Supplementary Information

Peptide modified gold nanoparticles that bind lanthanide ions

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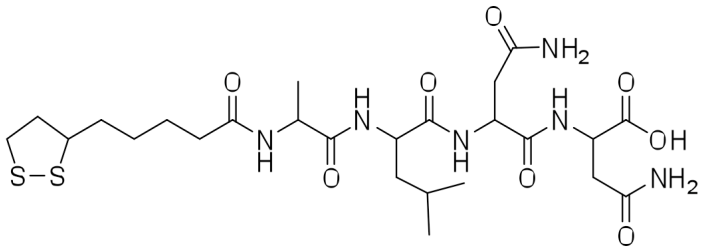
Synthetic details.

Preparation of ThiocticALNN Peptide



ThiocticALNN was synthesised using a CEM discover SPS microwave reactor. FMOC-Asn-(Trt)-Wang resin (0.208 g) was swollen in DMF (7 cm^3) for 15 minutes. The DMF was removed and the resin washed with DMF (5 x 7 cm^3). The FMOC protecting group of the amino acid was removed by adding 20% piperidine in DMF (7 cm^3) and placing in the microwave reactor (Conditions: 20 W, 75 ^oC, 3 min). The deprotection solution was removed and the resin washed with DMF (5 x 7 cm^3). FMOC-L-Asn-(trt)-OH (0.5 mmol) was added to the resin in DMF, along with the activator HBTU and the activator base DIEA and then coupled in the microwave reactor (Conditions: 20 W, 75 ^oC, 3 min). The resin was then washed with DMF (5 x 7 cm^3). The deprotection and coupling was repeated for each of the amino acids, FMOC-L-Leu-OH (0.5 mmol), FMOC-L-Ala-OH.H_2O (0.5 mmol) and thioctic acid (1 mmol). After the final coupling of the thioctic acid to the peptide, the resin was washed with DCM (5 x 7 cm^3). The peptide was cleaved from the resin in the microwave reactor (Conditions: 20 W, 35 ^oC, 25 minutes) using a cleavage solution of 90% TFA, 2% anisole, 5% thioanisole and 3% EDT. The final solution was filtered, reduced in volume under N_2 and cold diethyl ether (40 cm^3, -20 ^oC) was added which caused the formation of a white precipitate. The precipitate was isolated by filtration and washed with diethyl ether, redissolved in water (40 cm^3) and acetic acid (15 cm^3) and freeze dried. The crude Peptide was then purified by semi-prep HLPC (C18 column, Acetonitrile/Water/TFA). (5.2 mg, 8.4%) MS (MALDI) m/z 641 $[M+Na]^+$, 643 $[M+2H+Na]^+$, 657$[M+K]^+$, 659 $[M+2H+K]^+$. UV-vis (H_2O) λ_{max} 203 nm

ThioKEESLADLL was purchased from United Peptide Corporation, purified by HPLC, MS m/z 1206.

