Nanometric Resolution in the Hydrodynamic Size Analysis of Ligand-Stabilized Gold Nanorods: Supporting Information

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I. TEM size analysis of citrate-stabilized gold nanorods (Cit-GNRs)

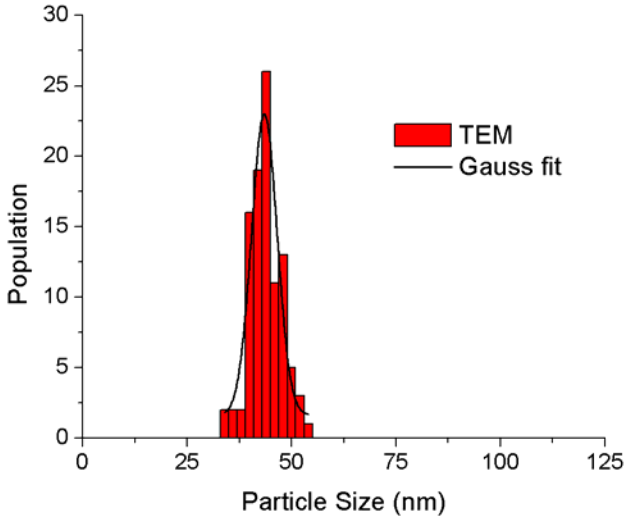

Figure S1. Histogram of cit-GNR length using TEM size analysis (taken from 3 images at a resolution of 1.4 pixels/nm). Particle count $N = 100$; mean = 44.4 nm; std. dev. = 3.9 nm

II. Ligand exchange with GNRs in the presence of PSS

Ligand exchange in the presence of PSS does not proceed as well as with fully purified cit-GNRs. Significant aggregation can be observed by NTA if the Na-PSS loading is above 1.5 mg/mL (0.15 wt%), prior to centrifugation and redispersion (C/R) in fresh surfactant solution (Figure S2a). Differences in the vis−NIR absorbance spectra are more subtle, but also indicate a modest degree of aggregation (Figure S2b). Surface functionalizations directly with PSS-GNRs (i.e. without citrate treatment) are variable in efficacy, and less reliable than with cit-GNRs (Figure S2c,d). We thus recommend using PSS as a detergent rather than as a stabilizing surfactant,[18] and to limit the PSS concentration to 0.15 wt% or less (*cf*. Ref. 20, Stage 5), prior to centrifugation and redispersion control in 5 mM citrate.

