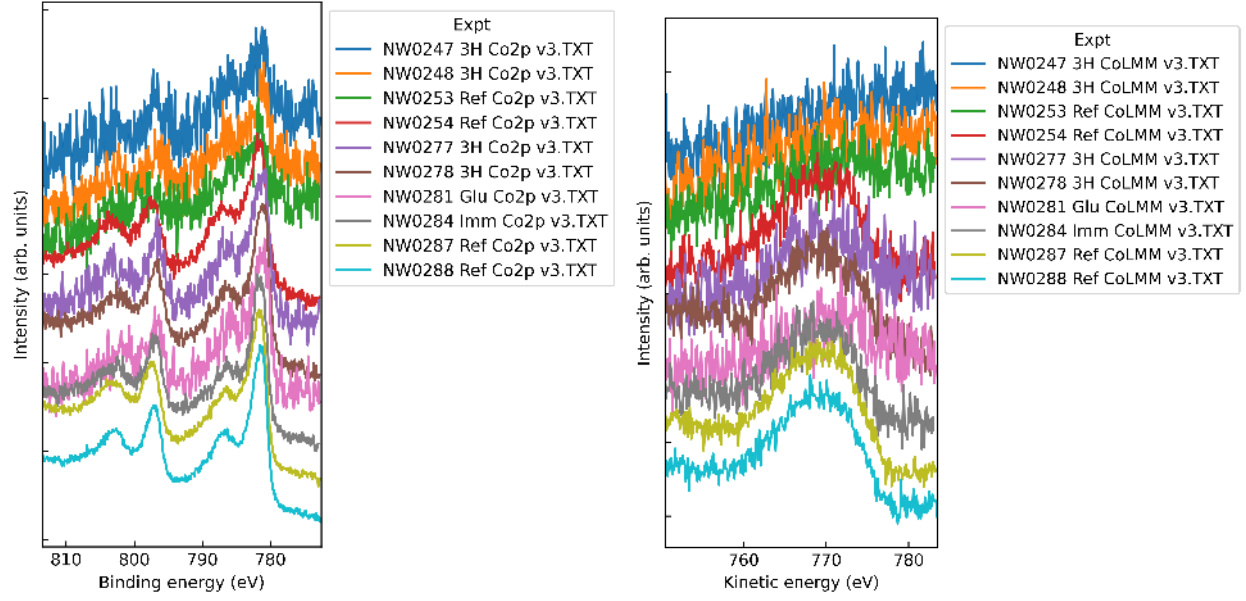


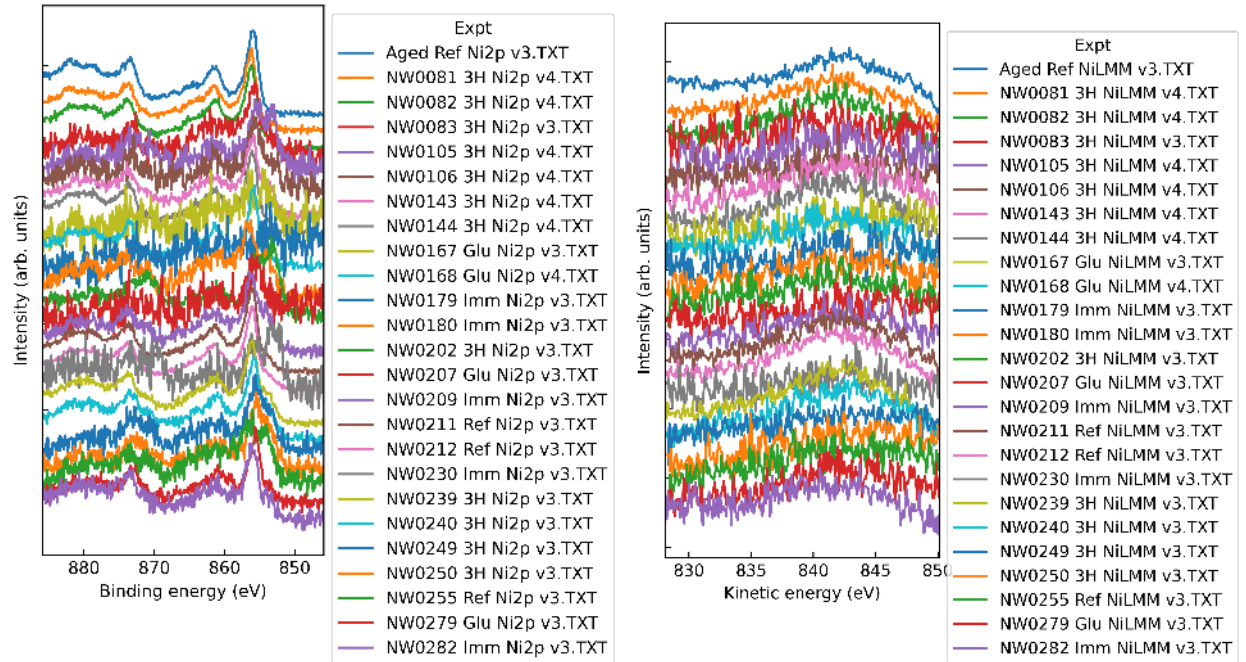
Figure 1: Spectra corresponding to Wagner plot 3H Fe



(a) Principle photoelectron emission spectra

(b) Auger photoemission spectra

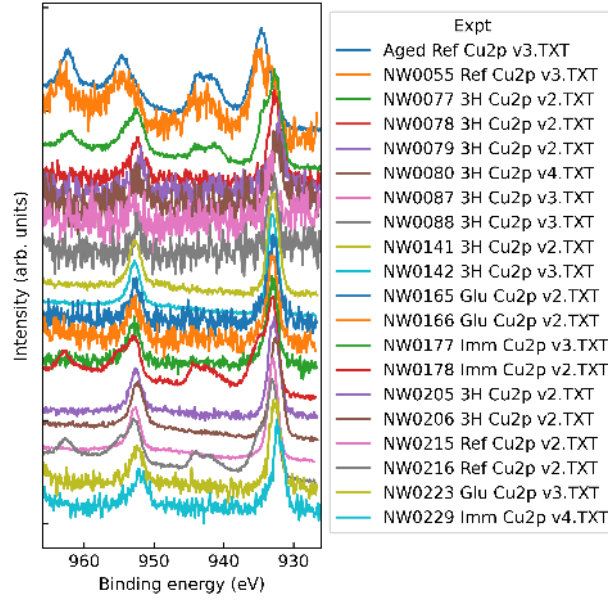
Figure 2: Spectra corresponding to Wagner plot 3H Co



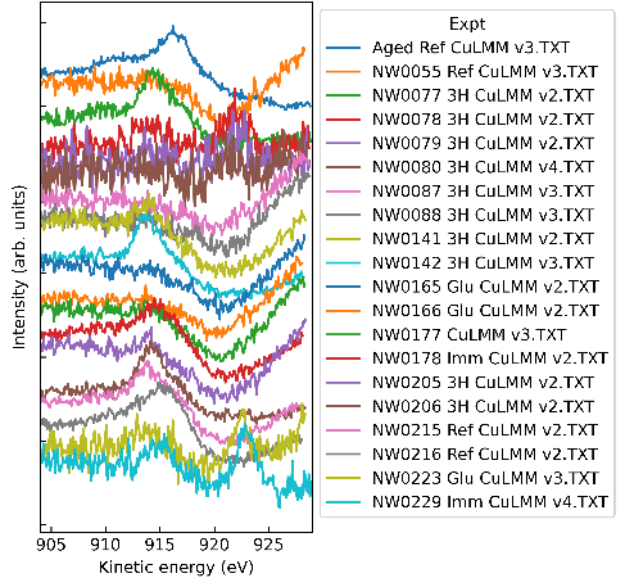
(a) Principle photoelectron emission spectra

