Electronic Supplementary Information

Solution processed CZTS solar cells using amine-thiol systems: under-standing the dissolution process and device fabrication

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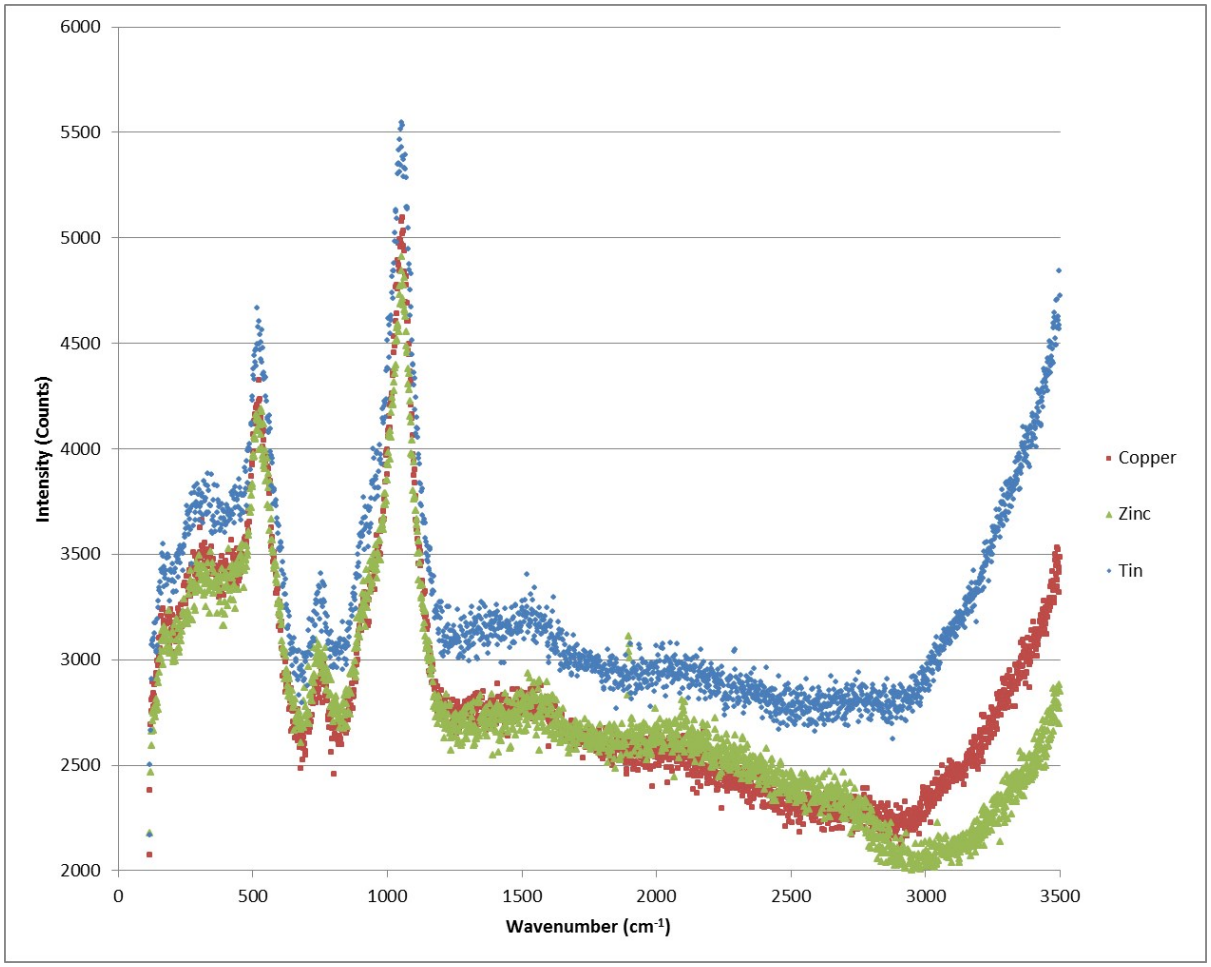


Figure S1: Raman spectroscopy data for three ethanolamine/cysteamine solutions containing one of the metals (Cu, Zn, and Sn).

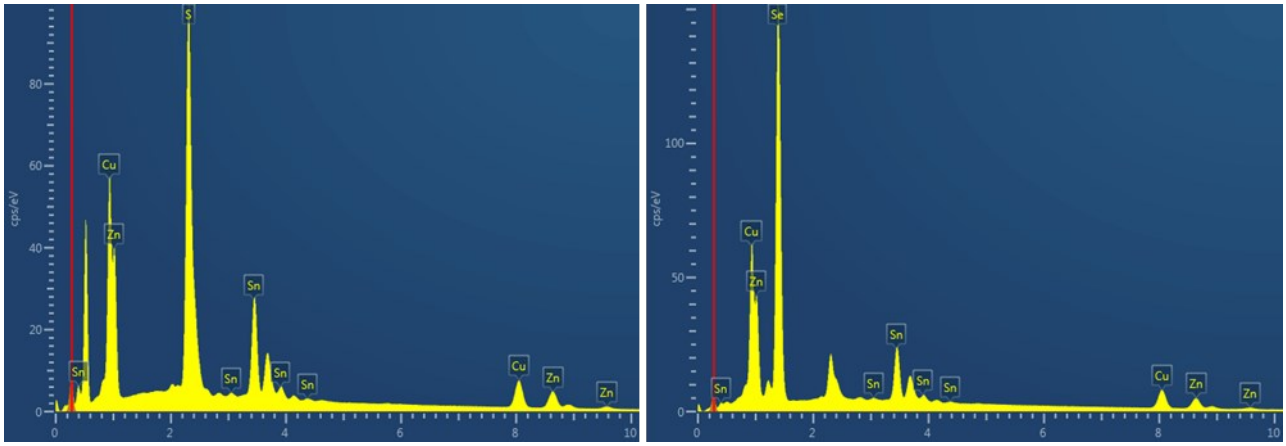


Figure S2: Surface EDX analysis (15 kV) of thin films after spin deposition (left), and after selenisation (right). The remaining peak at ~2.3 keV in the right EDX data could refer to S or Mo, but is most likely indicating Mo (See also Figure S24b).

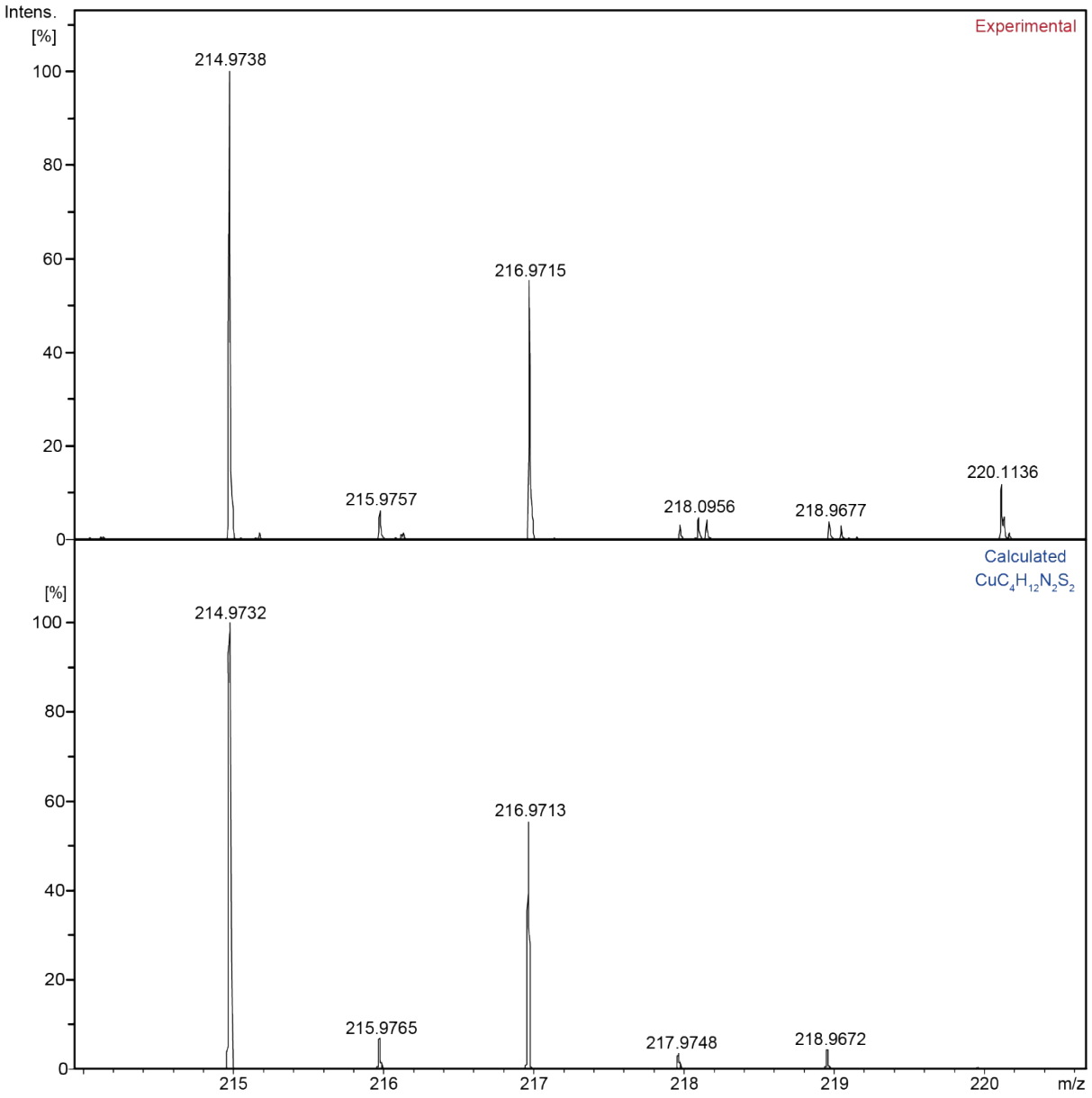


Figure S3: ESI-(+)MS spectrum of dissolved copper, expanded to the $CuC_4H_{12}N_2S_2$ complex. Accurate mass for $[M]^+$ 214.9738 Da, exact mass for $CuC_4H_{12}N_2S_2$ 214.9732 Da, Δ = 2.8 ppm.