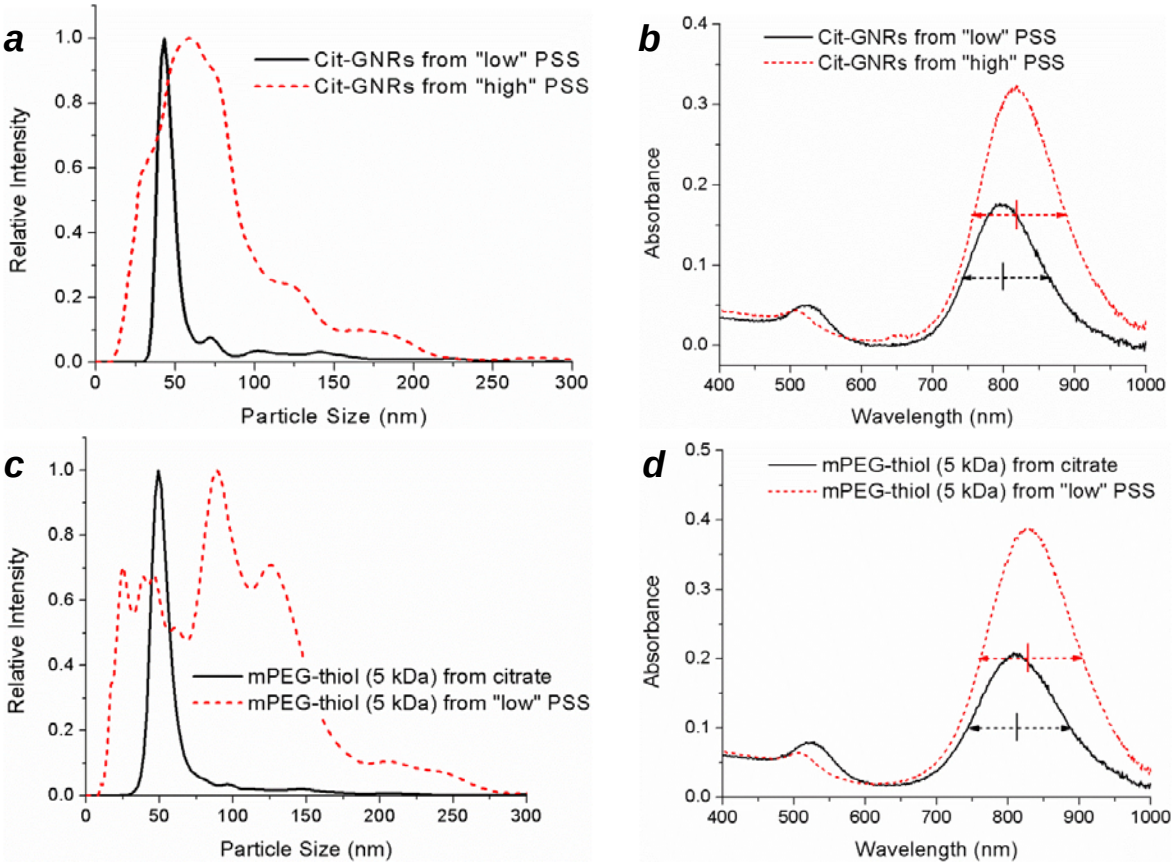

Figure S2. NTA plots and vis−NIR spectra of citrate-stabilized GNRs previously suspended in Na-PSS solutions at different concentrations. (a,b) GNRs redispersed in 5 mM Na_3-cit after 1 C/R cycle from 0.35 wt% Na-PSS ("high") or from < 0.15 wt% Na-PSS ("low"). (c,d) GNRs redispersed in 1.2 mM 5-kDa mPEG-SH after 1 C/R cycle from 5 mM Na_3-cit or after 1 C/R cycle from "low" PSS.

III. Ligand exchange with Cit-GNRs

All experiments were performed with cit-GNRs obtained after two C/R cycles with 5 mM Na_3-cit.[20] In most cases, cit-GNRs were centrifuged and separated from the supernatant, then redispersed into aqueous solutions containing surfactant and allowed to sit for 12−20 hours. Excess surfactant was removed by centrifugation and redispersion in pure water, prior to analysis.

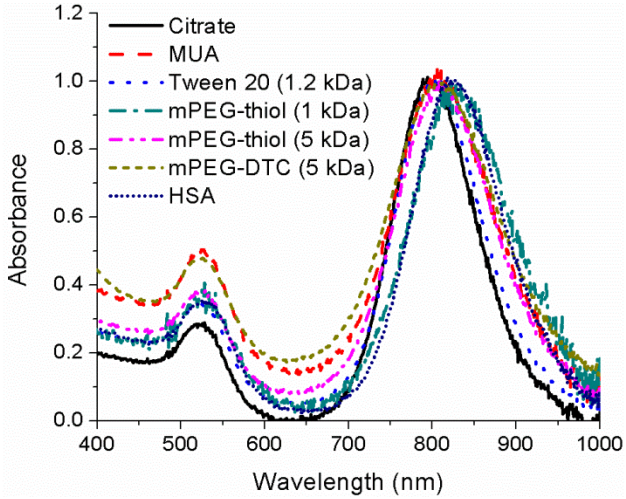

Figure S3. Normalized absorbance spectra of surfactant-stabilized GNRs, produced by surface exchange with cit-GNRs using a variety of ligands, surfactants, or proteins. Minor shifts in λ_{LPR} can be observed, consistent with changes in the surface dielectric.

IV. Ligand exchange as a function of PEG-thiol concentration

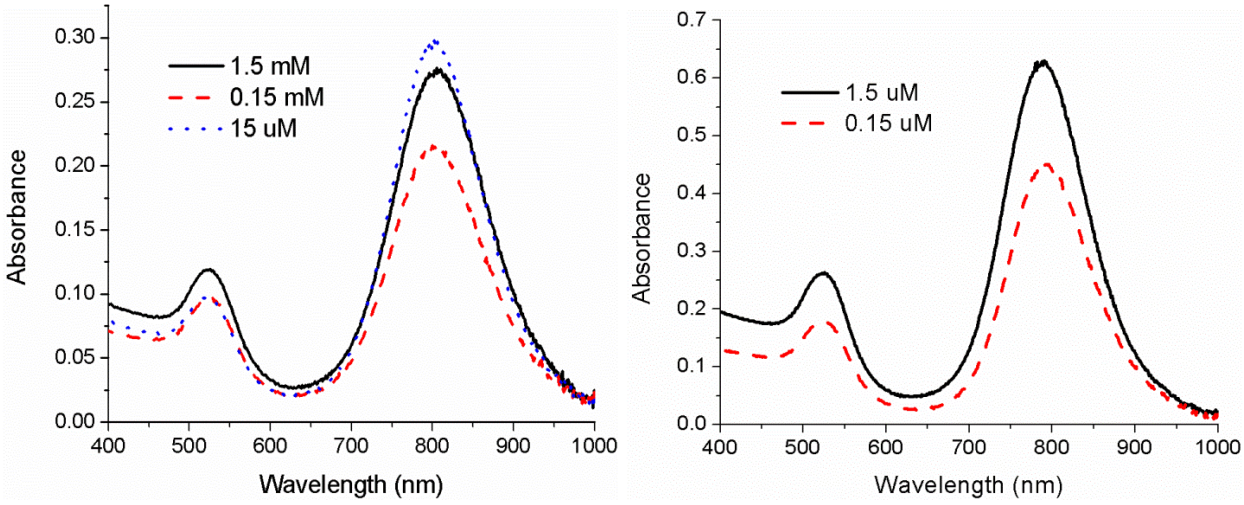

Figure S4. Vis−NIR absorbance spectra of cit-GNRs incubated for 12 hours with mPEG-thiol (5 kDa) at loadings ranging from 1.5 mM to 0.15 μM. Only minor differences in spectral profile can be discerned, in the visible region ($\lambda < 700$ nm).