Supplementary Information (SI) for Analyst.

Electronic supporting information for:

In-situ study of the interactions of metal surfaces with cationic surfactant corrosion inhibitors with surface-enhanced Raman spectroscopy coupled with visible spectroscopy

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Studies of the interaction between silver colloid and BAC-16

For the study of the interaction between the silver nanoparticle and the surfactants, four measurement series with different AgNP:BAC-16 ratios (1:9, 2:8, 5:5, 8:2) were carried out using the mixtures listed in Table S1 (equivalent to Table 1 in the main document). In Figure S1, the measurement sequence for the VIS-SERS measurements is illustrated. For the AgNP:BAC-16 mixtures, the BAC-16 concentrations in respect to the dilution with the AgNP colloid are shown in Table S2.

Table S1: Experimental parameters for the VIS-SERS measurements. BAC-16 concentrations refer to the samples before mixing.

Ratios	V($AgNO_3$)	V(NH_2OH)	V(BAC-16)	c(BAC-16) / mg L^{-1}								
1:9	0.9 mL	0.1 mL	9 mL	0.02	0.05	0.2	0.5	1	2	4		
2:8	1.8 mL	0.2 mL	8 mL	0.02	0.05	0.2	0.5	1	2	4		
5:5	4.5 mL	0.5 mL	5 mL	0.02	0.05	0.2	0.5	1	2	4	10	100
8:2	7.2 mL	0.8 mL	2 mL			0.2	0.5	1	2	4	10	100

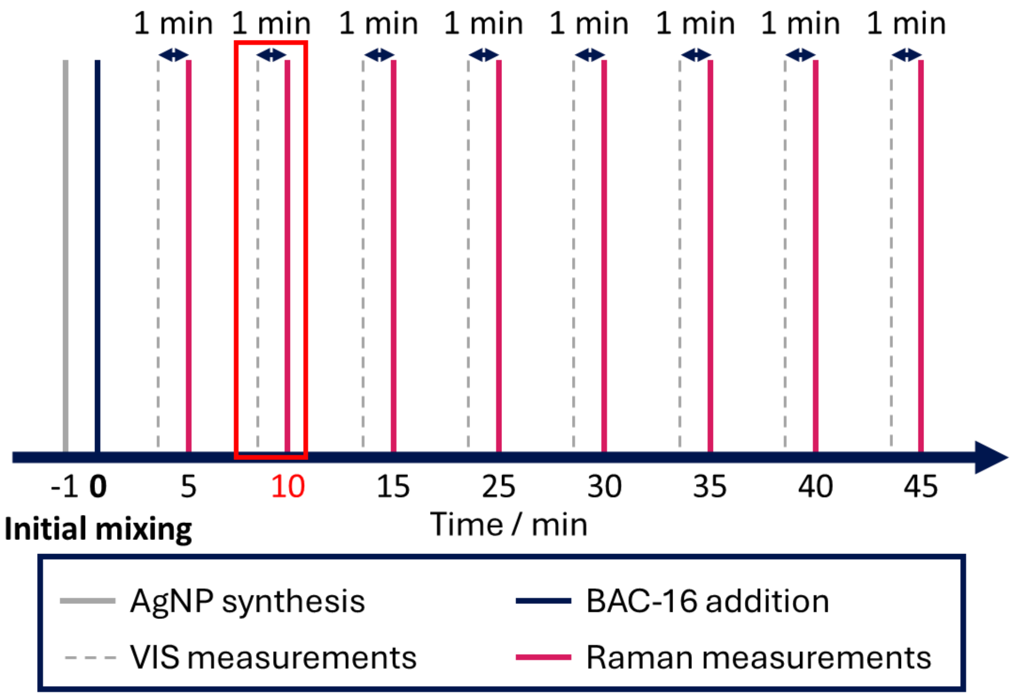

Figure S1: Illustration of the measurement sequence for the VIS-SERS measurements. Initial mixing refers to the addition of BAC-16 to the AgNP colloid, while the two measurements marked by the red box show the measurements taken 10 min after initial mixing (9 min in case of the VIS measurement) used for Figure 5 in the main manuscript.

Table S2: Experimental parameters for the VIS-SERS measurements. BAC-16 concentrations refer to the samples after mixing.

Ratios	c(BAC-16) / mg L^{-1}								
1:9	0.018	0.045	0.18	0.45	0.9	1.8	3.6		
2:8	0.016	0.04	0.16	0.4	0.8	1.6	3.2		
5:5	0.01	0.025	0.1	0.25	0.5	1	2	5	50
8:2			0.04	0.1	0.2	0.4	0.8	2	20

Considerations for the comparison of different volumetric ratios

To correlate the experiments with different colloid to surfactant volumetric ratios (Table 1), the concentrations were standardised to reflect the number of BAC-16 molecules per SERS particle. For this, the amount of AgNPs per mL colloid was calculated. Looking at the concentrations of the precursors ($AgNO_3$ and NH_2OH) in Table S3, $AgNO_3$ was the limiting reactant.

Table S3: Concentration of precursors for the AgNP synthesis.

	c / mol L^{-1}	V / mL	n / mmol
$AgNO_3$	1.11×10^{-3}	0.9	9.99×10^{-4}
NH_2OH	1.50×10^{-2}	0.1	1.50×10^{-3}

For 1 mL of AgNP suspension, calculating the number of AgNPs per mL colloid results in a number of 1.65×10^{10} mL^{-1}, using the following equations, a silver molar mass (M_{Ag}) of 107.87 g mol^{-1}, and a density of 10.49 g cm^{-3} for the calculations in Table S4:

$$m_{Ag} = M_{Ag} \cdot c_{Ag} \cdot V_{Ag} \quad \text{(S1)}$$

$$V_{Ag} = \frac{m_{Ag}}{\rho_{Ag}} \quad \text{(S2)}$$

$$V_{sphere} = \frac{4}{3}\pi r^3 \quad \text{(S3)}$$

$$n_{AgNP} = \frac{V_{Ag}}{V_{sphere}} \quad \text{(S4)}$$

Table S4: Calculation of the number of AgNPs per mL colloid.

m_{Ag} / g	V_{Ag} / cm^3	r_{AgNP} / nm	V_{sphere} /nm^3	V_{sphere} / cm^3	n_{AgNP} / a.u.
1.08×10^{-4}	1.03×10^{-5}	53	6.24×10^{5}	6.24×10^{-16}	1.65×10^{10}

Using the number of 1.65×10^{10} AgNP per mL colloid, the number of BAC-16 molecules per AgNP can be calculated using (1) in the main manuscript. The resulting ratios are shown in Table S5.

Table S5: Experimental parameters for the VIS-SERS measurements. BAC-16 concentrations refer to the number of BAC-16 molecules per AgNP.

Ratios	c^*_{BAC} / a.u.								
1:9	1.7×10^4	4.2×10^4	1.7×10^5	4.2×10^5	8.3×10^5	1.7×10^6	3.3×10^6		
2:8	7.4×10^3	1.9×10^4	7.4×10^4	1.9×10^5	3.7×10^5	7.4×10^5	1.5×10^6		
5:5	1.9×10^3	4.6×10^3	1.9×10^4	4.6×10^4	9.2×10^4	1.9×10^5	3.7×10^5	9.2×10^5	9.2×10^6
8:2			4.6×10^3	1.2×10^4	2.3×10^4	4.6×10^4	9.2×10^4	2.3×10^5	2.3×10^6