Supporting Information for:

Reversible assembly of metal nanoparticles induced by penicillamine. Dynamic formation of SERS hot spots

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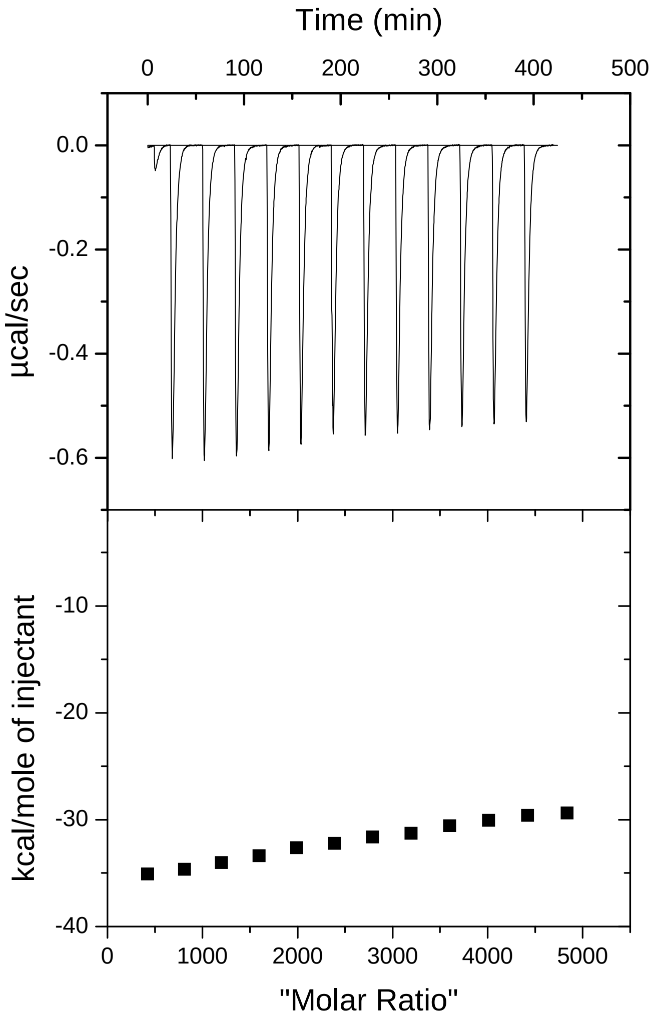


Figure S1. Heat effects for injection of water into Au@PEN at 25 °C, for ease of comparison molar heat effects and molar ratios are based on setting the ligand concentration in the syringe to 0.5 mM.

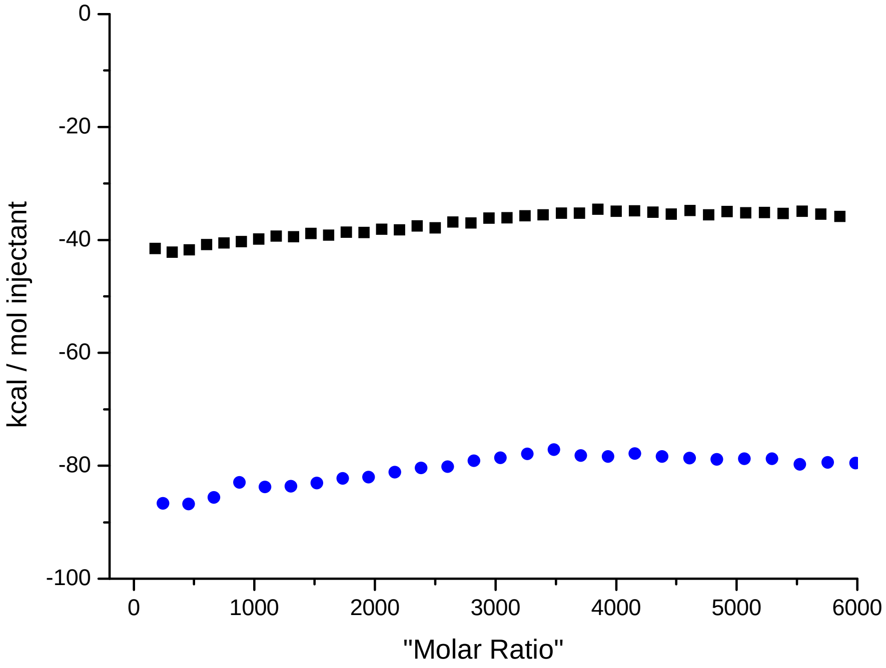


Figure S2. Integrated heat effects for injecting 0.5 mM PEN at pH 4.7 into water pH 6.5 (black squares) and for injecting 0.25 mM PEN at pH 4.4 into water pH 6.7 (blue circles), all injections are 4 μl in volume and titrations were carried out at 25 °C, for ease of comparison molar ratios are based on setting the host concentration in the sample cell to 9.77 nM.

