Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Understanding the Interaction of Gold and Silver Nanoparticles with Natural Organic Matter using Affinity Capillary Electrophoresis

Supporting information

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The electrophoretic mobility (μ) was calculated using Equation S-1:

$$\mu = \frac{l_d l_t}{V}\left(\frac{1}{t_m} - \frac{1}{t_{EOF}}\right) \tag{S-1}$$

where l_d is the length to the detection window (effective length), l_t is the total length of the capillary, V is the applied voltage, t_m is the migration time of the analyte at the peak maximum and t_{EOF} is the migration time of the electro-osmotic flow (EOF) marker.

The μ, when an internal standard was used, was calculated using Equation S-2:

$$\mu = \frac{l_d l_t}{V}\left(\frac{1}{t_m} - \frac{1}{t_{IS}} + \frac{V\mu_{IS}}{l_d l_t}\right) \tag{S-2}$$

where t_{IS} is the migration time of the internal standard at the peak maximum and μ_{IS} is the electrophoretic mobility of the internal standard.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Experiments were run employing an RF forward power of 1550 W, with argon gas flows of 1.00 L min^{-1} and 0.15 L min^{-1} for carrier and makeup flows, respectively. Indium (115) and iridium (193) were used as internal standards. Standards and samples were introduced using a peristaltic pump into a micromist nebulizer and Scott double pass spray chamber with a 0.3 rps uptake speed for an uptake time of 120 s followed by a 45 s stabilize time. The post run rinsing was 120 s of 2 % nitric acid followed 120 s of 4 % nitric acid when Ag was analyzed and 90 s of acidic aqueous thiourea solution (0.5 % w/v thiourea, 0.9 % v/v HCl and 0.03 % v/v HNO_3) and 30 s of 4 % nitric acid when Au was analyzed, all with a 0.4 rps rinse speed. For analysis of Au samples, Au standards and samples were diluted using a thiourea solution. The samples were diluted by taking 10 µL and diluting to 10 mL, which was further diluted by 100 µL being diluted to 10 mL and then being analyzed. Ag standards and samples were diluted in the same manner except 2 % HCl was used as the solvent. A humidifier was attached to the carrier gas when HCl was the solvent. The amount of Au and Ag were determined using the calibration curves y = 176401x + 140 (R^2 0.9999) and y = 181824x + 1278 (R^2 0.9997) respectively with concentrations ranging from 0.01 – 2 µg L^{-1}. Data acquisition and processing was performed in Mass Hunter version 4.4.

Table S1. Characterization of NP samples. Z-average diameters and zeta potential of NPs suspended in water and 40 mM phosphate buffer pH 6.8 with (PB40NOM) and without (PB40) 40 ppm of NOM present. Error is reported as the standard deviation (SD) of triplicate measurements. Poor fitting quality and low repeatability were found for the sizes of NP when not suspended in water. The ion content of the supernatant was determined by Ion Chromatography (IC) with the error reported as the SD of triplicate measurements.

Sample	DLS Diameters (nm)			Zeta potential (mV)		Ion content in supernatant	
	water	PB40	PB40NOM	water	PB40NOM	Citrate (mM)	Chloride (µM)
AuNP60	63.3 ± 0.5	~200	~480	-43 ± 2	-26 ± 5	1.96 ± 0.09	7.2 ± 0.3
AuNP10	16.0 ± 0.3	~96	~46	-43 ± 1	-23 ± 2	2.13 ± 0.03	4.6 ± 0.1
AuNP20S	28.0 ± 0.2	~43	~62	-33 ± 1	-11 ± 1	0.34 ± 0.02	64.9 ± 4.2
AgNP90	109.1 ± 0.9	~540	~755	-31 ± 1	-35 ± 2	2.25 ± 0.07	8.4 ± 0.3
AgNP60	65.0 ± 0.1	~760	~321	-62 ± 2	-33 ± 3	2.19 ± 0.10	5.1 ± 0.3
AgNP30	37.1 ± 0.7	~510	~598	-52 ± 1	-35 ± 2	2.25 ± 0.10	5.1 ± 0.3
AgNP10	21.7 ± 0.6	~109	~354	-39 ± 1	-35 ± 1	1.96 ± 0.02	4.2 ± 0.2
AgNP10S	23.3 ± 0.4	~145	~200	-44.0 ± 2	-38 ± 4	1.57 ± 0.03	7.9 ± 0.2

Recovery of citrate through membrane.

Citrate was found to adsorb onto the membrane used to concentrate the NPs and remove the unbound citrate. When 0.2 mM sodium citrate was passed through the membrane only 10 % of the citrate was recovered. When the membrane was pre-treated with 2 M sodium malate the recovery of a citrate through the membrane was 92 % although from the precision of the IC measurement there was no significant difference between the concentration of citrate measured before and after passing through the membrane.