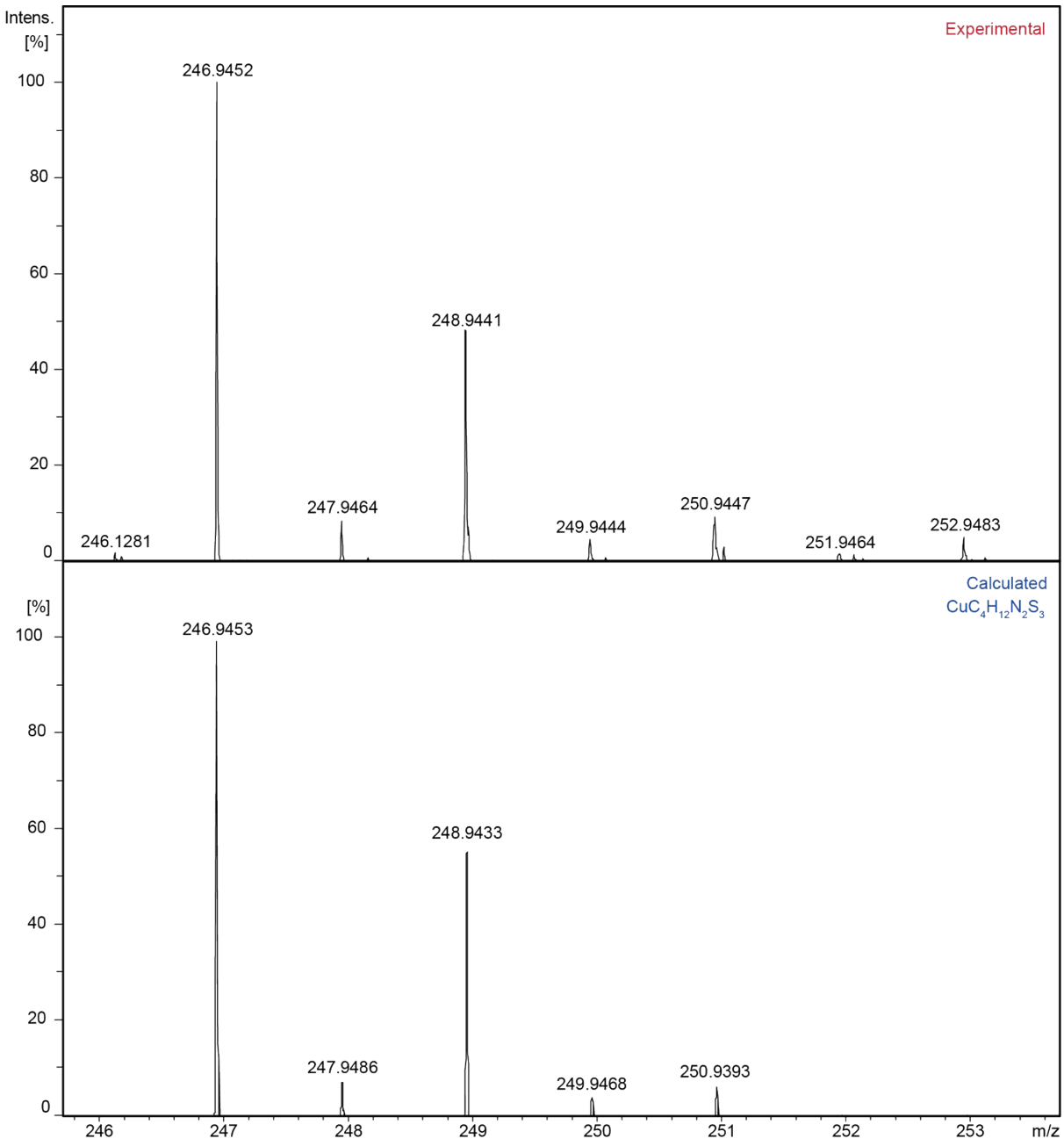


Figure S4: ESI-(+)MS spectrum of dissolved copper, expanded to the $CuC_4H_{12}N_2S_3$ complex. Accurate mass for $[M]^+$ 246.9452 Da, exact mass for $CuC_4H_{12}N_2S_3$ 246.9453 Da, Δ = 0.4 ppm.

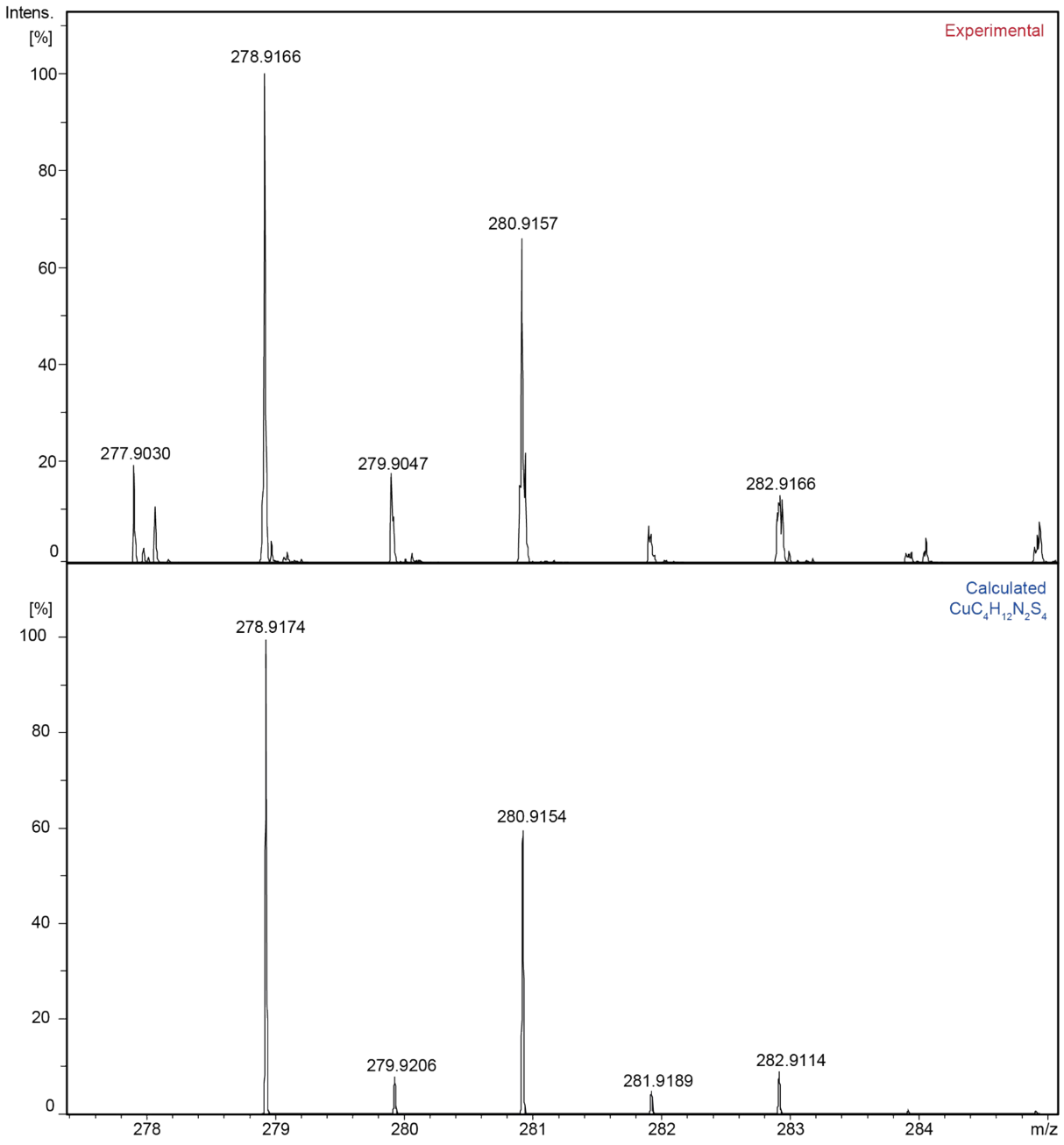


Figure S5: ESI-(+)MS spectrum of dissolved copper, expanded to the $CuC_4H_{12}N_2S_4$ complex. Accurate mass for $[M]^+$ 278.9166 Da, exact mass for $CuC_4H_{12}N_2S_4$ 278.9174 Da, Δ = 2.9 ppm.

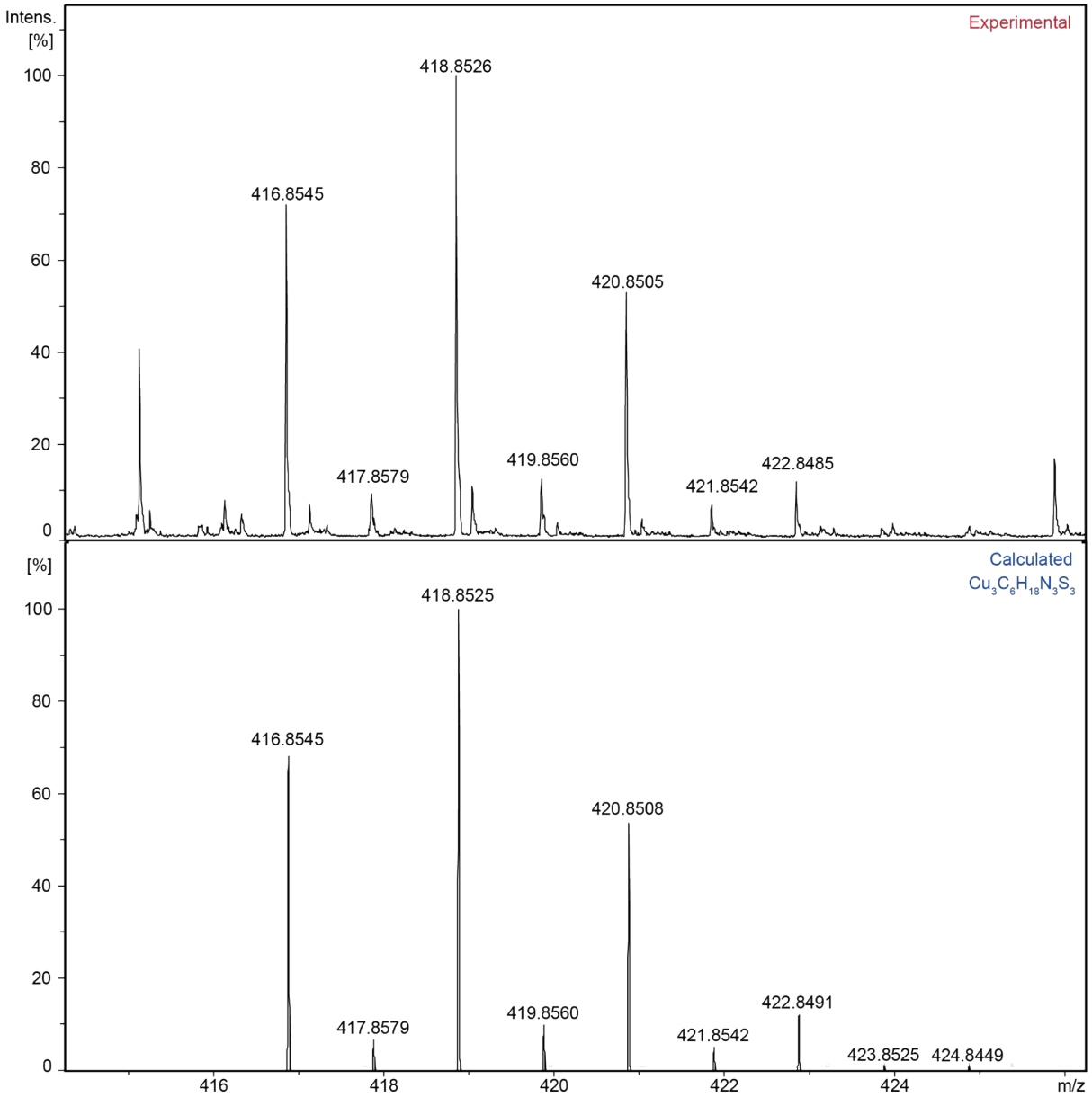


Figure S6: ESI-(+)MS spectrum of dissolved copper, expanded to the $Cu_3C_6H_{18}N_3S_3$ complex. Accurate mass for $[M]^+$ 418.8526 Da, exact mass for $Cu_3C_6H_{18}N_3S_3$ 418.8525 Da, Δ = 0.2 ppm. Low signal-to-noise ratio was observed for these ion signals, which suggests only plausible identification of the complex; however, in spite of low intensity isotopic pattern and accurate mass match reliably.

