Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Multivalency of PEG-Thiol Ligands Affects the Stability of NIR-absorbing Hollow Gold Nanospheres and Gold Nanorods

Julie Ruff[*a], *Julia Steitz*[b], *Anne Buchkremer*[a], *Michael Noyong*[a], *Heinrich Hartmann*[c], *Astrid Besmehn*[c], *Ulrich Simon*[*a]

[a] Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germany

[b] Institute for Laboratory Animal Science, University Hospital of the RWTH Aachen University, Aachen, Germany

[c] Central Institute for Engineering, Electronics and Analytics (ZEA-3), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

SUPPORTING INFORMATION

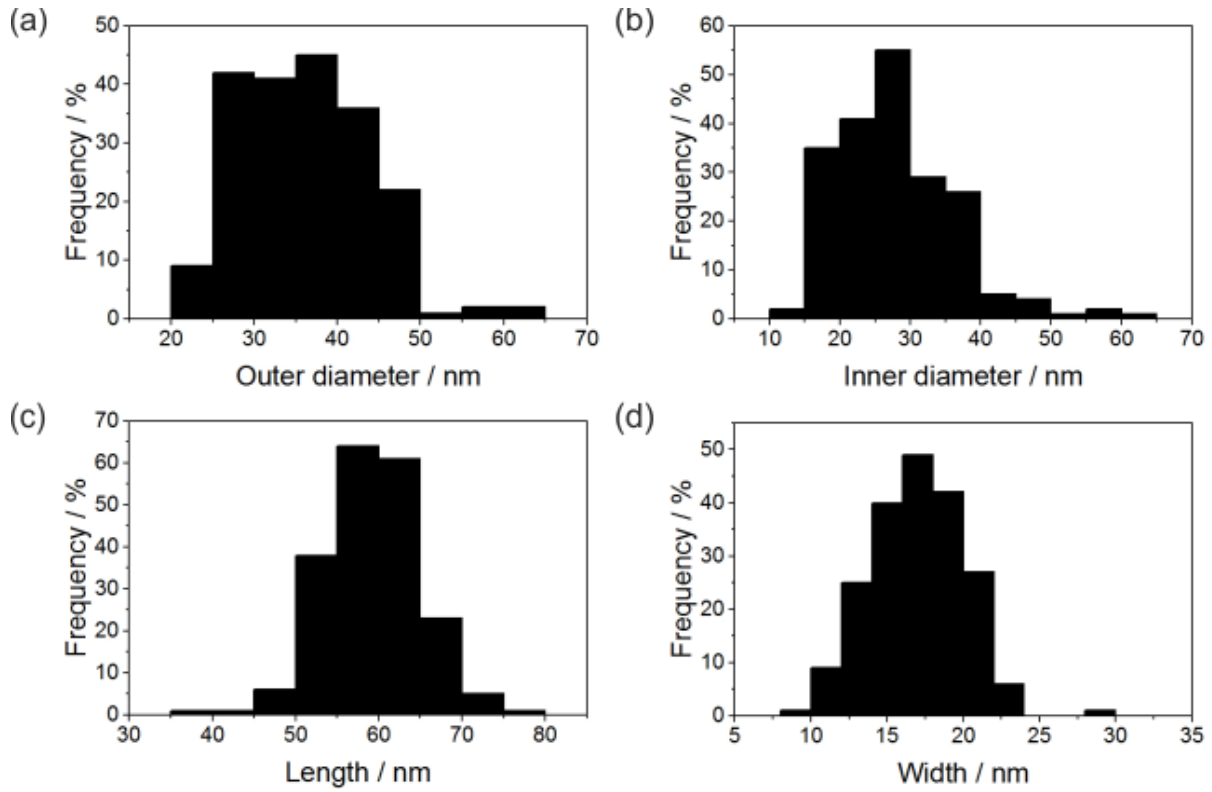

Figure S1. Histograms corresponding to the evaluation of the SEM-T images for HAuNS with (a) a shell diameter of 35 ± 6 nm and (b) and inner diameter of 28 ± 8 nm resulting in a shell thickness of 5 ± 4 nm and for AuNR with (c) the length of 59 ± 6 nm and a width of 17 ± 3 nm.

