Environmental Science: Nano

Electronic supplementary information for

Direct analysis of fulvic acids adsorbed onto capped gold nanoparticles by laser desorption ionization Fourier-transform ion cyclotron resonance mass spectrometry

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Materials and Methods

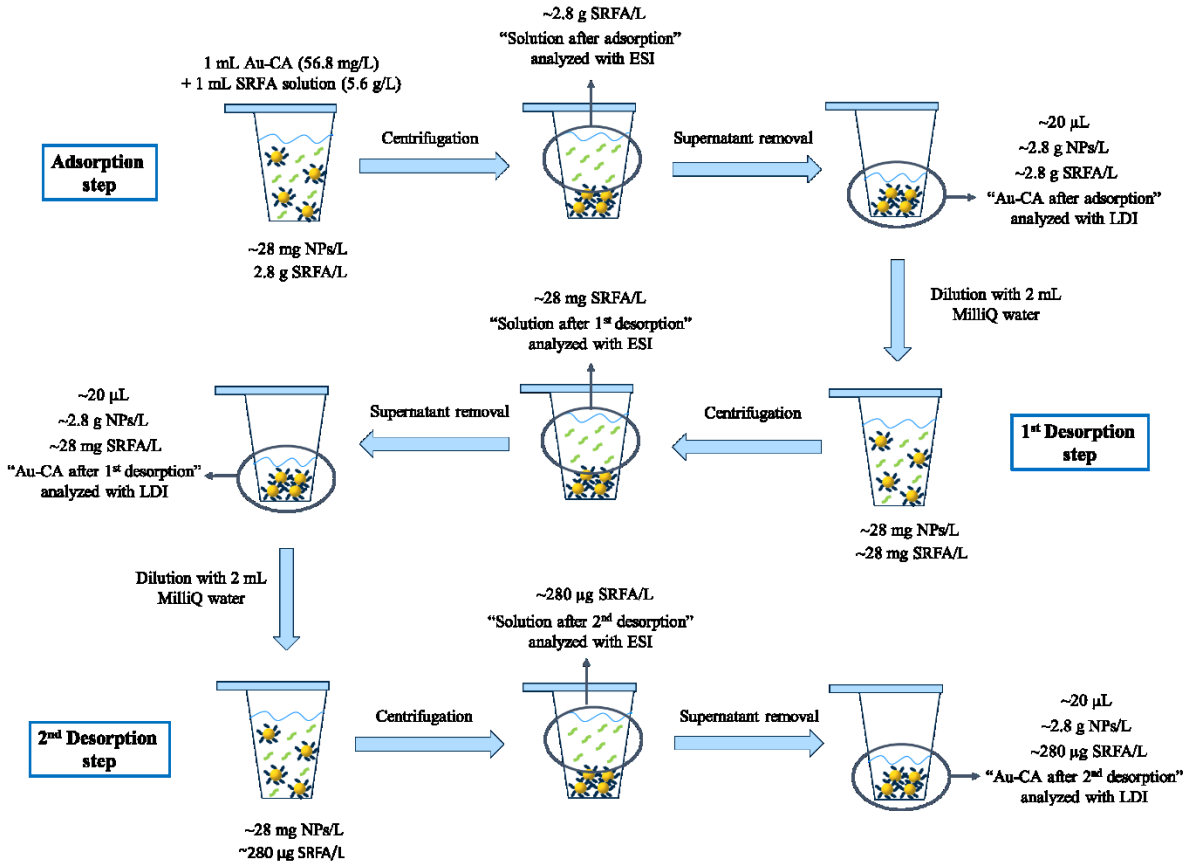


Figure S1. Experimental scheme for the adsorption and the following two desorption steps for Au-CA.

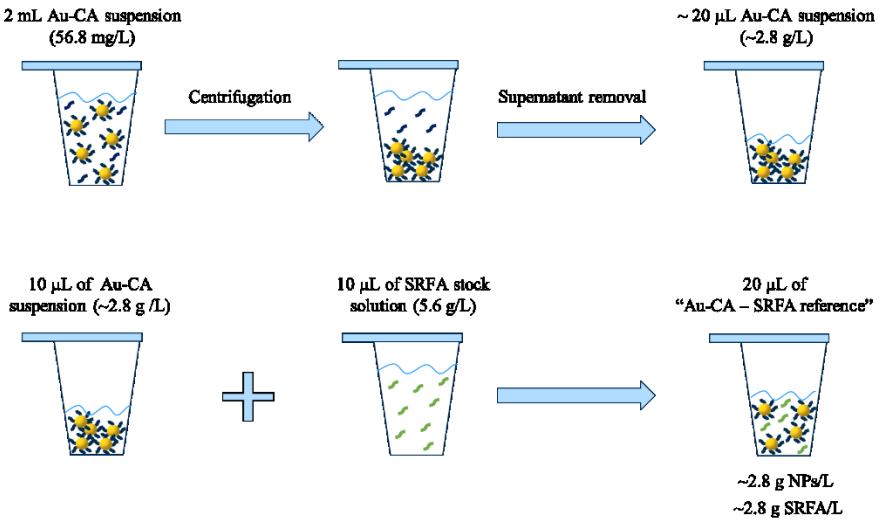


Figure S2. Experimental scheme for the preparation of the Au-CA – SRFA reference sample for LDI-FT-ICR-MS analysis.

Table S1. Spectra details for each sample for the LDI- and ESI-FT-ICR-MS measurements in the negative ionization mode.

Sample	Ionization mode	Ion accumulation time (IAT, [ms])	Total ion count (TIC, [x 10^{10}])	Total number of peaks	Number of assigned molecular formulas (MFs)	Fraction of assigned peaks [%]	Total assigned intensity (TAI, [x 10^{10}])
Au-CA – SRFA reference	LDI	60	21.6	18024	6977	39	13.0
Au-CA – SRFA reference	LDI	60	24.2	18956	7437	39	14.3
Au-CA – SRFA reference	LDI	60	18.7	17237	6721	39	11.1
Au-CA after adsorption	LDI	60	22.5	16968	6432	38	11.4
Au-CA after 1st desorption	LDI	60	18.4	16998	5996	35	7.8
Au-CA after 2nd desorption	LDI	60	10.4	13335	4171	31	3.5
Au-TA after adsorption	LDI	50	18.7	16731	6357	38	9.6
Au-TA after 1st desorption	LDI	50	13.8	13826	4424	32	5.0
Au-TA after 2nd desorption	LDI	50	11.6	9466	1809	19	1.4
Au-LA after adsorption	LDI	60	18.8	17040	6214	36	9.3
Au-LA after 1st desorption	LDI	60	14.6	15032	4802	32	5.3
Au-LA after 2nd desorption	LDI	60	12.1	13218	3934	30	3.3
Au-PVP after adsorption	LDI	50	12.2	14667	5265	36	6.3
Au-PVP after 1st desorption	LDI	50	9.4	12358	3670	30	3.3
Au-PVP after 2nd desorption	LDI	50	10.5	11166	2923	26	2.0
Au-(m-PEG-SH) after adsorption	LDI	60	10.6	12904	3925	30	3.9
Au-(m-PEG-SH) after 1st desorption	LDI	60	11.9	12065	2891	24	2.2
Au-(m-PEG-SH) after 2nd desorption	LDI	60	8.3	9702	1806	19	1.0
Au-BPEI after adsorption	LDI	50	17.4	16813	6372	38	9.7
Au-BPEI after 1st desorption	LDI	50	17.4	14851	4660	31	7.5
Au-BPEI after 2nd desorption	LDI	50	13.6	14766	4750	32	6.2
SRFA reference	ESI	20	10.1	14219*	2780	20	5.0
SRFA reference	ESI	20	10.4	14310*	2754	19	5.1
SRFA reference	ESI	20	10.3	14415*	2775	19	5.1
Solution after adsorption	ESI	20	10.5	14429*	2827	20	5.3
Solution after 1st desorption	ESI	10	11.9	14482*	3338	23	6.9
Solution after 2nd desorption	ESI	400	16.0	16460*	3407	21	4.7

* These values are blank-subtracted. The not blank-subtracted values starting in the table from the first SRFA reference sample to the solution after 2nd desorption are 14548, 14620, 14726, 14785, 14828, and 16831, respectively. The TIC represents the non-subtracted values whereby the MF assignment was performed from the blank-subtracted values.