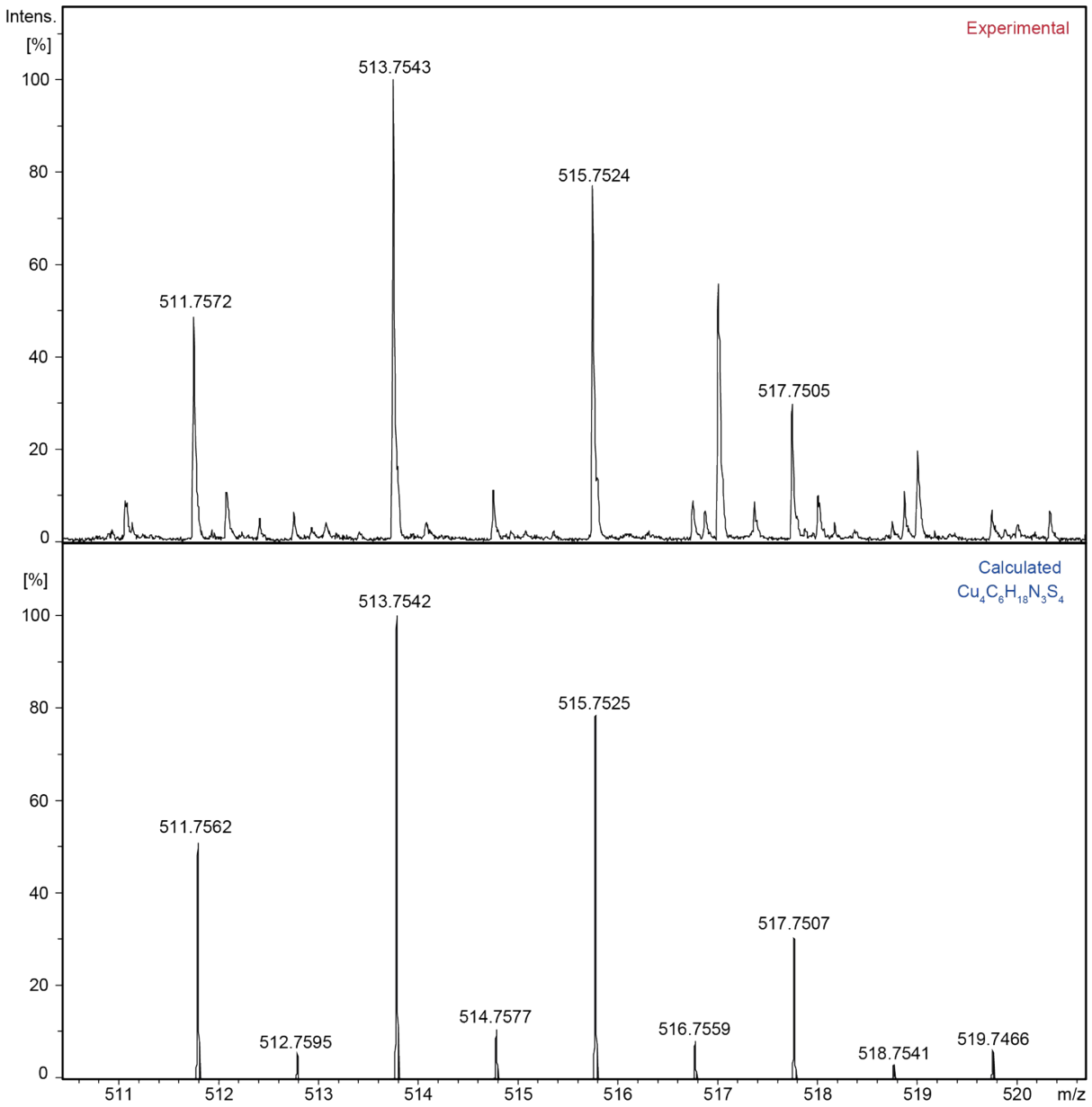


Figure S7: ESI-(+)MS spectrum of dissolved copper, expanded to the $Cu_4C_6H_{18}N_3S_3$ complex. Accurate mass for $[M]^+$ 513.7543 Da, exact mass for $Cu_4C_6H_{18}N_3S_3$ 513.7542 Da, Δ = 0.2 ppm. Low signal-to-noise ratio was observed for these *ion* signals, which suggests only plausible identification of the complex; however, in spite of low intensity isotopic pattern and accurate mass match reliably.

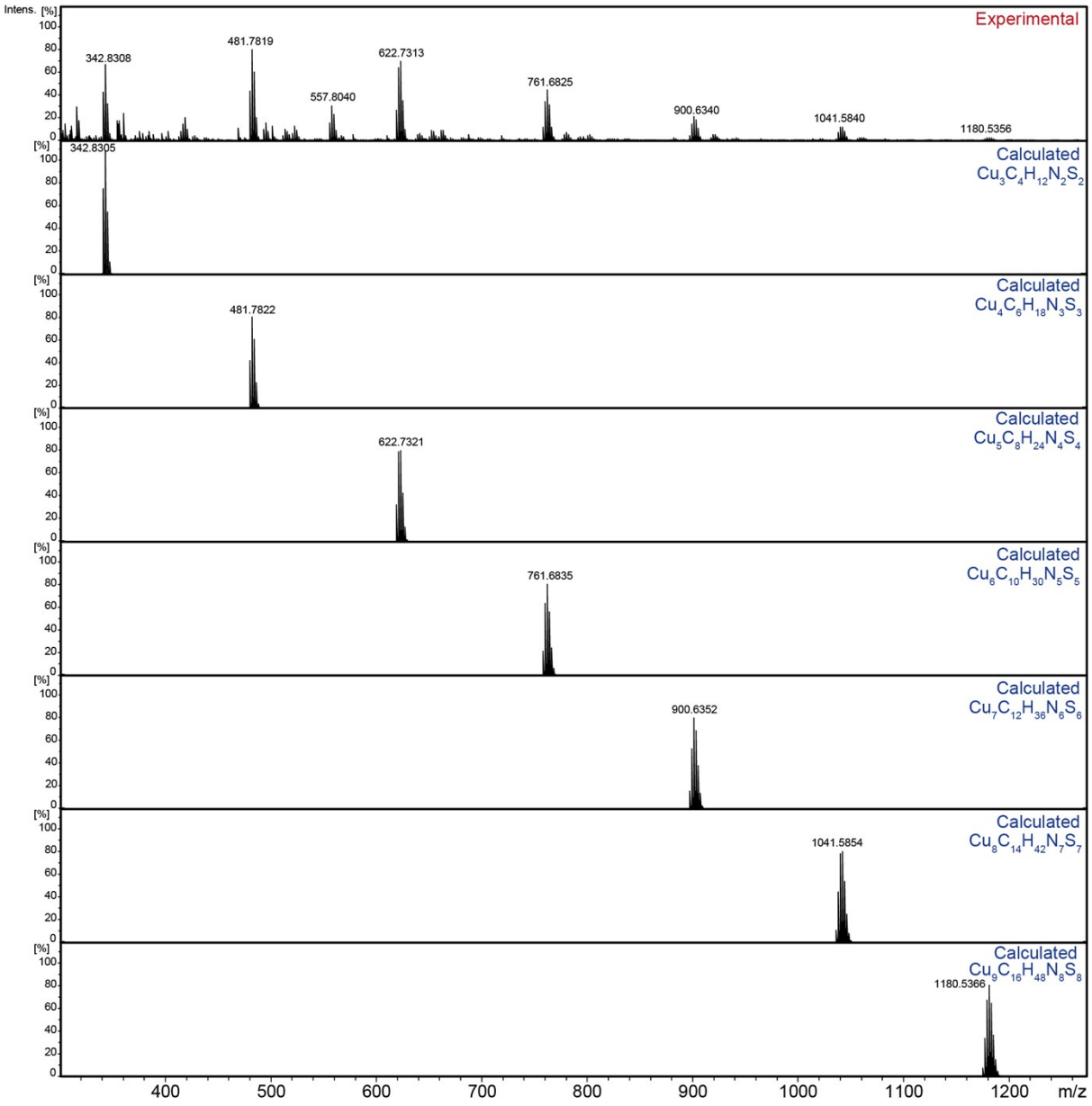


Figure S8: ESI-(+)MS spectrum of dissolved copper. Accurate mass for $[M]^+$ 342.8308 Da, exact mass for $Cu_3C_4H_{12}N_2S_2$ 342.8305 Da, Δ = 0.9 ppm; accurate mass for $[M]^+$ 481.7819 Da, exact mass for $Cu_4C_6H_{18}N_3S_3$ 481.7822 Da, Δ = 0.6 ppm; accurate mass for $[M]^+$ 622.7313 Da, exact mass for $Cu_5C_8H_{24}N_4S_4$ = 622.7321 Da, Δ = 1.3 ppm; accurate mass for $[M]^+$ 761.6825 Da, exact mass for $Cu_6C_{10}H_{30}N_5S_5$ 761.6835 Da, Δ = 1.3 ppm; accurate mass for $[M]^+$ 900.6340 Da, exact mass for $Cu_7C_{12}H_{36}N_6S_6$ 900.6352 Da, Δ = 1.3 ppm; accurate mass for $[M]^+$ 1041.5840 Da, exact mass for $Cu_8C_{14}H_{42}N_7S_7$ 1041.5854 Da, Δ = 1.3 ppm; accurate mass for $[M]^+$ 1180.5356 Da, exact mass for $Cu_9C_{16}H_{48}N_8S_8$ 1180.5366 Da, Δ = 0.9 ppm.

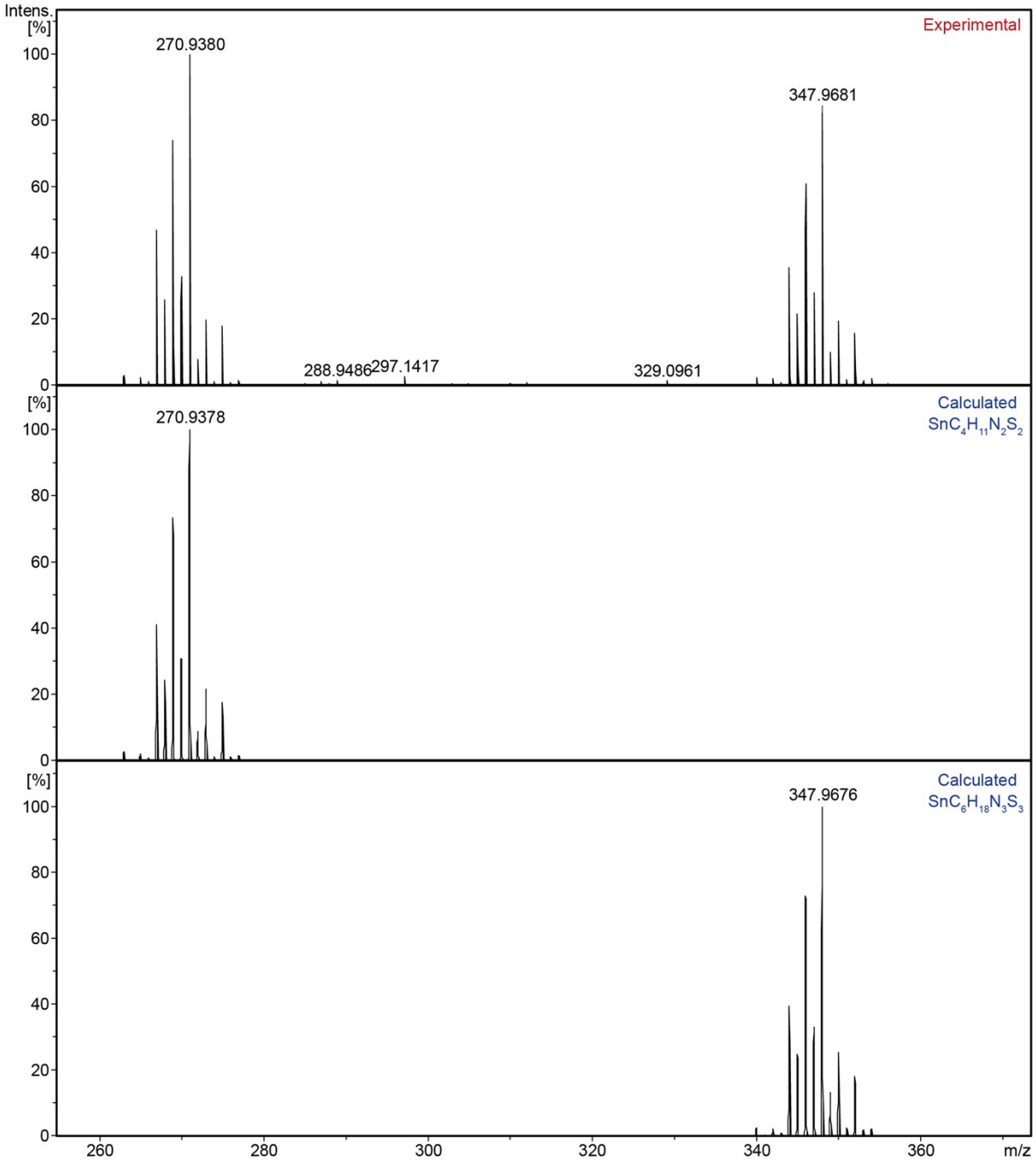


Figure S9: ESI-(+)MS spectrum of dissolved tin. Accurate mass for $[M]^+$ 270.9380 Da, exact mass for $SnC_4H_{11}N_2S_2$ 270.9378 Da, Δ = 0.7 ppm; accurate mass for $[M]^+$ 347.9681 Da, exact mass for $SnC_6H_{18}N_3S_3$ 347.9676 Da, Δ = 1.4 ppm.