(b) Auger photoemission spectra

Figure 3: Spectra corresponding to Wagner plot 3H Ni

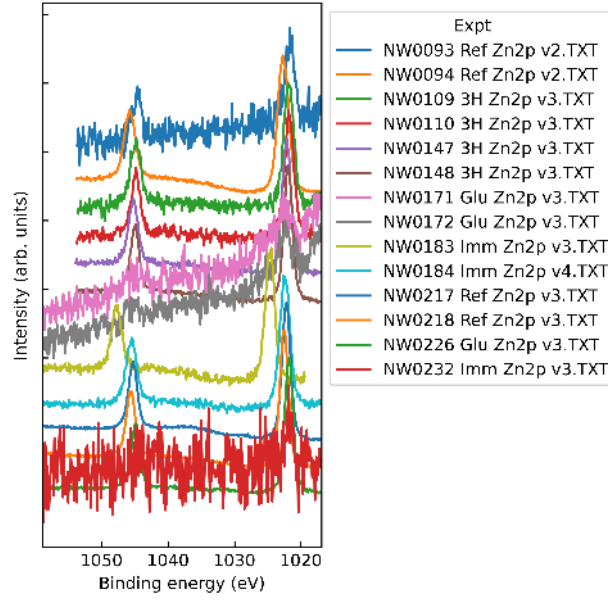


(a) Principle photoelectron emission spectra

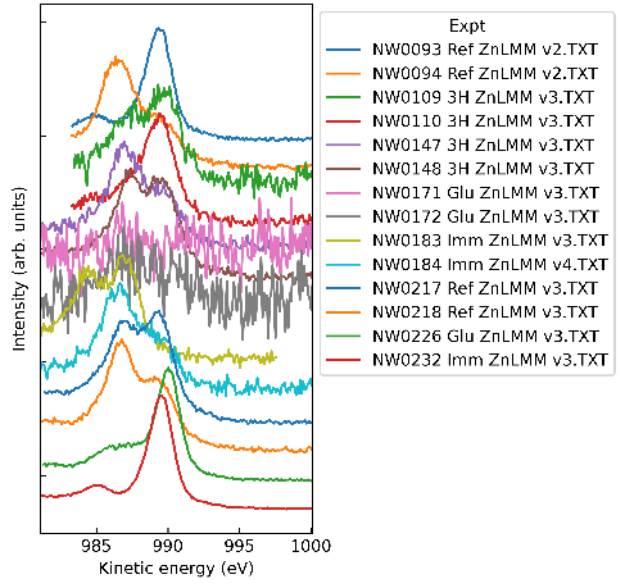


(b) Auger photoemission spectra

Figure 4: Spectra corresponding to Wagner plot 3H Cu



(a) Principle photoelectron emission spectra



(b) Auger photoemission spectra

Figure 5: Spectra corresponding to Wagner plot 3H Zn

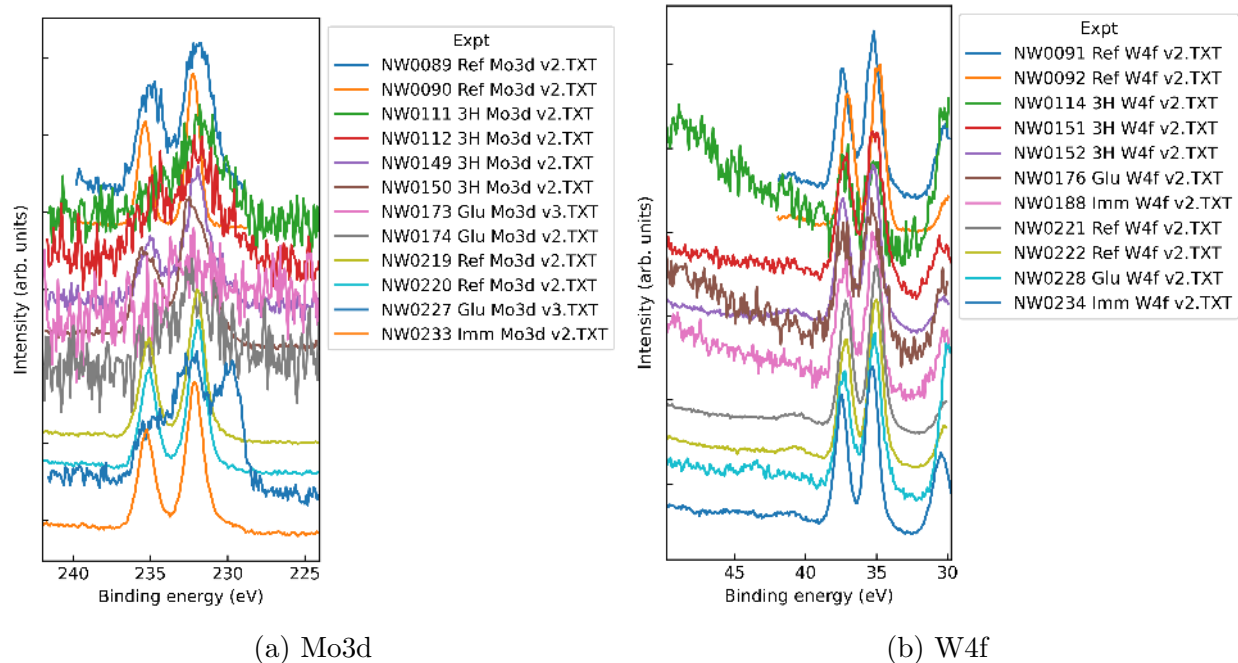


Figure 6: Spectra corresponding to binding energy plots

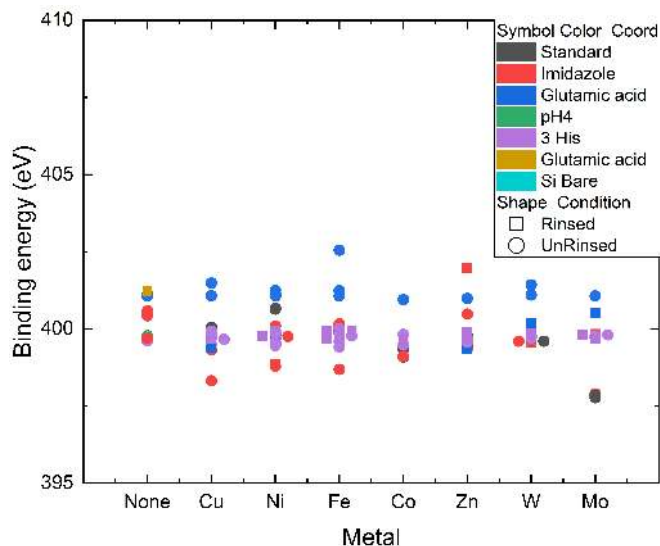


Figure 7: Binding energy comparison of N1s peak binding energy for all metals.

The N1s signal for the imidazole samples showed a significant shift for all samples except zinc. Therefore, the histidine residue had the potential to interact with all the metals except for zinc. There was no significant shift

in binding energy for the 3His measurements across all the metals, this is likely due to the proportion of backbone amide nitrogens to secondary amine imidazole nitrogens contained within the oligoamide. Therefore, looking at the highest intensity of the N1s peak is not a reliable measure for oligoamide interactions.

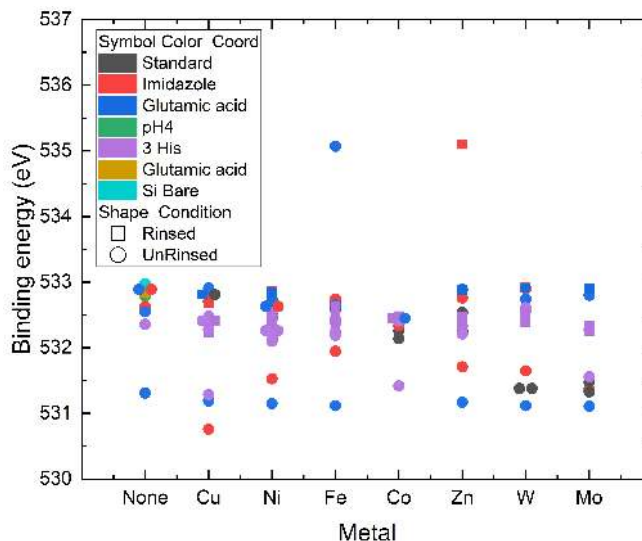


Figure 8: Binding energy comparison of O1s peak binding energy for all metals.

In respect to the O1s peak, W and Mo cause appreciable changes between reference measurements and those with the oligoamide. Indicating that the dominating signal is inline with the expected value of the bound oligoamide. Due to the presence of SiO_2 in the substrate, as confirmed by the detected presence of Si in the survey spectra. The use of O1s to determine the interactions between the oligoamide and the metals is tenuous.

Atomic Force Microscopy (AFM)

This section contains AFM images presented in the main text without the projection lighting, displaying the positions of line profiles used to determine features, in order of ascending atomic number.

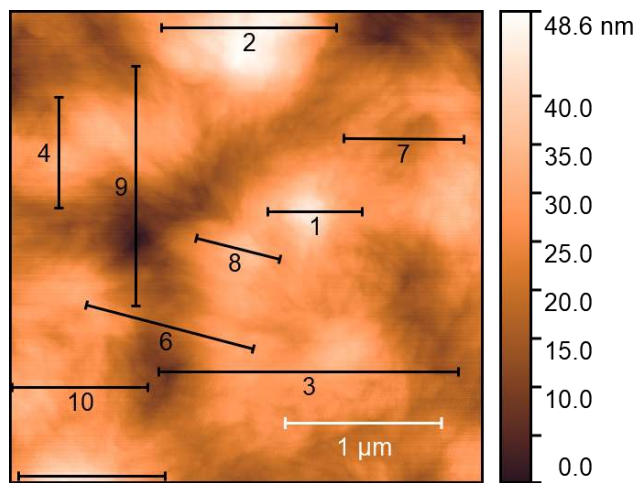
This table is the height feature measurements that were used to determine the reported dimensions.

Table 1: AFM Line profile measurements

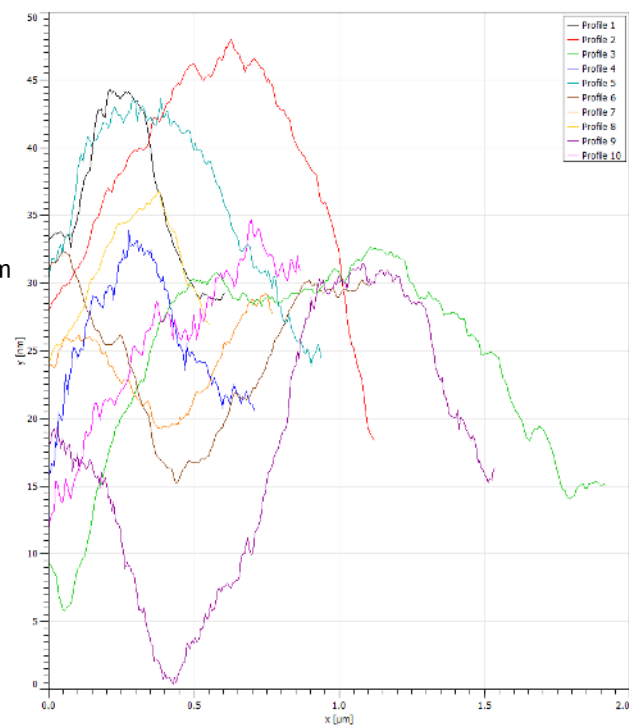
	Source file	Prof.1	Prof.2	Prof.3	Prof.4	Prof.5	Prof.6	Prof.7	Prof.8	Prof.9	Prof.10	Average	Stdev	Median
3H	Large	14.75	27.59	14.53	11.09	17.51	29.56	6.53	10.08	13.12	15.99	16.08	6.937	14.64
""	Zoomed	0.84	8.61	7	3.94	2.01	3.32	3.88	3.49	1.08	1.24	3.54	2.428	3.405
Cu	Large	0.5552	0.6182	0.5876	0.5875	0.7006	0.5826	0.5493	0.798	0.656	0.5524	0.62	0.075	0.58755
""	Zoomed	0.686	0.4595	0.8231	0.7552	0.736	0.8353	0.6178	1.658	0.8226	0.6275	0.80	0.306	0.7456
Fe	Large	1.791	2.466	3.069	2.003	1.515	2.011	1.562	1.666	2.099	1.273	1.95	0.495	1.897
""	Tall Strut.	112.7	126.3	83.7	53.4	41.7	34.8	65.1	79.3	79.6	72.7	74.93	27.319	76
""	Bot. right	10.27	6.47	6.372	6.46	5.054	5.922	4.3699	7.016	3.774	5.902	6.16	1.676	6.147
""	Zoomed	2.218	2.198	2.244	1.885	1.959	2.182	3.044	2.69	3.256	1.055	2.27	0.590	2.208
Co	Large	2.329	1.721	2.895	3.356	3.007	2.844	2.846	1.822	2.506	3.233	2.66	0.527	2.845
""	Zoomed	1.558	2.27	2.34	4.11	4.65	3.171	2.976	3.072	3.136	2.64	2.99	0.848	3.024
Ni	Large	1.732	1.668	1.096	1.691	1.216	1.838	1.334	1.547	0.9786	0.7491	1.38	0.348	1.4405
""	Zoomed	1.676	1.776	0.8156	1.292	1.165	1.51	1.524	1.24	0.5406	0.9052	1.24	0.377	1.266
Zn	Large	3.412	3.199	3.831	3.1799	3.383	3.316	3.01	3.135	3.535	3.432	3.34	0.222	3.3495
""	Zoomed	3.313	3.363	3.321	3.288	3.414	2.982	3.045	3.116	2.961	2.873	3.17	0.184	3.202
MoO4	Large	3.582	3.51	3.052	3.281	4.597	2.655	1.616	3.516	2.681	3.608	3.21	0.746	3.3955
""	Zoomed	2.701	2.198	2.714	2.02	3.295	2.05	3.422	2.738	1.779	2.83	2.57	0.522	2.7075
WO4	Large	57.78	60.33	85.24	64.39	61.31	160.99	71.33	127.6	38.95	144.02	87.19	39.582	67.86
	Zoomed	26.103	25.68	32.14	12.696	46.63	24.23	17.95	14.083	12.075	30.063	24.17	10.135	24.955

Table 2: Layer size measurements

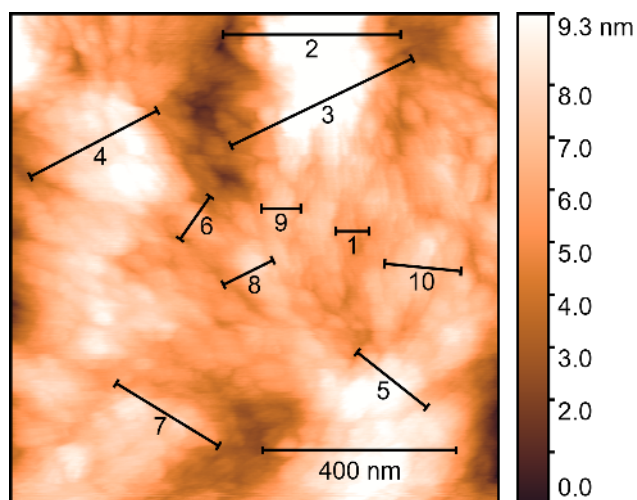
Metal	Dimension	Line 1	Line 2	Line 3	Line 4	Line 5	Average
Fe	Width (nm)	1307	2411	2204	2692	2479	2218.6
	Length (nm)	4651	4954	4987	4673	3876	4628.2
Ni	Width (nm)	533.3	481.4	401.2	623.2	691.6	546.14
	Length (nm)	2622.7	2517.7	2792.4	2981.8	3320.7	2847.06