Direct corona characterization on Au-CA by LDI-FT-ICR-MS

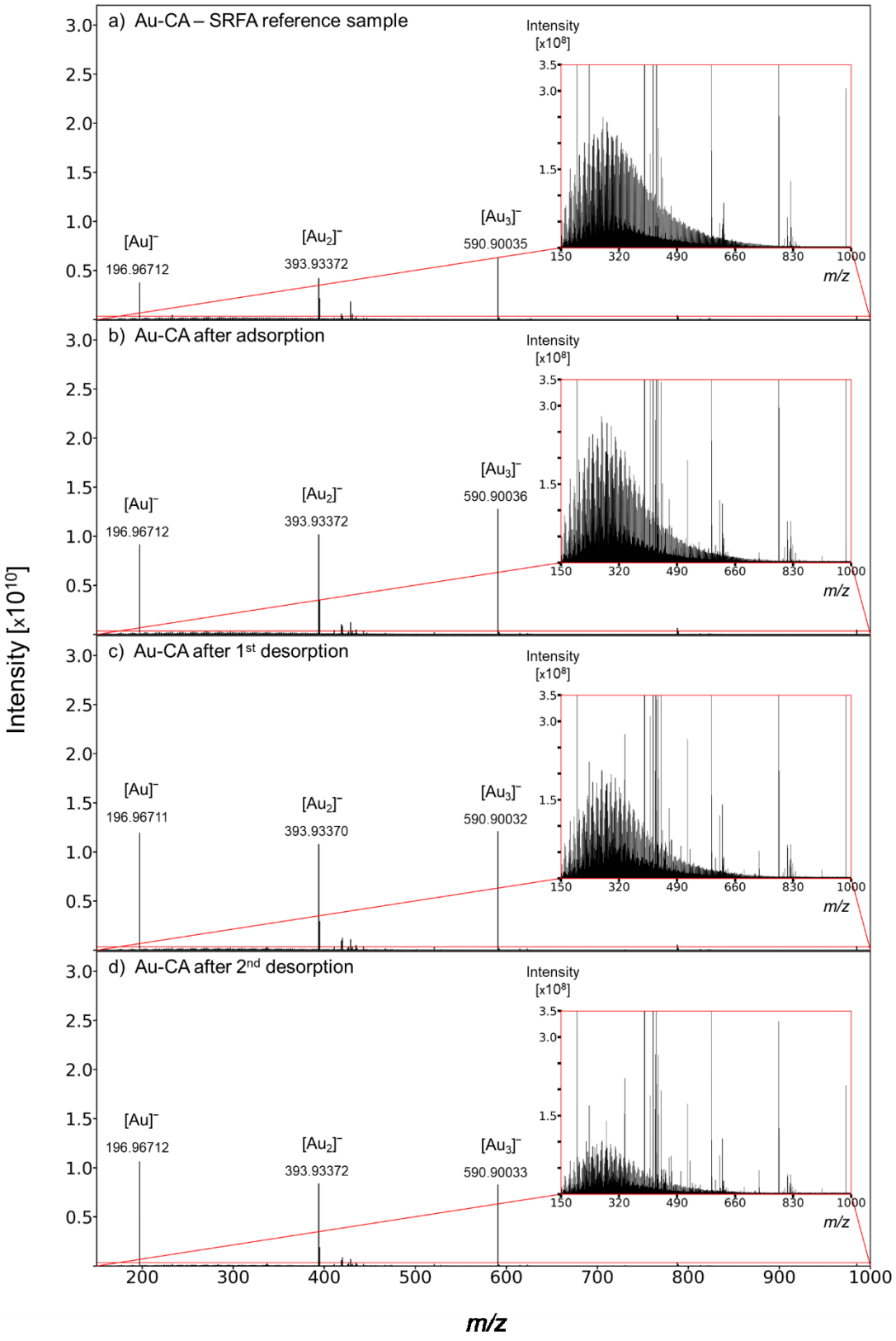


Figure S3. Raw LDI-FT-ICR mass spectra measured in the negative ionization mode for: a) Au-CA – SRFA reference sample, b) Au-CA after adsorption, c) Au-CA after 1st desorption, and d) Au-CA after 2nd desorption.