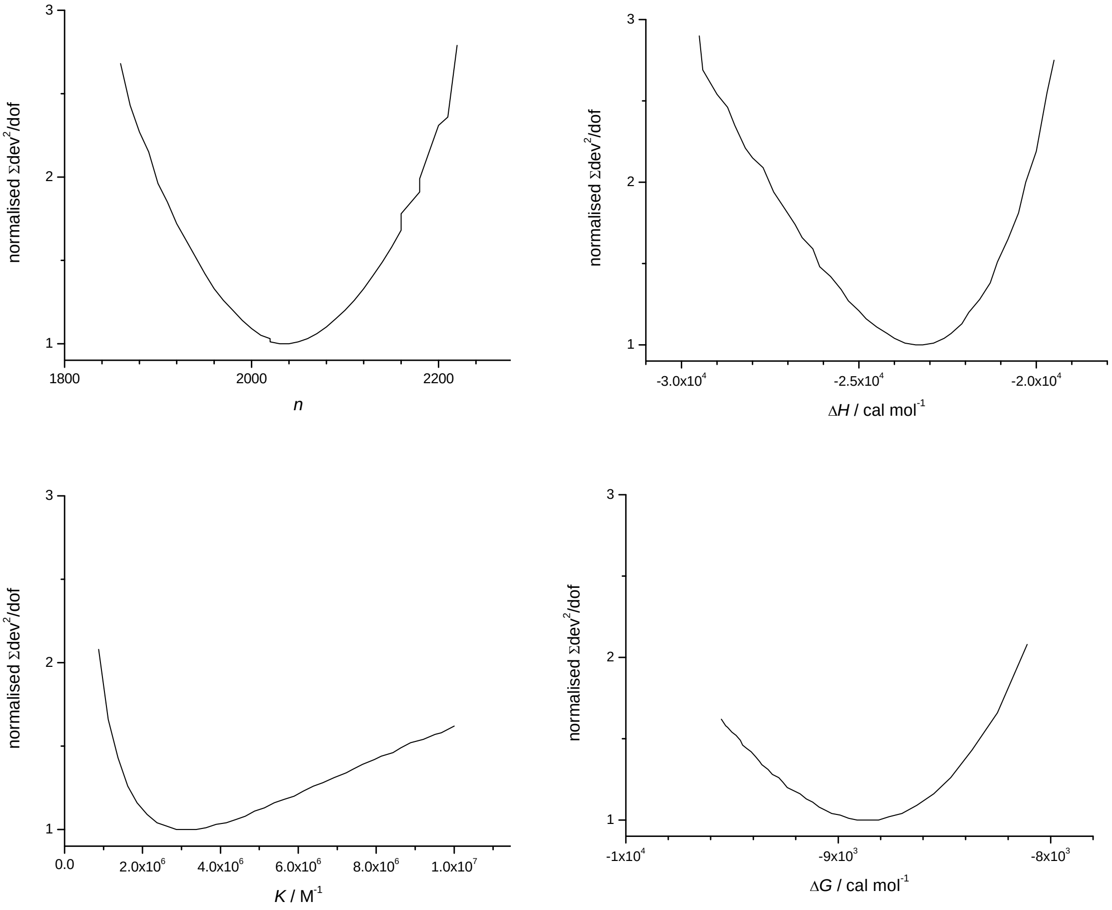


Figure S3A. Error margin evaluation for ITC data for 0.5 mM PEN titrated into 9.8 nM Au nanoparticles (corresponding to the data for PEN shown in Figure 1). Variable values for which the normalized Σdev^2/dof is below a value of 2 should be considered to be within error margins for this titration.