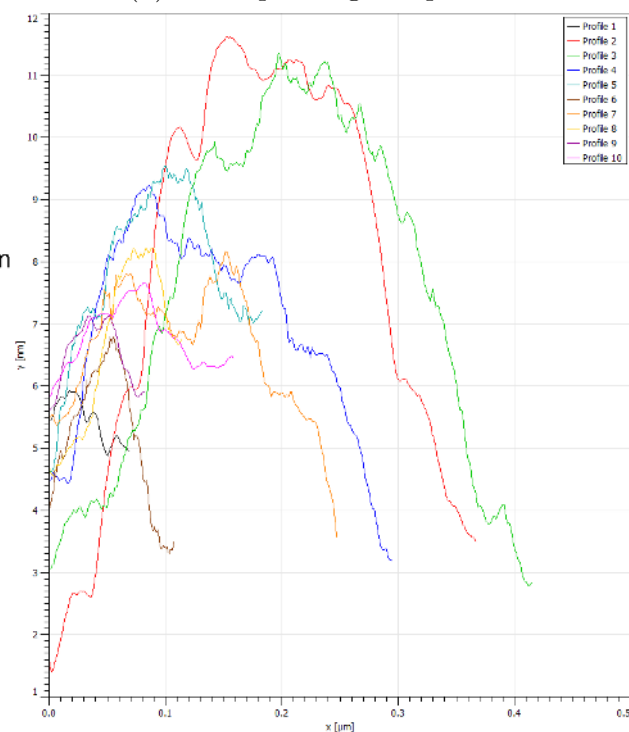
(a) AFM image with line profiles



(b) Corresponding line profiles



(c) Zoomed in AFM image with line profiles



(d) Corresponding line profiles

Figure 9: **3H** oligoamide on silicon

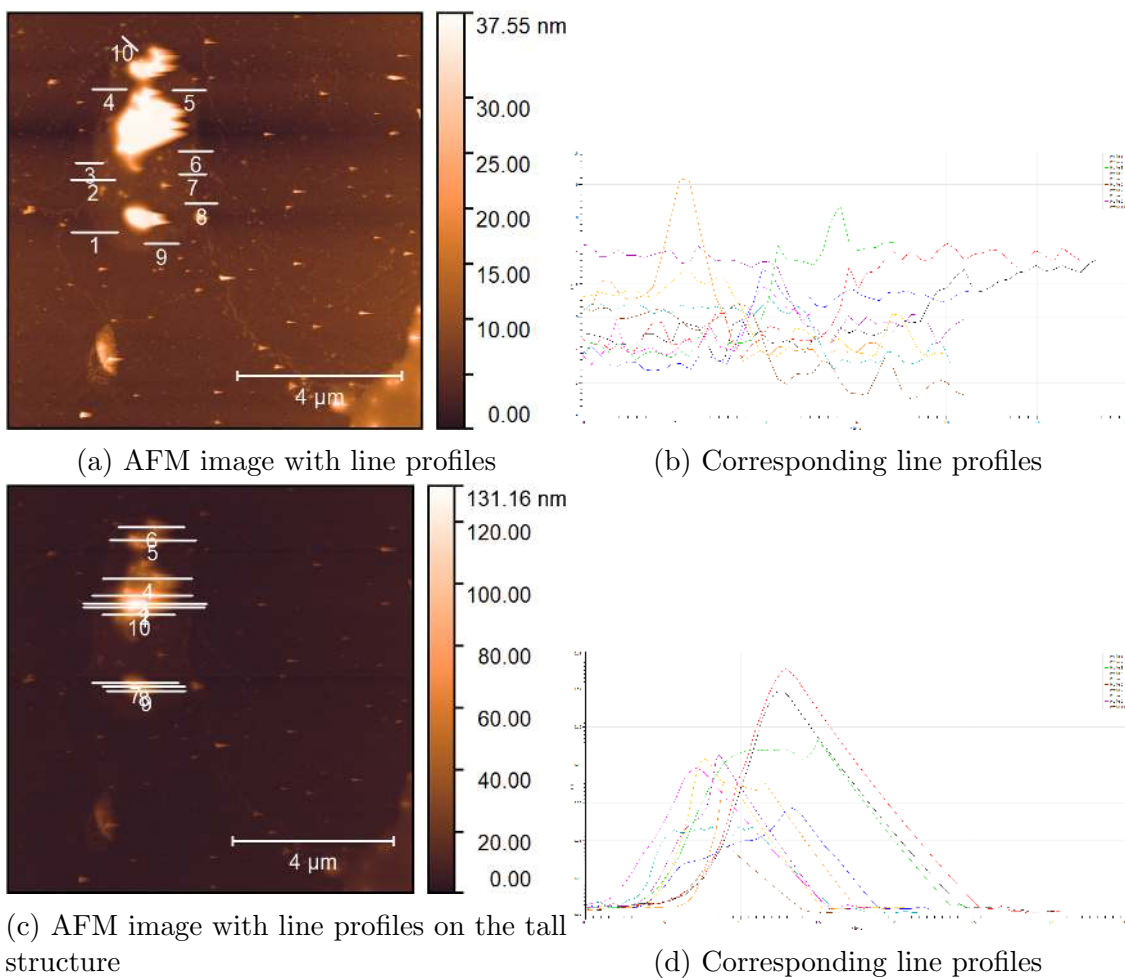


Figure 10: **3H** after surface coordination with Fe(II)

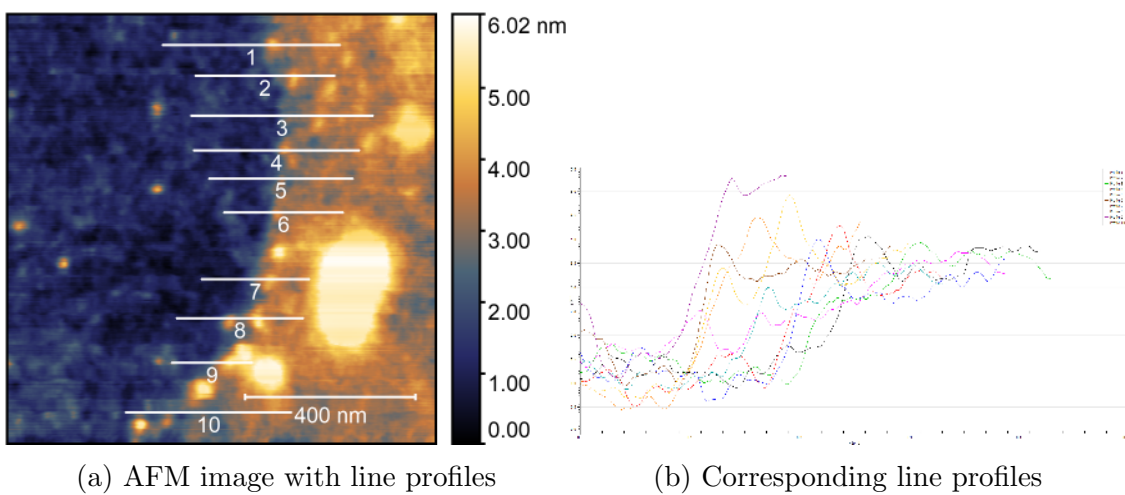


Figure 11: **3H** after surface coordination with Fe, the smaller scan area.

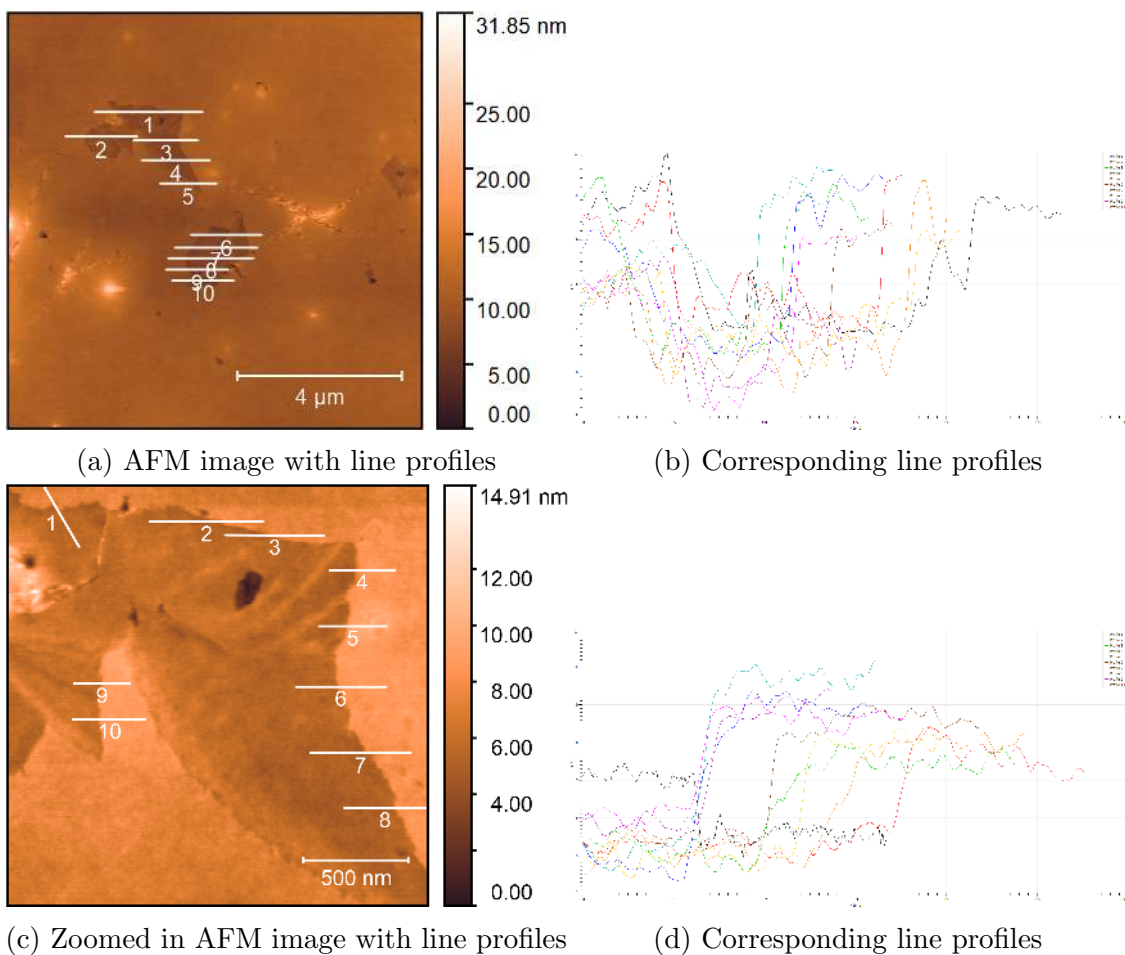


Figure 12: **3H** after surface coordination with Co(II)

