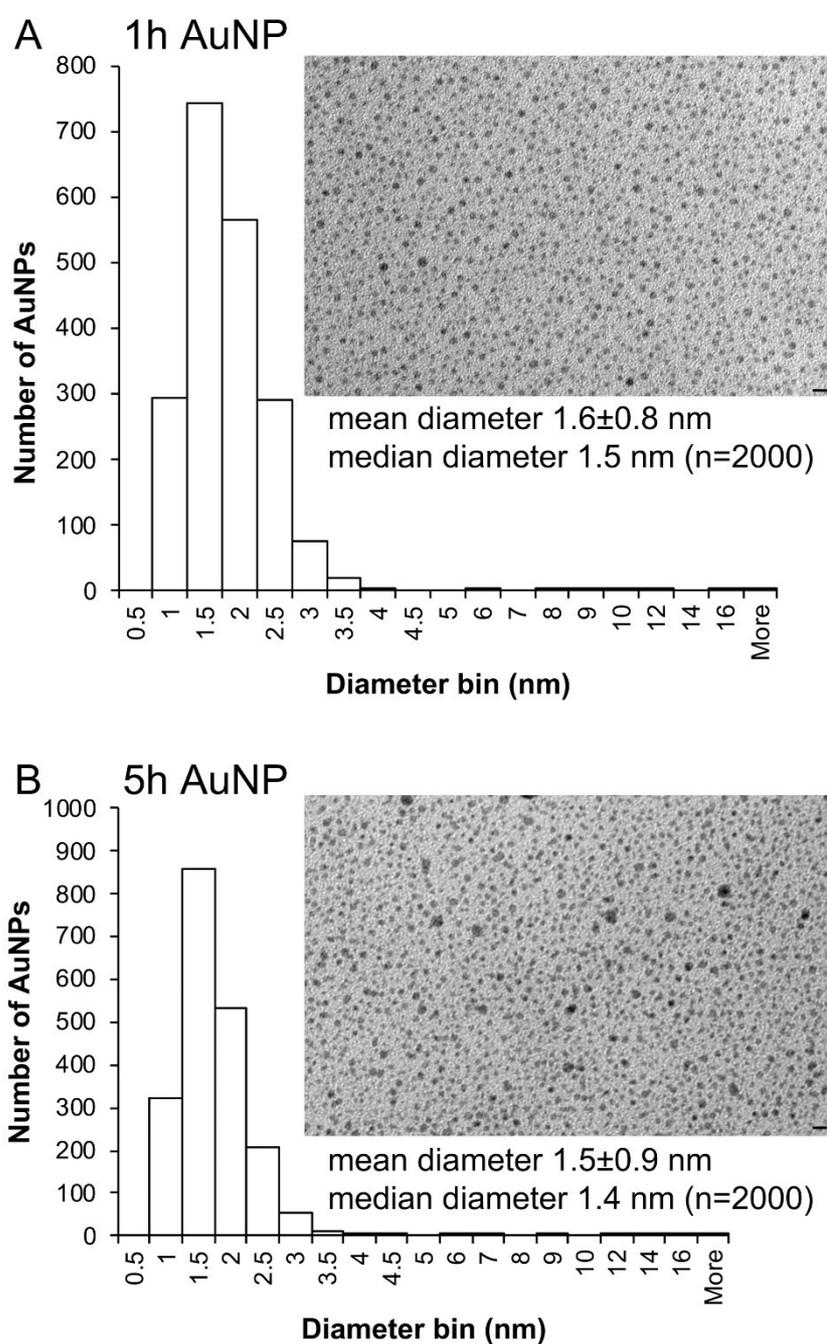
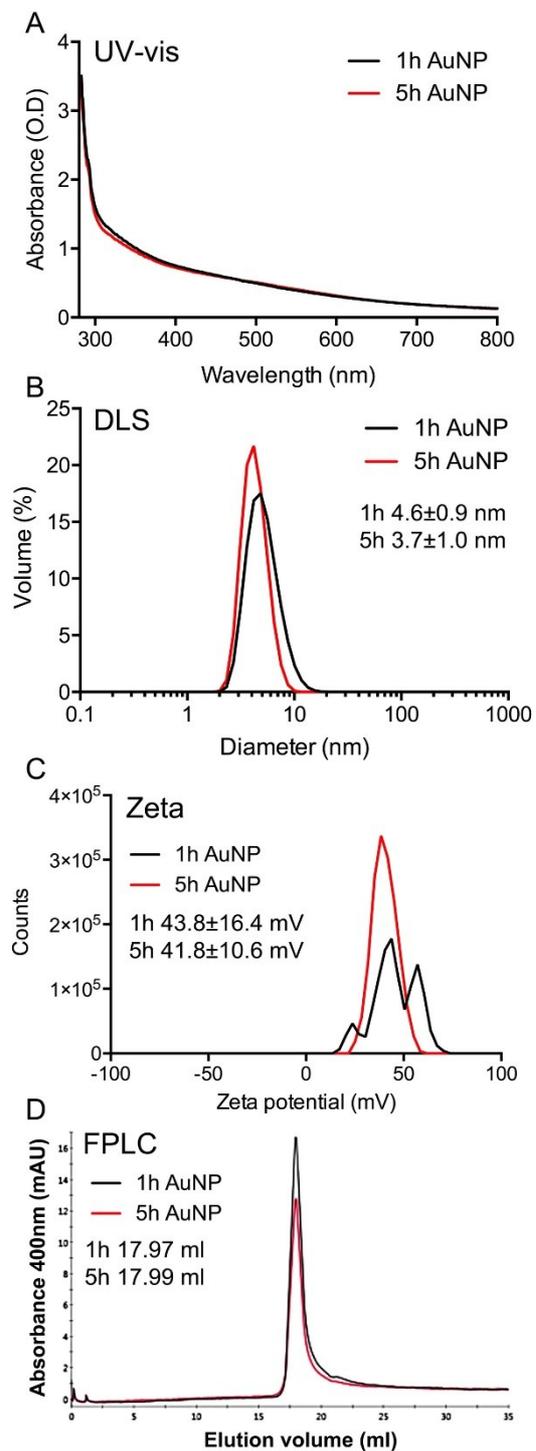