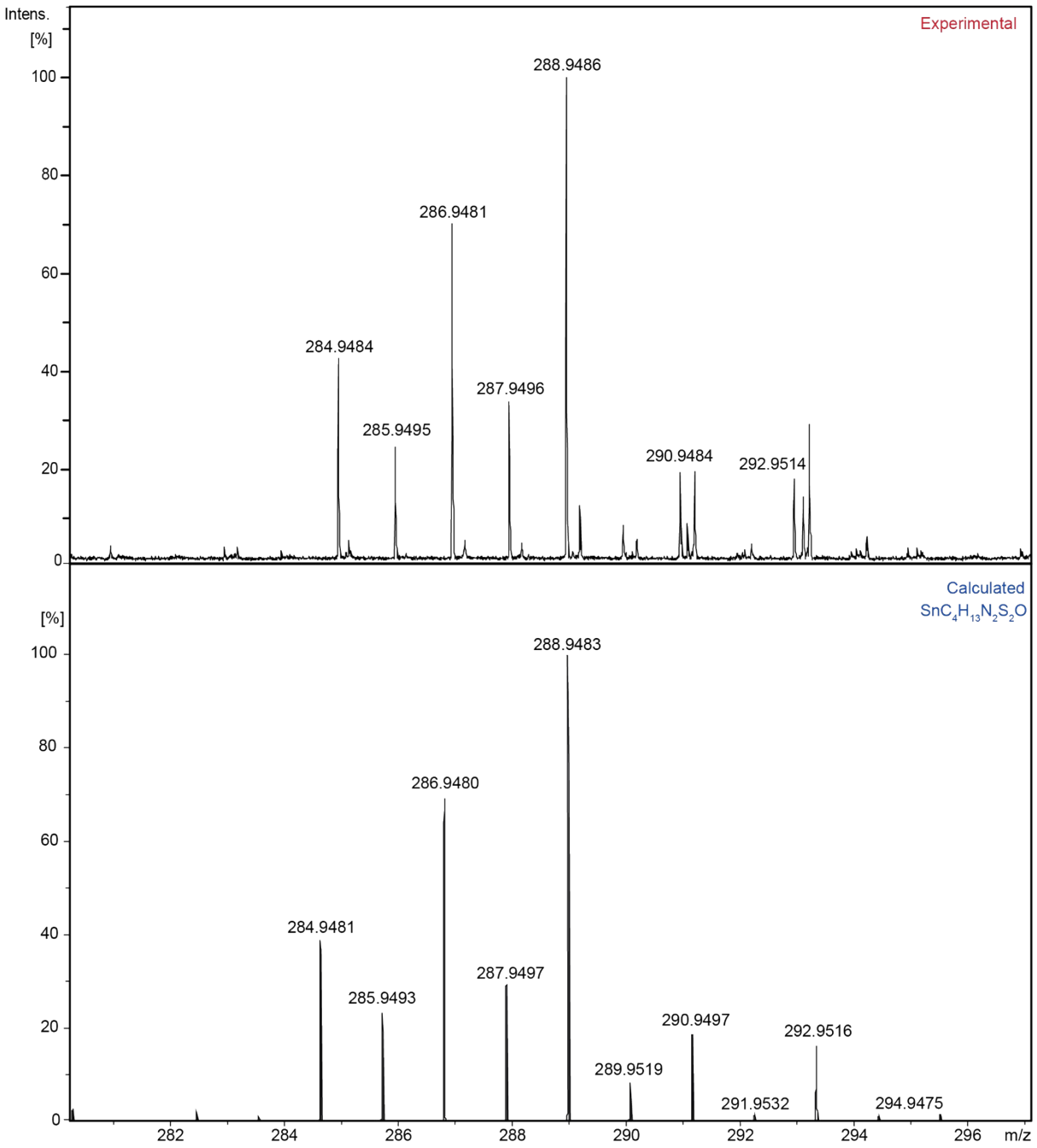


Figure S10: ESI-(+)MS spectrum of dissolved tin, expanded to the $SnC_4H_{13}N_2S_2O$ complex. Accurate mass for $[M]^+$ 288.9486 Da, exact mass for $SnC_4H_{13}N_2S_2O$ 288.9483 Da, Δ = 1 ppm.

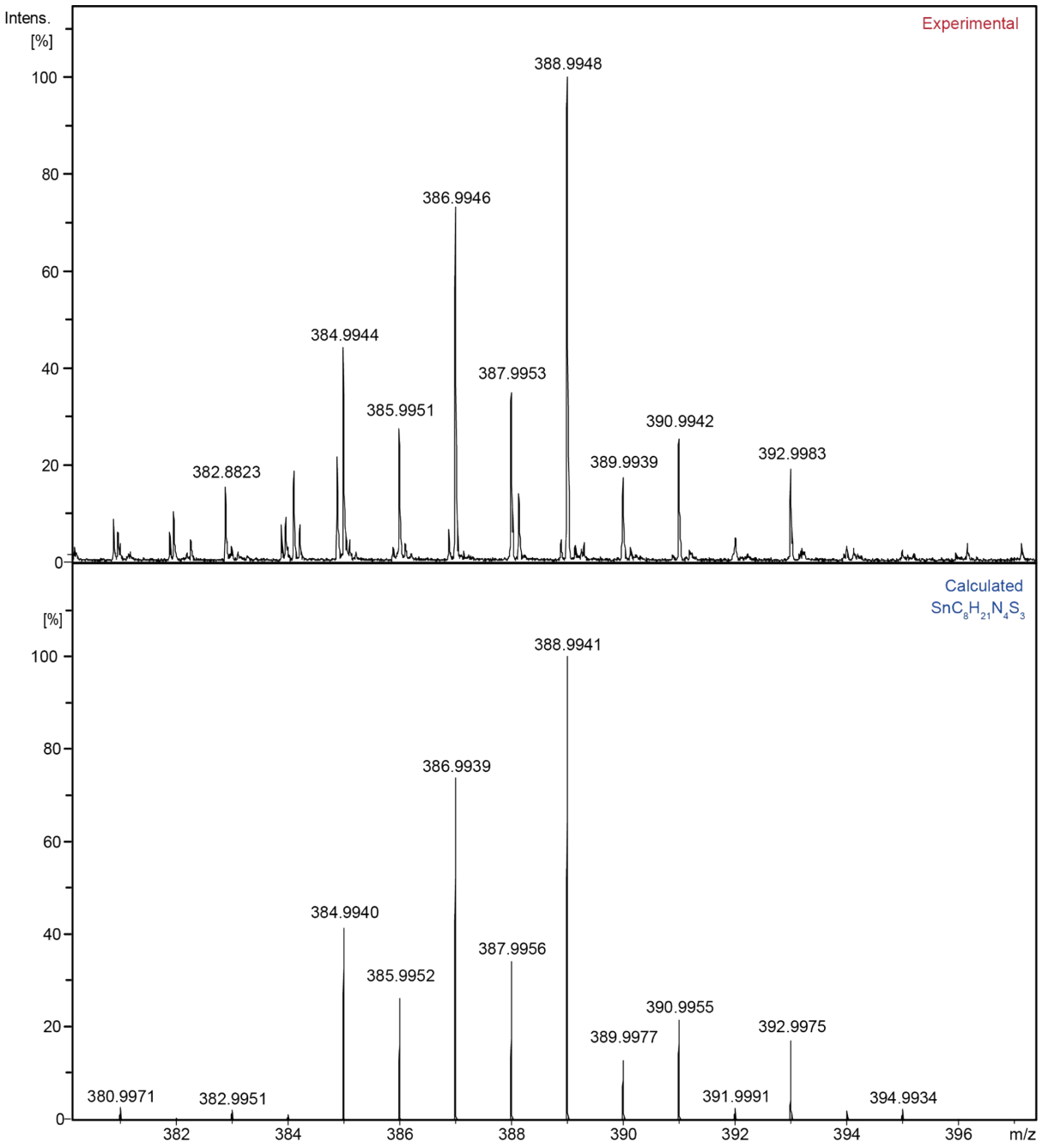


Figure S12: ESI-(+)MS spectrum of dissolved tin, expanded to the $SnC_8H_{21}N_4S_3$ complex. Accurate mass for $[M]^+$ 388.9948 Da, exact mass for $SnC_8H_{21}N_4S_3$ 388.9941 Da, Δ = 1.8 ppm. Low signal-to-noise ratio was observed for these ion signals, which suggests only plausible identification of the complex; however, in spite of low intensity isotopic pattern and accurate mass match reliably.

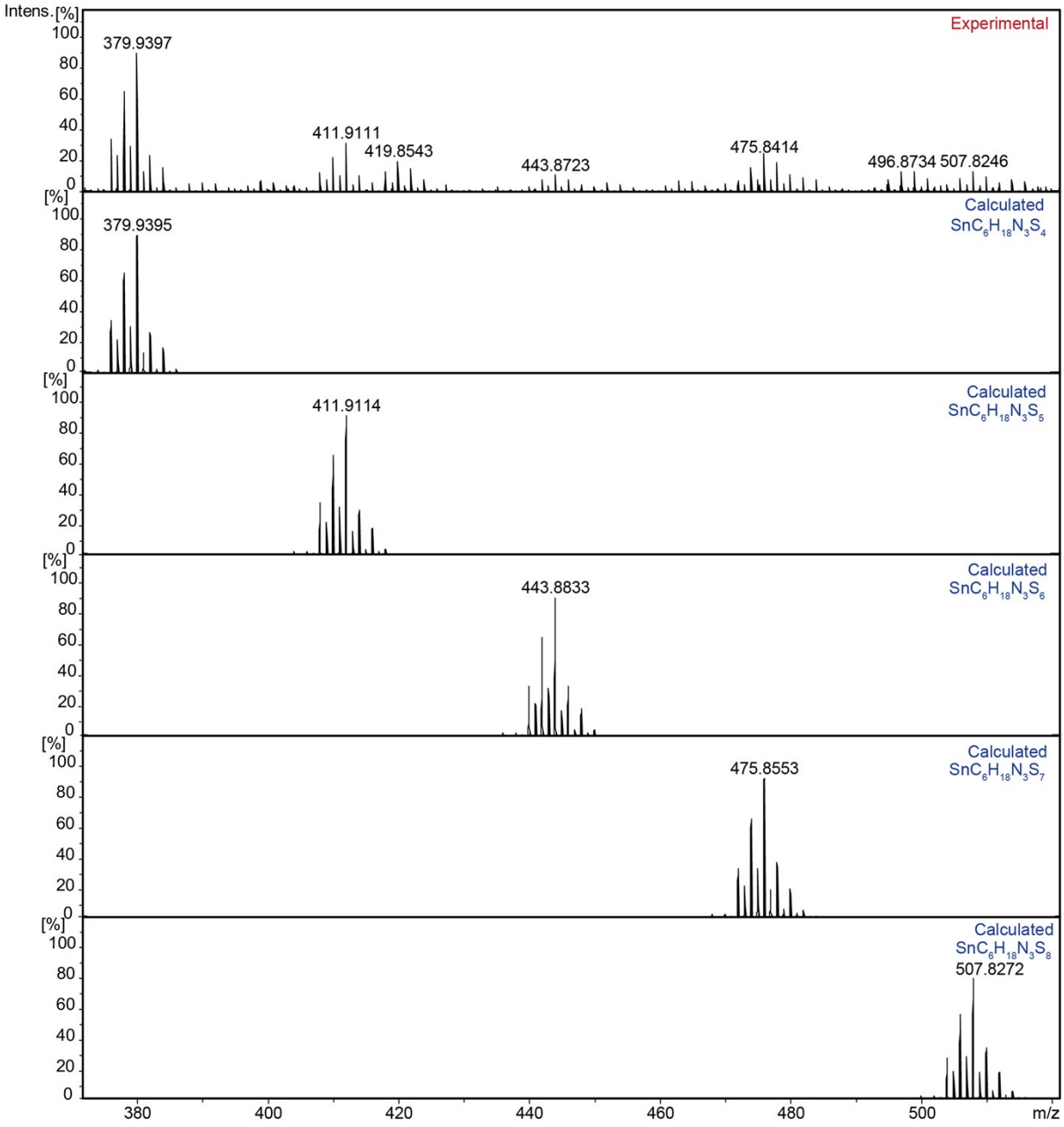


Figure S13: ESI-(+)MS spectrum of dissolved tin. Accurate mass for $[M]^+$ 379.9397 Da, exact mass for $SnC_6H_{18}N_3S_4$ = 379.9395 Da, Δ = 0.5 ppm; accurate mass for $[M]^+$ 411.9111 Da, exact mass for $SnC_6H_{18}N_3S_5$ = 411.9114 Da, Δ = 0.7 ppm; accurate mass for $[M]^+$ 443.8723 Da, exact mass for $SnC_6H_{18}N_3S_6$ 443.8833 Da, Δ = 25 ppm (experimental error is high due to low resolution as a result of signal overlapping); accurate mass for $[M]^+$ 475.8414 Da, exact mass for $SnC_6H_{18}N_3S_7$ 475.8553 Da, Δ = 29 ppm (experimental error is high due to low resolution as a result of signal overlapping); accurate mass for $[M]^+$ 507.8246 Da, exact mass for $SnC_6H_{18}N_3S_8$ 507.8272 Da, Δ = 5 ppm. Low signal-to-noise ratio was observed for these ions' signals, which suggests only plausible identification of the complexes; however, in spite of low intensity isotopic pattern and accurate mass match reliably.