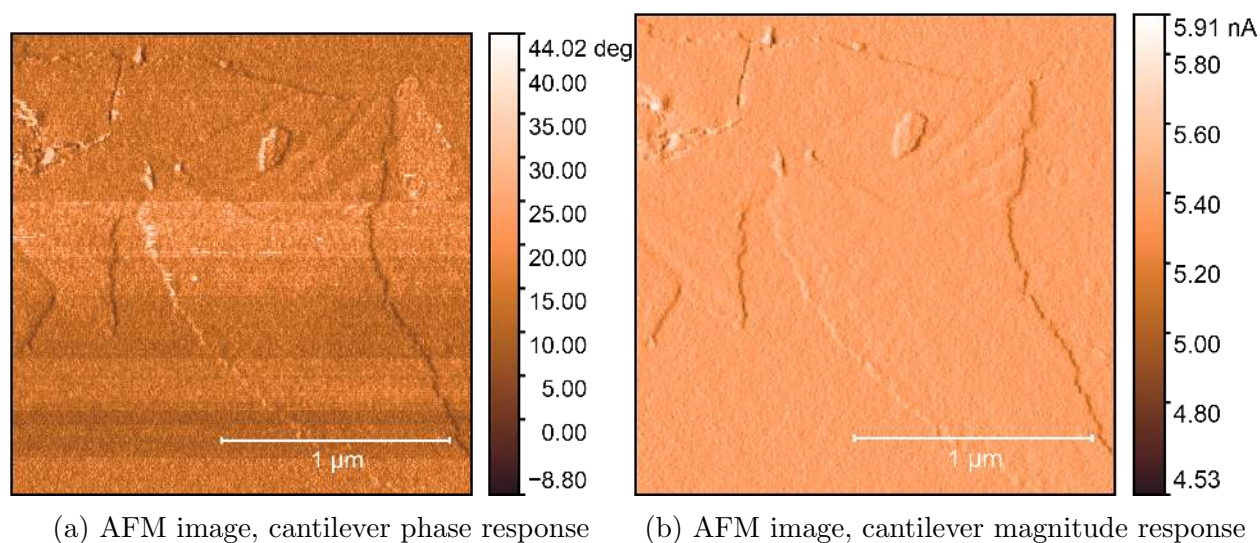
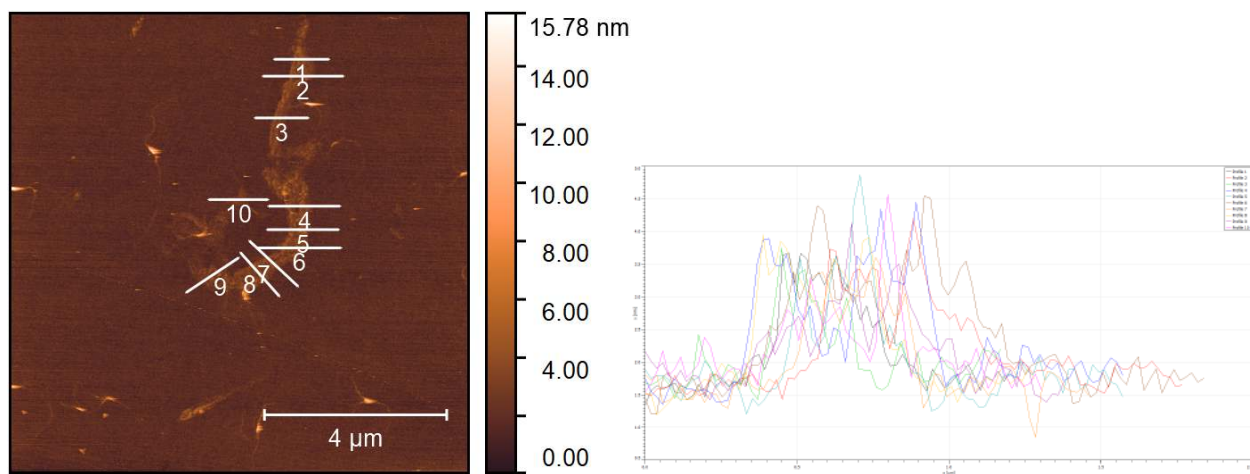
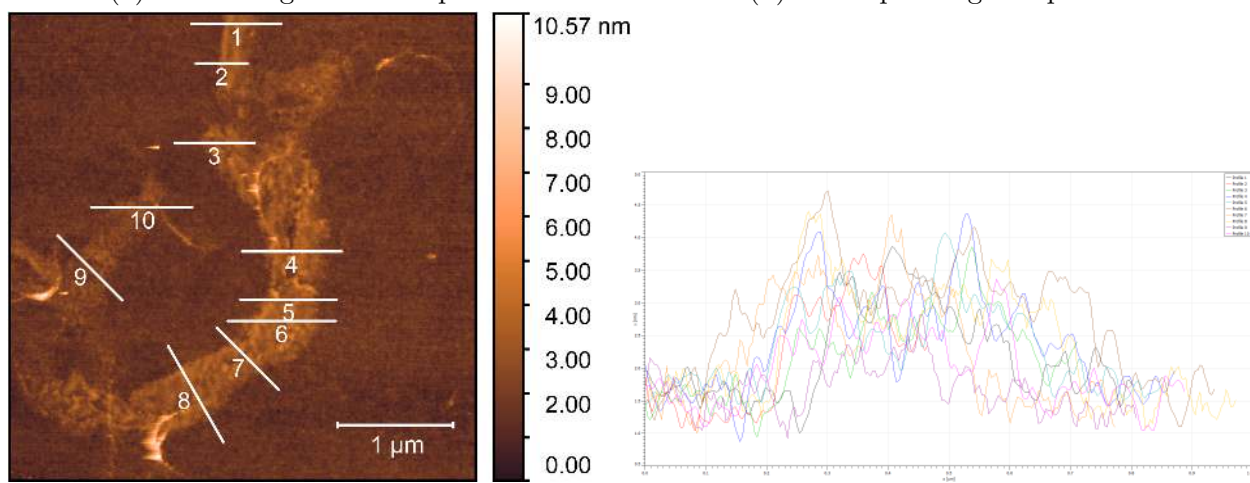


Figure 13: **3H** after surface coordination with Co(II)



(a) AFM image with line profiles

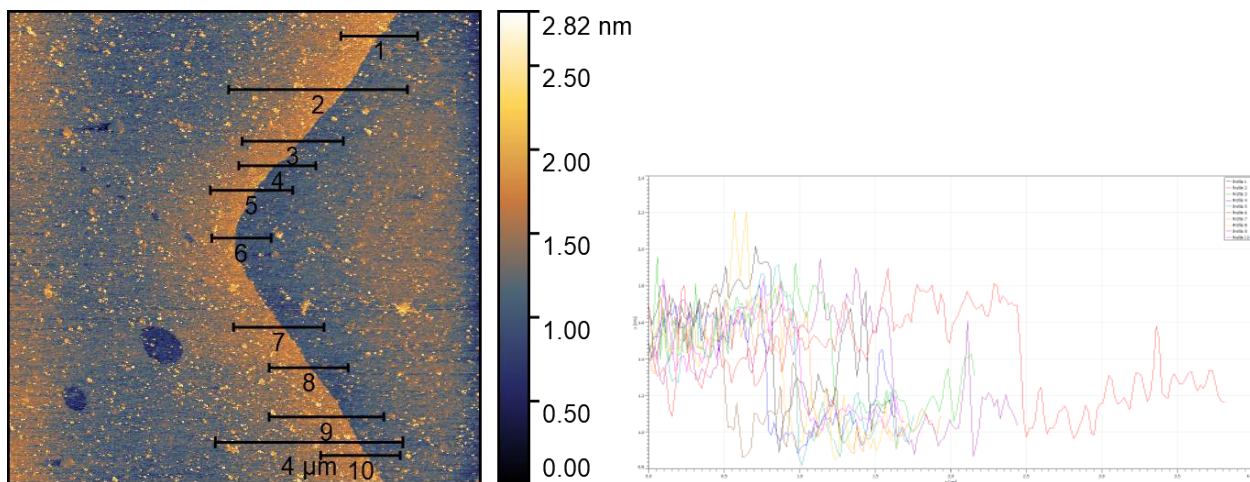
(b) Corresponding line profiles



(c) Zoomed in AFM image with line profiles

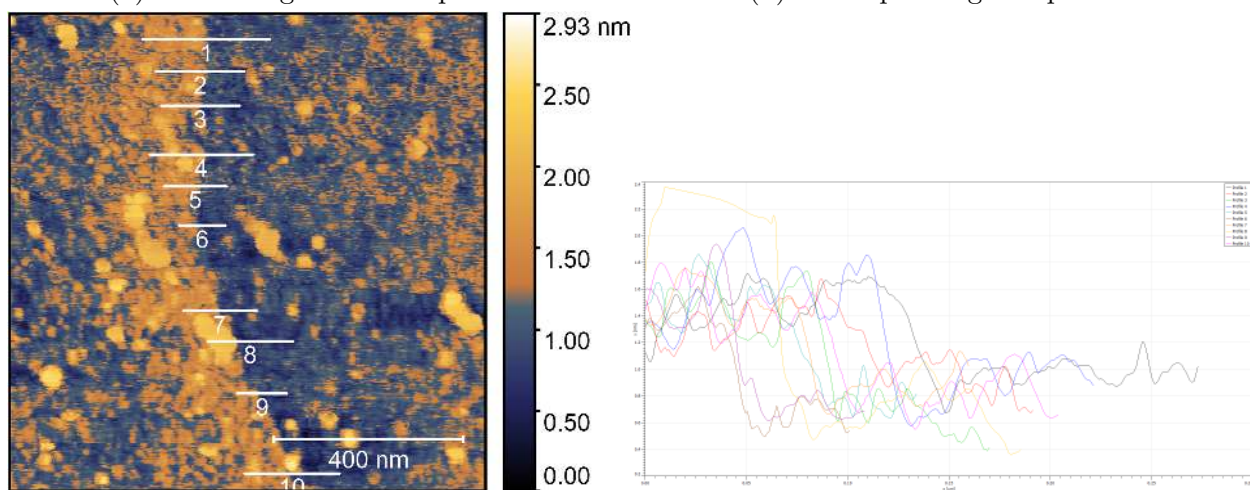
(d) Corresponding line profiles

Figure 14: **3H** after surface coordination with Ni(II)



(a) AFM image with line profiles

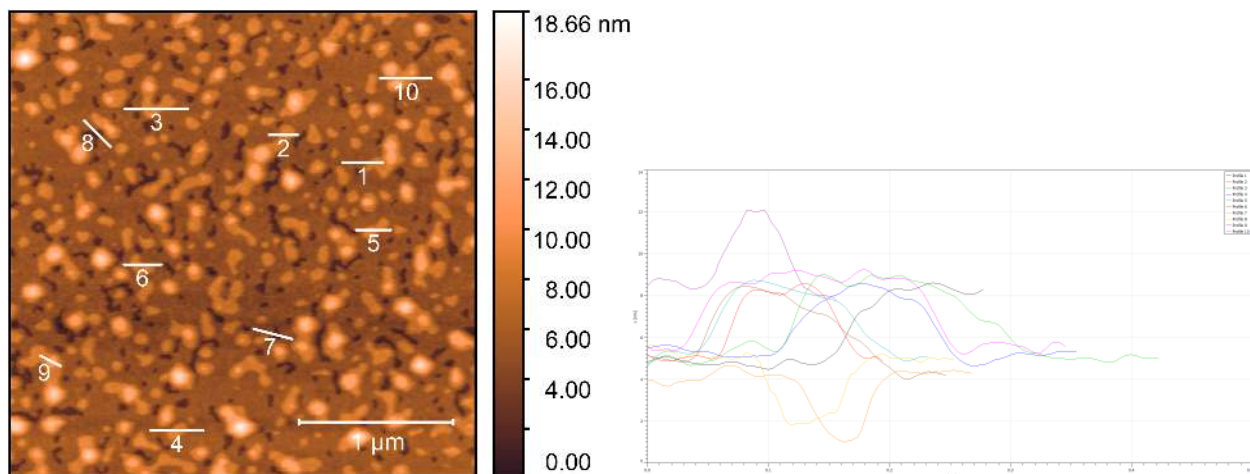
(b) Corresponding line profiles



(c) Zoomed in AFM image with line profiles

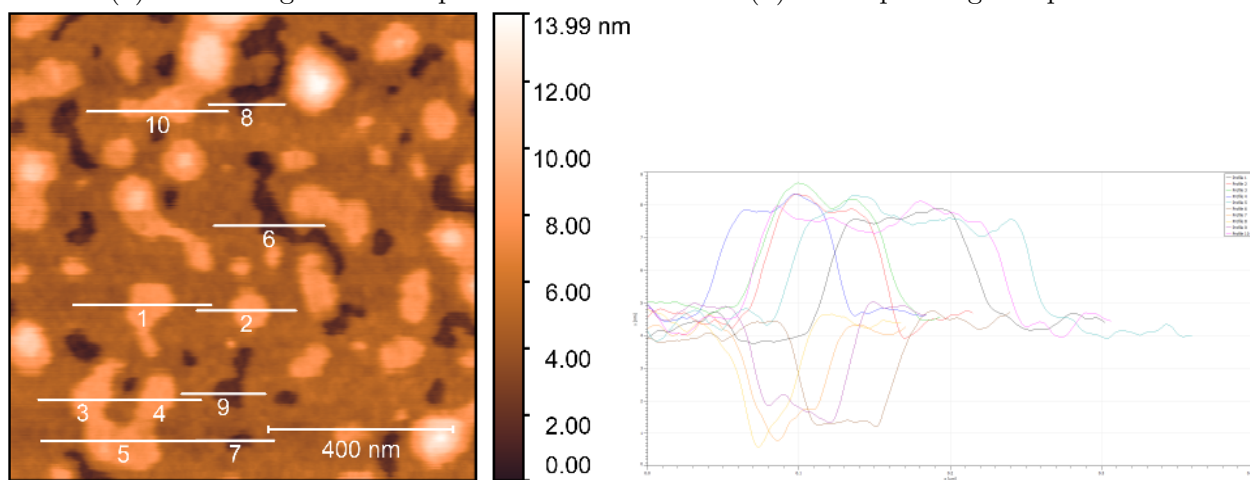
(d) Corresponding line profiles

Figure 15: **3H** after surface coordination with Cu(II)