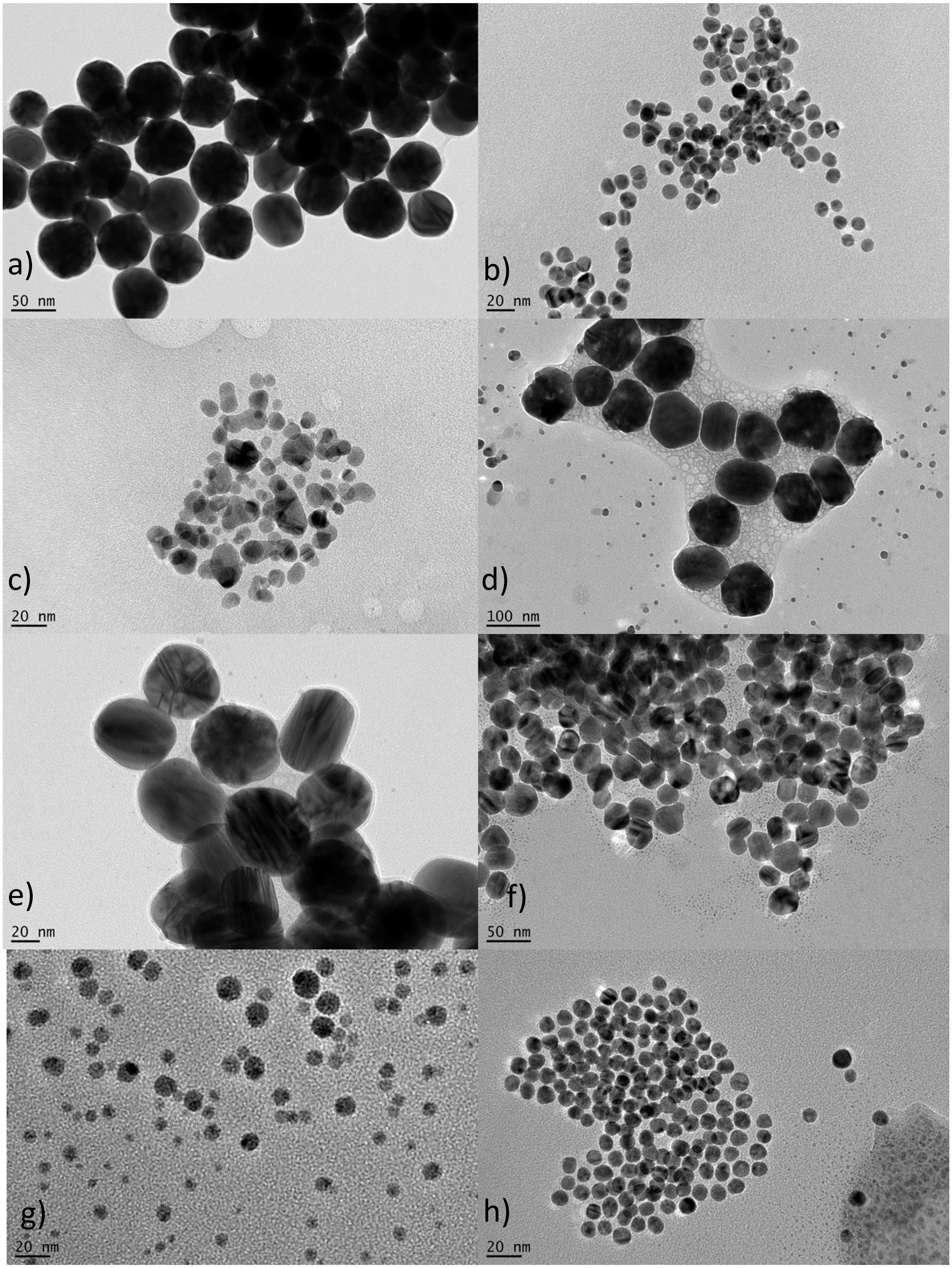

Figure S1. TEM images of NPs suspended in PB40. a) AuNP60, b) AuNP10, c) AuNP20S, d) AgNP90, e) AgNP60, f) AgNP30, g) AgNP10 and h) AgNP10S