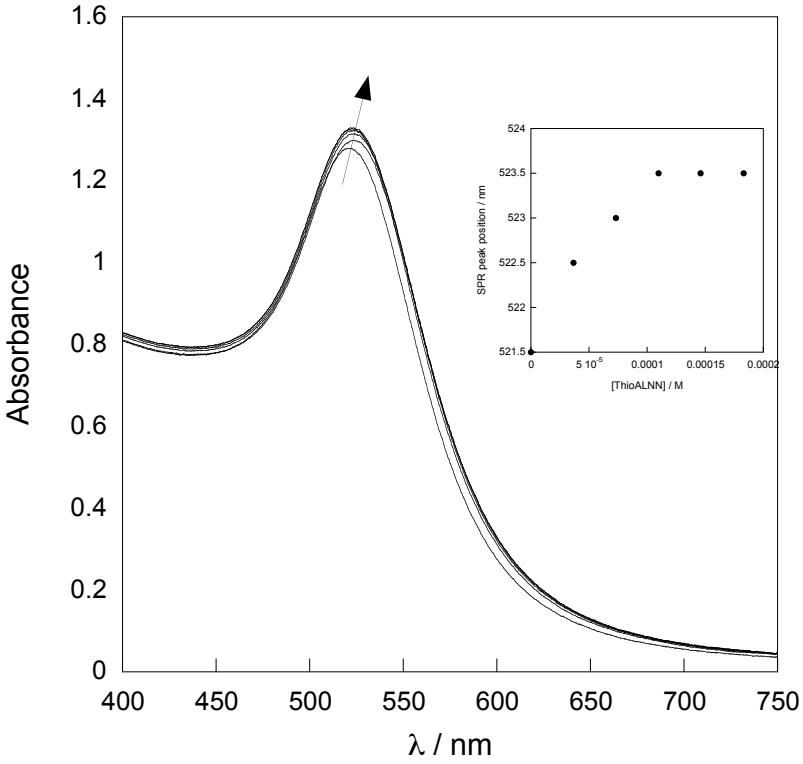


Figure S1. UV-vis spectra of gold nanoparticles upon incremental addition (in µl) of a 5 mM solution of ThioALNN in phosphate buffer (pH = 7.4, 160 mM NaCl, 3mM KCl, 8 mM Na_2HPO_4, 1 mM KH_2PO_4). Concentration of gold nanoparticles is 4.5 nM and the final concentration of ThioALNN is 0.183 mM. Inset: Plot of the SPR shift *vs*. concentration of peptide.

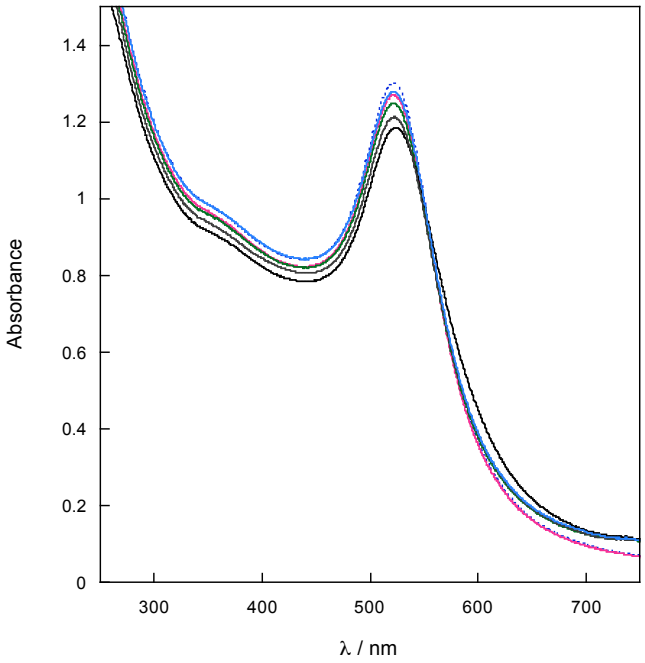


Figure S2. UV-vis spectra monitoring the addition of Eu^{3+} to Au-ThioALNN. Concentration of gold nanoparticles is 4.5 nM, [ThioALNN] = 0.183 mM. A 10 mM stock solution of Eu^{3+} is added in µl increments.

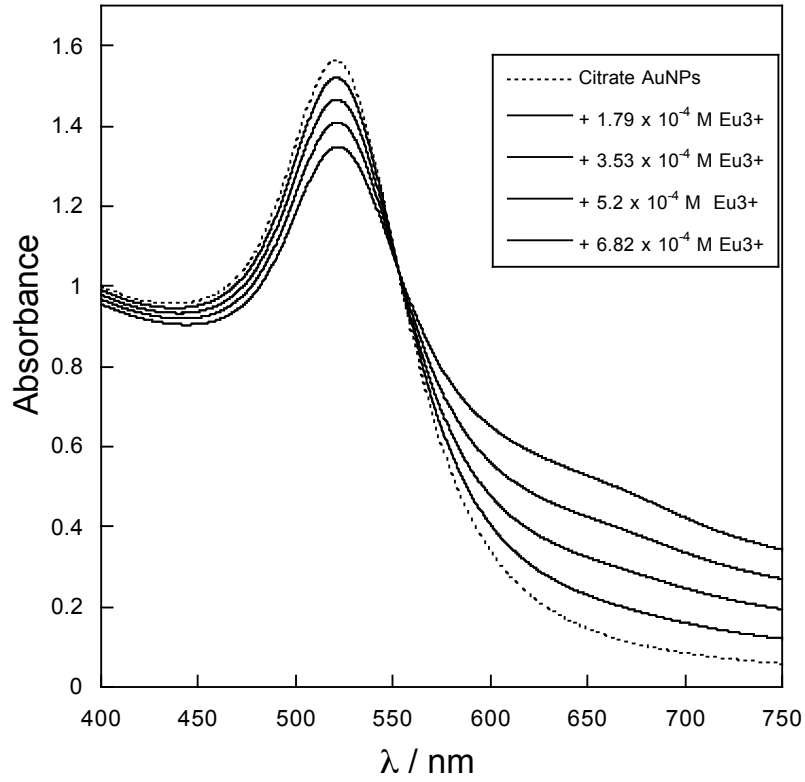


Figure S3. UV-vis spectra of titration of Eu^{3+} with Au-citrate nanoparticles. Concentration of citrate AuNPs = 4.5 nM. A 10 mM stock solution of Eu^{3+} is added in µl increments.