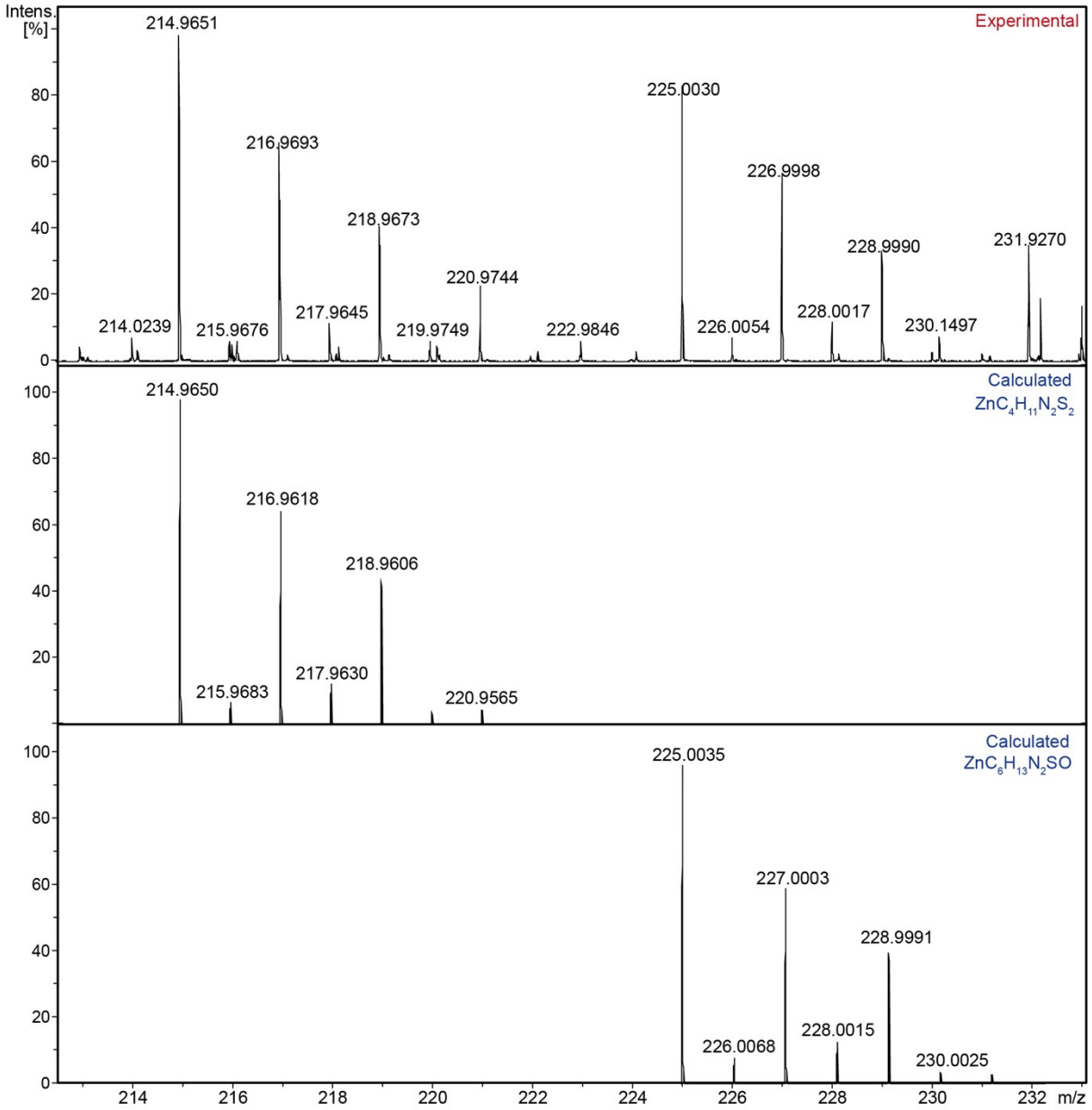


Figure S14: ESI-(+)MS spectrum of dissolved zinc. Accurate mass for $[M]^+$ 214.9651 Da, exact mass for $ZnC_4H_{11}N_2S_2$ 214.9650 Da, Δ = 0.5 ppm; accurate mass for $[M]^+$ 225.0030 Da, exact mass for $ZnC_6H_{13}N_2SO$ 225.0035 Da, Δ = 2.2 ppm.

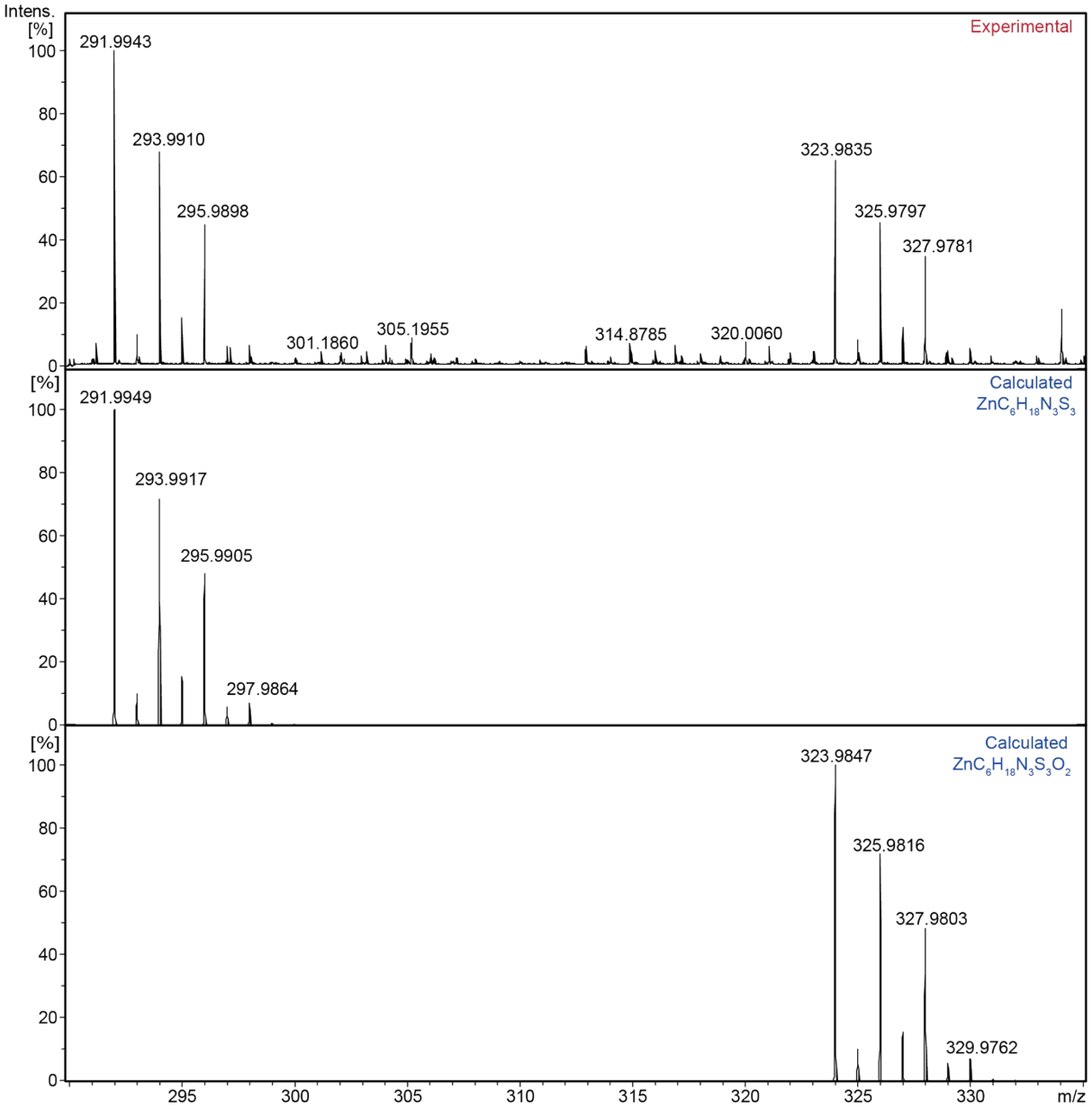


Figure S15: ESI-(+)MS spectrum of dissolved zinc. Accurate mass for $[M]^+$ 291.9943 Da, exact mass for $ZnC_6H_{18}N_3S_3$ 291.9949 Da, Δ = 2.0 ppm; accurate mass for $[M]^+$ 323.9835 Da, exact mass for $ZnC_6H_{18}N_3S_3O_2$ 323.9847 Da, Δ = 3.7 ppm.

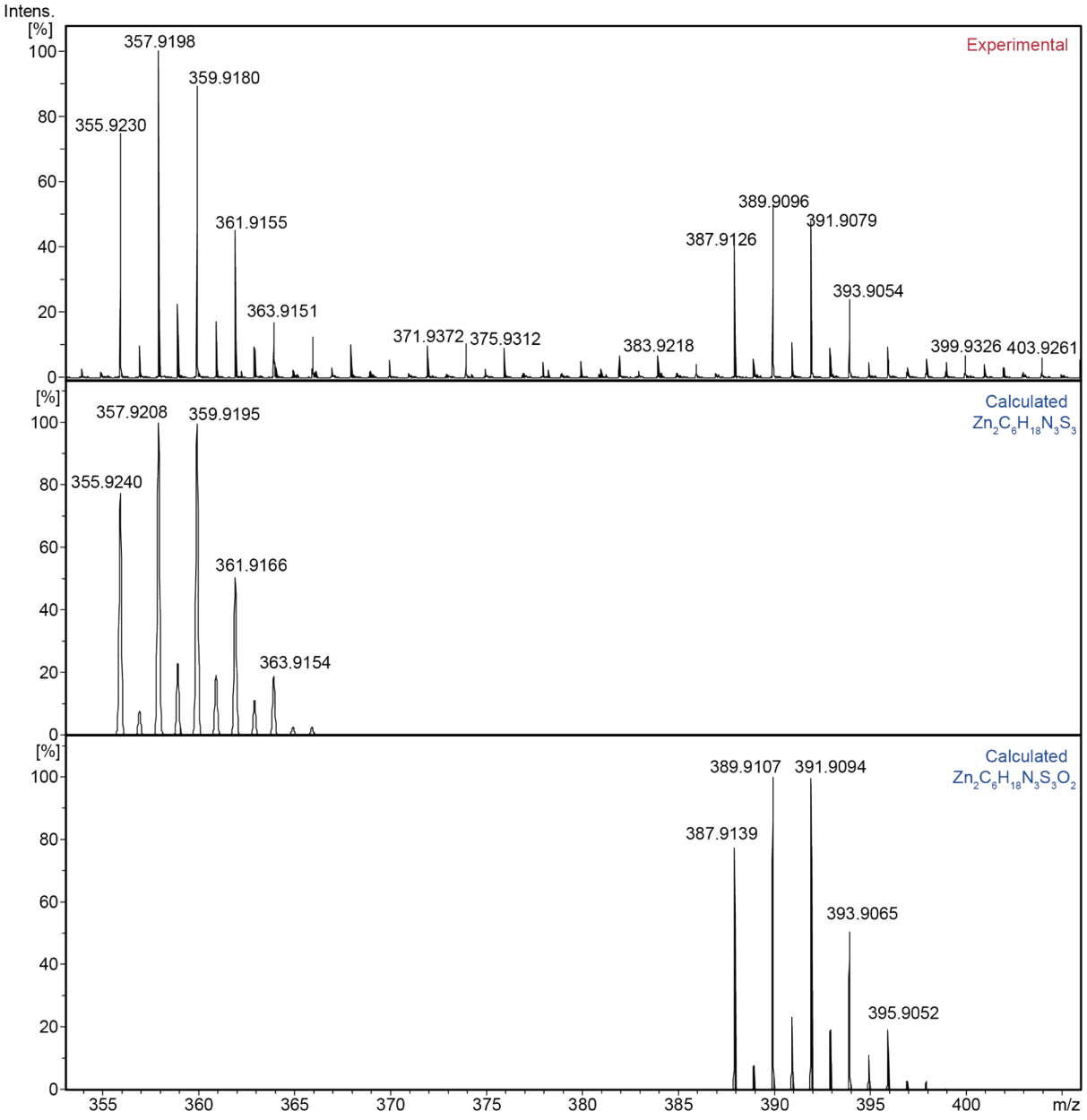


Figure S16: ESI-(+)MS spectrum of dissolved zinc. Accurate mass for $[M]^+$ 357.9198 Da, exact mass for $Zn_2C_6H_{18}N_3S_3$ 357.9208 Da, Δ = 2.8 ppm; accurate mass for $[M]^+$ 389.9096 Da, exact mass for $Zn_2C_6H_{18}N_3S_3O_2$ 389.9107 Da, Δ = 2.8 ppm.