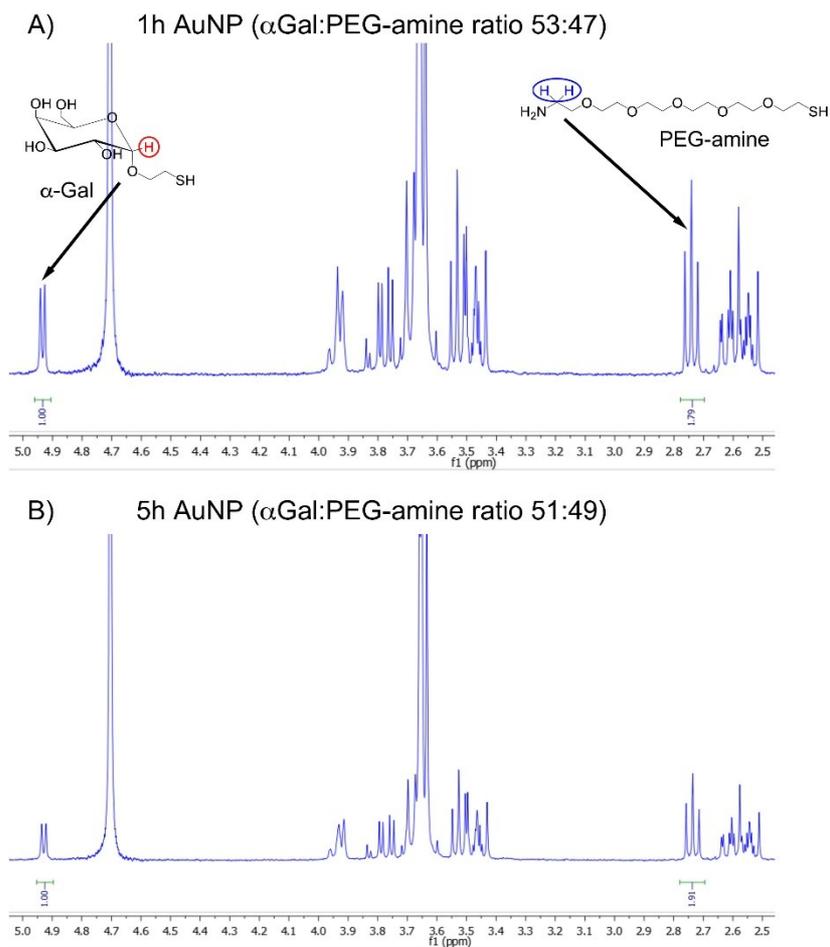
## Supporting information



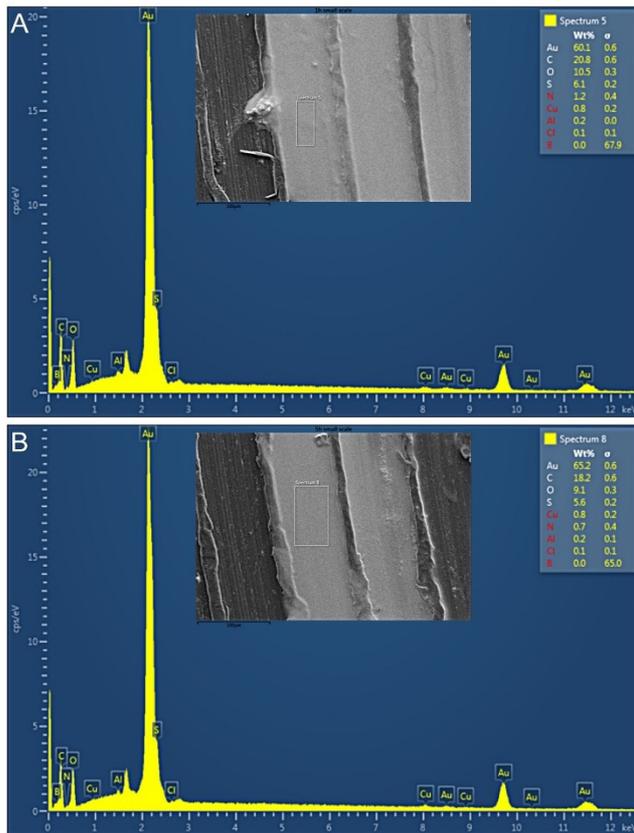
Supplementary Figure 1. TEM images of A) short synthesis (1h AuNPs) and B) long synthesis (5h AuNPs) with their corresponding core size distribution histograms. Error =  $\pm$ SD. Scale bars = 5 nm.



Supplementary Figure 2. Physico-chemical characterization of short synthesis and long synthesis AuNPs. A) UV-VIS spectra. B) Hydrodynamic diameter as measured by DLS. C) Zeta potential. D) FPLC in PBS. Errors =  $\pm$ SD.



Supplementary Figure 3. <sup>1</sup>H-NMR analysis of A) short synthesis (1h AuNPs) and B) long synthesis (5h AuNPs). The positions of the NMR doublet for  $\alpha$ -Galactose and the NMR triplet for PEGamine are marked with arrows and are quantified to calculate the  $\alpha$ -Galactose:PEGamine ligand ratio.



**C**

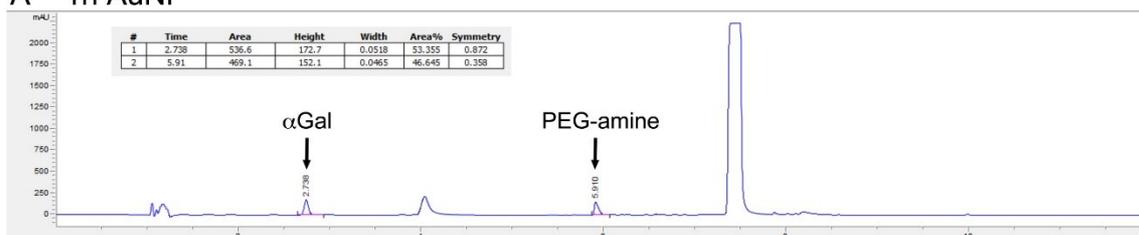
Au Wt% 1 h	S Wt% 1 h	O Wt% 1 h	C Wt% 1 h	S:Au 1 h	O:Au 1 h	C:Au 1 h
60.6	6.1	10.2	20.7	0.10066	0.16832	0.34158
60.1	6.1	10.5	20.8	0.10150	0.17471	0.34609
61.0	6.1	10.7	19.9	0.10000	0.17541	0.32623
61.2	6.3	10.3	20.9	0.10294	0.16830	0.34150
61.1	6.2	10.6	20.0	0.10147	0.17349	0.32733