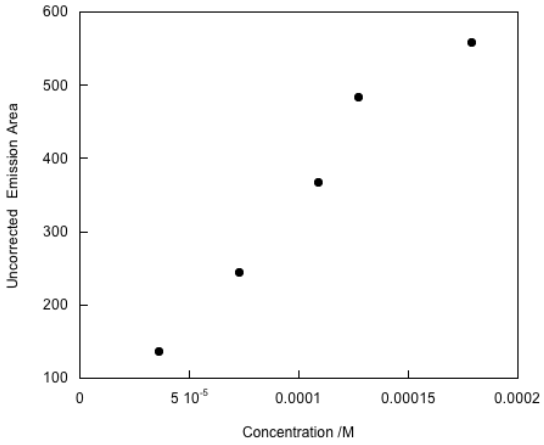


Figure S4. Plot of emission increase plot upon addition of Eu^{3+} to Au-citrate nanoparticles (4.5 nM), not corrected for residual Eu^{3+} emission, due to weak signal.

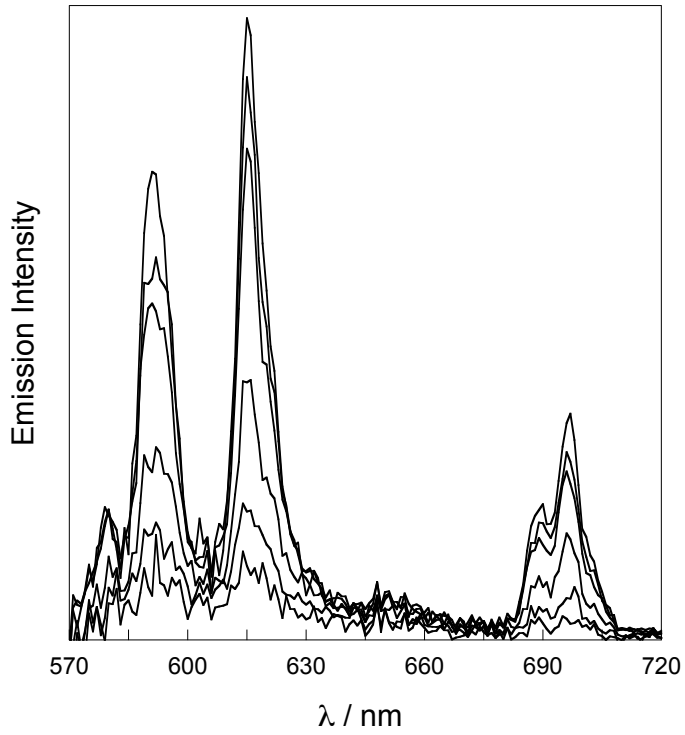


Figure S5. Emission spectra of titration of a solution of Eu^{3+} (5 mM) in µl increments to a solution of ThioALNN 0.18 mM.