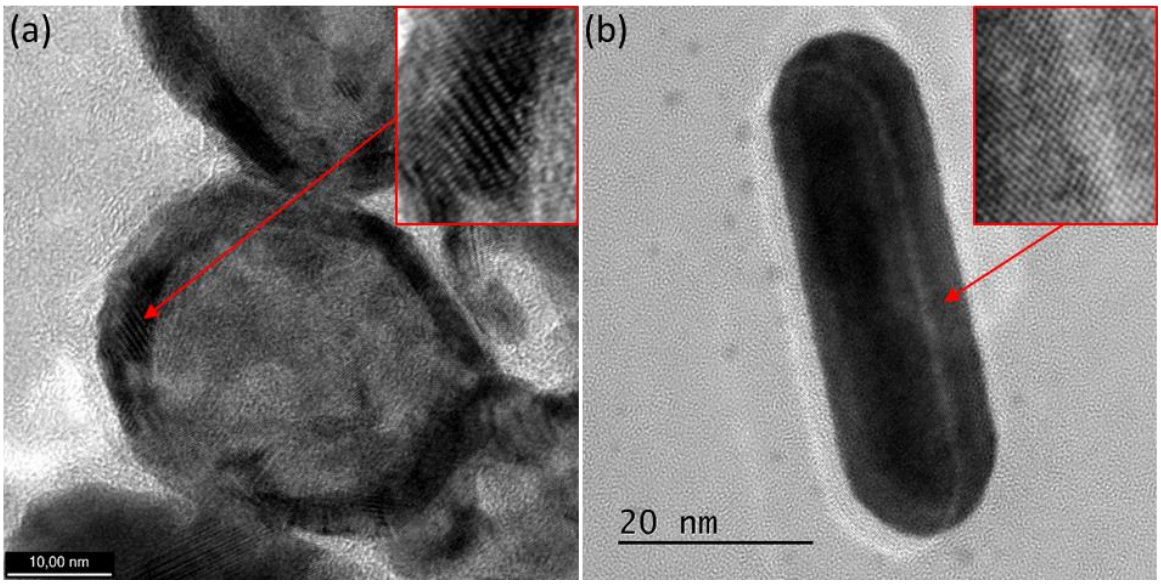

Figure S2. HR-TEM images of (a) HAuNS with an outer diameter of 35 ± 3 nm, an inner diameter of 27 ± 2 nm and a shell thickness of 4 ± 1 nm and of (b) AuNR with a length of 59 ± 6 nm and a width from 17 ± 2 nm. The insets show exemplary a crystalline domain in a larger magnification.