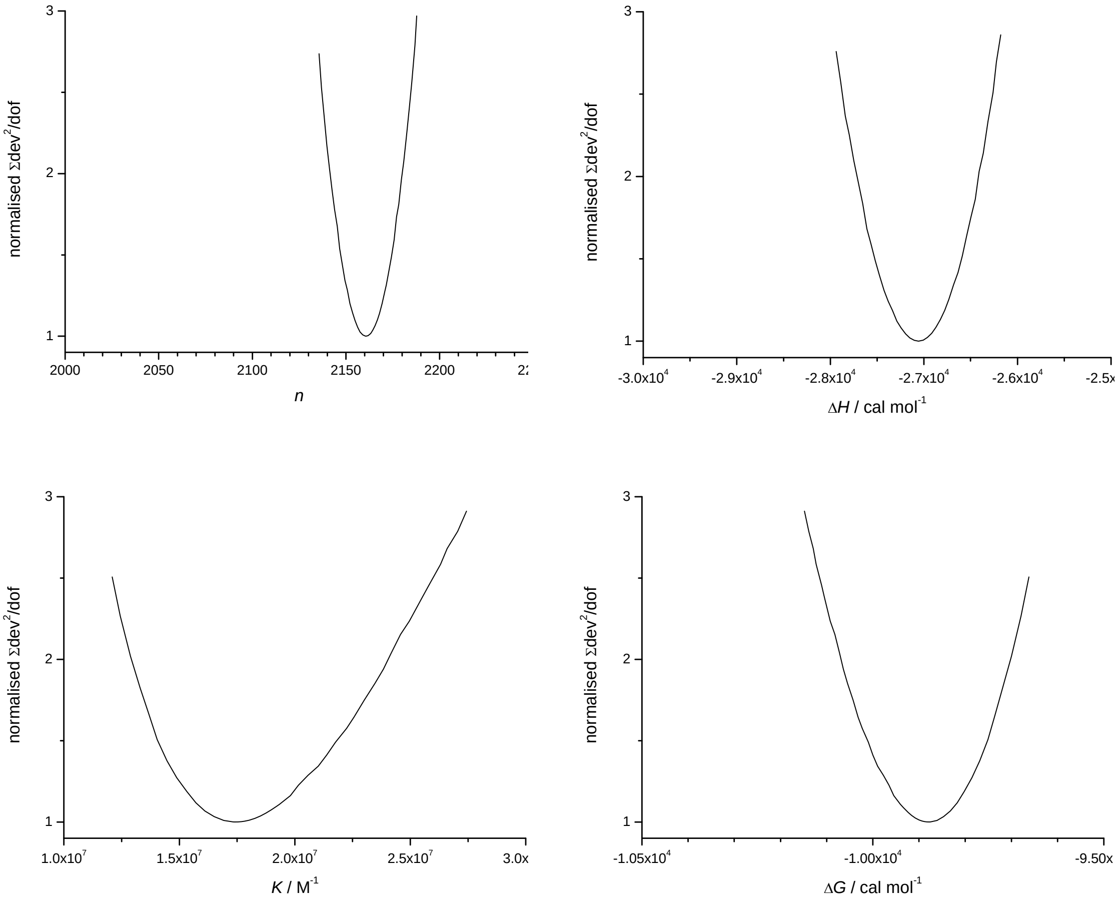


Figure S3B. Error margin evaluation for ITC data for 0.5 mM NAP titrated into 9.6 nM Au nanoparticles (corresponding to the data for NAP shown in Figure 1). Variable values for which the normalized $\Sigma dev^2/dof$ is below a value of 2 should be considered to be within error margins for this titration.

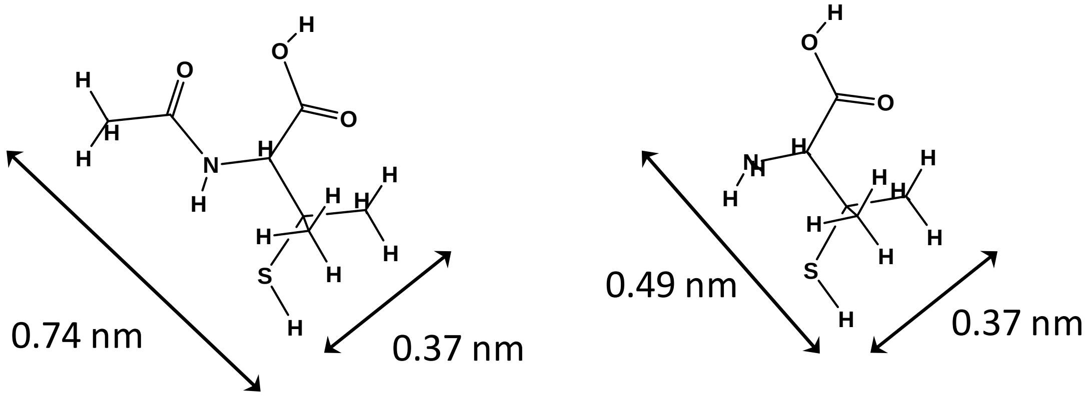


Figure S4. NAP (left) and PEN (right) dimensions derived from molecular mechanics calculations. The structures have been tilted for sake of clarity.