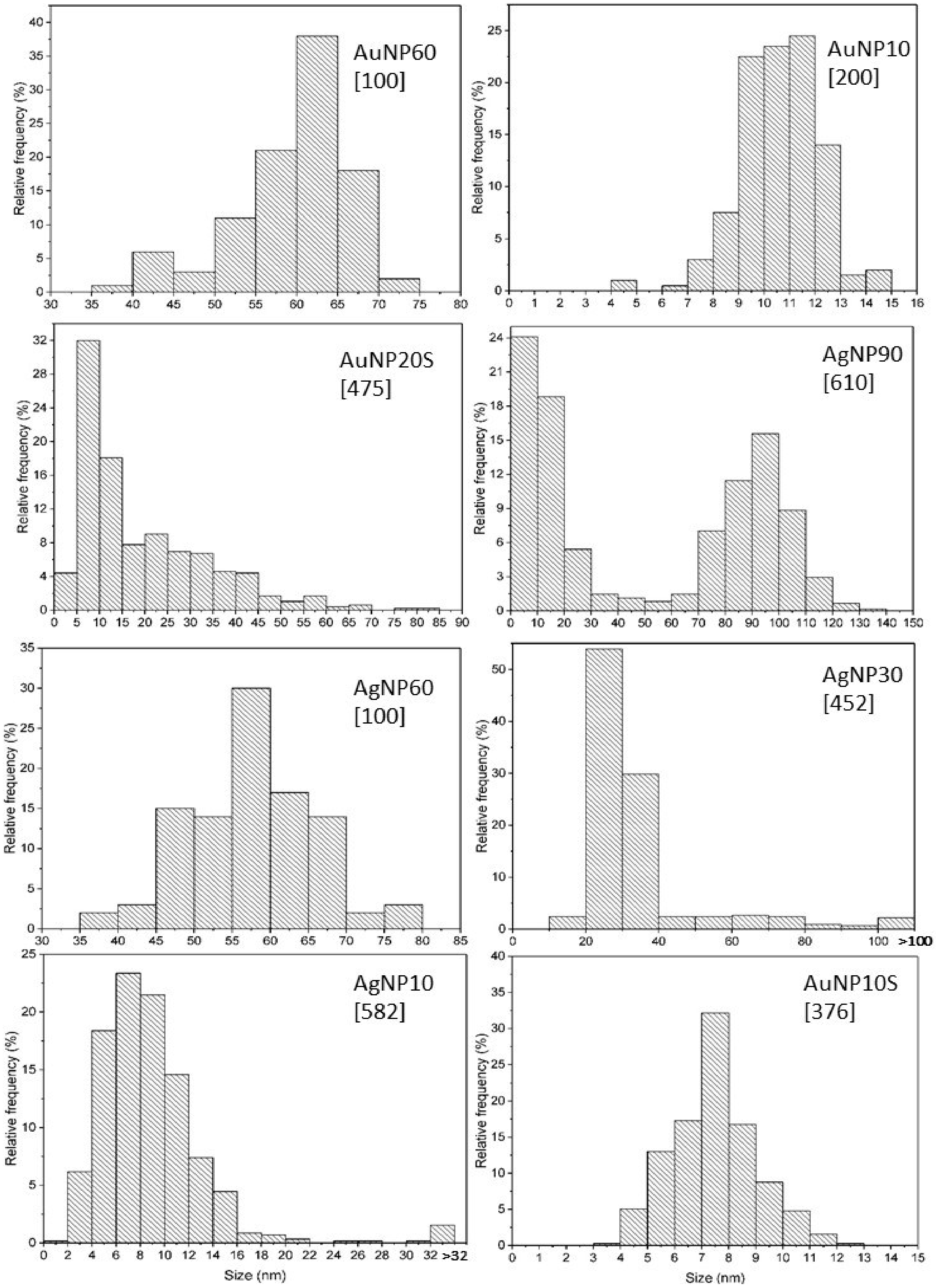

Figure S2. Particle Size Distributions (PSDs) of NPs suspended in PB40 by Transmission Electron Microscopy (TEM). Number of particles counted shown in brackets.

Table S2. Calculated surface area and citrate quantities from TEM and Ion Chromatography (IC) experiments. The surface area was calculated by converting the size distributions in Figure S2 to surface area and mass distributions and taking the sum from the distribution which assumes the TEM particle distribution is representative of the sample. The densities of gold or silver were 19.32 and 10.49 g cm^{-3} respectively. Total citrate refers to the amount of citrate in the suspension after degradation. Error determined from the SD of the citrate quantification.

NM	TEM, Surface area (m^2 g^{-1})	Total citrate molecules in suspension (10^6) per particle	Total citrate per surface area of particle (mmol m^{-2})
AuNP60	5.07	53.9 ± 1.3	8.2 ± 0.2
AuNP10	28.15	0.4 ± 0.1	1.8 ± 0.3
AuNP20S	7.77	0.3 ± 0.1	0.8 ± 0.1
AgNP90	6.12	309.2 ± 18.0	19.6 ± 1.1
AgNP60	9.61	71.5 ± 0.6	12.0 ± 0.1
AgNP30	9.48	15.3 ± 0.7	12.2 ± 0.5
AgNP10	17.92	0.3 ± 0.1	6.4 ± 0.2
AgNP10S	70.65	0.1 ±<0.1	1.0 ± 0.1

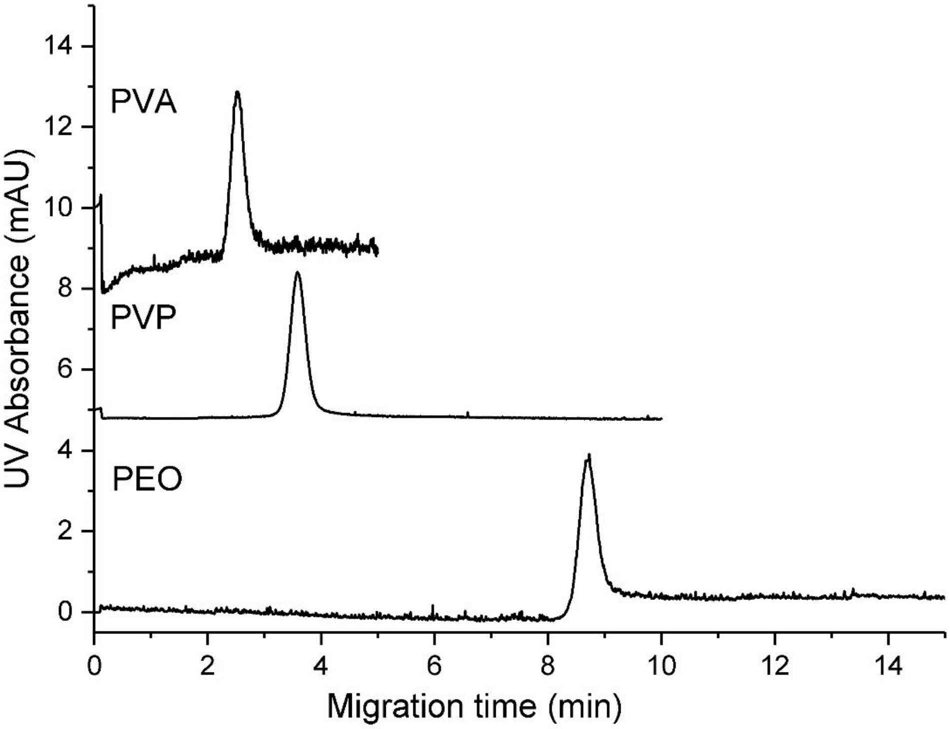

Figure S3. Pressure mobilization of NOM with different coated capillaries. Poly(vinyl alcohol), PVA, coated Agilent capillary with 75 µm i.d. and a total length of 34.0 cm (effective length 25.5 cm). Poly(*N*-vinylpyrrolidone), PVP, coated capillary with 75 µm i.d. and a total length of 40.4 cm (effective length 31.9 cm). Poly(ethylene oxide), PEO, WAX Agilent capillary 50 µm i.d. and a total length of 48.5 cm (effective length 40.0 cm). The BGE was PB40 at 25 °C with 30 mbar of internal pressure. The injection concentration was 5 g L^{-1}. Detection at 254 nm.