(a) AFM image with line profiles

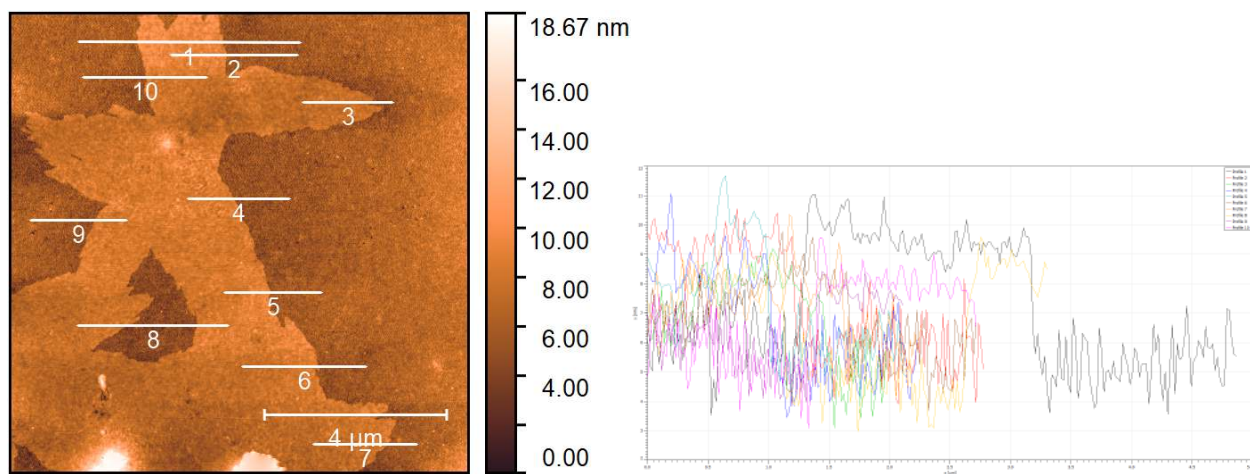
(b) Corresponding line profiles



(c) Zoomed in AFM image with line profiles

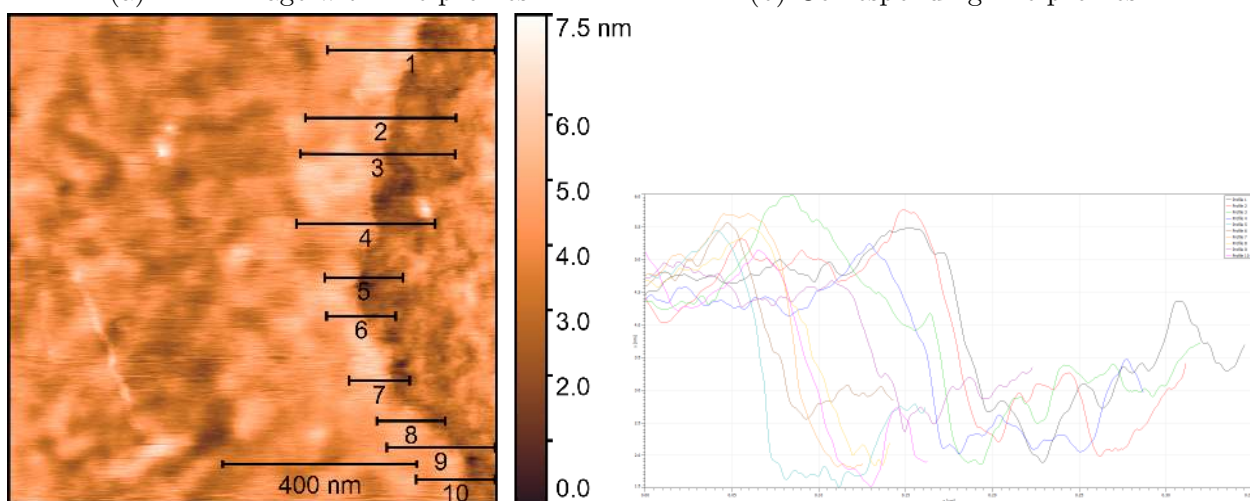
(d) Corresponding line profiles

Figure 16: **3H** after surface coordination with Zn(II)



(a) AFM image with line profiles

(b) Corresponding line profiles



(c) Zoomed in AFM image with line profiles

(d) Corresponding line profiles

Figure 17: **3H** after surface coordination with MoO₄

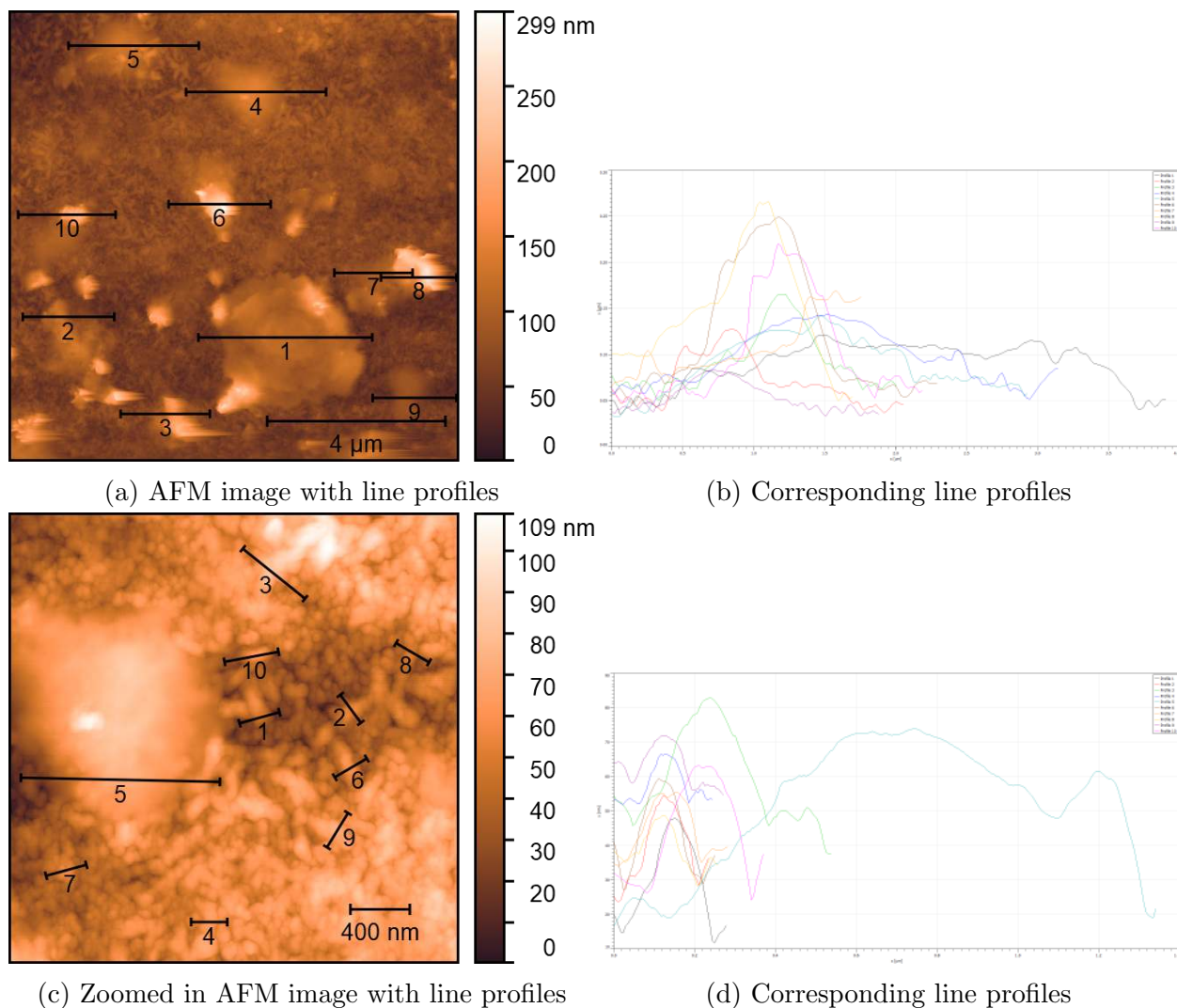
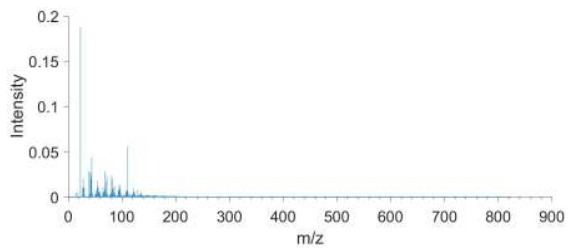


Figure 18: **3H** after surface coordination with WO₄

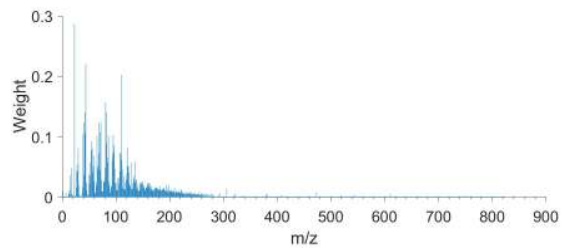
Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

ToF-SIMS mass spectra

This section contains the raw mass spectra from the ToF-SIMS measurements and corresponding weights from the machine learning analysis. The accompanying tables contain the ToF-SIMS mass assignments with corresponding normalised intensity.