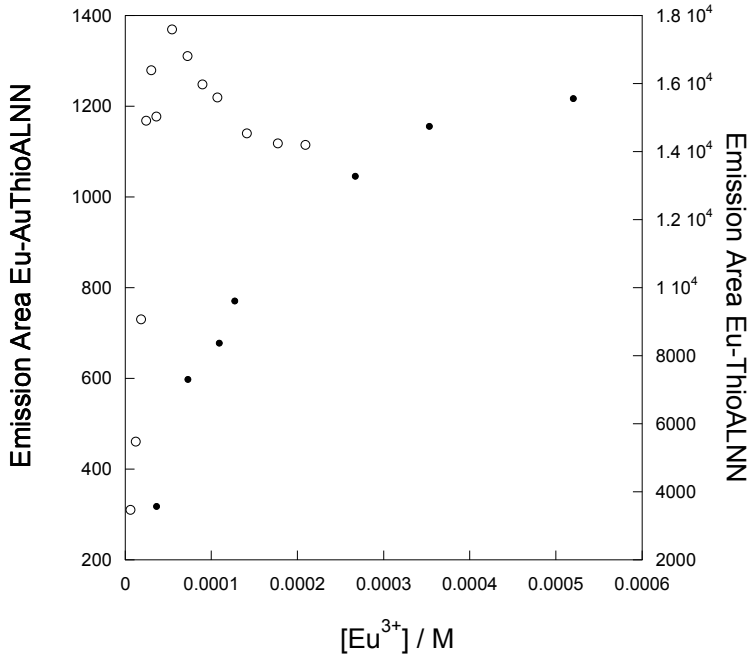


Figure S6. Comparison of relative emission increase upon addition of Eu3+ solution in Au-ThioALNN (black circles) and ThioALNN (open circles).

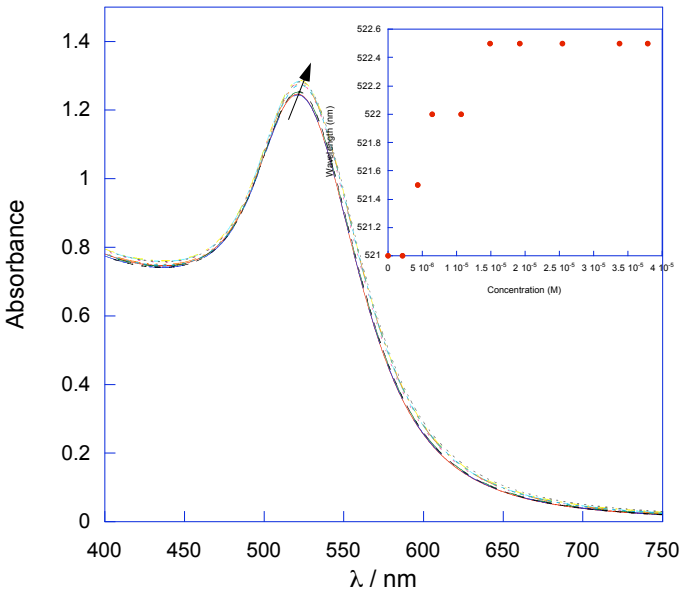


Figure S7. UV-vis spectra of gold nanoparticles upon increment addition (in μl) of a 5 mM solution of ThioKEESLADLL in phosphate buffer (pH = 7.4, 160 mM NaCl, 3mM KCl, 8 mM Na_2HPO_4, 1 mM KH_2PO_4). Concentration of gold nanoparticles is 4.5 nM. Inset: Plot of the SPR shift *vs*. concentration of peptide.

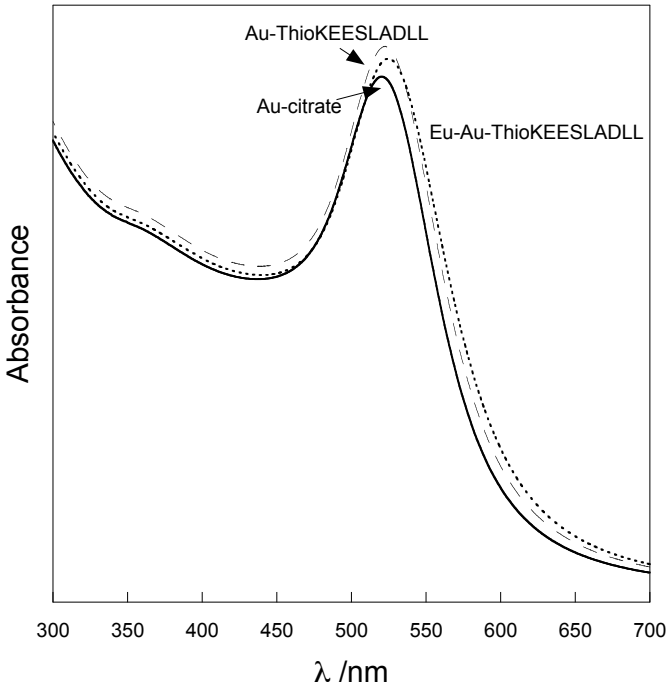


Figure S8. Selected UV-vis spectra featuring the SPR band of citrate modified nanoparticles 4.5 nM (—) upon addition of ThioKEESLADLL 0.18 mM in phosphate buffer, (--) and Eu^{3+} 0.68 mM in water (…).