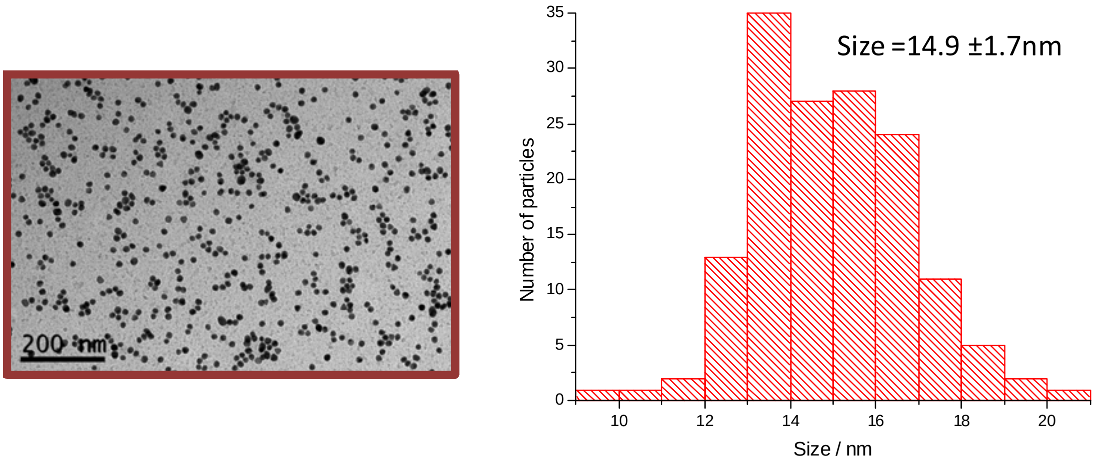
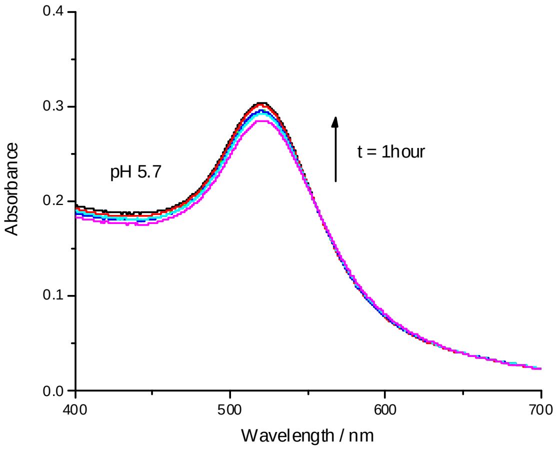