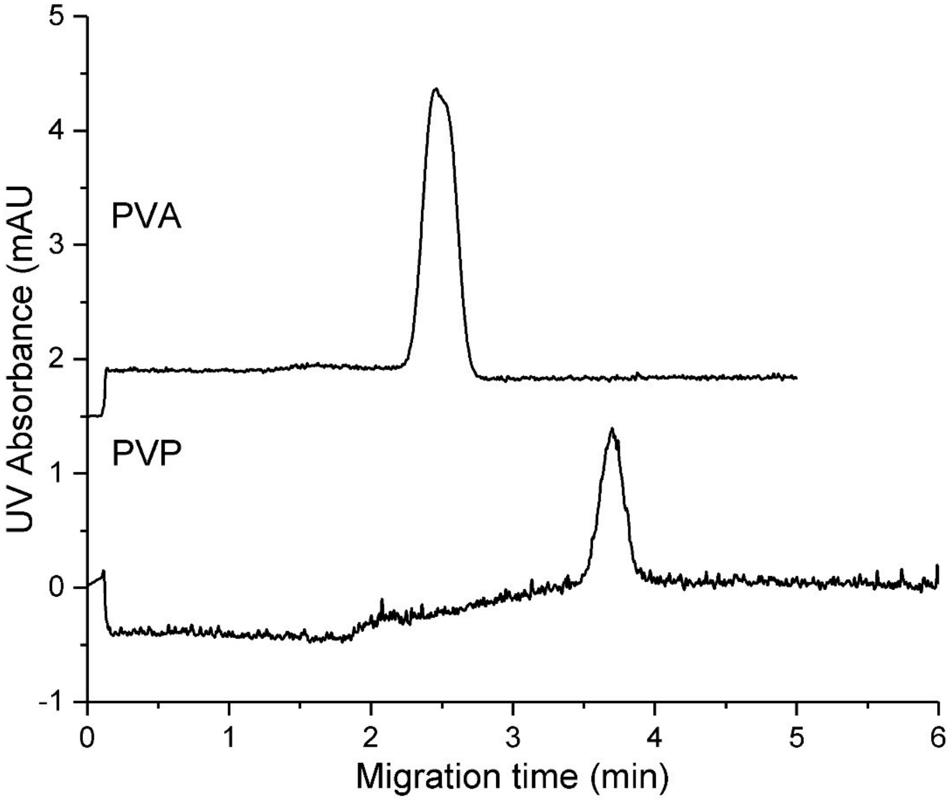

Figure S4. Pressure mobilization of AuNP60 with different coated capillaries. Poly(vinyl alcohol), PVA, coated Agilent capillary with 75 µm i.d. and a total length of 34.0 cm (effective length 25.5 cm). Poly(*N*-vinylpyrrolidone), PVP, coated capillary with 75 µm i.d. and a total length of 40.4 cm (effective length 31.9 cm). The BGE was PB40 at 25 °C with 30 mbar of internal pressure. The injection concentration was 40 mg L^{-1}. Detection at 200 nm.