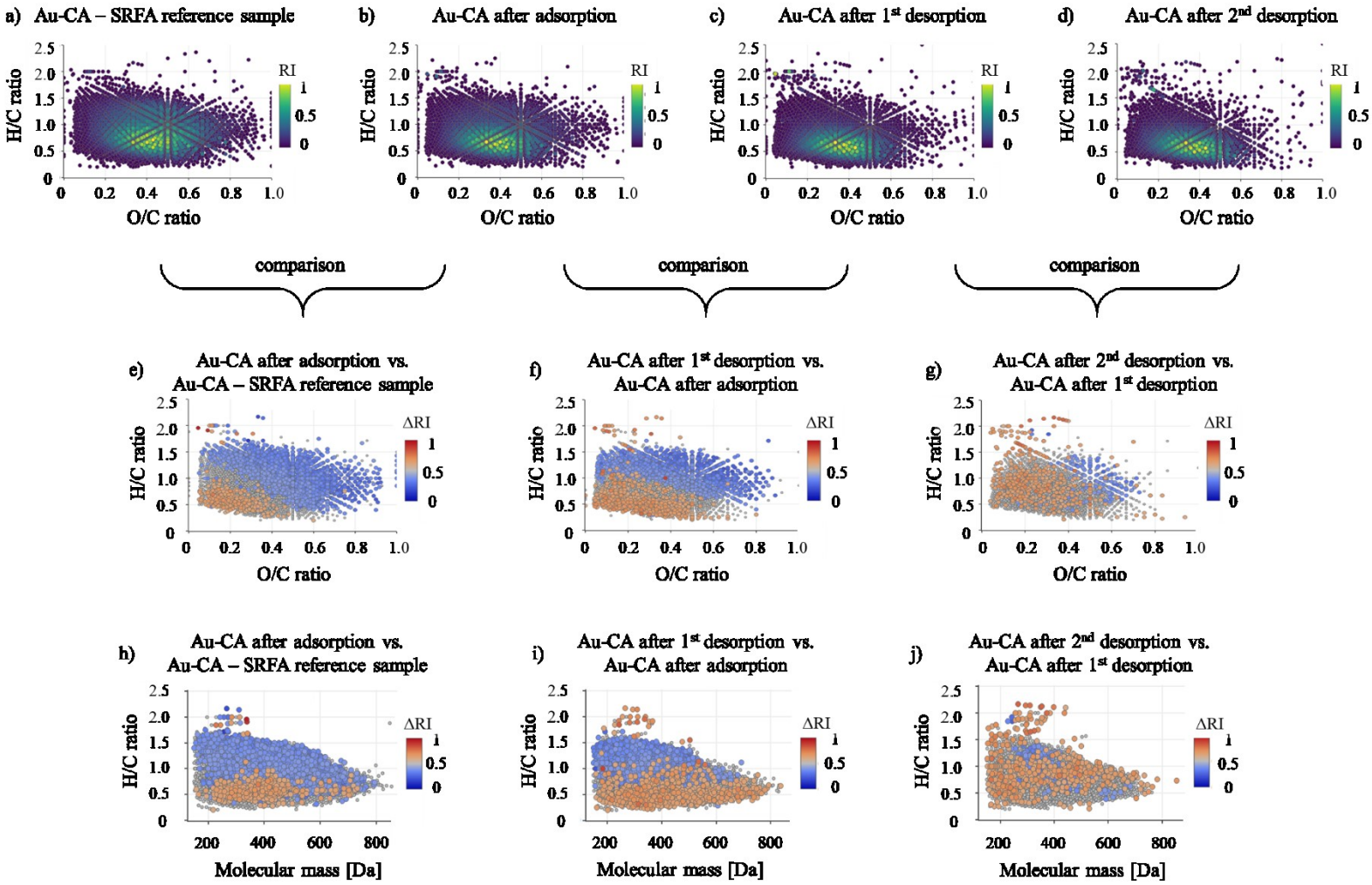


Figure S4. In the upper row (a-d), VKDs of molecular formulas detected by LDI-FT-ICR-MS measurements of a) Au-CA – SRFA reference sample, b) Au-CA after adsorption, c) Au-CA after 1st desorption and d) Au-CA after 2nd desorption with relative peak intensity ($0 \leq RI \leq 1$) shown as color scale. In the middle row (e-g) and lower row (h-j), the cVKD and comparison H/C vs. molecular mass diagrams, respectively of Au-CA after adsorption vs. Au-CA – SRFA reference sample (e, h), Au-CA after 1st desorption vs. Au-CA after adsorption (f, i), and Au-CA after 2nd vs. Au-CA after 1st desorption (g,j). The ΔRI values calculated from relative peak intensities are shown as color scale whereby red colors ($0.6 \leq \Delta RI \leq 1$) represent formulas more abundant in the first-mentioned sample, blue colors ($0 \leq \Delta RI \leq 0.4$) represent formulas more abundant in the second-mentioned sample, and the grey color indicates similar relative intensities ($0.4 \leq \Delta RI \leq 0.6$) for the common assigned MFs in both samples. The curly braces visually show which samples are compared.

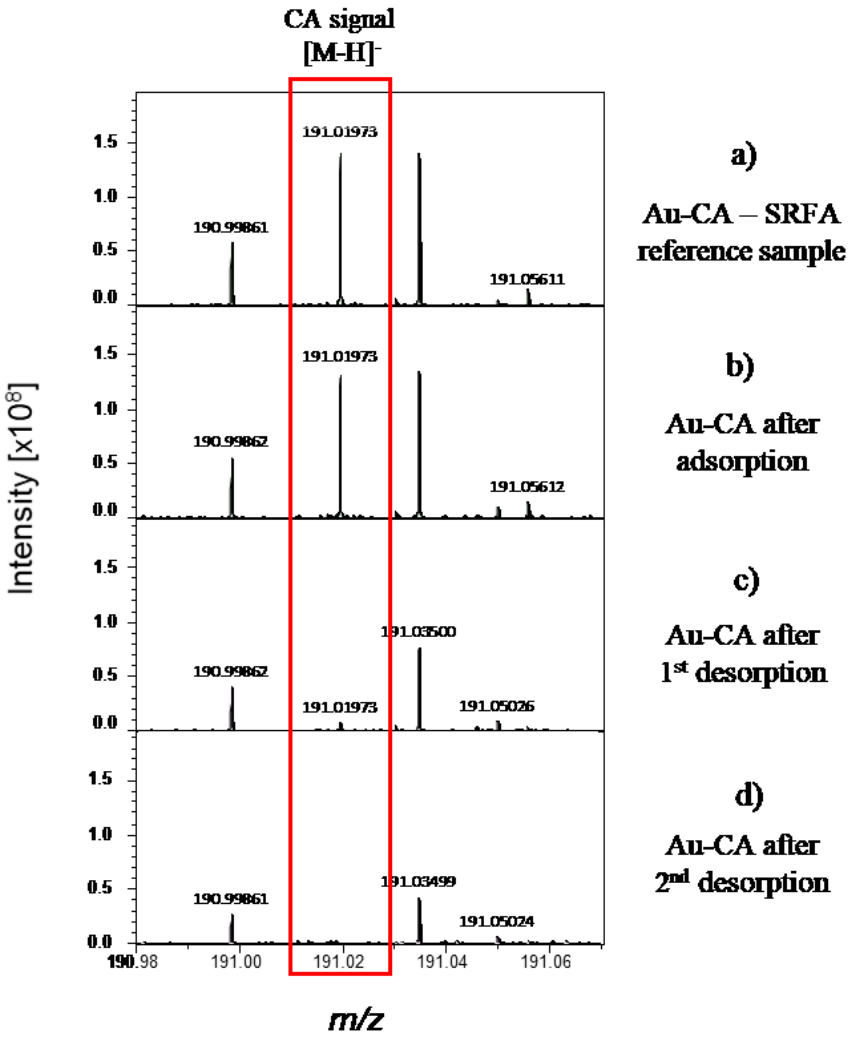


Figure S5. LDI-FT-ICR mass spectra in negative ionization mode demonstrating that CA is detached from the NP surface after the three treatment steps: a) Au-CA – SRFA reference sample, b) Au-CA after adsorption, c) Au-CA after 1st desorption, and d) Au-CA after 2nd desorption.