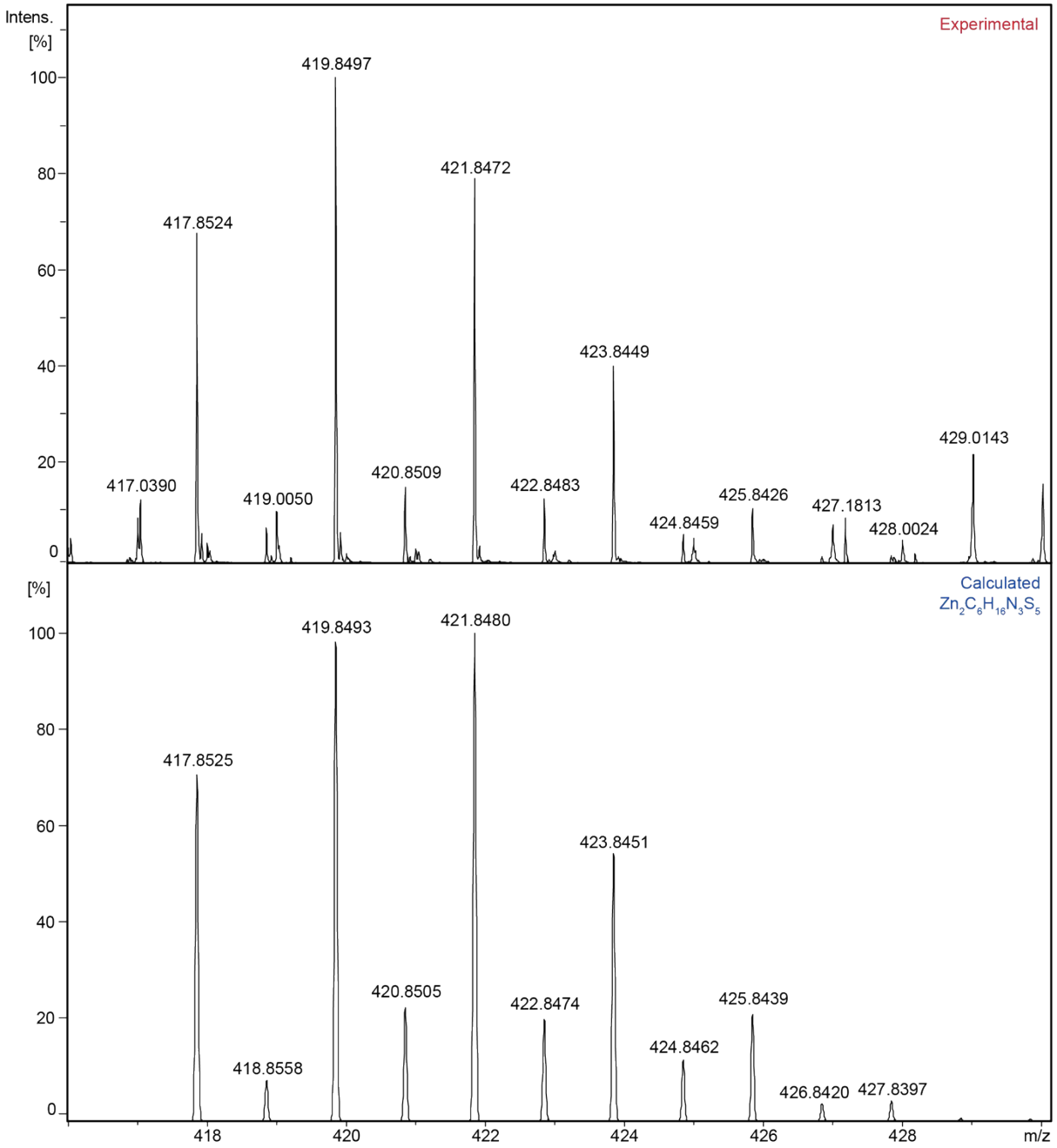


Figure S17: ESI-(+)MS spectrum of dissolved zinc, expanded to the $Zn_2C_6H_{16}N_3S_5$ complex. Accurate mass for $[M]^+$ 421.8472 Da, exact mass for $Zn_2C_6H_{16}N_3S_5$ 421.8480 Da, Δ = 1.9 ppm.

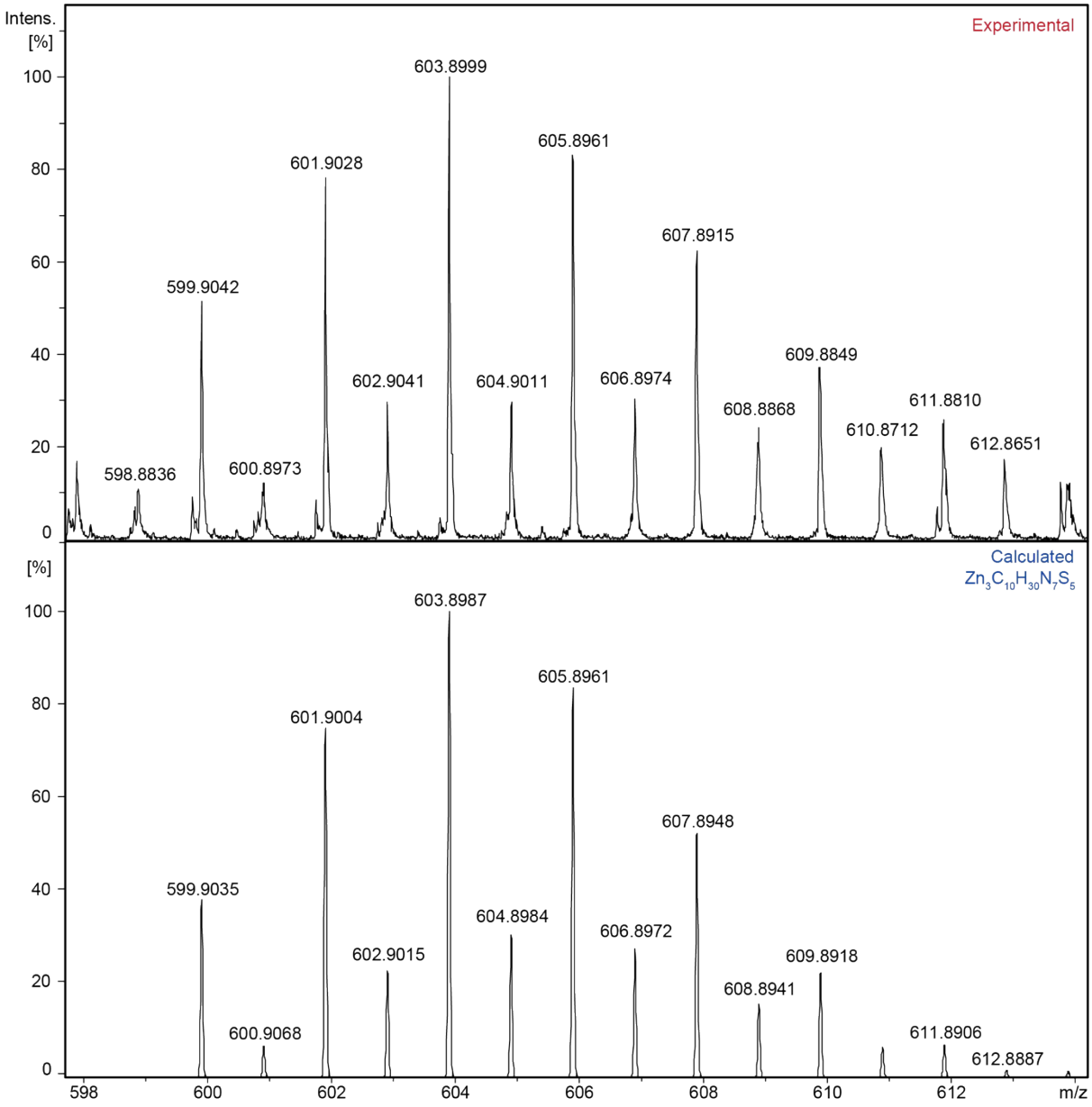


Figure S18: ESI-(+)MS spectrum of dissolved zinc, expanded to the $Zn_3C_{10}H_{30}N_7S_5$ complex. Accurate mass for $[M]^+$ 603.8999 Da, exact mass for $Zn_3C_{10}H_{30}N_7S_5$ 603.8987 Da, Δ = 2 ppm. Low signal-to-noise ratio was observed for these ion signals, which suggests only plausible identification of the complex; however, in spite of low intensity, the isotopic pattern and accurate mass match reliably.

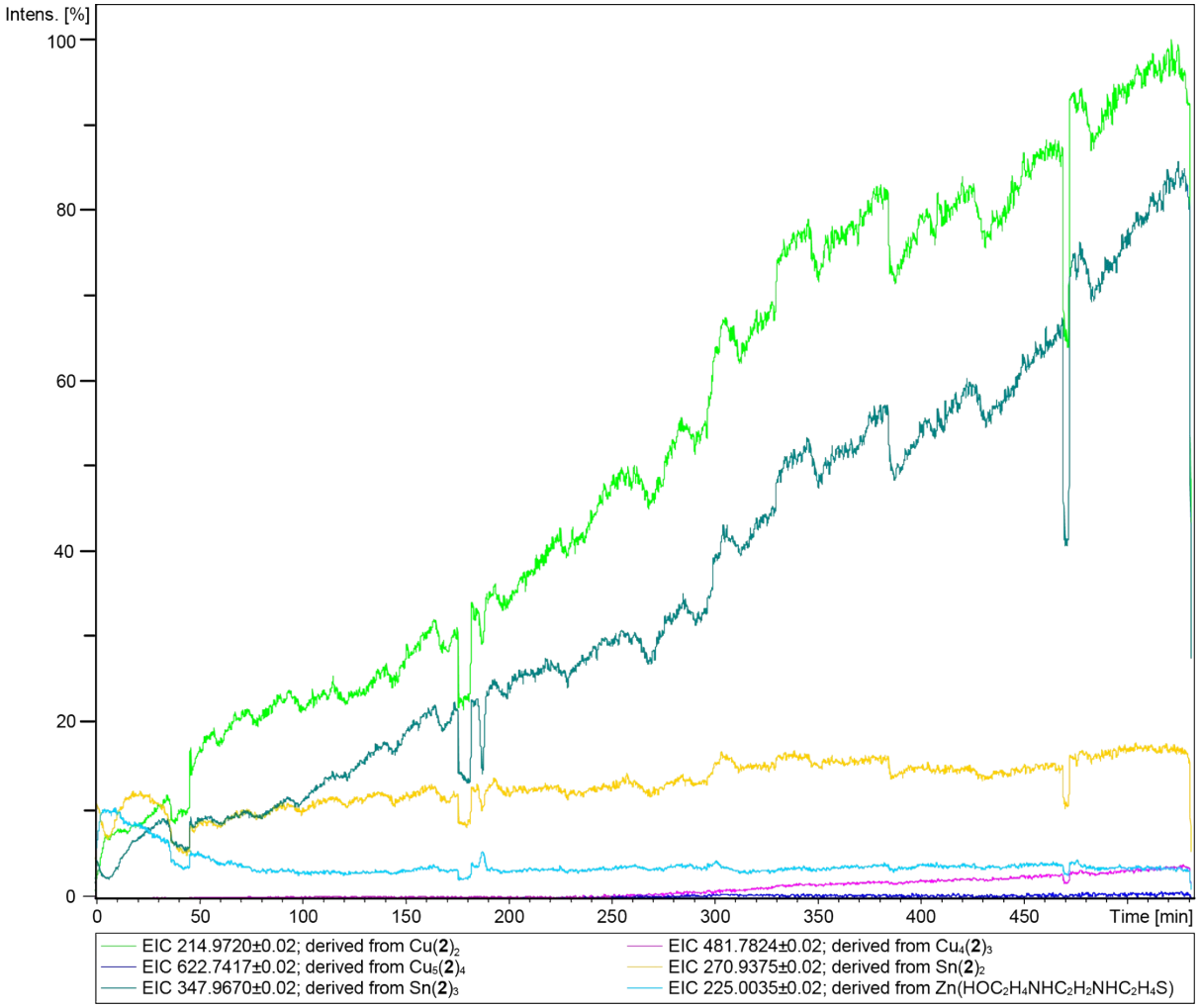


Figure S19: Gauss-smoothed curves (3 sec, 5 cycles) for the real-time abundances of ions in ethanolamine/cysteamine solution containing Cu, Zn, Sn and S.