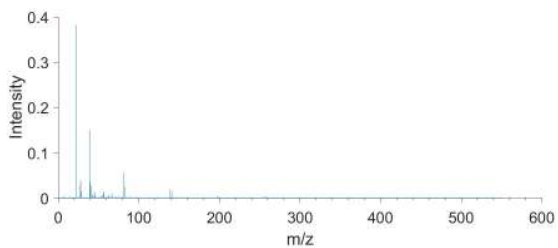


(a) Mass spectrum

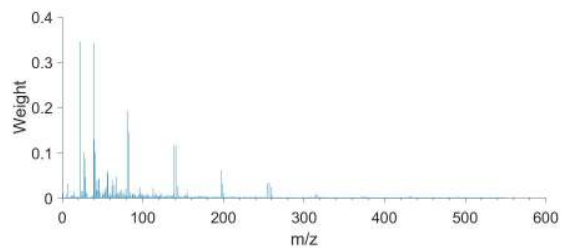


(b) Machine learning weights

Figure 19: 3H Pos

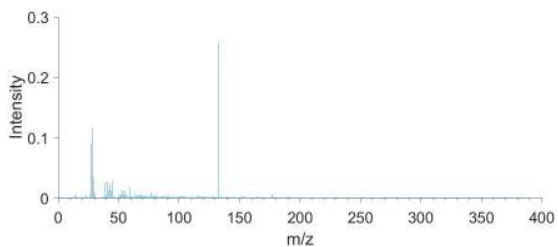


(a) Mass spectrum

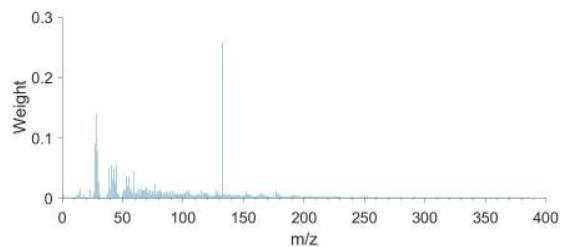


(b) Machine learning weights

Figure 20: Fe Pos

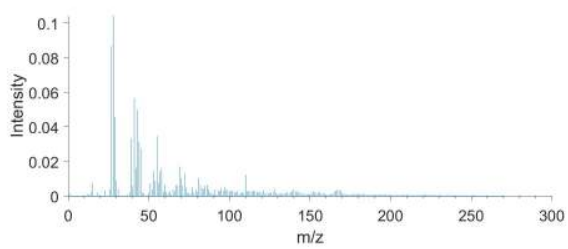


(a) Mass spectrum

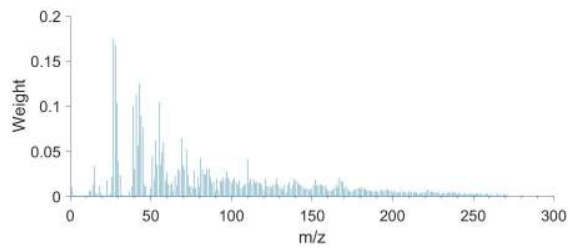


(b) Machine learning weights

Figure 21: Co Pos

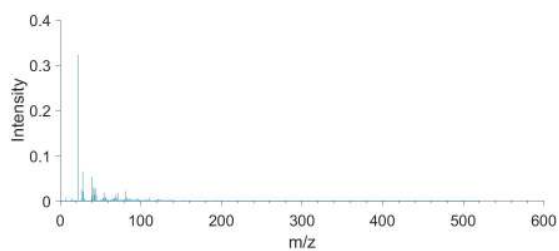


(a) Mass spectrum

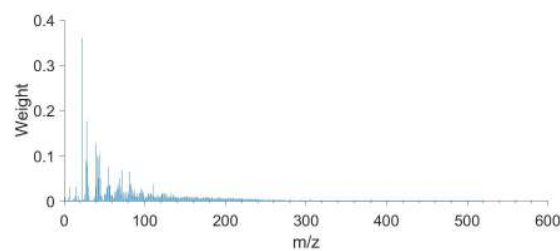


(b) Machine learning weights

Figure 22: Ni Pos

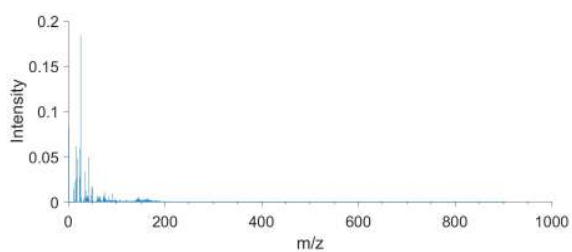


(a) Mass spectrum

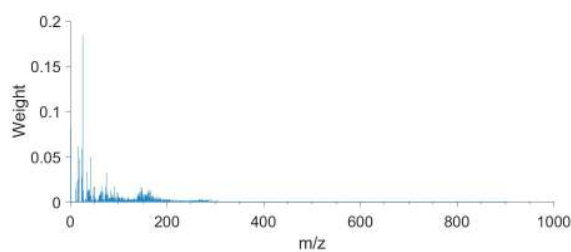


(b) Machine learning weights

Figure 23: Zn Pos

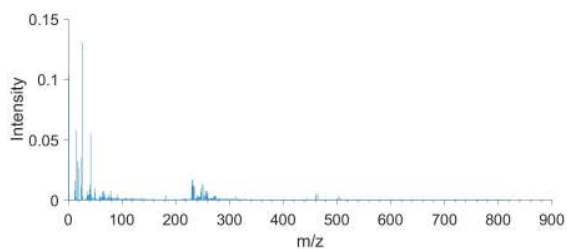


(a) Mass spectrum

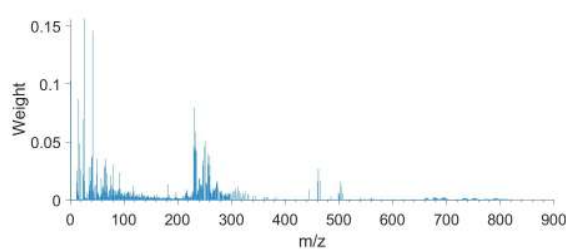


(b) Machine learning weights

Figure 24: MoO4 Neg



(a) Mass spectrum



(b) Machine learning weights

Figure 25: WO4 Neg

ToF-SIMS mass spectra peak assignments

Table 3: ToF-SIMS mass assignment for **3H** in positive
ion mode. Total Counts 88550596

Assignment	Mass (u)	Normalized Intensity
H+	1.0033	7.08E-04
H_2^+	2.016	5.57E-05
C+	11.9966	2.29E-04
CH+	13.0041	2.74E-04
CH ₂ +	14.0116	6.74E-04
CH ₃ +	15.0214	3.76E-03
O+	16.0173	9.80E-05
OH+	17.0234	2.26E-04
H ₂ O+	18.0353	3.64E-03
Na+	22.9777	2.04E-01
CN+	26.0142	1.17E-03
CHN+	27.0167	9.33E-03
Si+	28.003	1.62E-02
CHO+	29.0235	8.03E-03
CH ₂ O+	30.0285	8.43E-03
CH ₃ O+	31.018	1.29E-03
CH ₄ O+	32.0421	1.09E-04
C ₃ H+	37.0065	2.76E-04

Continued on next page

Table 3: ToF-SIMS mass assignment for **3H** in positive ion mode. Total Counts 88550596 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_2N+	38.0122	1.09E-03
C_2HN+	38.993	2.45E-02
C_2H_2N+	40.0194	2.89E-03
C_3H_5+	41.0356	2.50E-02
C_2H_4N+	42.0378	1.73E-02
C_2H_5N+	43.0346	2.19E-02
C_2H_6N+	44.0508	4.00E-02
SiCH_5+	45.0442	4.08E-03
C_3N+	50.0096	2.60E-03
C_4H_3+	51.0237	2.42E-03
C_4H_4+	52.0271	3.12E-03
C_4H_5+	53.0379	6.17E-03
C_4H_6+	54.0385	9.23E-03
C_3H_5N+	55.0458	1.54E-02
C_3H_6N+	56.0533	9.45E-03
C_3H_7N+	57.0506	5.13E-03
C_3H_6O+	58.07	4.32E-03
C_2H_5NO+	59.0395	1.75E-03

Continued on next page

Table 3: ToF-SIMS mass assignment for **3H** in positive
ion mode. Total Counts 88550596 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_2H_6NO+	60.0584	5.60E-03
C_4N+	62.0077	5.56E-04
C_4HO+	64.9999	9.88E-03
C_4H_5N+	67.0447	5.22E-03
C_3H_4N_2+	68.0465	7.46E-03
C_3H_5N_2+	69.0524	2.56E-02
C_3H_4NO+	70.0489	1.46E-02
C_3H_6NO+	72.0719	2.07E-02
C_5H_3N+	77.036	2.11E-03
C_6H_6+	78.0461	1.48E-03
C_5H_5N+	79.0478	2.31E-03
C_6H_8+	80.0576	4.15E-03
C_4H_5N_2+	81.0502	2.04E-02
C_5H_6O+	82.057	1.72E-02
C_5H_9N+	83.07	7.68E-03
C_4H_6NO+	84.0642	8.12E-03
C_4H_7NO+	85.0638	3.95E-03
C_4H_8NO+	86.0723	1.03E-02

Continued on next page

Table 3: ToF-SIMS mass assignment for **3H** in positive ion mode. Total Counts 88550596 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_5N_2+	88.0064	2.88E-03
C_6H_7N+	93.0689	5.72E-03
C_5H_4NO+	94.0573	6.53E-03
C_6H_7O+	95.0691	1.19E-02
C_6H_8O+	96.0768	6.79E-03
C_6H_9O+	97.0904	9.68E-03
C_6H_10O+	98.0829	3.62E-03
C_6H_8NO+	110.1012	5.18E-02
C_5HN_2O_2+	121.0753	7.86E-03
C_6H_4NO_2+	122.0644	3.85E-03

Table 4: ToF-SIMS mass assignment for **3H** plus Fe in positive ion mode. Total Counts 44531963

Assignment	Mass (u)	Normalized Intensity
H+	1.0031	1.04E-03
H_2+	2.0167	7.94E-05
$\hat{6}$ Li+	6.013	3.15E-04
Li+	7.0138	3.62E-03

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Table 4: ToF-SIMS mass assignment for **3H** plus Fe in positive ion mode. Total Counts 44531963 (Continued)

Assignment	Mass (u)	Normalized Intensity
$\hat{10}\text{B}^+$	10.011	9.19E-05
B^+	11.0069	3.44E-04
C^+	11.9976	3.98E-04
CH^+	13.0064	4.46E-04
CH_2^+	14.0136	9.66E-04
CH_3^+	15.0211	2.59E-03
O^+	16.0037	2.09E-04
OH^+	17.01	1.18E-04
H_2O^+	18.0279	1.32E-04
Na^+	22.9623	4.47E-01
Mg^+	23.9863	1.25E-03
CN^+	26.0126	1.72E-03
CHN^+	26.9983	2.51E-02
Si^+	27.9772	6.50E-02
CHO^+	29.0006	2.09E-02
CH_2O^+	29.9896	3.20E-03
CH_3O^+	31.0103	1.29E-03

Continued on next page

Table 4: ToF-SIMS mass assignment for **3H** plus Fe in positive ion mode. Total Counts 44531963 (Continued)

Assignment	Mass (u)	Normalized Intensity
CH ₄ O ⁺	32.0226	6.40E-05
C ₃ H ⁺	37.0067	3.23E-04
C ₂ N ⁺	38.0152	9.25E-04
K ⁺	38.9647	1.18E-01
Ca ⁺	39.9647	3.02E-02
BNO ⁺	41.0057	2.43E-02
C ₂ H ₄ N ⁺	42.029	3.16E-03
C ₂ H ₅ N ⁺	43.0353	1.08E-02
C ₂ H ₆ N ⁺	44.0203	3.23E-03
SiCH ₅ ⁺	45.0097	1.58E-02
NO ₂ ⁺	45.9865	4.60E-03
C ₃ N ⁺	50.016	1.00E-03
C ₄ H ₃ ⁺	51.0226	2.33E-03
C ₄ H ₄ ⁺	52.028	9.36E-04
C ₄ H ₅ ⁺	53.0332	3.88E-03
C ₄ H ₆ ⁺	54.0173	1.87E-03
C ₃ H ₅ N ⁺	55.0494	5.99E-03

Continued on next page

Table 4: ToF-SIMS mass assignment for **3H** plus Fe in positive ion mode. Total Counts 44531963 (Continued)

Assignment	Mass (u)	Normalized Intensity
Fe+	55.9508	1.38E-02
C_3H_7N+	57.0204	8.61E-03
C_3H_6O+	58.0532	7.47E-04
C_2H_5NO+	59.0279	1.22E-03
C_2H_6NO+	60.0308	2.57E-04
C_4N+	61.9923	2.56E-03
C_4HO+	65.0085	2.73E-03
C_4H_5N+	67.0091	8.93E-03
C_3H_4N_2+	68.0225	9.58E-04
C_3H_5N_2+	69.0445	1.85E-03
C_3H_4NO+	70.0287	6.71E-04
C_3H_6NO+	72.0148	2.04E-03
C_3H_5O_2+	73.0261	1.91E-03
C_5H_3N+	77.0364	2.14E-03
C_6H_6+	78.0306	8.95E-04
C_5H_5N+	79.023	2.45E-03
C_6H_8+	80.0406	5.39E-04

Continued on next page

Table 4: ToF-SIMS mass assignment for **3H** plus Fe in positive ion mode. Total Counts 44531963 (Continued)

Assignment	Mass (u)	Normalized Intensity
C ₄ H ₅ N ₂ ⁺	80.9949	1.26E-02
C ₅ H ₆ O ⁺	82.0312	5.40E-04
C ₅ H ₉ N ⁺	83.0148	5.19E-03
C ₄ H ₆ NO ⁺	84.0158	6.24E-04
C ₄ H ₇ NO ⁺	85.0232	8.49E-04
C ₄ H ₈ NO ⁺	86.0412	3.07E-04
C ₅ N ₂ ⁺	87.9938	1.10E-03
C ₆ H ₇ N ⁺	93.0511	4.50E-04
C ₅ H ₄ NO ⁺	94.038	2.47E-04
C ₆ H ₇ O ⁺	95.0286	8.61E-04
C ₆ H ₈ O ⁺	96.0204	7.78E-04
C ₆ H ₉ O ⁺	97.0269	1.20E-03
C ₆ H ₁₀ O ⁺	98.0382	4.67E-04
C ₆ H ₈ NO ⁺	110.072	2.28E-04
C ₂ H ₃ NOFe ⁺	112.9637	1.58E-03
C ₅ HN ₂ O ₂ ⁺	121.0376	4.94E-04
C ₆ H ₄ NO ₂ ⁺	121.994	3.55E-04

Continued on next page

Table 4: ToF-SIMS mass assignment for **3H** plus Fe in positive ion mode. Total Counts 44531963 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_4H_3O_2Fe+	138.9489	3.91E-03
C_4H_5O_2Fe+	140.9538	2.49E-03
C_4H_5NO_2Fe+	154.9646	1.25E-03
C_6H_5O_4Fe+	196.9397	5.92E-04
C_6H_7O_4Fe+	198.936	5.84E-04
C_8H_7O_6Fe+	254.9099	5.38E-04
C_8H_9O_6Fe+	256.9059	6.62E-04

Table 5: ToF-SIMS mass assignment for **3H** plus Co in positive ion mode. Total Counts 19467807

Assignment	Mass (u)	Normalized Intensity
H+	1.0047	1.47E-03
H_2+	2.0186	1.53E-04
C+	11.9991	9.15E-04
CH+	13.0084	1.08E-03
CH_2+	14.0152	2.13E-03
CH_3+	15.0234	5.41E-03

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Table 5: ToF-SIMS mass assignment for **3H** plus Co in
positive ion mode. Total Counts 19467807
(Continued)