Indirect SRFA-corona characterization of Au-CA by ESI-FTICR-MS

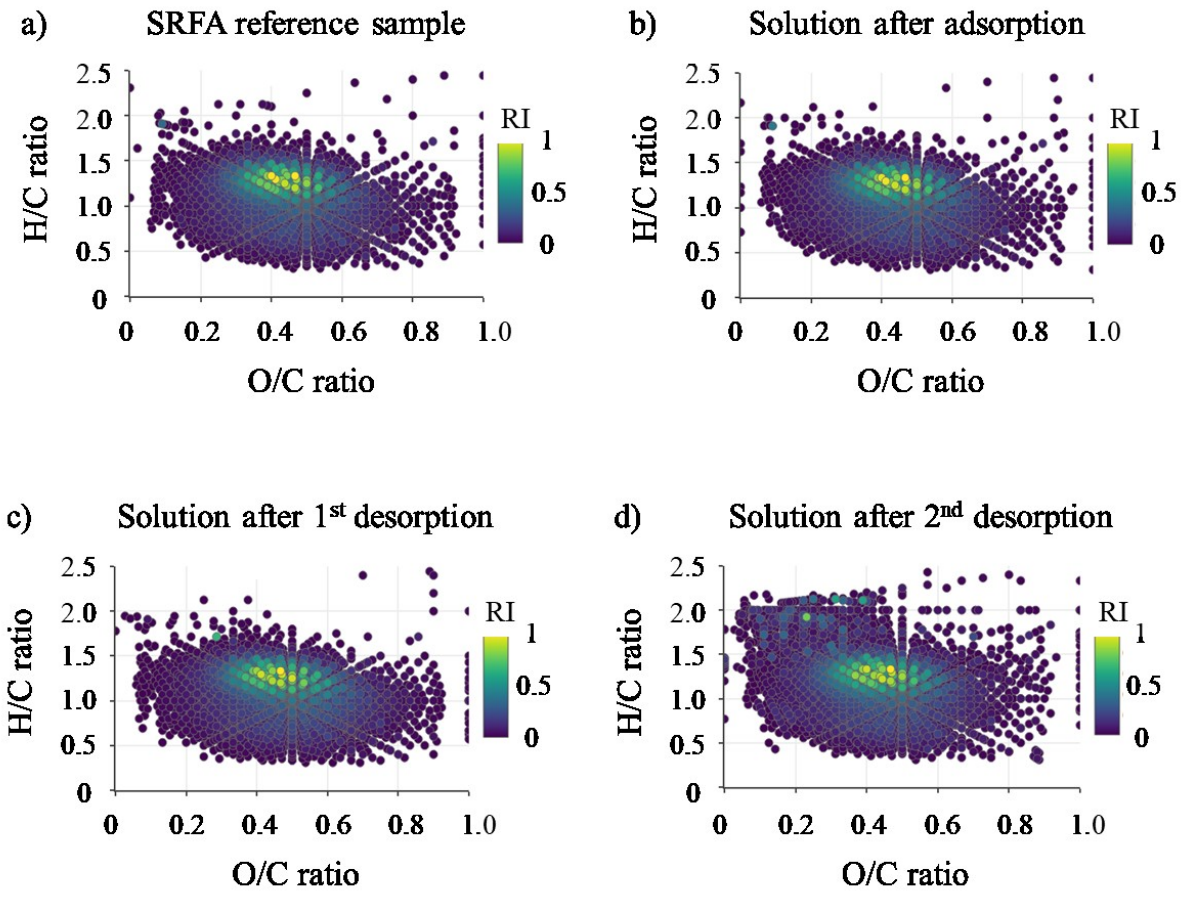


Figure S6. VKDs of molecular formulas detected by ESI-FT-ICR-MS measurements of a) SRFA reference sample, b) solution after adsorption, c) solution after 1st desorption, and d) solution after 2nd desorption with relative peak intensity ($0 \leq RI \leq 1$) shown as color scale.

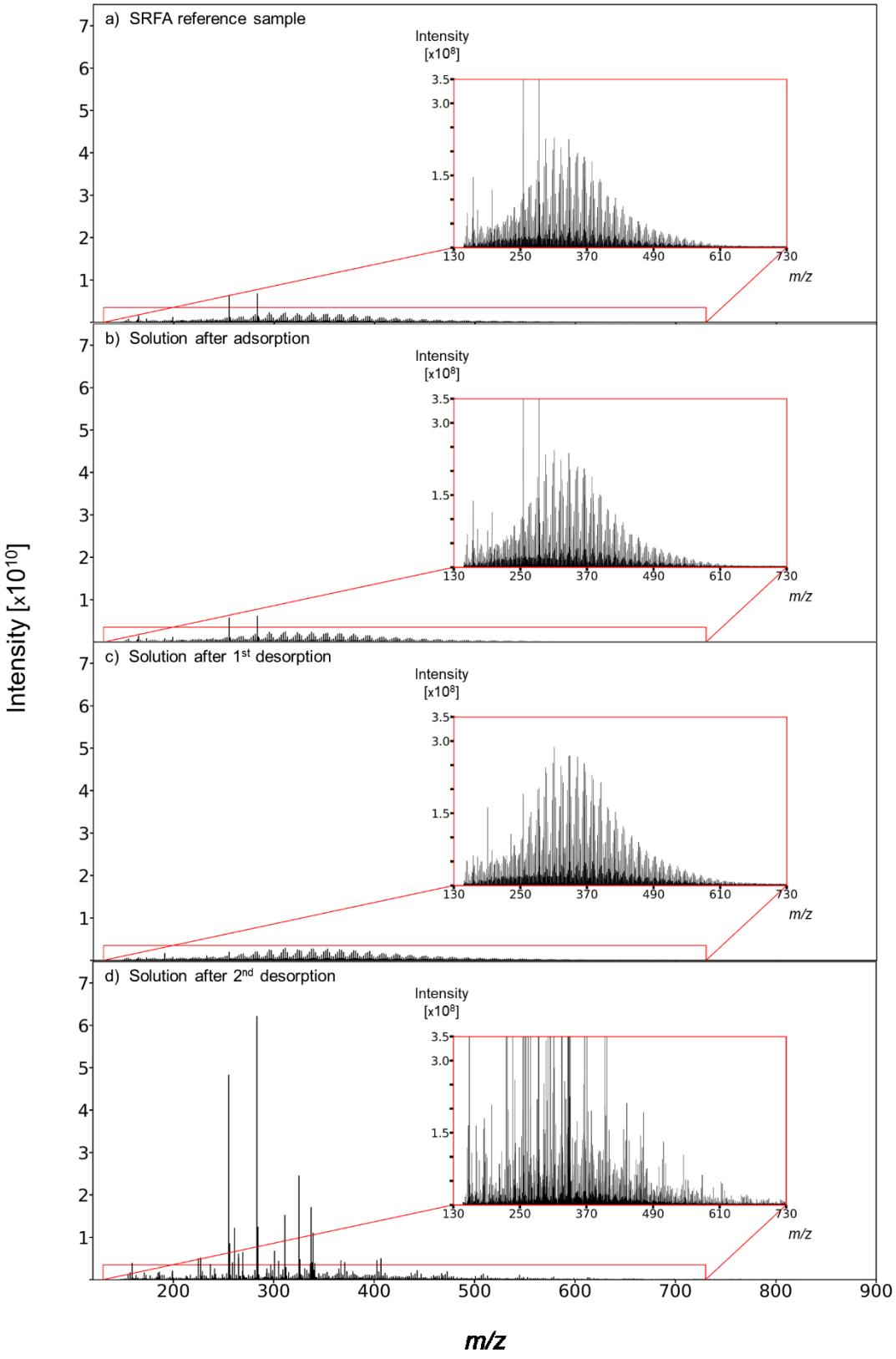


Figure S7. Raw ESI-FT-ICR mass spectra in the negative ionization mode for: a) SRFA reference sample, b) solution after adsorption, c) solution after 1st desorption, and d) solution after 2nd desorption for Au-CA.

Indirect SRFA-corona characterization of Au-CA by ESI-FTICR-MS

Comparison between LDI- and ESI-FTICR-MS

Comparing the obtained solutions and NPs among each other after these three treatment steps, a trend can be observed (Figure S8a-d). Initially, molecules with high O/C and low H/C are desorbed (Figure S8b and c). Then, molecules with low O/C and high H/C are desorbed, showing the remaining SRFA-corona to be consisting of molecules with low O/C and low H/C (Figure S8d). The trend of preferential adsorption and desorption of certain groups of molecules displayed in Figure S8 is in agreement with the results separately obtained with LDI (Figure S4d-j) and with ESI (Figure 2c-f).