Figure S5. Representative TEM image (left) and size distribution (right) of the Au@citrate nanoparticles.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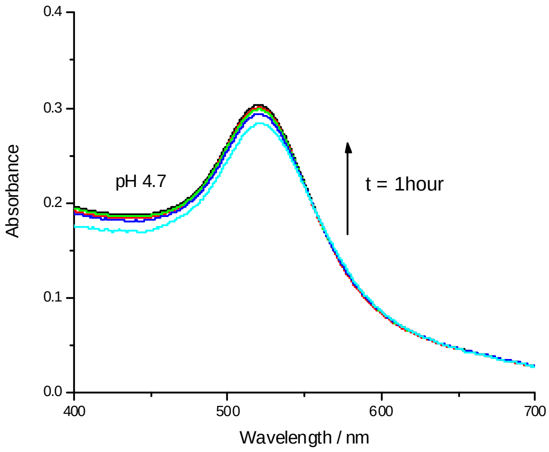
t = 1hour
Absorbance
0.0
0.1
0.2
0.3
0.4
400
500
600
700
Wavelength / nm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t = 1hour
Absorbance
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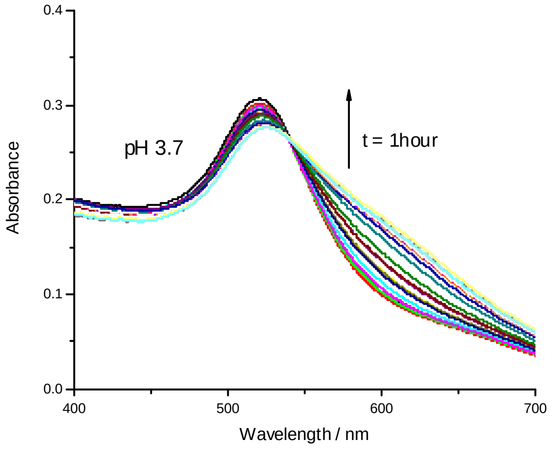
0.2
0.3
0.4
400
500
600
700
Wavelength / nm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t = 1hour
Absorbance
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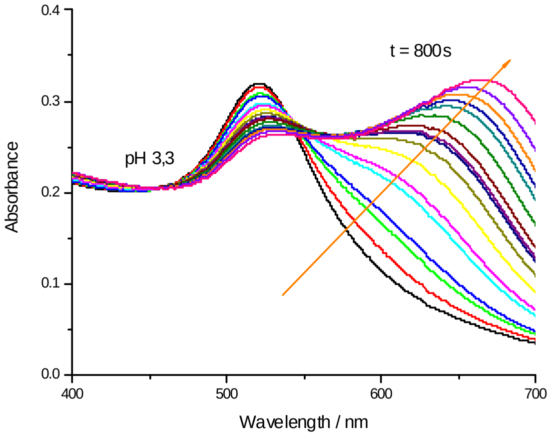
0.1
0.2
0.3
0.4
400
500
600
700
Wavelength / nm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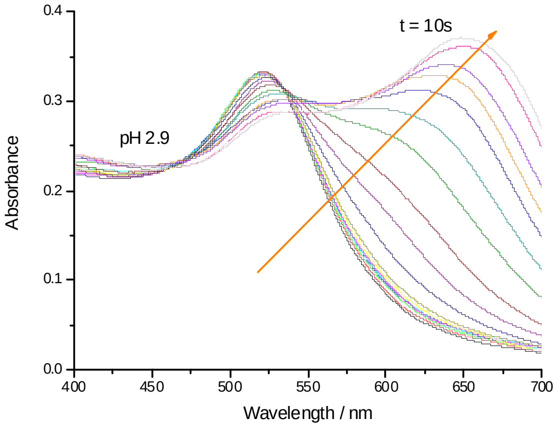
t = 800s
Absorbance
0.0
0.1
0.2
0.3
0.4
400
500
600
700
Wavelength / nm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Absorbance
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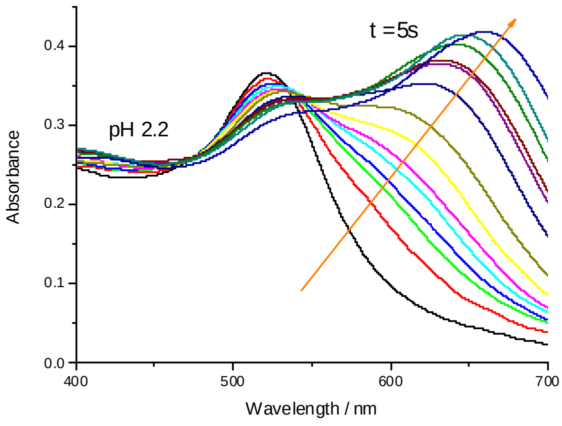
0.1
0.2
0.3
0.4
400
450
500
550
600
650
700
Wavelength / nm


pH 2.2
t =5s
Absorbance
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0.1
0.2
0.3
0.4
400
500
600
700
Wavelength / nm

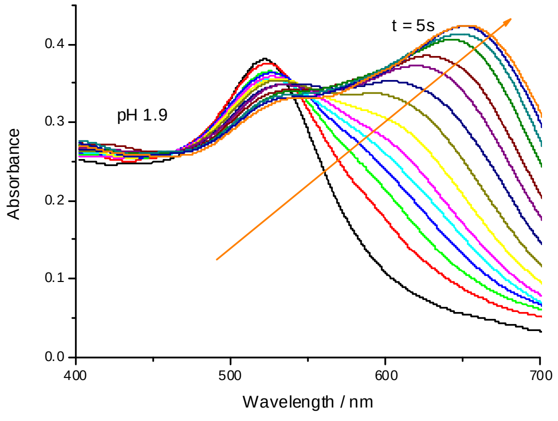
pH 1.9
t = 5s
Absorbance
0.0
0.1
0.2
0.3
0.4
400
500
600
700
Wavelength / nm

Figure S6A. Time evolution of the aggregation at different pH (as indicated in the labels) for PEN stabilized gold nanoparticles.