Assignment	Mass (u)	Normalized Intensity
O+	16.0092	2.72E-04
OH+	17.0185	1.68E-04
H ₂ O+	18.0366	8.15E-04
Na+	22.9921	3.91E-03
CN+	26.0149	3.23E-03
CHN+	26.9924	8.01E-02
Si+	27.9793	1.08E-01
CHO+	28.9962	3.33E-02
CH ₂ O+	30.0011	7.37E-03
CH ₃ O+	31.005	1.69E-03
CH ₄ O+	32.0222	9.73E-05
C ₃ H+	37.0028	8.68E-04
C ₂ N+	38.0115	2.46E-03
C ₂ HN+	39.0035	2.32E-02
C ₂ H ₂ N+	40.0122	4.24E-03
C ₃ H ₅ +	41.0343	2.38E-02
C ₂ H ₄ N+	42.0293	1.15E-02

Continued on next page

Table 5: ToF-SIMS mass assignment for **3H** plus Co in
positive ion mode. Total Counts 19467807
(Continued)

Assignment	Mass (u)	Normalized Intensity
C ₂ H ₅ N ⁺	43.024	1.97E-02
C ₂ H ₆ N ⁺	44.0323	1.08E-02
SiCH ₅ ⁺	44.9787	2.37E-02
C ₃ N ⁺	50.0099	2.78E-03
C ₄ H ₃ ⁺	51.0219	6.57E-03
C ₄ H ₄ ⁺	52.0191	4.28E-03
C ₄ H ₅ ⁺	53.0263	1.11E-02
C ₄ H ₆ ⁺	54.027	5.69E-03
C ₃ H ₅ N ⁺	55.0398	1.01E-02
C ₃ H ₆ N ⁺	56.0334	3.87E-03
C ₃ H ₇ N ⁺	57.0351	2.39E-03
C ₃ H ₆ O ⁺	58.0499	1.45E-03
Co ⁺	58.9373	1.50E-02
C ₂ H ₆ NO ⁺	60.0124	1.34E-03
C ₄ N ⁺	62.0017	1.77E-03
C ₄ HO ⁺	65.0161	4.81E-03
C ₄ H ₅ N ⁺	67.0314	4.87E-03

Continued on next page

Table 5: ToF-SIMS mass assignment for **3H** plus Co in
positive ion mode. Total Counts 19467807
(Continued)

Assignment	Mass (u)	Normalized Intensity
C_3H_4N_2+	68.0312	3.37E-03
C_3H_5N_2+	69.0343	4.56E-03
C_3H_4NO+	70.0249	3.47E-03
C_3H_6NO+	72.0196	3.24E-03
C_5H_3N+	77.0233	7.63E-03
C_6H_6+	78.0348	2.50E-03
C_5H_5N+	79.0354	3.30E-03
C_6H_8+	80.0406	2.14E-03
C_4H_5N_2+	81.0365	4.02E-03
C_5H_6O+	82.0382	2.03E-03
C_5H_9N+	83.0473	1.18E-03
C_4H_6NO+	84.0263	1.92E-03
C_4H_7NO+	85.0175	1.25E-03
C_4H_8NO+	86.0061	2.73E-03
C_5N_2+	87.9793	1.58E-03
C_6H_7N+	93.0404	1.72E-03
C_5H_4NO+	94.0347	1.52E-03

Continued on next page

Table 5: ToF-SIMS mass assignment for **3H** plus Co in
positive ion mode. Total Counts 19467807
(Continued)

Assignment	Mass (u)	Normalized Intensity
C_6H_7O+	95.0455	1.96E-03
C_6H_8O+	96.0463	1.18E-03
C_6H_9O+	97.04	1.18E-03
C_6H_10O+	98.0328	1.20E-03
CHN_2Co+	99.9592	1.33E-03
CO_2Co+	102.9574	3.62E-03
CHO_2Co+	103.982	1.59E-03
C_6H_8NO+	110.0604	1.02E-03
C_5HN_2O_2+	121.0303	1.44E-03
C_6H_4NO_2+	121.9941	8.56E-04
Cs+	132.8841	2.57E-01
C_4H_5N_2Co+	139.9831	9.58E-04

Table 6: ToF-SIMS mass assignment for **3H** plus Ni in pos-
itive ion mode. Total Counts 31223581

Assignment	Mass (u)	Normalized Intensity
H+	1.0049	1.24E-03

Continued on next page

Table 6: ToF-SIMS mass assignment for **3H** plus Ni in positive ion mode. Total Counts 31223581 (Continued)

Assignment	Mass (u)	Normalized Intensity
H ₂ ⁺	2.0176	1.33E-04
C ⁺	11.9997	5.40E-04
CH ⁺	13.0081	7.38E-04
CH ₂ ⁺	14.0159	1.81E-03
CH ₃ ⁺	15.025	6.68E-03
O ⁺	16.0134	2.75E-04
OH ⁺	17.0233	2.17E-04
H ₂ O ⁺	18.0384	1.93E-03
Na ⁺	22.9944	2.80E-03
CN ⁺	26.0157	3.35E-03
CHN ⁺	26.9977	7.13E-02
Si ⁺	27.9819	1.05E-01
CHO ⁺	29.0039	4.78E-02
CH ₂ O ⁺	30.0093	9.85E-03
CH ₃ O ⁺	31.011	3.40E-03
CH ₄ O ⁺	32.0262	1.43E-04
C ₃ H ⁺	37.0067	5.81E-04
C ₂ N ⁺	38.0128	1.95E-03

Continued on next page

Table 6: ToF-SIMS mass assignment for **3H** plus Ni in positive ion mode. Total Counts 31223581 (Continued)

Assignment	Mass (u)	Normalized Intensity
C ₂ HN ⁺	39.0079	2.38E-02
C ₂ H ₂ N ⁺	40.0153	5.32E-03
C ₃ H ₅ ⁺	41.037	4.77E-02
C ₂ H ₄ N ⁺	42.0346	1.84E-02
C ₂ H ₅ N ⁺	43.0375	4.55E-02
C ₂ H ₆ N ⁺	44.045	2.99E-02
SiCH ₅ ⁺	45.0115	2.67E-02
C ₃ N ⁺	50.013	1.57E-03
C ₄ H ₃ ⁺	51.0229	3.95E-03
C ₄ H ₄ ⁺	52.0243	3.06E-03
C ₄ H ₅ ⁺	53.0311	1.02E-02
C ₄ H ₆ ⁺	54.0337	7.73E-03
C ₃ H ₅ N ⁺	55.0441	2.50E-02
C ₃ H ₆ N ⁺	56.0446	8.95E-03
C ₃ H ₇ N ⁺	57.0529	1.25E-02
Ni ⁺	57.9582	1.18E-02
C ₂ H ₅ NO ⁺	59.03	2.62E-03
C ₂ H ₆ NO ⁺	60.0158	4.93E-03

Continued on next page

Table 6: ToF-SIMS mass assignment for **3H** plus Ni in positive ion mode. Total Counts 31223581 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_4N+	61.9893	1.55E-03
C_4HO+	65.0164	3.27E-03
C_4H_5N+	67.039	5.74E-03
C_3H_4N_2+	68.0373	5.29E-03
C_3H_5N_2+	69.0446	1.86E-02
C_3H_4NO+	70.0371	9.23E-03
C_3H_6NO+	72.0633	9.66E-03
C_5H_3N+	77.0266	4.53E-03
C_6H_6+	78.033	1.67E-03
C_5H_5N+	79.033	3.38E-03
C_6H_8+	80.0446	1.99E-03
C_4H_5N_2+	81.0419	1.16E-02
C_5H_6O+	82.0441	7.70E-03
C_5H_9N+	83.0553	3.73E-03
C_4H_6NO+	84.0391	3.89E-03
C_4H_7NO+	85.0196	4.84E-03
C_4H_8NO+	86.0459	5.76E-03
C_5N_2+	87.9886	1.72E-03

Continued on next page

Table 6: ToF-SIMS mass assignment for **3H** plus Ni in positive ion mode. Total Counts 31223581 (Continued)

Assignment	Mass (u)	Normalized Intensity
NiO_2+	89.9956	8.24E-04
NiO_2H+	91.0402	3.28E-03
NiO_2H_2+	92.0341	8.49E-04
C_6H_7N+	93.0519	3.03E-03
C_5H_4NO+	94.043	2.54E-03
C_6H_7O+	95.0536	4.13E-03
C_6H_8O+	96.0516	2.45E-03
C_6H_9O+	97.0659	4.50E-03
C_6H_10O+	98.0416	2.79E-03
C_6H_8NO+	110.0843	1.09E-02
C_5HN_2O_2+	121.0391	3.05E-03
C_6H_4NO_2+	122.0102	1.29E-03
C_2H_2N_2O_2Ni+	143.9539	1.74E-03
C_6HN_2O_2Ni+	190.9643	6.96E-04
C_4H_4N_8Ni+	221.9661	8.16E-04

Table 7: ToF-SIMS mass assignment for **3H** plus Cu in positive ion mode. Total Counts 32864224

Assignment	Mass (u)	Normalized Intensity
H+	1.0063	1.51E-03
O+	16.0144	2.82E-04
Na+	22.9949	5.63E-03
CN+	26.0164	3.25E-03
CHN+	27.0019	5.00E-02
Si+	27.9808	1.14E-01
CHO+	29.0026	4.95E-02
CH ₂ O+	30.0035	8.77E-03
CH ₃ O+	31.0127	3.93E-03
SiHO+	44.9899	3.74E-02
C ₄ N+	62.0029	1.09E-03
Cu+	62.9363	2.95E-02
CuH ₂ +	64.943	1.47E-02
C ₄ H ₅ N+	67.04	5.22E-03
C ₃ H ₄ N ₂ +	68.0371	3.77E-03
C ₃ H ₅ N ₂ +	69.0466	1.23E-02
C ₃ H ₄ NO+	70.0374	6.56E-03
C ₃ H ₆ NO+	72.0582	6.81E-03

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Table 7: ToF-SIMS mass assignment for **3H** plus Cu in positive ion mode. Total Counts 32864224 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_4H_5N_2+	81.0394	9.01E-03
C_5H_6O+	82.0414	3.70E-03
C_4H_6NO+	84.0491	2.33E-03
C_4H_8NO+	86.0579	3.03E-03
CHNCu+	89.9465	4.81E-03
COCu+	91.0081	4.47E-03
CHOCu+	91.9565	3.32E-03
C_5H_4NO+	94.0282	1.77E-03
C_6H_7O+	95.0493	2.61E-03
CHN_2Cu+	103.9666	2.99E-03
CHO_2Cu+	107.9801	2.32E-03
CH_3O_2Cu+	110.0654	2.89E-03
C_6H_4NO_2+	122.0064	1.61E-03
C_4OCu+	126.9064	2.38E-03
C_4H_5N_2Cu+	143.961	2.94E-03
C_5H_8N_2O_2Cu+	190.906	1.75E-03
C_4H_4N_8Cu+	226.9367	7.40E-04

Table 8: ToF-SIMS mass assignment for **3H** plus Cu in
negative ion mode. Total Counts 46938036

Assignment	Mass (u)	Normalized Intensity
H-	1.0096	1.40E-01
C-	12.0055	6.59E-03
CH-	13.0134	1.47E-02
CH ₂ -	14.0218	2.68E-03
CH ₃ -	15.0255	8.51E-04
O-	15.9994	1.15E-01
OH-	17.008	5.89E-02
H ₂ O-	18.0052	2.49E-04
F-	19.0061	1.18E-03
C ₂ -	24.0068	8.87E-03
C ₂ H-	25.0144	2.71E-02
CN-	26.009	9.99E-02
CHN-	27.0168	2.18E-03
Si-	27.9849	2.05E-03
SiH-	28.9909	1.97E-03
SiH ₂ -	29.997	6.10E-04
Cl-	34.9762	1.11E-02
NaN-	36.9805	4.63E-03

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Table 8: ToF-SIMS mass assignment for **3H** plus Cu in
negative ion mode. Total Counts 46938036
(Continued)

Assignment	Mass (u)	Normalized Intensity
CH_3Na-	38.0127	2.67E-03
C_2HN-	39.0186	2.61E-03
C_2H_2N-	40.0152	6.11E-03
CHN_2-	41.0122	1.00E-02
CNO-	42.0069	4.57E-02
CHO_2-	44.9979	2.55E-03
C_4-	47.9998	1.44E-03
C_4H_2-	50.0124	4.33E-03
C_4H_3-	51.0213	7.23E-04
C_2H_4NO-	58.0299	3.22E-03
SiO_2-	59.9743	1.82E-02
SiHO_2-	60.9824	1.08E-02
C_4HO-	65.006	4.01E-03
SiO_3-	75.9688	1.02E-02
SiHO_3-	76.9765	2.03E-02
PO_3H-	79.9661	1.10E-02
C_2H_3OCu-	105.9471	6.01E-03