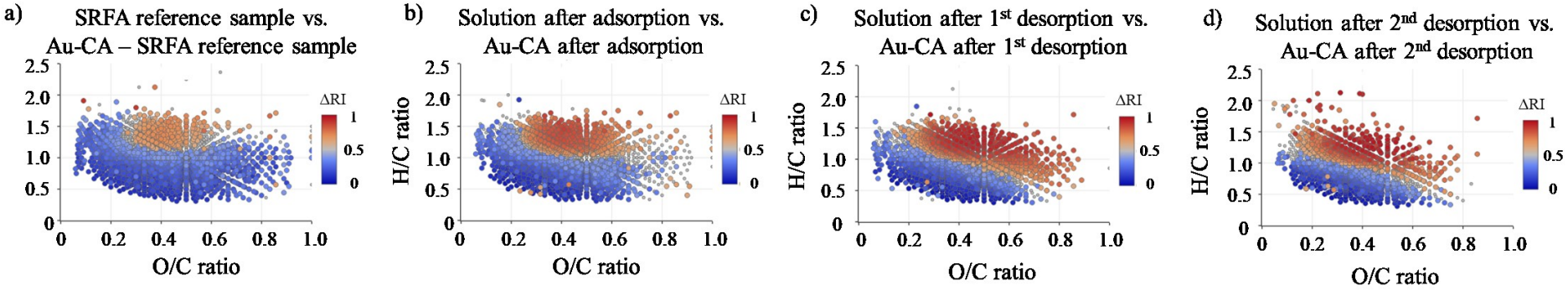
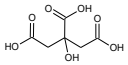
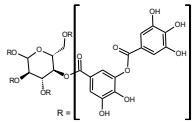
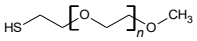
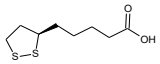
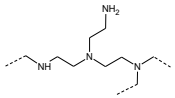


Figure S8. Van Krevelen diagrams for comparisons of LDI- and ESI-FT-ICR-MS measurements of the a) SRFA reference sample vs. Au-CA – SRFA reference sample, b) solution after adsorption vs. Au-CA after adsorption c) solution after 1st desorption vs. Au-CA after 1st desorption, and d) solution after 2nd desorption vs. Au-CA after 2nd desorption. The red dots (< 1 - 0.6) represent formulas more abundant in the ESI samples, whereas blue dots (0.4 - > 0) represent formulas that are more abundant in the LDI samples. Grey dots indicate similar relative intensities (between 0.4 and 0.6) for the common assigned molecular formulas in both samples.

Influence of the capping agent on corona composition

Table S2. Capping agents used in this study.

Name	Abbreviation	Chemical strucutre	Molecular weight	Type	Charge	Linkage to NP core	Zeta potential of stock NP[§] [mV]	Zeta potential after adsorption[†] [mV]	pH of stock NP[§]	pH after adsorption[§]
Citric acid	CA		192.0 Da	small molecule	negative	weak electrostatic	-51.3 ± 1.5	-30.4 ± 1.9	7.0 ± 0.1	2.5 ± 0.2
Tannic acid	TA		1700.2 Da	small molecule	negative	MLCT & vdW forces[#]	-35.4 ± 1.4	-19.7 ± 1.9	5.1 ± 0	2.6 ± 0
Polyvinyl-pyrrolidone	PVP		40 kDa	polymer	weak negative	MLCT & vdW forces[#]	-35.1 ± 0.7	-30.2 ± 0.8	4.8 ± 0	2.5 ± 0
Methoxy polyethylene glycol sulfhydryl	m-PEG-SH		5 kDa	polymer	negative	covalent	-50.2 ± 1.4	-27.8 ± 1.0	4.8 ± 0.1	2.5 ± 0
Lipoic acid	LA		206.0 Da	small molecule	negative	covalent	-44.4 ± 1.2	-26.3 ± 0.9	4.6 ± 0	2.5 ± 0
Branched polyethylenimine	BPEI		25 kDa	polymer	positive	covalent via LA as linker molecule	45.1 ± 2.0	-31.4 ± 0.8	5.2 ± 0	2.6 ± 0

[#] metal-to-ligand charge transfer (MLCT) & van der Waals (vdW) forces

[§] Mean ± SD of three replicates.

[†] Mean ± SD of three replicates. NP stock solution (50 – 56.8 mg/L) was mixed with SRFA (1:1 v/v) to obtain a concentration ratio [SRFA:Au NPs] of ~100:1 (m/m) according to the procedure described in the main text. The zeta potential of SRFA (5.0 g/L) before mixing was -24.1 ± 1.4 mV (n = 3).

Table S3. Molecular descriptors of all capping agents on Au NPs after adsorption, after 1st desorption and after 2nd desorption derived from the LDI-FT-ICR-MS measurements. The LDI measurement error (4.2%) was calculated from triplicate sample preparation of the Au-CA – SRFA reference sample and was used for all LDI measurements.

	Sample name	M_w [Da]	O/C	H/C	N/C [x10^3]	S/C [x10^3]	N/S [x10^3]	DBE	DBE-O	AI
Au-BPEI	after adsorption	**462** ± 19	**0.41** ± 0.02	**0.72** ± 0.03	**5.59** ± 0.23	**1.39** ± 0.06	**4.02** ± 0.17	**14.20** ± 0.60	**6.00** ± 0.25	**0.47** ± 0.02
	after 1st desorption	**443** ± 19	**0.34** ± 0.01	**0.60** ± 0.03	**5.76** ± 0.24	**1.21** ± 0.05	**4.78** ± 0.20	**15.90** ± 0.67	**8.85** ± 0.37	**0.62** ± 0.03
	after 2nd desorption	**442** ± 19	**0.35** ± 0.01	**0.61** ± 0.03	**6.83** ± 0.29	**1.97** ± 0.08	**3.47** ± 0.15	**15.75** ± 0.66	**8.54** ± 0.36	**0.61** ± 0.03
Au-CA	after adsorption	**446** ± 19	**0.37** ± 0.02	**0.78** ± 0.03	**6.04** ± 0.25	**0.81** ± 0.03	**7.48** ± 0.31	**13.33** ± 0.56	**6.09** ± 0.26	**0.45** ± 0.02
	after 1st desorption	**440** ± 18	**0.34** ± 0.01	**0.71** ± 0.03	**7.55** ± 0.32	**1.43** ± 0.06	**5.27** ± 0.22	**14.69** ± 0.62	**7.69** ± 0.32	**0.54** ± 0.02
	after 2nd desorption	**413** ± 17	**0.33** ± 0.01	**0.70** ± 0.03	**8.06** ± 0.34	**1.97** ± 0.08	**4.09** ± 0.17	**14.29** ± 0.60	**7.76** ± 0.33	**0.55** ± 0.02
Au-LA	after adsorption	**466** ± 20	**0.39** ± 0.02	**0.71** ± 0.03	**5.38** ± 0.23	**1.51** ± 0.06	**3.56** ± 0.15	**14.61** ± 0.61	**6.75** ± 0.28	**0.49** ± 0.02
	after 1st desorption	**438** ± 18	**0.35** ± 0.01	**0.68** ± 0.03	**6.15** ± 0.26	**2.52** ± 0.11	**2.44** ± 0.10	**14.99** ± 0.63	**7.87** ± 0.33	**0.56** ± 0.02
	after 2nd desorption	**408** ± 17	**0.34** ± 0.01	**0.70** ± 0.03	**6.91** ± 0.29	**4.19** ± 0.18	**1.65** ± 0.07	**14.09** ± 0.59	**7.51** ± 0.32	**0.55** ± 0.02
Au-PVP	after adsorption	**454** ± 19	**0.39** ± 0.02	**0.73** ± 0.03	**5.95** ± 0.25	**0.98** ± 0.04	**6.09** ± 0.26	**14.14** ± 0.59	**6.34** ± 0.27	**0.48** ± 0.02
	after 1st desorption	**407** ± 17	**0.35** ± 0.01	**0.68** ± 0.03	**8.19** ± 0.34	**1.47** ± 0.06	**5.59** ± 0.23	**14.23** ± 0.60	**7.48** ± 0.31	**0.56** ± 0.02
	after 2nd desorption	**365** ± 15	**0.33** ± 0.01	**0.72** ± 0.03	**14.68** ± 0.62	**2.94** ± 0.12	**4.99** ± 0.21	**12.90** ± 0.54	**7.07** ± 0.30	**0.55** ± 0.02
Au-(m-PEG-SH)	after adsorption	**413** ± 17	**0.36** ± 0.02	**0.77** ± 0.03	**4.86** ± 0.20	**0.82** ± 0.03	**5.92** ± 0.25	**13.01** ± 0.55	**6.30** ± 0.26	**0.48** ± 0.02
	after 1st desorption	**389** ± 16	**0.32** ± 0.01	**0.71** ± 0.03	**7.93** ± 0.33	**2.19** ± 0.09	**3.63** ± 0.15	**13.61** ± 0.57	**7.63** ± 0.32	**0.56** ± 0.02
	after 2nd desorption	**362** ± 15	**0.30** ± 0.01	**0.75** ± 0.03	**6.97** ± 0.29	**3.59** ± 0.15	**1.94** ± 0.08	**12.52** ± 0.53	**7.12** ± 0.30	**0.55** ± 0.02
Au-TA	after adsorption	**452** ± 19	**0.41** ± 0.02	**0.74** ± 0.03	**6.76** ± 0.28	**1.23** ± 0.05	**5.51** ± 0.23	**13.67** ± 0.57	**5.75** ± 0.24	**0.46** ± 0.02
	after 1st desorption	**416** ± 17	**0.40** ± 0.02	**0.59** ± 0.02	**6.85** ± 0.29	**1.72** ± 0.07	**3.99** ± 0.17	**14.63** ± 0.61	**7.16** ± 0.30	**0.60** ± 0.03
	after 2nd desorption	**392** ± 16	**0.42** ± 0.02	**0.55** ± 0.02	**6.10** ± 0.26	**1.65** ± 0.07	**3.69** ± 0.15	**13.93** ± 0.59	**6.70** ± 0.28	**0.64** ± 0.03