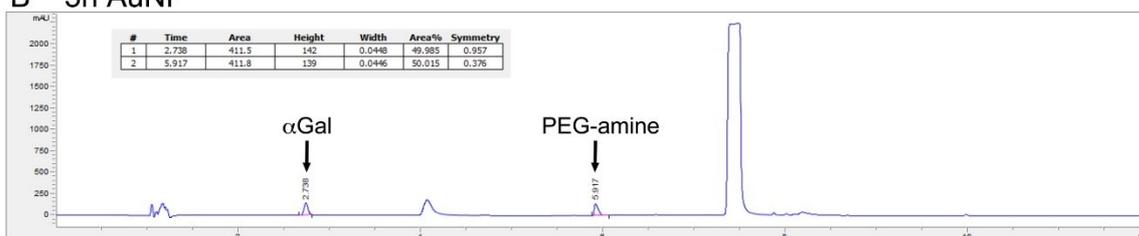
Au Wt% 5 h	S Wt% 5 h	O Wt% 5 h	C Wt% 5 h	S:Au 5 h	O:Au 5 h	C:Au 5 h
64.7	5.4	9.4	19.3	0.08346	0.14529	0.29830
65.2	5.6	9.1	18.2	0.08589	0.13957	0.27914
64.6	5.6	9.1	18.5	0.08669	0.14087	0.28638
65.5	5.8	9.1	18.2	0.08855	0.13893	0.27786
65.4	5.6	9.3	17.5	0.08563	0.14220	0.26758

Supplementary Figure 4. SEM-EDS elemental analysis of A) Short synthesis (1h AuNPs) and B) Long synthesis (5h AuNPs). Representative EDS spectra are shown with element peaks marked. Inset are SEM images showing the region analysed for each spectrum. C) Each sample was analysed in 5 different regions. The Wt% of Au, S, O, C and the S:Au, O:Au and C:Au ratios for each region are tabulated.