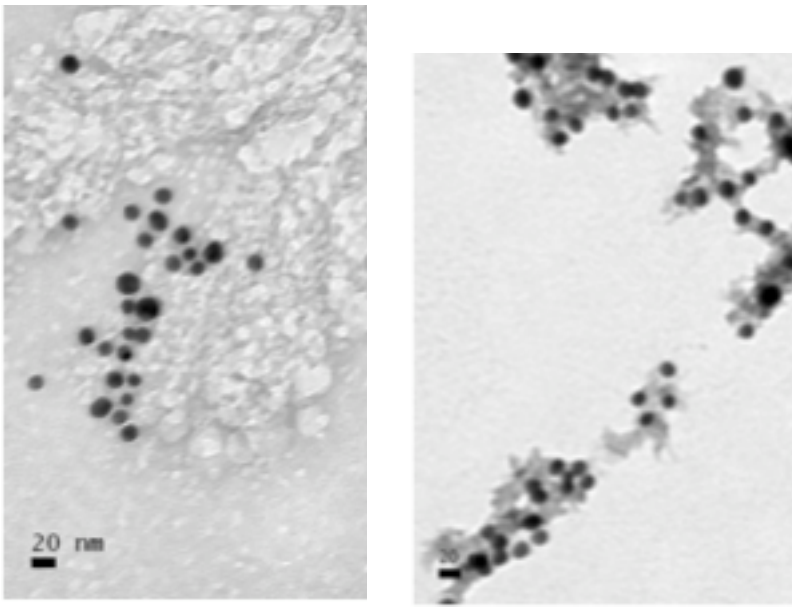


Figure S9. TEM images of Au-ThioKEESLADLL (left) and Eu Au-ThioKEESLADLL (right).

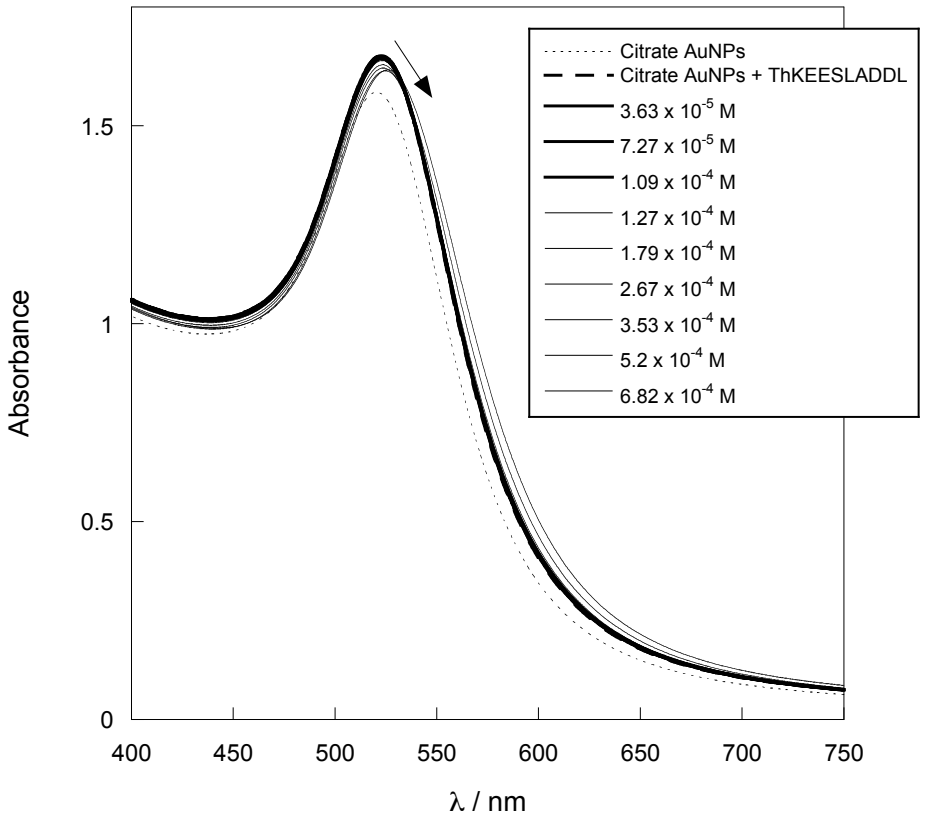


Figure S10. UVvis spectra monitoring the addition of Eu^{3+} to Au-ThioKEESLADLL, [nanoparticles]= 4.5 nM, [ThioKEESLADLL] 0.18 mM .