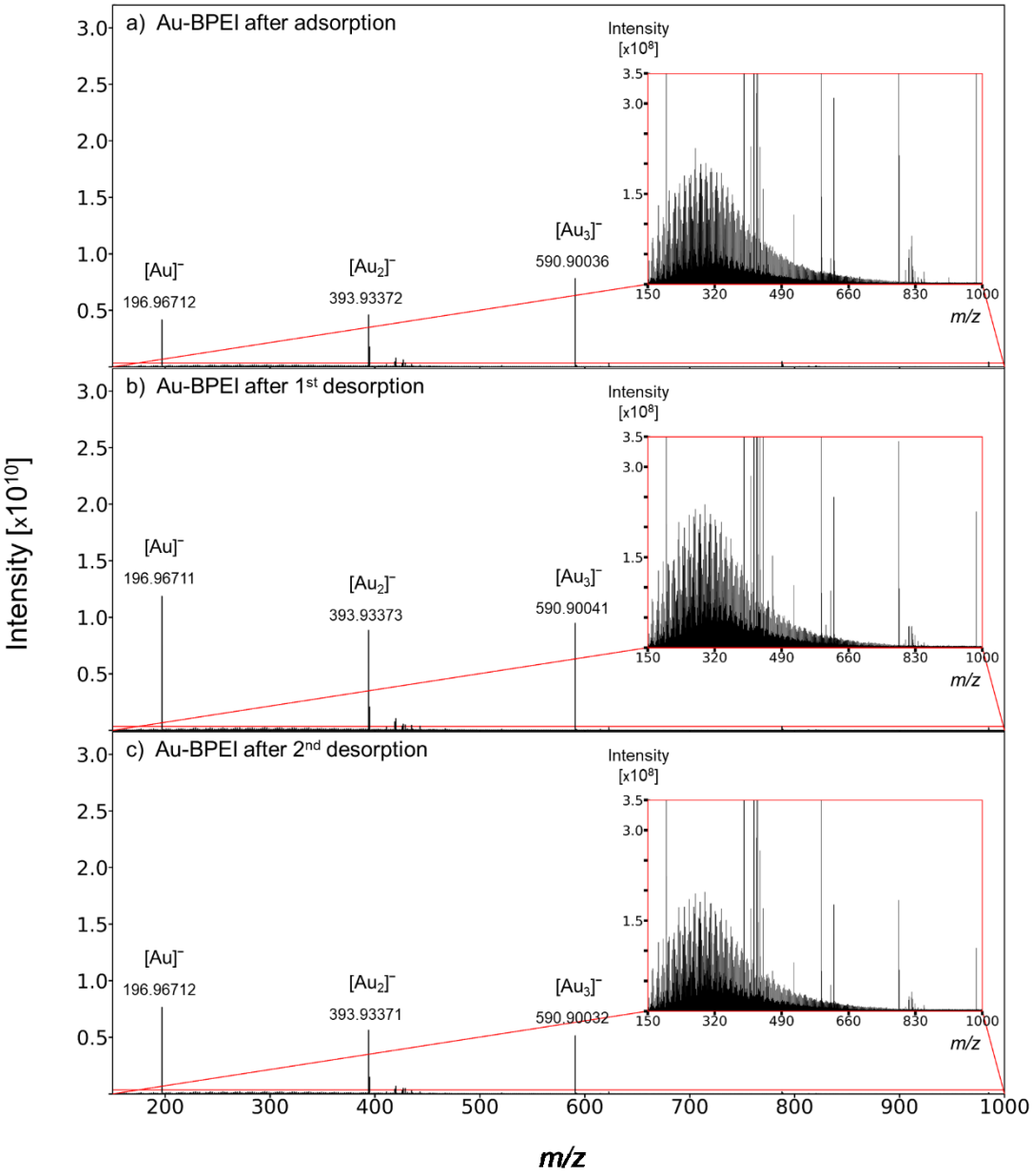


Figure S9. Raw LDI-FT-ICR mass spectra measured in the negative ionization mode for: a) Au-BPEI after adsorption, b) Au-BPEI after 1st desorption, and c) Au-BPEI after 2nd desorption.