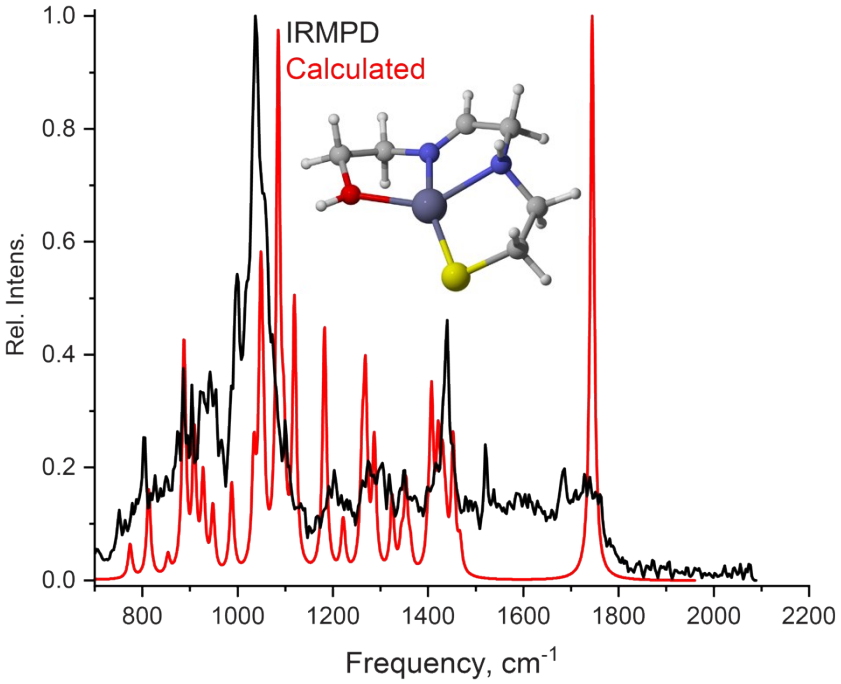


Figure S20: Alternative zinc imine complex Zn($HOC_2H_4NHC_2H_2NHC_2H_4S$) with *m/z* 225.0035 observed in ESI-MS: Structure of the complex optimised by DFT calculations; experimental IRMPD and calculated spectrum (both normalized) of this ion.

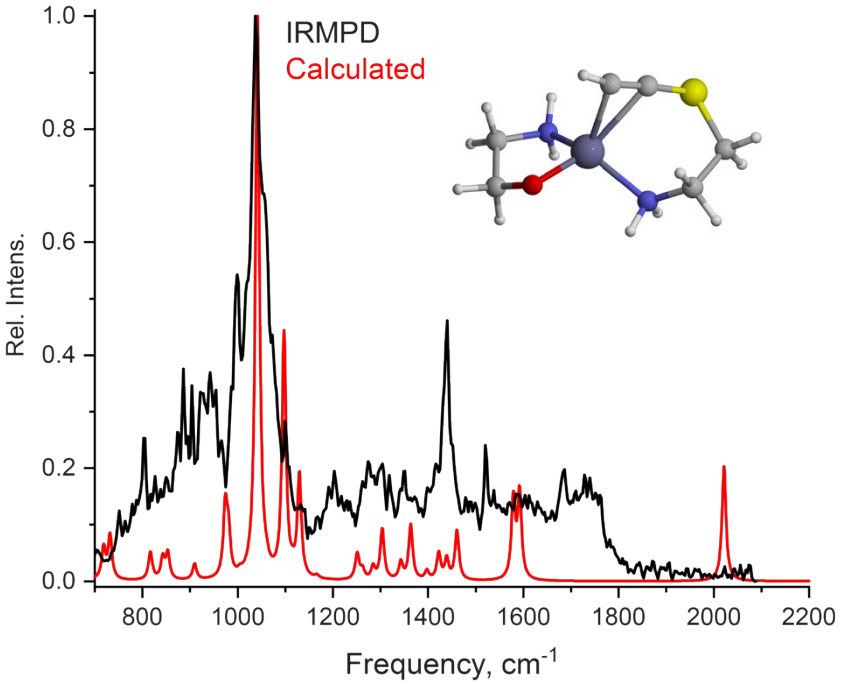
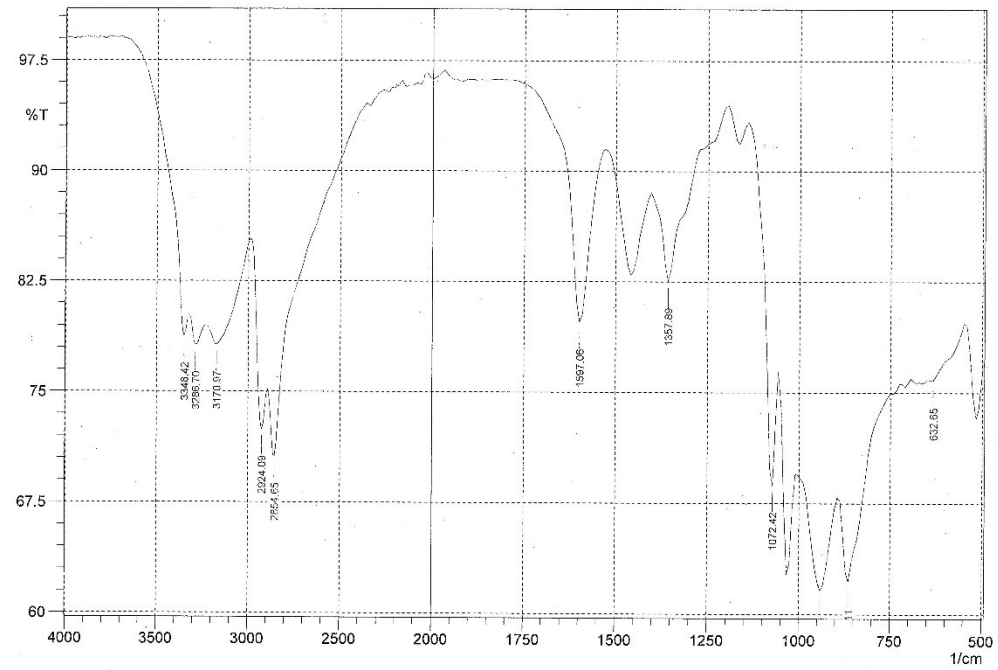


Figure S21: Alternative zinc/acetylene complex Zn(**1**)(**2**)C_2H with *m/z* 225.0035 observed in ESI-MS: Structure of the complex optimised by DFT calculations; experimental IRMPD and calculated spectrum (both normalized) of this ion.



No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	632.65	75.841	0.629	648.08	547.78	11.176	0.322
2	864.11	62.212	6.587	887.26	725.23	25.095	1.946
3	941.26	61.592	6.943	1002.98	894.97	20.033	2.342
4	1072.42	68.737	10.759	1141.86	1056.99	7.747	1.436
5	1357.89	82.548	7.326	1404.18	1203.58	10.279	2.552
6	1597.06	79.741	12.867	1782.23	1535.34	10.5	3.638
7	2854.65	70.609	5.987	2893.22	2360.87	36.772	1.522
8	2924.09	72.433	5.215	2985.81	2900.94	9.605	1.179
9	3170.97	78.177	2.664	3224.98	2993.52	21.736	2.313
10	3286.7	78.155	1.78	3317.56	3232.7	8.746	0.433
11	3348.42	78.775	2.603	3695.61	3325.28	13.376	0.409

Figure S22: IR spectrum of solution used in this work, ethanolamine/cysteamine containing Cu, Zn, Sn, and S.

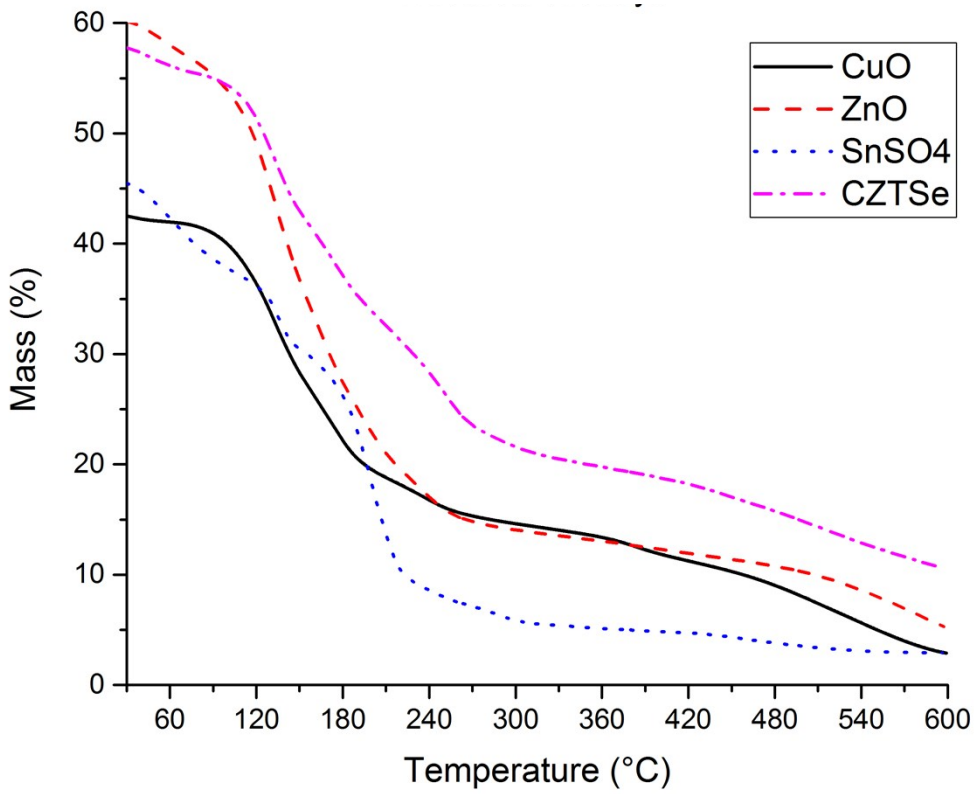


Figure S23: Thermogravimetric analysis of water based solution: Water, cysteamine, thiourea, copper (II) oxide, zinc oxide, tin (II) sulphate.