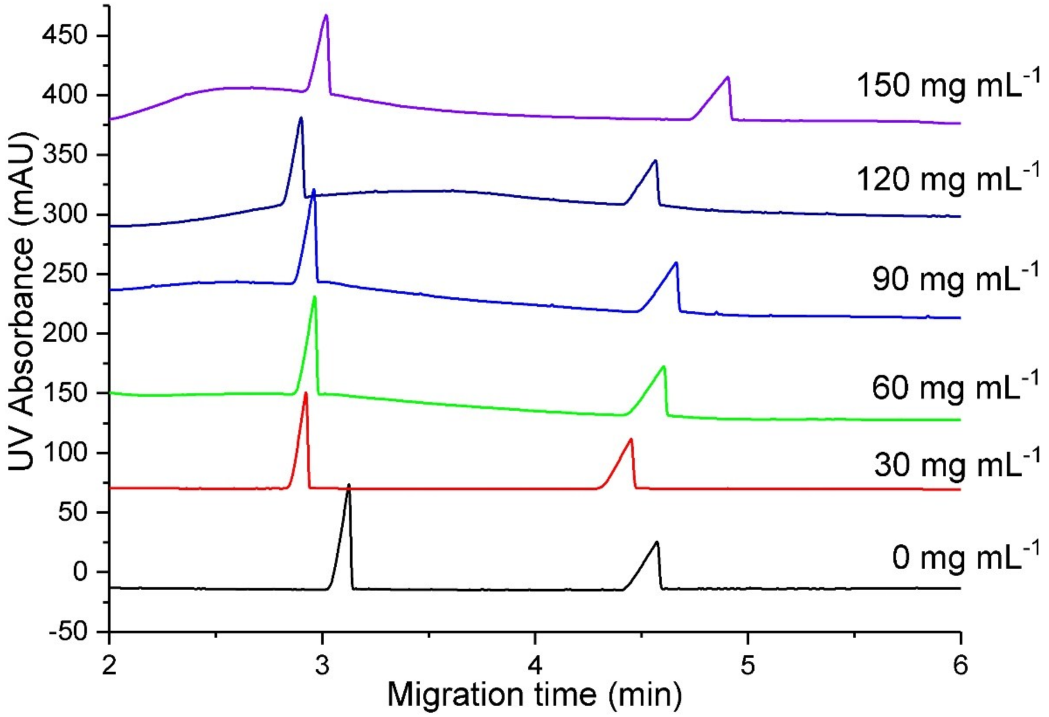

Figure S5. Electrophoretograms of AuNP60 as a function of migration time with changing NOM concentration in the BGE. The peak around 3 min is the bromide internal standard and the peak around 4.5 min is the NPs.

Table S3. Comparison of the binding parameters obtained from fitting the ACE data of NOM adsorbing onto to AuNPs and AgNPs to three different models (Equations 6-8).

Sample	Hill			Langmuir		Freundlich		
	K_D (mg L^{-1})	n	R^2	K_L (L μg^{-1})	R^2	K_F (L μg^{-1})	n_F	R^2
AuNP60	28.6 ± 2.2	1.7 ± 0.2	0.96	48.9 ± 7.6	0.88	99.2 ± 18.7	2.1 ± 0.2	0.96
AuNP10	18.1 ± 5.4	1.2 ± 0.3	0.80	63.1 ± 14.3	0.81	258.6 ± 101.7	3.8 ± 1.3	0.75
AuNP20S	34.9 ± 4.3	2.6 ± 0.7	0.85	48.7 ± 14.5	0.71	69.3 ± 33.9	1.8 ± 0.3	0.83
AgNP90	32.9 ± 7.0	1.1 ± 0.3	0.73	31.9 ± 5.7	0.75	103.4 ± 42.0	2.3 ± 0.5	0.80
AgNP60	27.3 ± 2.8	1.3 ± 0.2	0.93	43.5 ± 4.9	0.92	131.2 ± 29.0	2.5 ± 0.3	0.93
AgNP30	35.9 ± 6.7	1.6 ± 0.4	0.74	32.9 ±7.4	0.72	113.8 ± 72.4	2.4 ± 0.8	0.63
AgNP10	15.9 ± 3.3	1.3 ± 0.2	0.90	78.0 ± 15.0	0.90	281.8 ± 86.6	4.0 ± 1.1	0.85
AgNP10S	15.3 ± 2.5	3.4 ± 1.3	0.83	178.1 ± 94.4	0.66	398.9 ± 150.1	4.7 ± 1.9	0.67

K_D is the Hill dissociation constant, n is the Hill coefficient, K_L is the Langmuir adsorption isotherm constant, K_F is the Freundlich isotherm constant and n_F is the Freundlich constant.

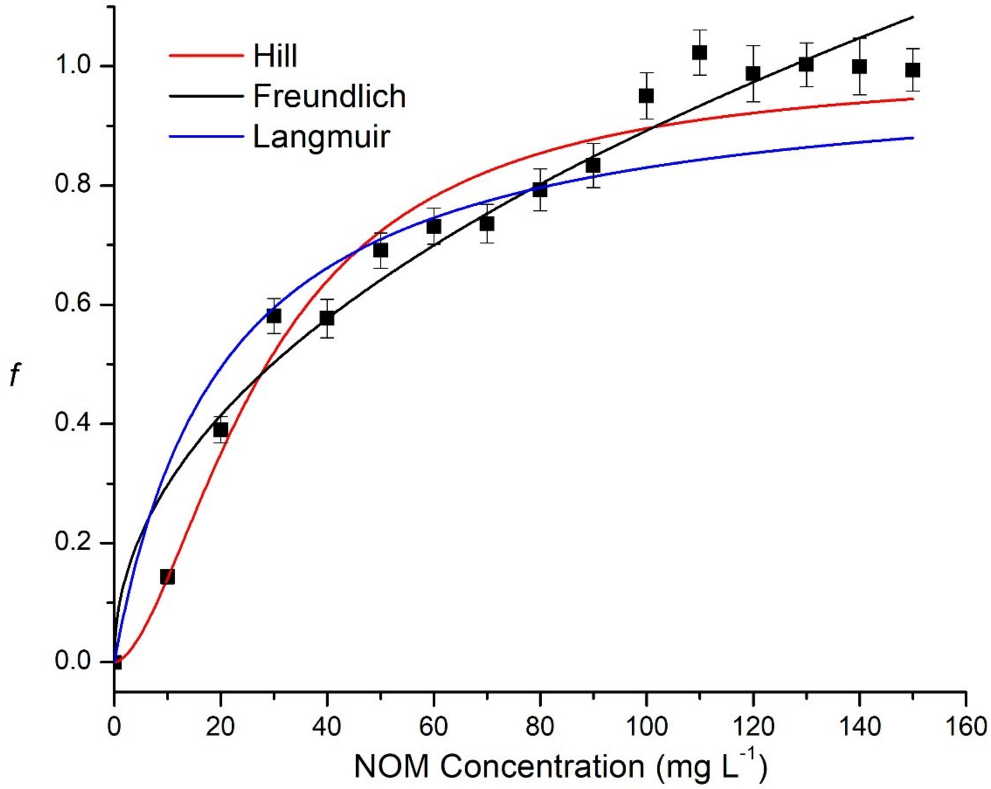

Figure S6. Comparison of the fitting the change in electrophoretic mobility of AuNP60 with changing NOM concentration in the BGE according to three different adsorption models shown in Equations 6-8.