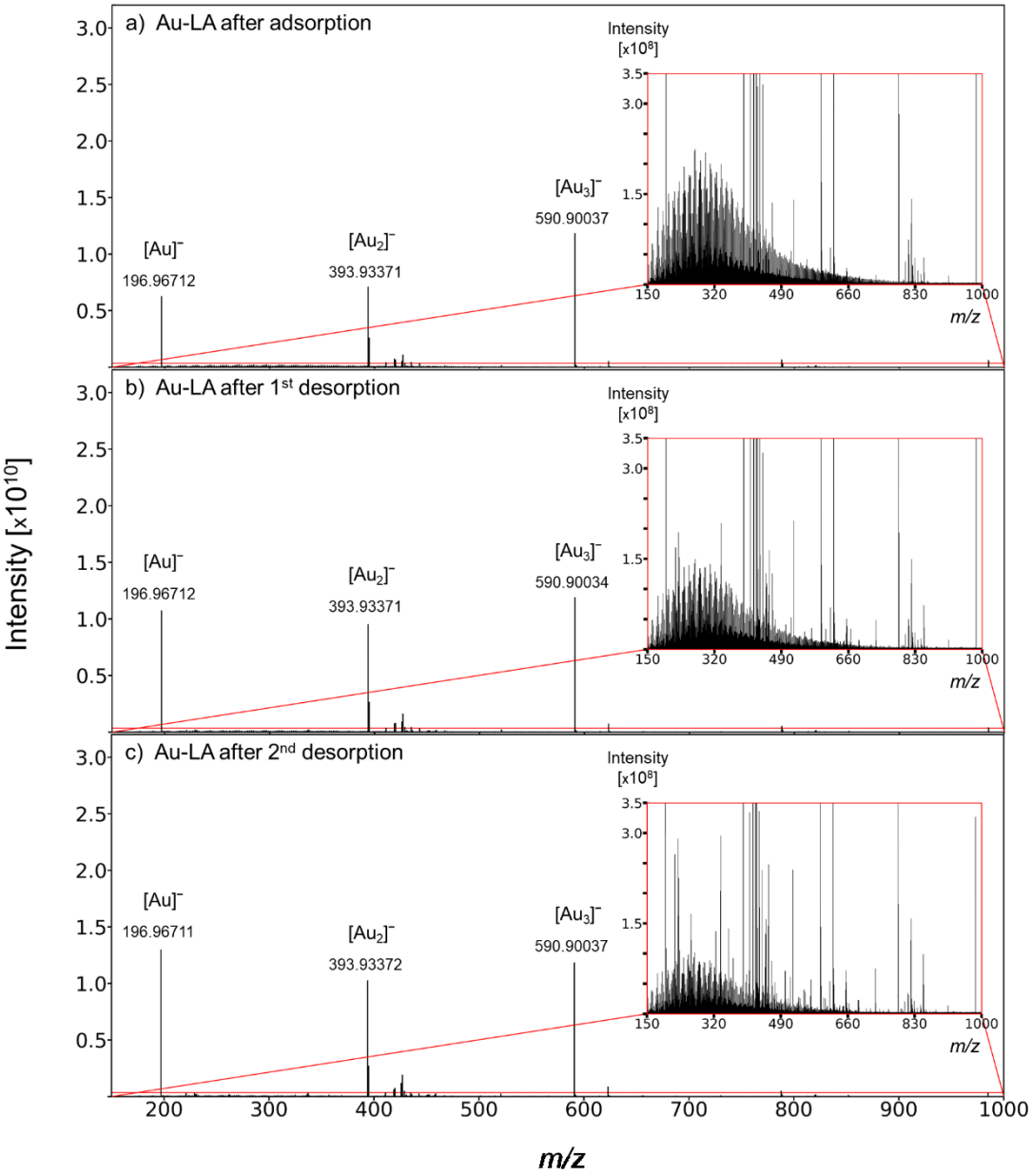


Figure S10. Raw LDI-FT-ICR mass spectra measured in the negative ionization mode for: a) Au-LA after adsorption, b) Au-LA after 1st desorption, and c) Au-LA after 2nd desorption.

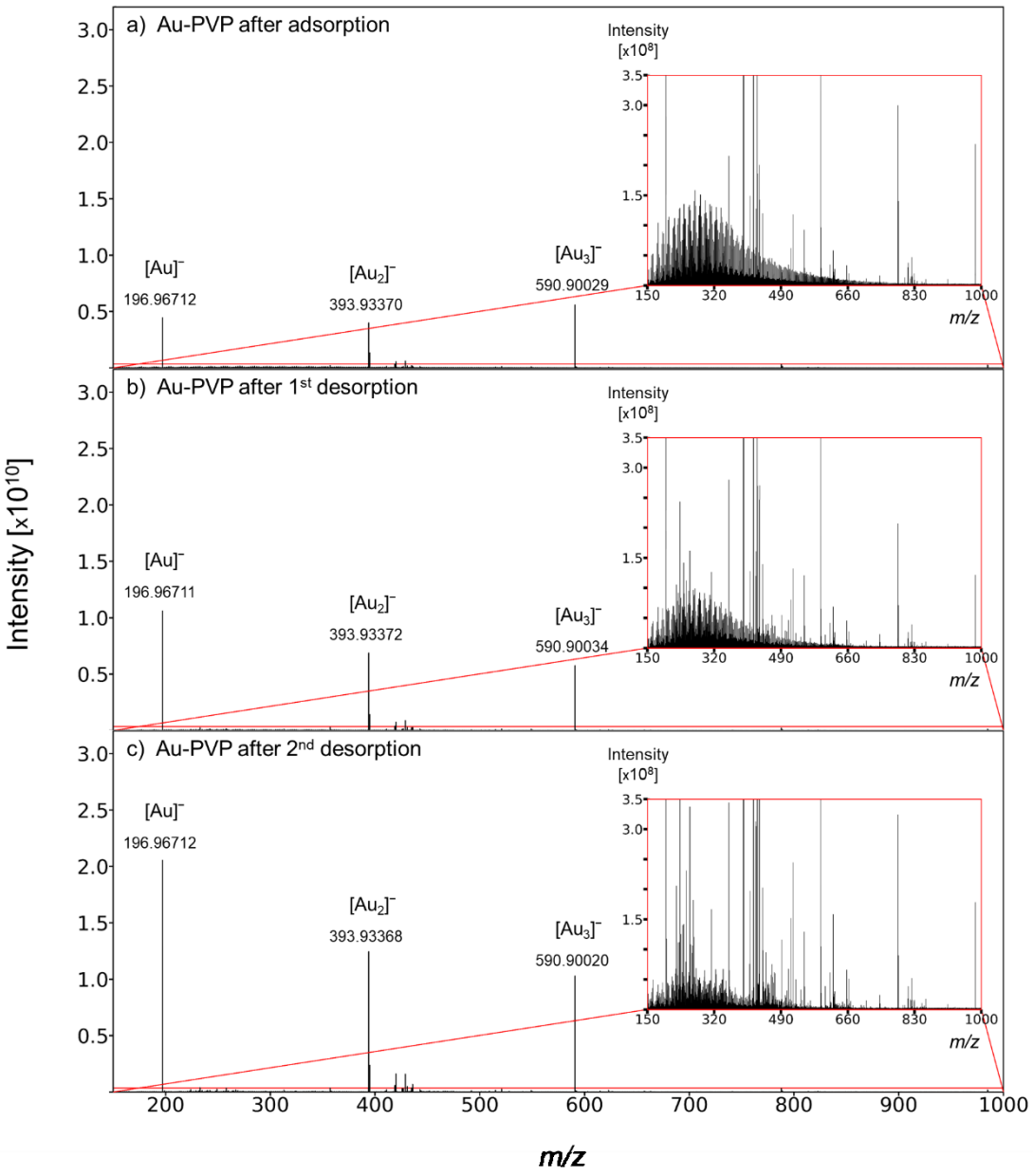


Figure S11. Raw LDI-FT-ICR mass spectra measured in the negative ionization mode for: a) Au-PVP after adsorption, b) Au-PVP after 1st desorption, and c) Au-PVP after 2nd desorption.