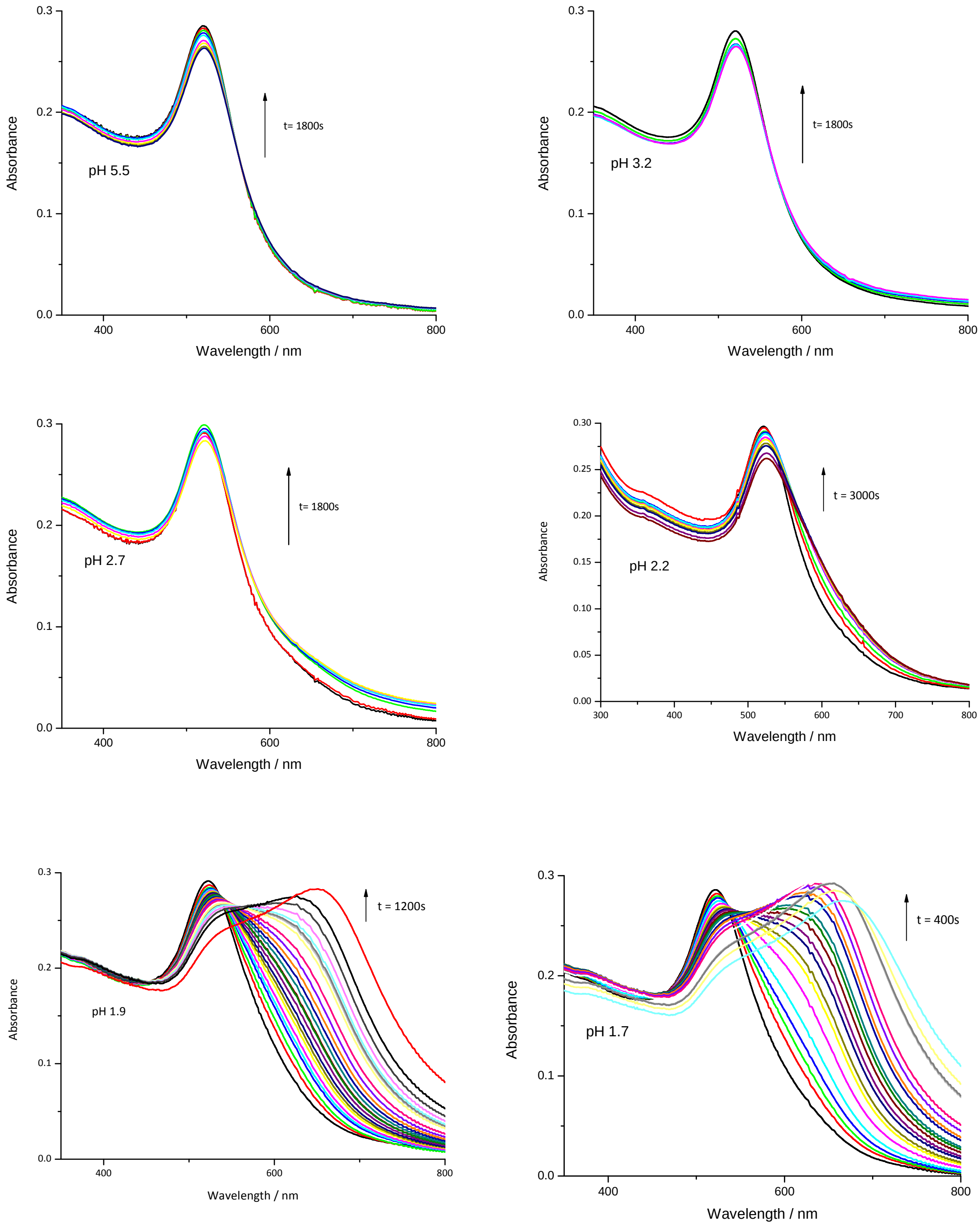

Figure S6B. Time evolution of the aggregation at different pH (as indicated in the labels) for NAP stabilized gold nanoparticles.