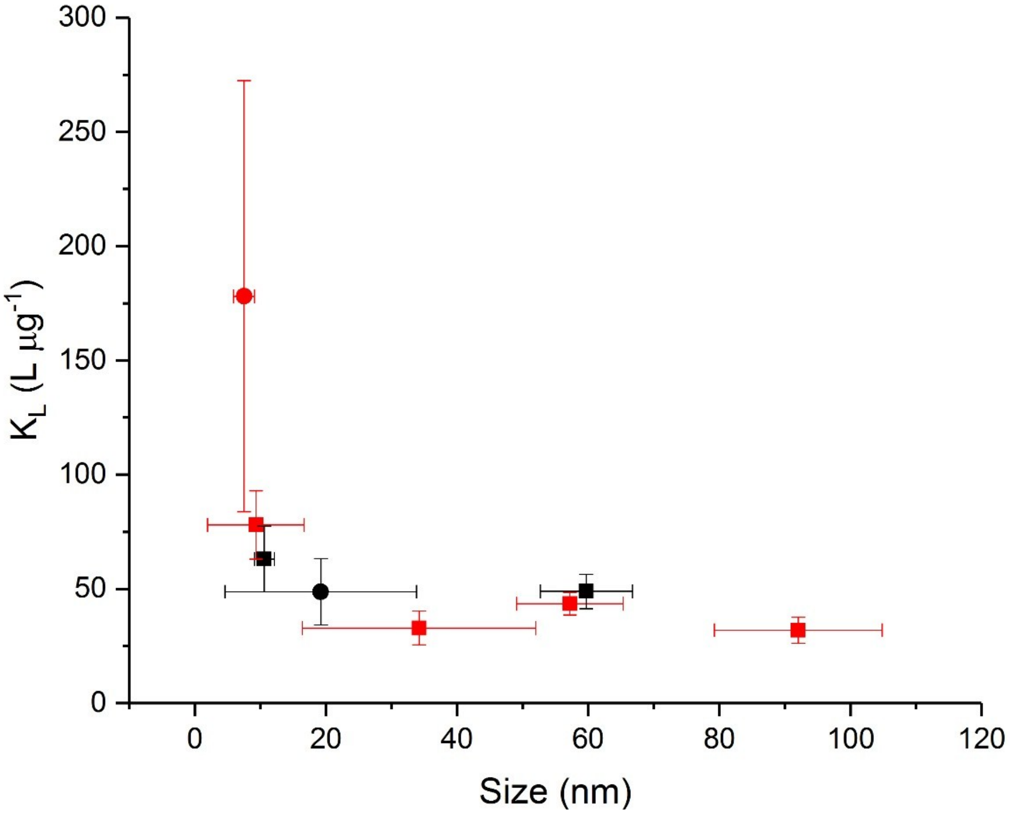

Figure S7. The correlation of K_L with the size of the NPs. AuNPs are shown as in black and AgNPs are shown in red. NPs supplied by Nanocomposix are shown as squares and those from Sigma are shown as circles. Error bars were calculated from the error in fitting to Equation 6 and the SD of the TEM sizing.