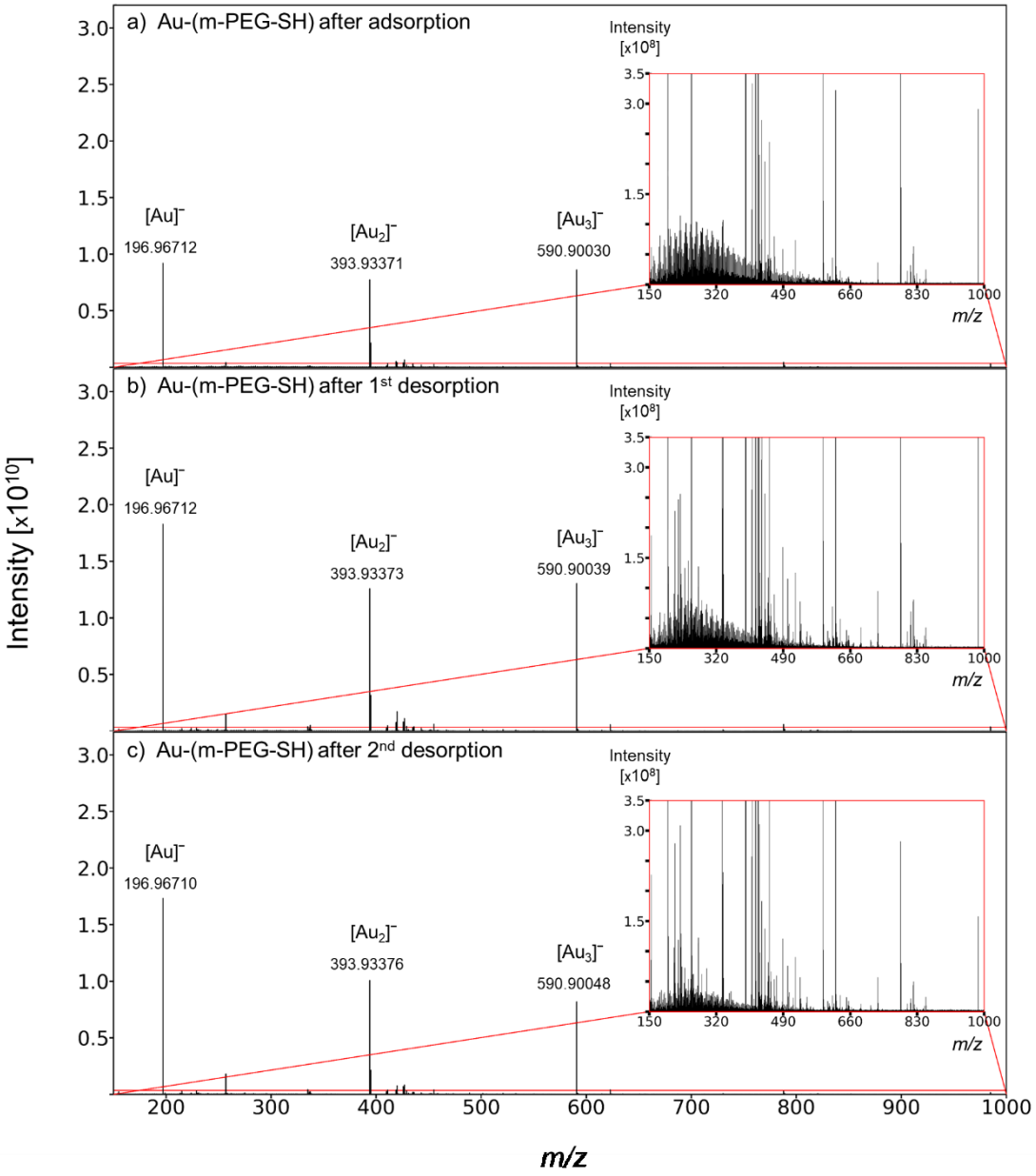


Figure S12. Raw LDI-FT-ICR mass spectra measured in the negative ionization mode for: a) Au-(m-PEG-SH) after adsorption, b) Au-(m-PEG-SH) after 1st desorption, and c) Au-(m-PEG-SH) after 2nd desorption.

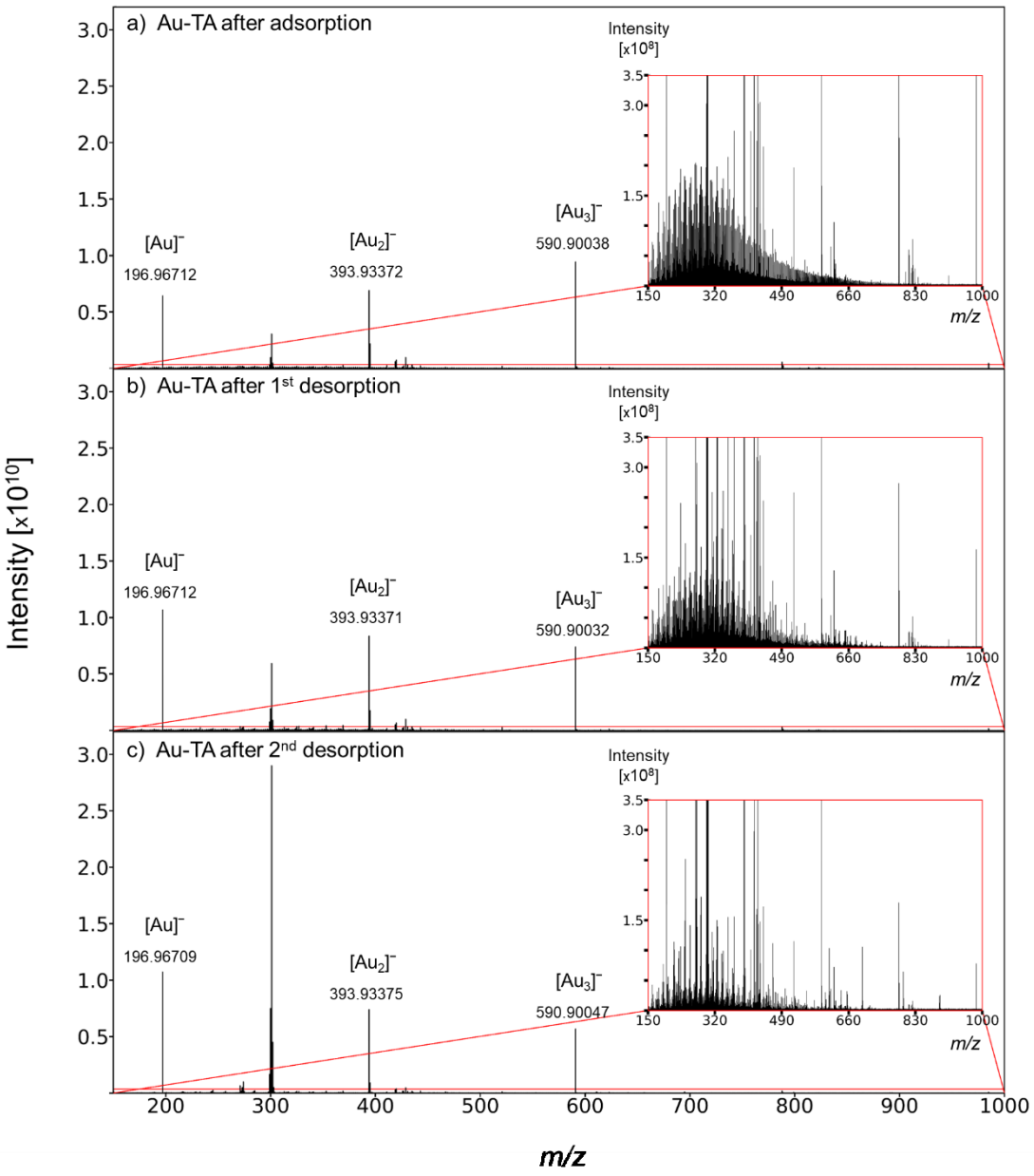


Figure S13. Raw LDI-FT-ICR mass spectra measured in the negative ionization mode for: a) Au-TA after adsorption, b) Au-TA after 1st desorption, and c) Au-TA after 2nd desorption.