### A 1h AuNP



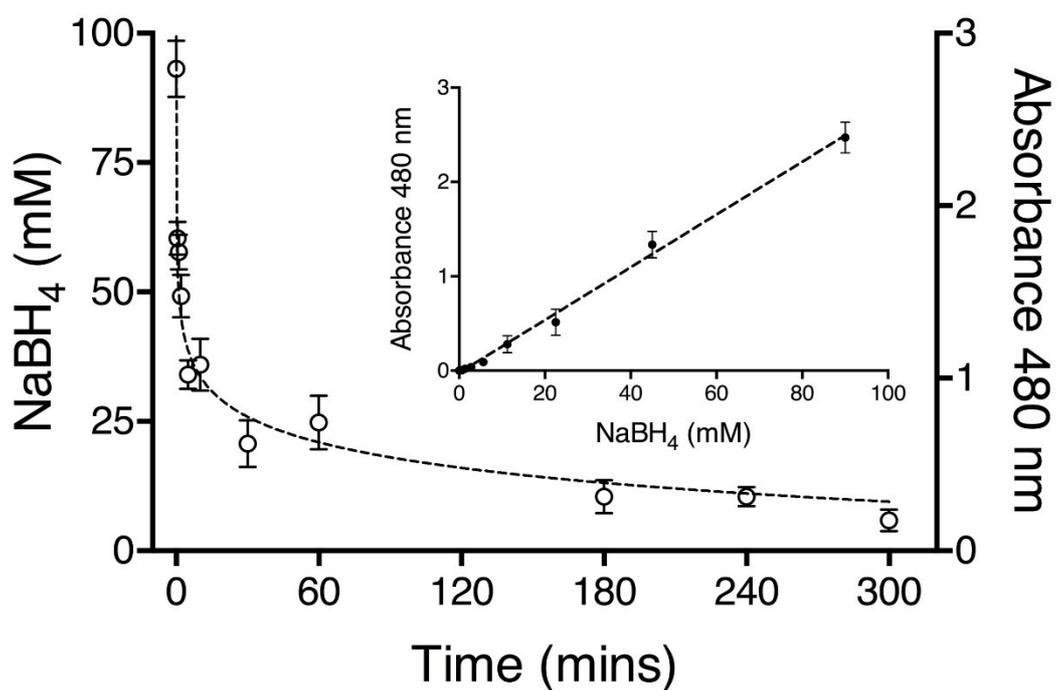
### B 5h AuNP



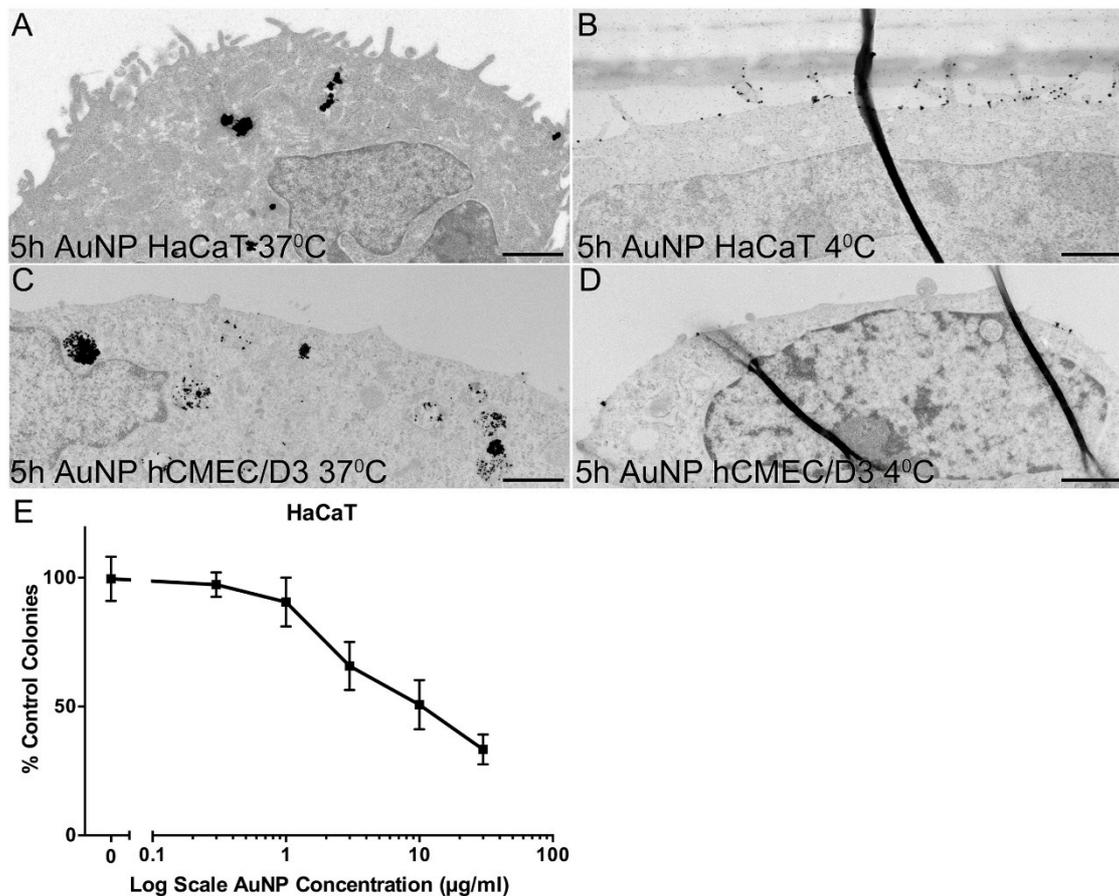
### C

AuNP	n moles $\alpha$ Gal/ $\mu$ g Au	n moles PEGamine/ $\mu$ g Au	$\alpha$ Gal %	$\alpha$ Gal/ 100 Au	PEGamine/ 100 Au	Total ligands/ 100 Au
1h	1.11	0.96	53.4	21.8	19.0	40.8
5h	0.92	0.85	52.0	18.1	16.7	34.8

Supplementary Figure 5. HPLC quantitation of thiol ligands released from AuNPs. A) Short synthesis (1h AuNPs) and B) Long synthesis (5h AuNPs). The positions of the  $\alpha$ -Galactose and PEGamine thiol elution peaks are marked and quantified. C) Summary table of  $\alpha$ -Galactose and PEGamine thiol concentrations relative to gold in nanomoles/ $\mu$ g Au or in molar terms (thiols/100 Au atoms). The  $\alpha$ -Galactose:PEGamine ligand ratio is also shown as the percentage  $\alpha$ -Galactose.



Supplementary Figure 6. TNBS assay of sodium borohydride at various time intervals during AuNP synthesis reaction. The data approximate a logarithmic curve (dotted line). Right Y-axis shows absorbance value at 480 nm, while left Y-axis shows corresponding molar concentration of sodium borohydride, interpolated from the calibration curve (inset graph). Data are mean  $\pm$ SEM,  $n=3$ .



Supplementary Figure 7. A,B) TEM images of long synthesis AuNPs on HaCaT cells following 3h incubation with 10  $\mu\text{g/ml}$  AuNPs at either A) 37 °C or B) 4 °C. C,D) TEM images of long synthesis AuNPs on hCMEC/D3 cell surface following 3h incubation with 8  $\mu\text{g/ml}$  AuNPs at either C) 37 °C or D) 4 °C. Scale bars = 1000 nm.

E) Clonogenic assay of HaCaT cells following acute 3h exposure with 10  $\mu\text{g/ml}$  long synthesis AuNPs. Mean  $\pm$  SEM  $n=9$ .