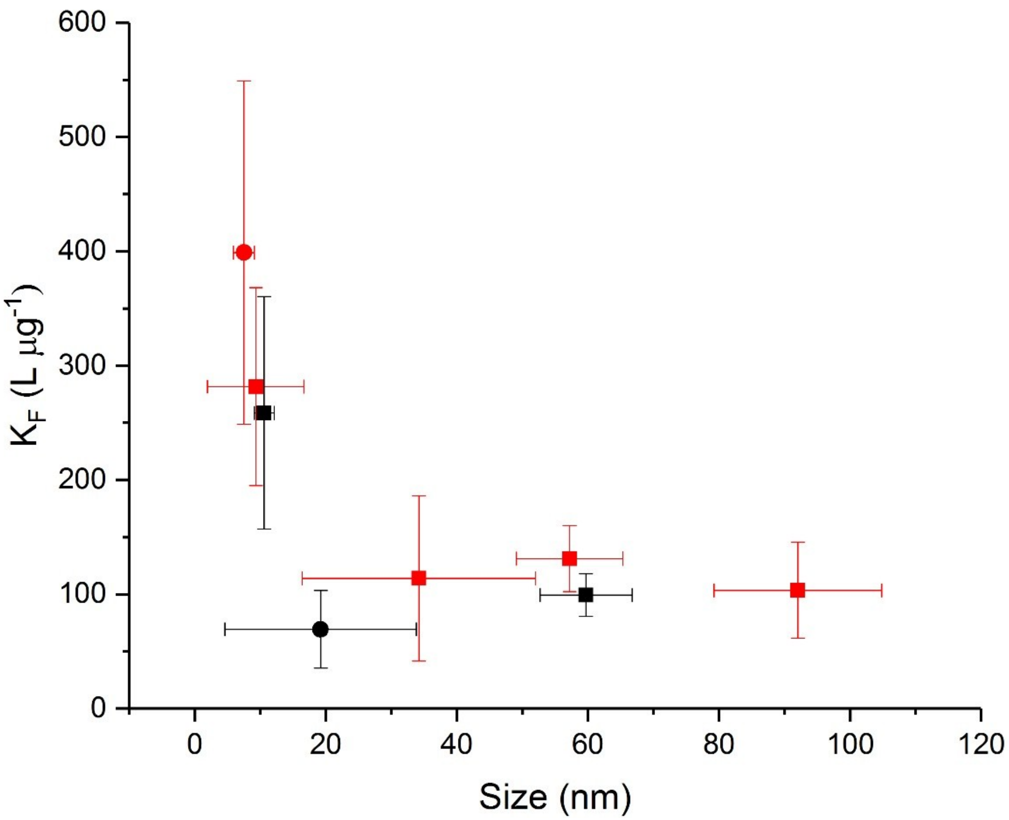

Figure S8. The correlation of K_F with the size of the NPs. AuNPs are shown as in black and AgNPs are shown in red. NPs supplied by Nanocomposix are shown as squares and those from Sigma are shown as circles. Error bars were calculated from the error in fitting to Equation 7 and the SD of the TEM sizing.

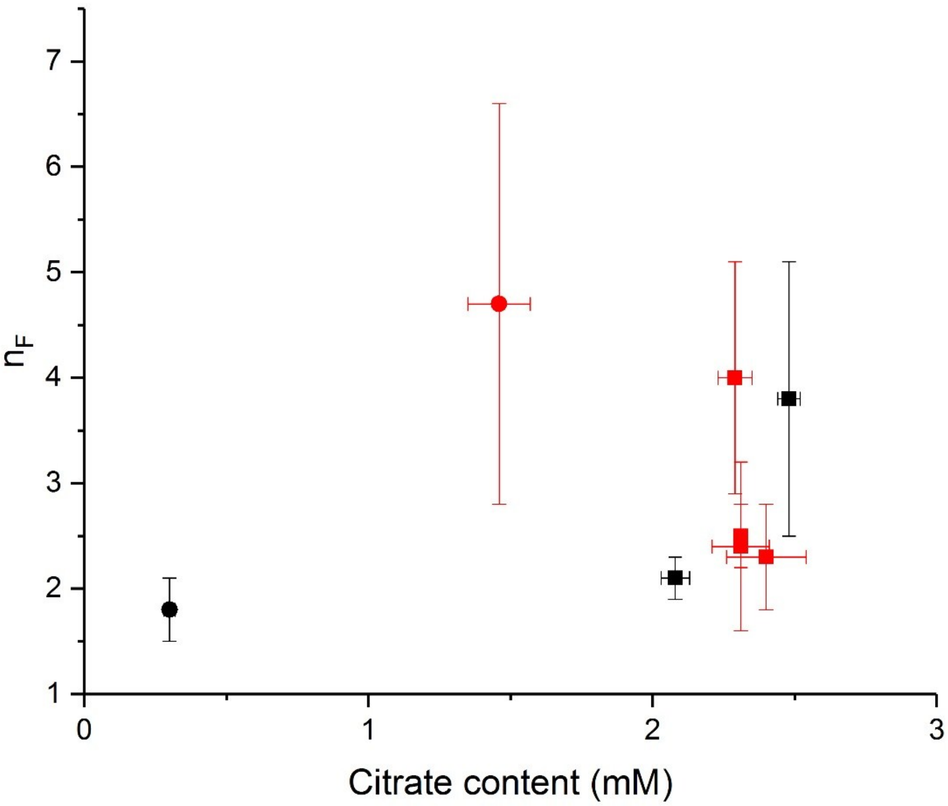

Figure S9. Difference in the heterogeneity of binding shown by the Freundlich constant (n_F) of NOM binding to NPs with different amount of total citrate. AuNPs are shown as in black and AgNPs are shown in red. NPs supplied by Nanocomposix are shown as squares and those from Sigma are shown as circles. Error bars were calculated from the error in fitting to Equation 7 and the SD of the IC quantification.