Continued on next page

Table 8: ToF-SIMS mass assignment for **3H** plus Cu in
negative ion mode. Total Counts 46938036
(Continued)

Assignment	Mass (u)	Normalized Intensity
C_2N_2Cu-	114.9419	1.06E-02
C_2HN_2Cu-	115.952	1.70E-03
C_2H_2N_2Cu-	116.9425	5.45E-03
C_3O_2Cu-	130.9419	8.49E-03
C_3HO_2Cu-	131.9534	1.58E-03
C_3H_2O_2Cu-	132.9401	4.42E-03

Table 9: ToF-SIMS mass assignment for **3H** plus Zn in pos-
itive ion mode. Total Counts 44258597

Assignment	Mass (u)	Normalized Intensity
H+	1.0049	8.60E-04
H_2+	2.0185	9.30E-05
C+	11.9992	4.85E-04
CH+	13.0079	5.70E-04
CH_2+	14.0156	1.27E-03
CH_3+	15.0241	4.57E-03
O+	16.0133	1.92E-04

Continued on next page

Table 9: ToF-SIMS mass assignment for **3H** plus Zn in positive ion mode. Total Counts 44258597 (Continued)

Assignment	Mass (u)	Normalized Intensity
OH+	17.022	1.70E-04
H ₂ O+	18.0365	1.63E-03
Na+	22.9726	2.36E-01
CN+	26.0157	2.17E-03
CHN+	27.005	2.57E-02
Si+	27.9839	4.55E-02
CHO+	29.0086	2.10E-02
CH ₂ O+	30.0159	5.79E-03
CH ₃ O+	31.0129	1.35E-03
CH ₄ O+	32.0277	7.13E-05
C ₃ H+	37.0029	4.24E-04
C ₂ N+	38.0118	1.37E-03
C ₂ HN+	38.9772	7.49E-02
C ₂ H ₂ N+	39.9928	1.23E-02
C ₃ H ₅ +	41.0282	3.43E-02
C ₂ H ₄ N+	42.0338	1.28E-02
C ₂ H ₅ N+	43.035	2.22E-02
C ₂ H ₆ N+	44.0441	2.45E-02

Continued on next page

Table 9: ToF-SIMS mass assignment for **3H** plus Zn in positive ion mode. Total Counts 44258597 (Continued)

Assignment	Mass (u)	Normalized Intensity
SiCH ₅ ⁺	45.0123	9.48E-03
C ₃ N ⁺	50.0068	1.65E-03
C ₄ H ₃ ⁺	51.0196	2.70E-03
C ₄ H ₄ ⁺	52.0224	2.47E-03
C ₄ H ₅ ⁺	53.0304	6.25E-03
C ₄ H ₆ ⁺	54.0318	5.98E-03
C ₃ H ₅ N ⁺	55.0427	1.42E-02
C ₃ H ₆ N ⁺	56.0397	6.02E-03
C ₃ H ₇ N ⁺	57.0315	7.84E-03
C ₃ H ₆ O ⁺	58.0589	2.36E-03
C ₂ H ₅ NO ⁺	59.0244	1.28E-03
C ₂ H ₆ NO ⁺	60.0465	2.32E-03
C ₄ N ⁺	61.9915	1.30E-03
C ₄ HN ⁺	62.9898	5.02E-03
Zn	63.9426	3.06E-03
C ₄ HO ⁺	64.9969	4.28E-03
C ₄ H ₅ N ⁺	67.0171	6.38E-03
C ₃ H ₄ N ₂ ⁺	68.0223	4.89E-03

Continued on next page

Table 9: ToF-SIMS mass assignment for **3H** plus Zn in positive ion mode. Total Counts 44258597 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_3H_5N_2+	69.0404	1.38E-02
C_3H_4NO+	70.0338	6.74E-03
C_3H_6NO+	72.0339	1.60E-02
C_3H_7NO+	73.0451	1.96E-03
C_5H_3N+	77.0181	2.56E-03
C_6H_6+	78.0251	1.29E-03
C_5H_5N+	79.0189	2.81E-03
C_6H_8+	80.0361	2.08E-03
C_4H_5N_2+	81.0035	2.90E-02
C_5H_6O+	82.0353	6.98E-03
C_5H_9N+	83.0144	7.98E-03
C_4H_6NO+	84.039	2.98E-03
C_4H_7NO+	85.0361	1.81E-03
C_4H_8NO+	86.0515	4.67E-03
C_5N_2+	87.9838	4.66E-03
C_6H_5N+	91.0175	2.12E-03
COZn+	92.0191	9.37E-04
SiCH_9N_2O+	93.0372	2.63E-03

Continued on next page

Table 9: ToF-SIMS mass assignment for **3H** plus Zn in positive ion mode. Total Counts 44258597 (Continued)

Assignment	Mass (u)	Normalized Intensity
C_5H_4NO+	94.0343	2.56E-03
C_6H_7O+	95.0457	3.65E-03
C_6H_8O+	96.0532	2.18E-03
C_6H_9O+	96.9738	8.13E-03
C_6H_10O+	98.0298	2.27E-03
ZnO_2H_3+	98.938	2.50E-03
C_5N_2O+	103.9872	2.04E-03
CHN_2Zn+	104.9996	1.63E-03
C_5H_4N_2O+	108.0237	2.47E-03
CH_5N_2Zn+	109.0391	1.86E-03
C_6H_8NO+	110.0783	9.37E-03
CH_3O_2Zn+	111.0243	1.64E-03
C_6H_3NO_2+	121.0193	3.03E-03
C_6H_4NO_2+	122.0018	1.86E-03
NaN_2Cl_2OH_2+	138.935	1.50E-03
NaClO_5H_3+	140.9413	1.08E-03
C_2H_4N_2O_2Zn+	152.0166	9.27E-04
C_2H_2O_4Zn+	153.9883	6.13E-04

Table 10: ToF-SIMS mass assignment for **3H** plus MoO4

in negative ion mode, Total Counts 56996280

Assignment	Mass (u)	Normalized Intensity
H-	1.0099	1.08E-01
C-	12.0066	1.43E-02
CH-	13.0147	2.45E-02
CH ₂ -	14.0233	2.29E-03
CH ₃ -	15.0262	4.30E-04
O-	16.0024	5.00E-02
OH-	17.0109	2.22E-02
H ₂ O-	18.006	1.07E-04
F-	19.0067	4.17E-02
C ₂ -	24.0092	2.69E-02
C ₂ H-	25.0171	6.46E-02
CN-	26.0065	1.71E-01
CHN-	27.0192	3.32E-03
Si-	27.9895	5.13E-04
SiH-	28.9962	3.70E-04
SiH ₂ -	30.0002	2.08E-04
CH ₃ O-	31.0124	1.10E-04
O ₂ -	31.9903	3.24E-03

Continued on next page

Table 10: ToF-SIMS mass assignment for **3H** plus MoO4
in negative ion mode, Total Counts 56996280
(Continued)

Assignment	Mass (u)	Normalized Intensity
O_2H-	32.9972	1.58E-03
Cl-	34.9793	2.67E-02
NaN-	36.9839	1.06E-02
CH_3Na-	38.0171	4.02E-03
C_2HN-	39.0229	3.30E-03
C_2H_2N-	40.0219	5.47E-03
CHN_2-	41.0189	6.28E-03
CNO-	42.0137	4.17E-02
C_2H_3O-	43.0266	2.78E-03
C_2H_4O-	44.0277	3.39E-04
CHO_2-	45.0087	9.34E-04
C_4-	48.0108	6.36E-03
C_4H_2-	50.0303	1.36E-02
C_4H_3-	51.0302	1.51E-03
C_4H_4-	52.0379	7.20E-04
C_4H_5-	53.0314	4.55E-04
C_2H_4NO-	58.0177	1.29E-03

Continued on next page

Table 10: ToF-SIMS mass assignment for **3H** plus MoO4

in negative ion mode, Total Counts 56996280

(Continued)

Assignment	Mass (u)	Normalized Intensity
SiO_2-	59.9889	5.78E-03
SiHO_2-	60.9998	3.19E-03
C_5H_4-	64.0235	4.47E-03
C_4HO-	65.0253	4.74E-03
C_4H_4N-	66.0318	4.87E-03
C_3H_3NO-	69.0298	6.08E-04
SiO_3-	75.9863	2.56E-03
SiHO_3-	76.9885	2.66E-03
PO_3H-	79.9831	2.43E-03
C_4H_3N_2O_2-	111.0207	7.32E-04
C_4H_5N_2O_2-	113.0258	7.47E-04
MoO_2-	129.9562	7.23E-04
MoO_3-	145.9409	3.76E-03
C_7H_11N_2O_2-	155.0036	1.18E-03
MoO_4-	161.9396	2.32E-03
CO_5Mo-	189.9361	5.68E-04

Table 11: ToF-SIMS mass assignment for **3H** plus WO4
in negative ion mode, Total Counts 67278795

Assignment	Mass (u)	Normalized Intensity
H-	1.0081	9.09E-02
C-	12.0022	5.80E-03
CH-	13.0099	1.24E-02
CH ₂ -	14.0174	1.94E-03
CH ₃ -	15.0211	6.10E-04
O-	15.9962	4.86E-02
OH-	17.0045	2.62E-02
H ₂ O-	18.0006	1.07E-04
F-	19.0011	2.08E-02
Na-	22.9923	1.26E-04
C ₂ -	24.0027	8.71E-03
C ₂ H-	25.0105	2.91E-02
CN-	26.0031	1.16E-01
CHN-	27.013	2.57E-03
Si-	27.9897	2.27E-04
SiH-	28.992	1.85E-04
SiH ₂ -	29.9979	1.81E-04
CH ₃ O-	31.0116	1.54E-04

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Table 11: ToF-SIMS mass assignment for **3H** plus WO4
in negative ion mode, Total Counts 67278795
(Continued)

Assignment	Mass (u)	Normalized Intensity
O_2-	31.9869	1.82E-03
O_2H-	32.9918	7.00E-04
Cl-	34.9737	5.65E-03
C_3-	36.0022	2.03E-03
NaN-	36.9844	3.15E-03
CH_3Na-	38.0095	3.29E-03
C_2HN-	39.0145	3.48E-03
C_2H_2N-	40.015	7.04E-03
CHN_2-	41.0103	1.02E-02
CNO-	42.0046	4.60E-02
C_2H_3O-	43.0185	3.34E-03
C_2H_4O-	44.0205	6.55E-04
CHO_2-	45.0012	1.89E-03
C_4-	47.9973	2.05E-03
C_4H_2-	50.0177	7.97E-03
C_4H_3-	51.021	1.05E-03
C_4H_4-	52.0279	7.61E-04

Continued on next page

Table 11: ToF-SIMS mass assignment for **3H** plus WO4
in negative ion mode, Total Counts 67278795
(Continued)

Assignment	Mass (u)	Normalized Intensity
C_4H_5-	53.0227	4.65E-04
C_2H_4NO-	58.0269	2.12E-03
SiO_2-	59.9772	2.70E-03
SiHO_2-	60.9855	1.90E-03
C_5H_4-	64.0111	4.66E-03
C_4HO-	65.016	5.60E-03
C_4H_4N-	66.0213	5.33E-03
C_3H_3NO-	69.0123	3.60E-03
SiO_3-	75.9771	1.51E-03
SiHO_3-	76.979	2.59E-03
PO_3H-	79.9723	6.27E-03
C_4H_3N_2O_2-	111.01	7.35E-04
C_4H_5N_2O_2-	113.0179	1.27E-03
C_7H_11N_2O_2-	155.0222	2.99E-04
WO-	199.9807	1.67E-04
WO_2-	215.9702	9.78E-04
WO_3-	231.9688	1.38E-02

Continued on next page

Table 11: ToF-SIMS mass assignment for **3H** plus WO4
in negative ion mode, Total Counts 67278795
(Continued)

Assignment	Mass (u)	Normalized Intensity
WO_4-	247.9783	5.54E-03
CO_5W-	275.9823	2.06E-03