## Supporting Information for

## Quantifying the Coverage Density of Poly(ethylene glycol) Chains on the Surface of Gold Nanostructures

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**Figure S1.** UV-vis spectra of 50-nm AuNCs before and after functionalization with HS-PEG<sub>3000</sub>-NH<sub>2</sub> or HS-PEG<sub>3000</sub>-COOH at two different temperatures: (A) 4 °C and (B) 22 °C.



**Figure S2.** Scheme of the reaction between fluorescamine and a primary amine that generates a fluorescent product.



**Figure S3.** Typical excitation and emission spectra of the chromophore generated from the reaction between fluorescamine and HS-PEG<sub>5000</sub>-NH<sub>2</sub>.



**Figure S4.** (A) Fluorescence spectra of the chromophore derived from fluorescamine by reacting with different concentration of HS-PEG<sub>5000</sub>-NH<sub>2</sub> at pH = 10: (a) 0.25, (b) 0.38, (c) 0.50, (d) 1.0, (e) 1.5, (f) 2.0 (g) 2.5, and (h) 3.0  $\mu$ M. By plotting the fluorescence intensity at 565 nm against the concentration of HS-PEG<sub>5000</sub>-NH<sub>2</sub>, we obtained the calibration curve shown in Figure 4A. (B) UV-vis spectra of the chromophore derived from ninhydrin by reacting with different concentrations of HS-PEG<sub>5000</sub>-NH<sub>2</sub>: (a) 0.5, (b) 5, (c) 10, (d) 20, (e) 33.3, (f) 66.7, and (g) 100  $\mu$ M. By plotting the absorbance at 565 nm against the concentration of HS-PEG<sub>5000</sub>-NH<sub>2</sub>: (a) 0.5, (b) 5, (c) 10, (d) 20, (e) 33.3, (f) 66.7, and (g) 100  $\mu$ M. By plotting the absorbance at 565 nm against the concentration of HS-PEG<sub>5000</sub>-NH<sub>2</sub>, we obtained the calibration curve shown in Figure 5A.



**Figure S5.** Calibration curve for fluorescamine-based assay using HS-PEG<sub>5000</sub>-NH<sub>2</sub>, which was obtained by plotting the fluorescence intensity at 480 nm against the concentration of HS-PEG<sub>5000</sub>-NH<sub>2</sub> at pH = 6.5.



**Figure S6.** Scheme of the reaction between ninhydrin and a primary amine that generates a colored product.



**Figure S7.** Calibration curve for FITC that was obtained by plotting the fluorescence intensity at 520 nm against the concentration of FITC.



**Figure S8.** Calculations of surface areas (S) for the four different types of Au nanostructures: (A) AuNC (only outer surface was considered in the calculation), (B) CTAC-capped AuNP, (C) citrate-capped AuNP, and (D) CTAB-capped AuNR. The sizes and morphologies were obtained from the TEM images shown in Figure 2, A, D, E, and F, respectively.

	Temperature	Hydrodynamic diameter (nm)	Polydispersity index	Zeta potential (mV)
AuNC-PVP	4 °C	96.1	0.188	-47.9
AuNC-PVP	22 °C	99.2	0.197	-57.1
AuNC-PEG <sub>3000</sub> -NH <sub>2</sub>	4 °C	108.1	0.241	20.3
AuNC-PEG <sub>3000</sub> -NH <sub>2</sub>	22 °C	190.6	0.296	14.6
AuNC-PEG <sub>5000</sub> -NH <sub>2</sub>	4 °C	130.7	0.226	11.7
AuNC-PEG <sub>5000</sub> -NH <sub>2</sub>	22 °C	204.9	0.287	-2.6
AuNC-PEG <sub>20000</sub> -NH <sub>2</sub>	4 °C	113.9	0.154	-35
AuNC-PEG <sub>20000</sub> -NH <sub>2</sub>	22 °C	115.6	0.143	-31.2
AuNC-PEG <sub>3000</sub> -COOH	4 °C	104.0	0.212	-40.4
AuNC-PEG <sub>3000</sub> -COOH	22 °C	101.9	0.206	-36.7

**Table S1.** Characterization of the 50-nm AuNCs with different surface coatings. PEGylation ofAuNCs was conducted at 4 °C and 22 °C for each sample.