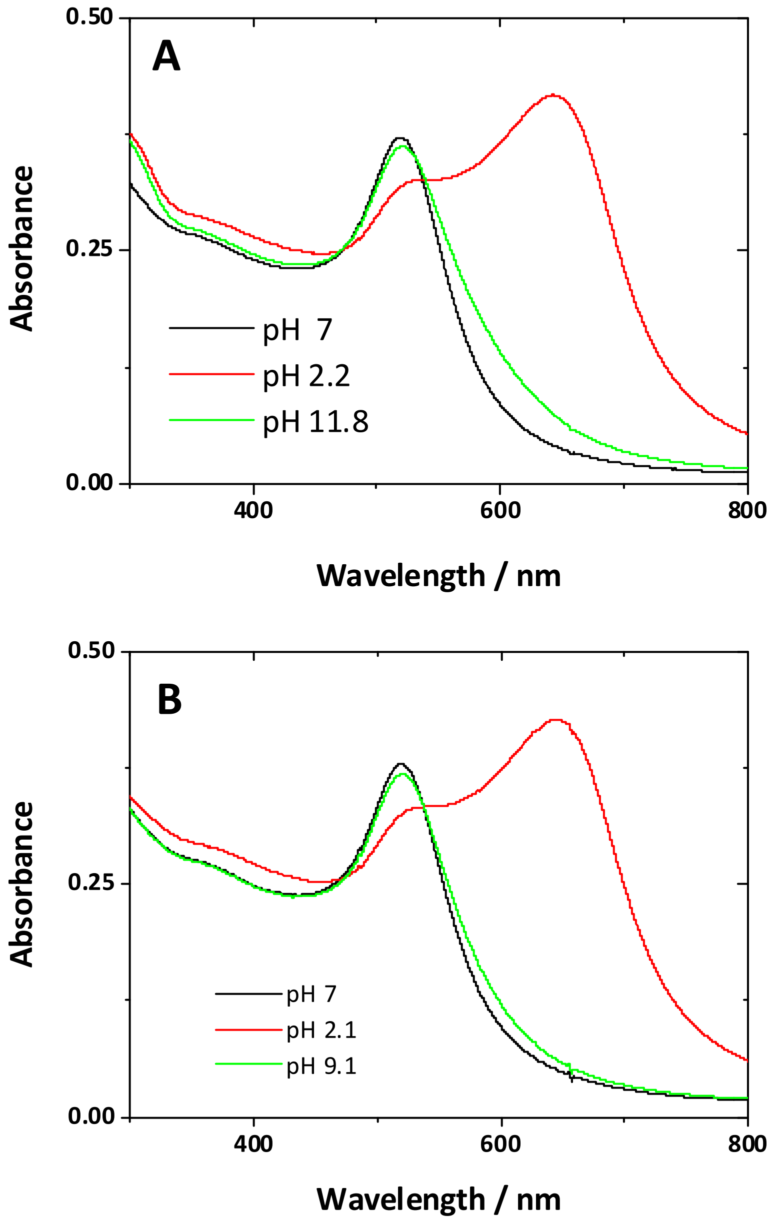

Figure S7. Reversible assembly of Au@PEN ([Au]=[PEN]=0.1mM) induced by HNO_3 (A) and H_2SO_4 (B).

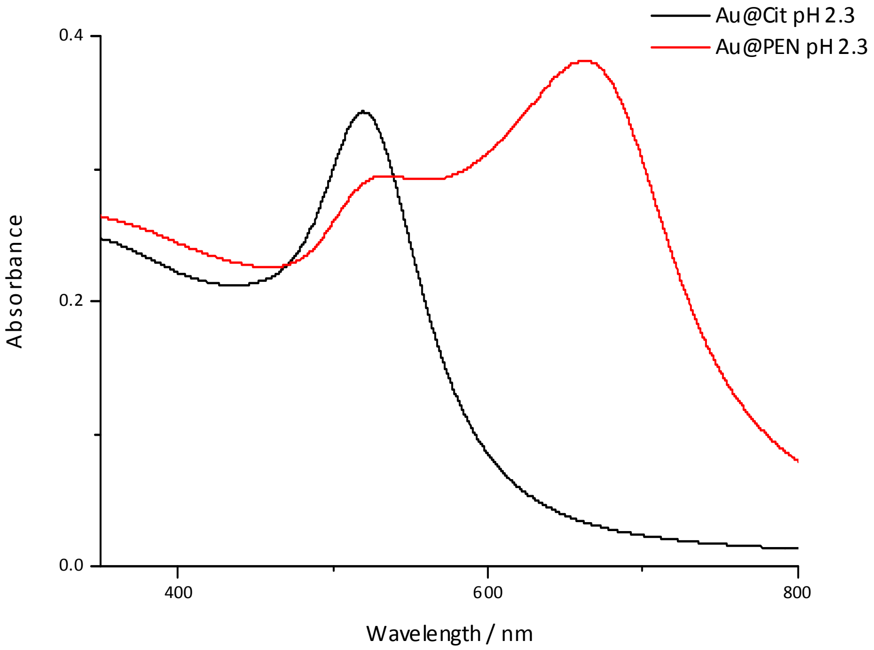

Figure S8. pH effect on the citrate stabilized gold nanoparticles. Even at a pH as low as 2.3 the gold dispersion show pH independent optical properties (black spectrum). The addition of PEN (20µL, 0.01M) to citrate stabilized gold nanoparticles at pH 2.3 led to fast aggregation of the particles (red spectrum).