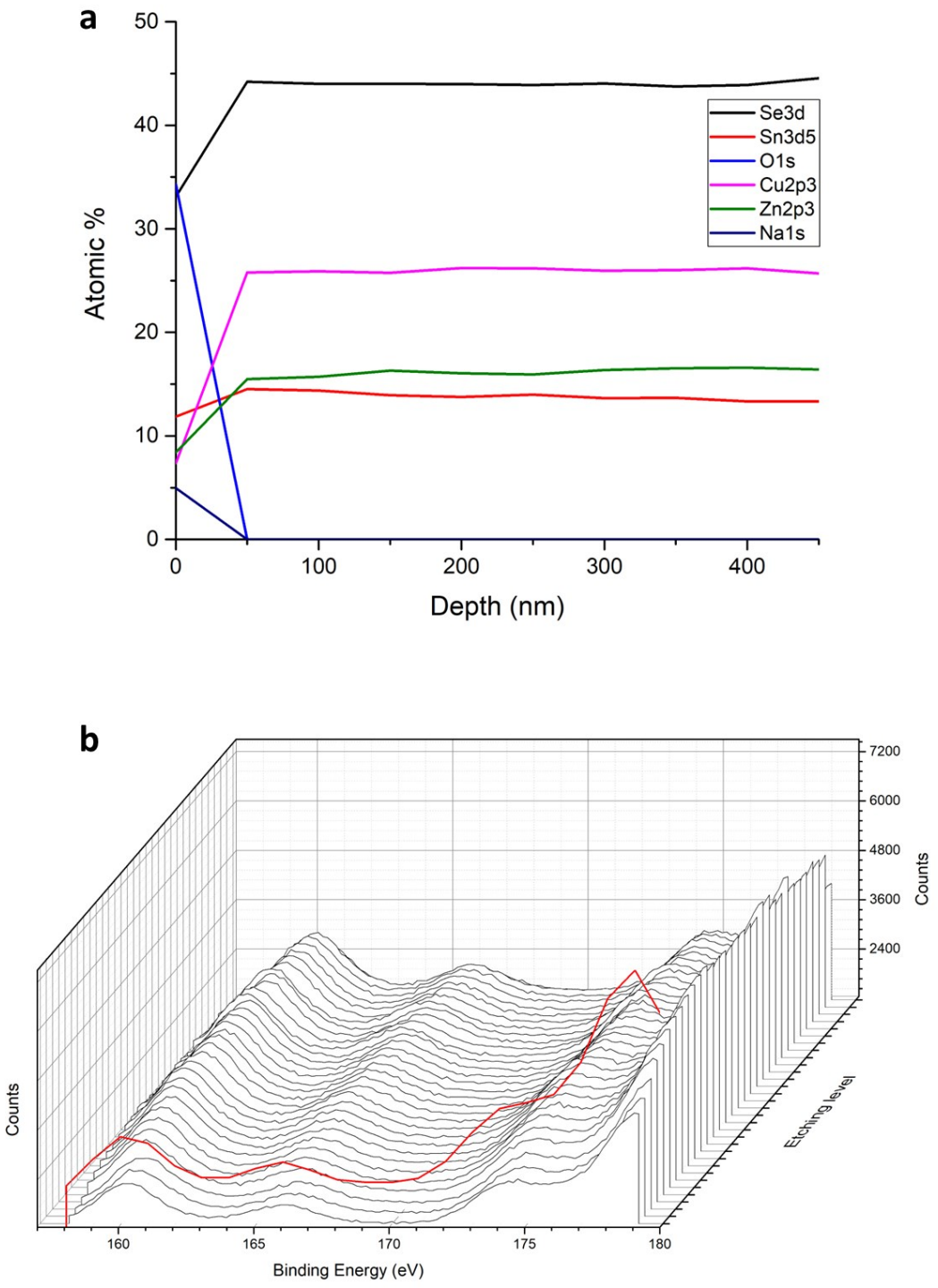


Figure S24: a) XPS analysis of a selenized CZTSe sample, Atomic % was recorded every 50 nm. b) XPS data displaying the region where peaks characteristic of S would appear, the red line is the background, the black lines are data from the sample throughout the bulk of the film. At no point is there a peak greater than the background counts, showing there is negligible levels of S in the film.

Table S1: Cartesian coordinates (Å) and total DFT energy (a.u.) of the Zinc enamine complex Zn($HOC_2H_4NHC_2H_2NHC_2H_4S$) with m/z 225.0035.

Energy (D3-B3LYP/def2-SVP): -2598.035038916

C	2.87022	-0.03184	0.13861
C	2.21627	1.34101	0.02607
N	0.82668	1.33030	0.59720
H	2.12571	1.61850	-1.03415
H	2.82376	2.10985	0.53394
S	1.95961	-1.37348	-0.76510
H	3.00289	-0.31410	1.19604
H	3.87441	0.02751	-0.30576
Zn	0.02578	-0.50080	-0.16680
O	-1.57064	-1.50003	0.74311
C	-2.83851	-1.11155	0.18389
C	-2.77957	0.39516	0.01383
N	-1.58085	0.77321	-0.79073
C	-0.01358	2.39033	0.11353
C	-1.13336	2.13067	-0.56863
H	0.89373	1.37611	1.61830
H	-1.51808	-2.45509	0.90172
H	0.29982	3.42585	0.28432
H	-1.75698	2.94229	-0.95582
H	-1.79281	0.64878	-1.78491
H	-3.71298	0.76719	-0.43826
H	-2.67240	0.86685	1.00118
H	-3.00089	-1.62445	-0.78025
H	-3.65568	-1.38088	0.87008

Table S2: Cartesian coordinates (Å) and total DFT energy (a.u.) of the Zinc imine complex Zn(HOC2H4NHC2H2NHC2H4S) with m/z 225.0035.

Energy (D3-B3LYP/def2-SVP): -2598.045414992

C	2.96228	0.04654	0.50655
C	2.22688	1.30476	0.05883
N	0.91915	1.43336	0.75150
H	2.02437	1.24468	-1.02185
H	2.85107	2.19827	0.24062
S	2.05795	-1.53268	0.15232
H	3.19708	0.10166	1.58257
H	3.92155	-0.00872	-0.02801
Zn	0.08051	-0.60462	0.39348
O	-1.66170	-1.81347	0.75655
C	-2.93030	-1.16899	0.56837
H	-3.69044	-1.89611	0.24542
H	-3.25903	-0.70245	1.51277
C	-2.72108	-0.10821	-0.51397
N	-1.48429	0.58761	-0.20393
H	-3.58996	0.56709	-0.57476
H	-2.59358	-0.60366	-1.49093
C	-0.00413	2.44353	0.22860
C	-1.32185	1.84753	-0.20267
H	0.43185	2.97315	-0.63780
H	-0.21794	3.23255	0.97027
H	1.08749	1.59544	1.74519
H	-2.12742	2.53767	-0.50313
H	-1.73579	-2.63854	1.25730

Table S3: Cartesian coordinates (Å) and total DFT energy (a.u.) of the Zinc acetylene complex Zn(HOC2H4NHC2H2NHC2H4S) with m/z 225.0035.

Energy (D3-B3LYP/def2-SVP): -2597.966636293

C	2.96884	-0.85473	-0.45465
C	3.08277	0.34990	0.49596
N	1.78346	0.52995	1.22523
H	3.24268	1.26555	-0.09453
H	3.91917	0.24315	1.20523
O	1.83821	-0.77239	-1.26154
H	2.97997	-1.78550	0.16223
H	3.89625	-0.88479	-1.05886
Zn	0.46206	0.06347	-0.32697
H	1.73195	-0.12884	2.00746
H	1.72228	1.46124	1.64129
S	-2.32172	1.58879	0.66789
C	-3.22383	0.06837	0.08415
H	-4.11244	0.39234	-0.47491
H	-3.56414	-0.38696	1.02727
C	-2.42032	-0.90786	-0.75997
N	-1.12915	-1.29569	-0.14678
H	-2.20450	-0.47187	-1.74637
H	-3.05911	-1.79042	-0.93204
H	-0.71386	-2.06906	-0.67810
H	-1.27595	-1.66291	0.79800
C	-1.22165	1.81298	-0.58306
C	-0.33874	1.90154	-1.43578
H	0.26186	2.15915	-2.29681

Table S4: Cartesian coordinates (Å) and total DFT energy (a.u.) of conformer 1 of the tin complex $Sn(2)_2$ with m/z 270.9378.

Energy (D3-B3LYP/def2-SVP): -1278.758968114

C	3.00349	-0.01812	0.96144
C	2.68865	0.53907	-0.42974
N	1.38500	1.19744	-0.45393
H	2.76349	-0.27462	-1.17682
H	3.47253	1.27760	-0.66856
S	1.65022	-1.09475	1.68329
H	3.19282	0.79087	1.68107
H	3.88460	-0.67357	0.92419
Sn	-0.00364	0.29899	0.66564
H	1.21764	1.89984	-1.16663
S	-2.11947	1.29323	1.19704
C	-3.11547	-0.19850	0.73541
H	-4.14642	0.17260	0.64137
H	-3.09850	-0.92354	1.56367
C	-2.67924	-0.82941	-0.58145
N	-1.26289	-1.27389	-0.51076
H	-2.76096	-0.09589	-1.39649
H	-3.33328	-1.68300	-0.82256
H	-0.86562	-1.42616	-1.44266
H	-1.17123	-2.16777	-0.01559

Table S5: Cartesian coordinates (Å) and total DFT energy (a.u.) of conformer 2 of the tin complex $Sn(2)_2$ with m/z 270.9378.

Energy (D3-B3LYP/def2-SVP): -1278.760214134

C	-3.09576	-0.02391	0.18591
C	-2.59768	-0.33413	-1.23823
N	-1.29578	-1.00938	-1.31792
H	-2.54339	0.61602	-1.79786
H	-3.35707	-0.95730	-1.73709
S	-1.85158	0.89861	1.22941
H	-3.38257	-0.93654	0.72921
H	-3.96805	0.64429	0.14027
Sn	-0.08090	-0.31343	0.16430
H	-1.36485	-2.02294	-1.40564
S	2.06992	-1.17562	0.79458
C	2.97314	-0.31445	-0.57797
H	4.02955	-0.33587	-0.27228
H	2.88268	-0.90264	-1.50405
C	2.53199	1.13029	-0.78078
N	1.08364	1.19801	-1.11073
H	3.12454	1.59182	-1.58667
H	2.69246	1.70897	0.14014
H	0.90175	0.92746	-2.08429
H	0.70935	2.14443	-0.99406

Table S6: Cartesian coordinates (Å) and total DFT energy (a.u.) of the mer-isomer of the tin complex $Sn(2)_3$ with m/z 347.9676.

Energy (D3-B3LYP/def2-SVP): -1812.038136774

C	-1.44629	-2.87859	-0.72814
C	-2.33521	-2.15790	0.28072
S	-1.34801	-1.30347	1.57478
H	-2.96627	-2.88705	0.80809
H	-2.99598	-1.43500	-0.22224
N	-0.58590	-1.91642	-1.44352
H	-2.07270	-3.44705	-1.43635
H	-0.79659	-3.59279	-0.20163
Sn	0.09366	-0.07429	0.00725
S	-1.44639	1.34017	-1.27995
C	-1.87081	2.44463	0.12826
H	-2.55170	1.92645	0.82249
H	-2.41515	3.29784	-0.30062
C	-0.63107	2.94949	0.85466
N	0.11592	1.82084	1.46476
H	-0.91661	3.67871	1.63149
H	0.04028	3.45085	0.14311
H	-0.34767	1.51736	2.32589
H	1.06660	2.10425	1.71027
N	1.81314	-0.88171	1.71106
S	2.19219	0.23734	-1.20634
C	3.33902	-0.79784	-0.20884
C	3.18726	-0.57777	1.29142
H	1.63640	-1.88936	1.73892
H	4.35197	-0.51128	-0.52665
H	3.20525	-1.86130	-0.46505
H	3.92657	-1.19415	1.83209
H	3.39370	0.47693	1.52923
H	1.61785	-0.54971	2.65716
H	-1.11436	-1.43252	-2.17542
H	0.20575	-2.36748	-1.90612

Table S7: Cartesian coordinates (Å) and total DFT energy (a.u.) of the fac-isomer of the tin complex $Sn(2)_3$ with m/z 347.9676.

Energy (D3-B3LYP/def2-SVP): -1812.027535626

C	-0.76169	-3.17328	0.08145
C	-1.93491	-2.34806	0.58712
N	-1.45367	-1.12584	1.27071
H	-2.55485	-2.95375	1.26939
H	-2.56510	-2.02208	-0.25296
S	0.28010	-2.29283	-1.16047
H	-1.14406	-4.07268	-0.42202
H	-0.13588	-3.51532	0.92321
Sn	-0.00383	0.00692	-0.32021
H	-2.23594	-0.48736	1.42787
S	-2.06389	0.93185	-1.29577
C	-2.41044	2.21509	-0.01921
H	-3.03291	1.79317	0.78898
H	-3.01625	2.98545	-0.51767
C	-1.15500	2.86110	0.55130
N	-0.29963	1.85316	1.22027
H	-1.43064	3.66328	1.25627
H	-0.56323	3.31190	-0.25878
H	-0.64925	1.64503	2.15880
H	0.65248	2.21304	1.31879
N	1.73708	-0.59812	1.33748
S	1.87363	1.28193	-1.24413
C	3.21236	0.32479	-0.42125
C	2.98895	0.14750	1.07478
H	1.85687	-1.57772	1.05797
H	4.14067	0.88910	-0.59006
H	3.32407	-0.65171	-0.91801
H	3.85203	-0.37672	1.51987
H	2.91143	1.13180	1.56192
H	1.52176	-0.59568	2.33611
H	-1.06490	-1.36088	2.18758