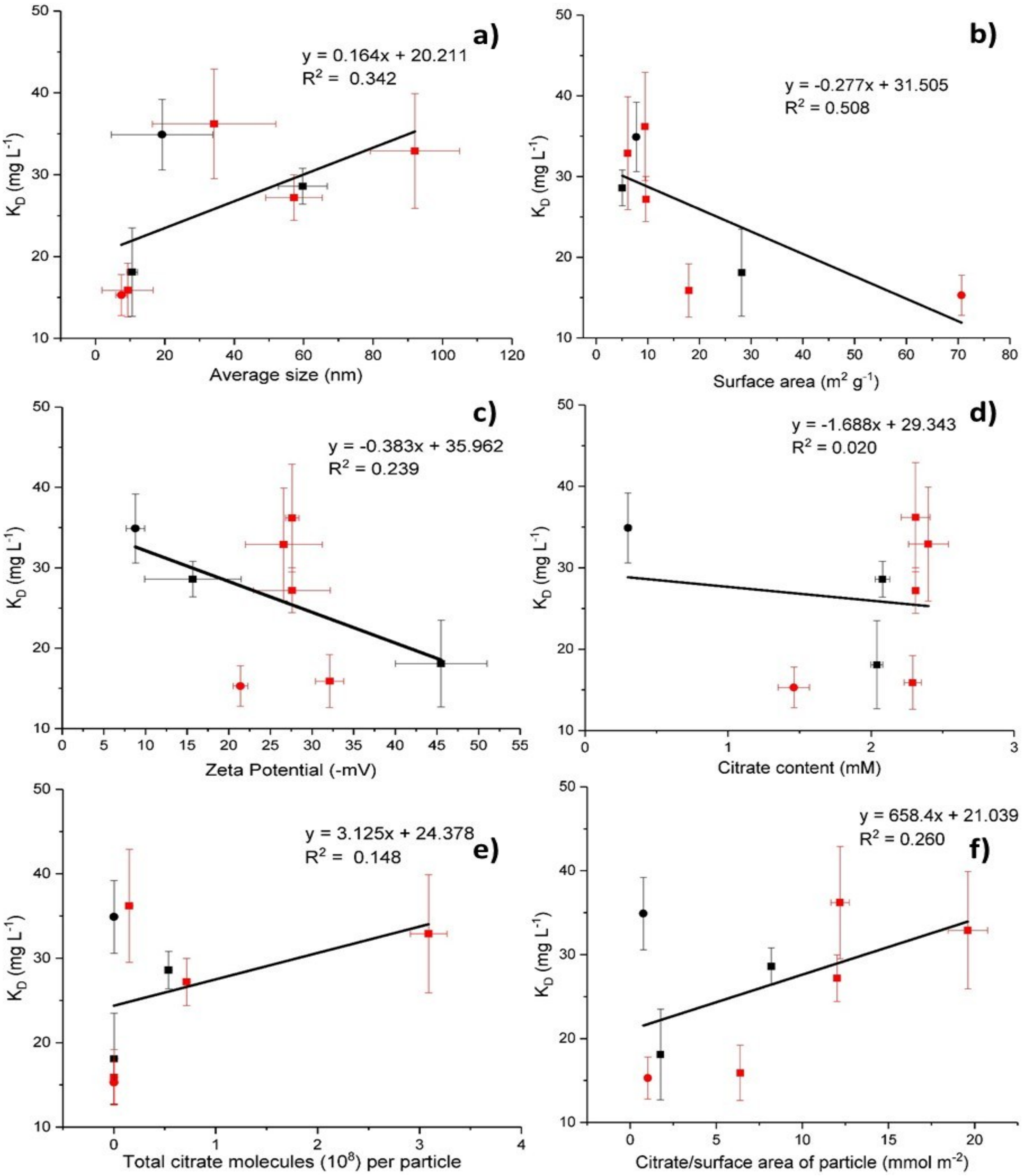

Figure S10. The correlation of K_D with the physiochemical properties a) size, b) surface area, c) zeta potential, d) total citrate content, e) total citrate molecules per particle and total citrate per surface area of the particle. AuNPs are shown as in black and AgNPs are shown in red. NPs supplied by Nanocomposix are shown as squares and those from Sigma are shown as circles. Error bars were calculated from the SD of the TEM, IC and zeta potential measurements. The surface area was calculated from the TEM particle distribution. Total citrate refers to the amount of citrate in the suspension after degradation.

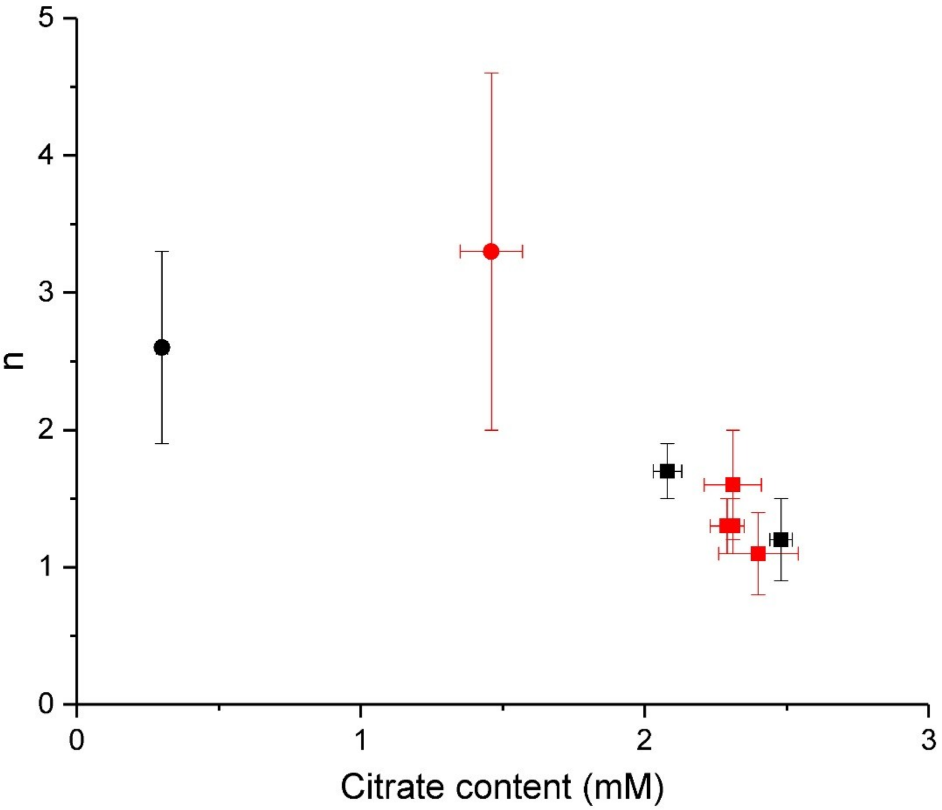

Figure S11. Difference in the cooperativeness shown by the Hills coefficient (*n*) of NOM binding to NPs with different amount of total citrate. AuNPs are shown as in black and AgNPs are shown in red. NPs supplied by Nanocomposix are shown as squares and those from Sigma are shown as circles. Error bars were calculated from the error in fitting to Equation 8 and the SD of the IC quantification.