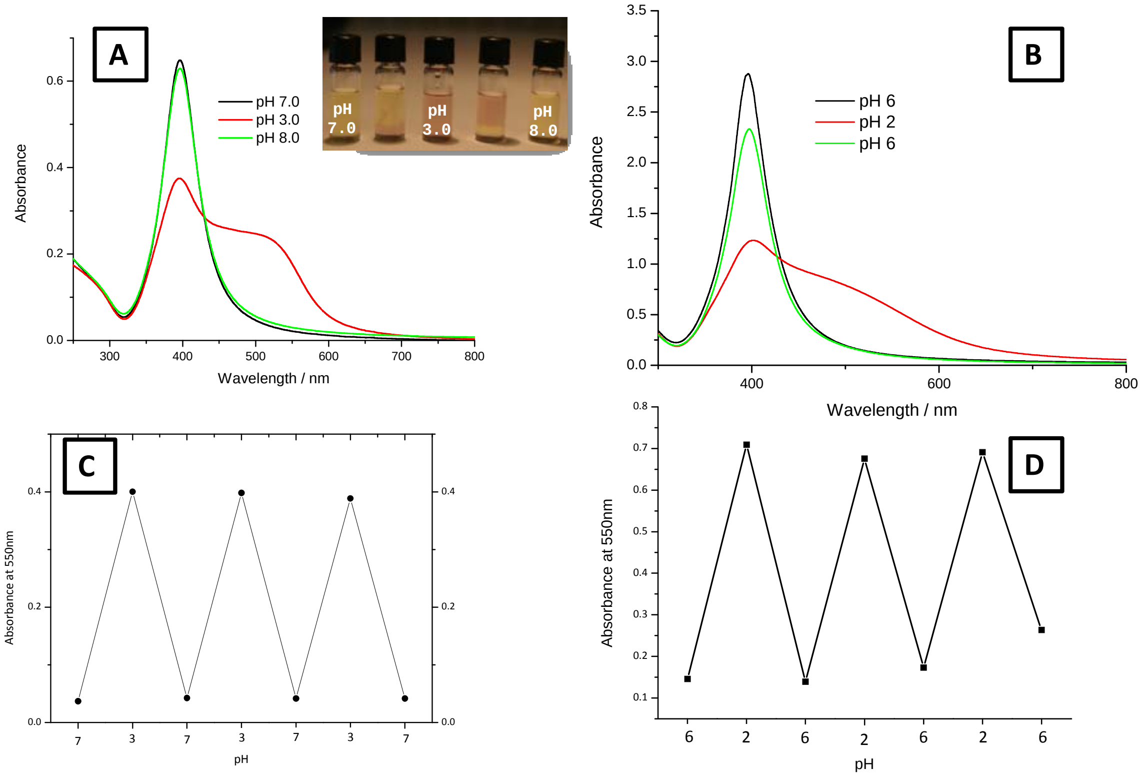

Figure S9. (A and B) UV-VIS spectra of the same silver nanoparticle dispersion at three different and cycled pHs, as indicated in the labels, stabilized by PEN (A) and NAP (B). Variation of the absorbance at 550 nm when the pH is cycled between 7 and 3 for Ag@PEN (C) and between 6 and 2 for Ag@NAP (D). In all case [Ag]= 0.1mM and the amount of PEN/NAP added correspond to 0.1mM.

Table S1. Thermodynamic parameters for the interaction of PEN and NAP with gold nanoparticles at 25 ºC and pH 7[a].

	stoichiometry	K_a / M^{-1}	ΔG / kcal mol^{-1}	ΔH / kcal mol^{-1}	ΔS / J K^{-1} mol^{-1}
PEN[b]	$(2.0 \pm 0.6) \times 10^{3}$	5×10^{6} [c]	-9.0±1.0	-26±7	-57±24
NAP[d]	$(2.3 \pm 0.2) \times 10^{3}$	4×10^{6} [c]	-9.0±0.6	-24±2	-50±7

a) Titrations involving PEN were carried out in 0.5 mM phosphate buffer at pH 7, titrations involving NAP were carried out in 0.1 mM phosphate buffer at pH 7.

b) Errors are estimated based on the behaviour of $\Sigma \mathrm{dev}^2/\mathrm{dof}$ for two titrations.

c) Errors are not standard, i.e. not symmetrically distributed around the average K_a.

d) Errors are estimated based on the behaviour of $\Sigma \mathrm{dev}^2/\mathrm{dof}$ for one titration.