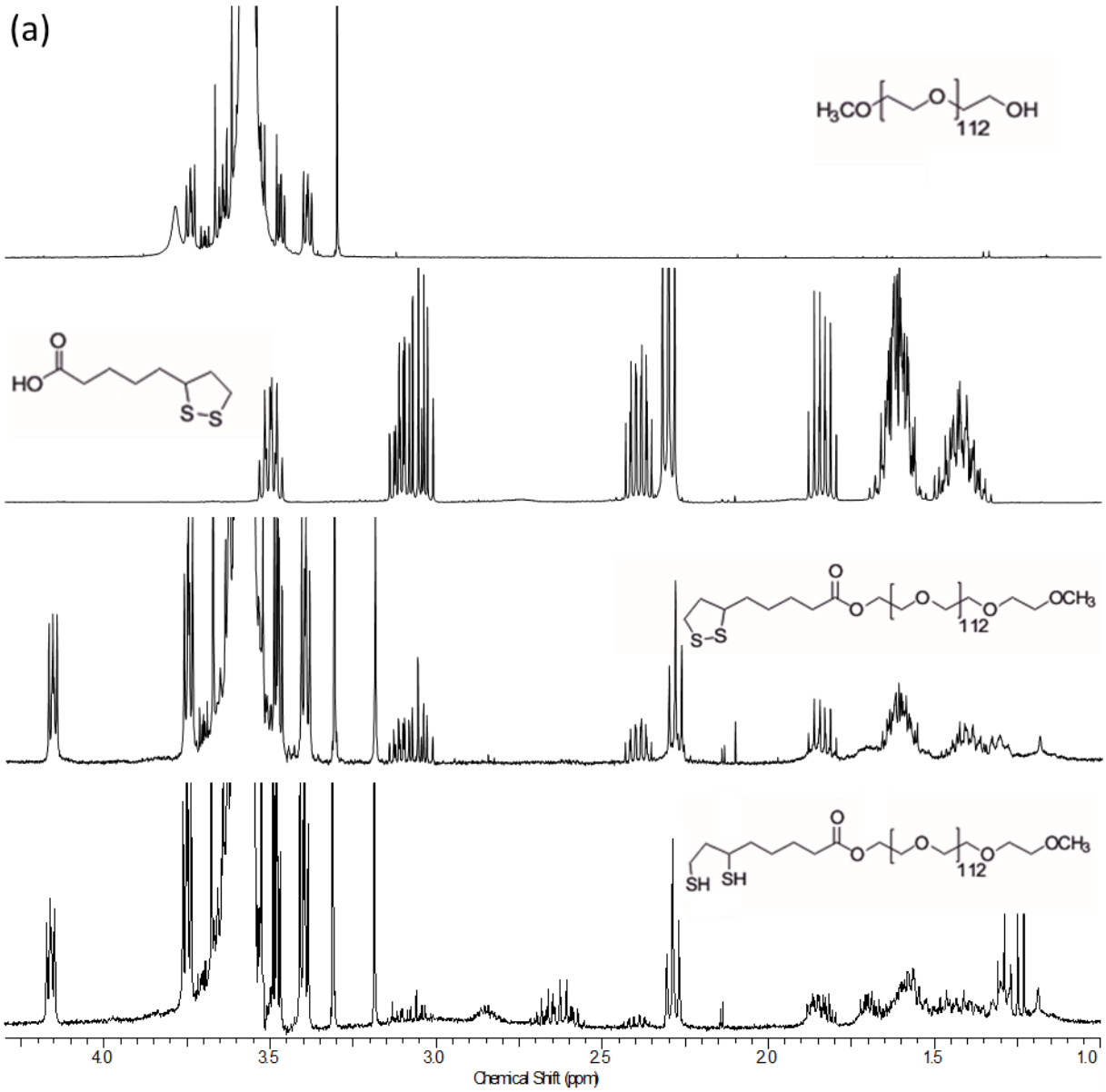

Figure S3a. ^{1}H-NMR spectrum from up to down of PEG_{5000} methyl ether, lipoic acid, bidentate $(HS)_2$-PEG_{5000}-OCH_3 prior to ring opening and bidentate $(HS)_2$-PEG_{5000}-OCH_3 after ring opening.

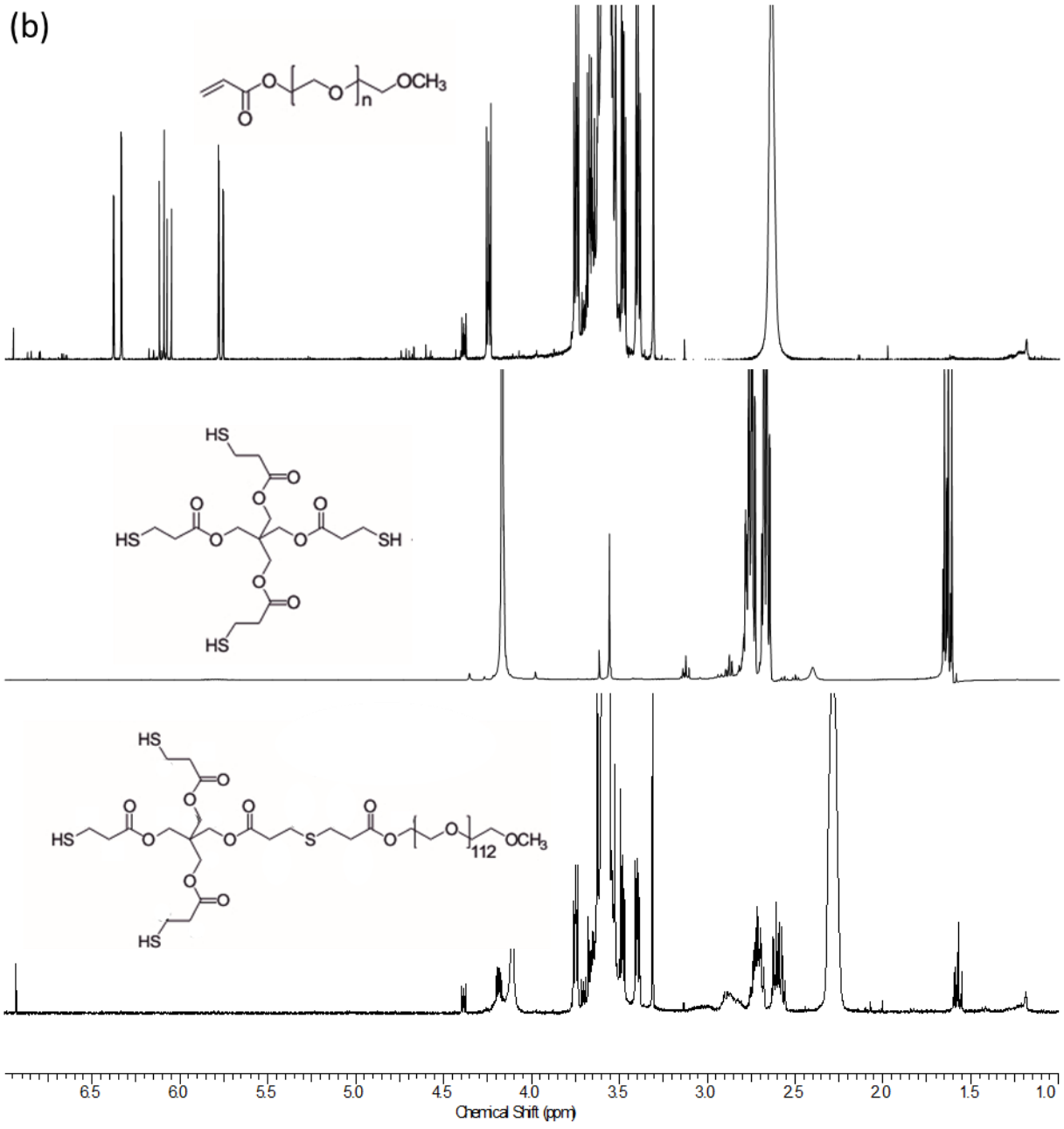

Figure S3b. ^{1}H-NMR spectrum from up to down of PEG_{5000} methyl ether acrylate, pentaerathritol tetrakis(3-mercaptopropionate) (PETM) and $(HS)_3$-PEG_{5000}-OCH_3.

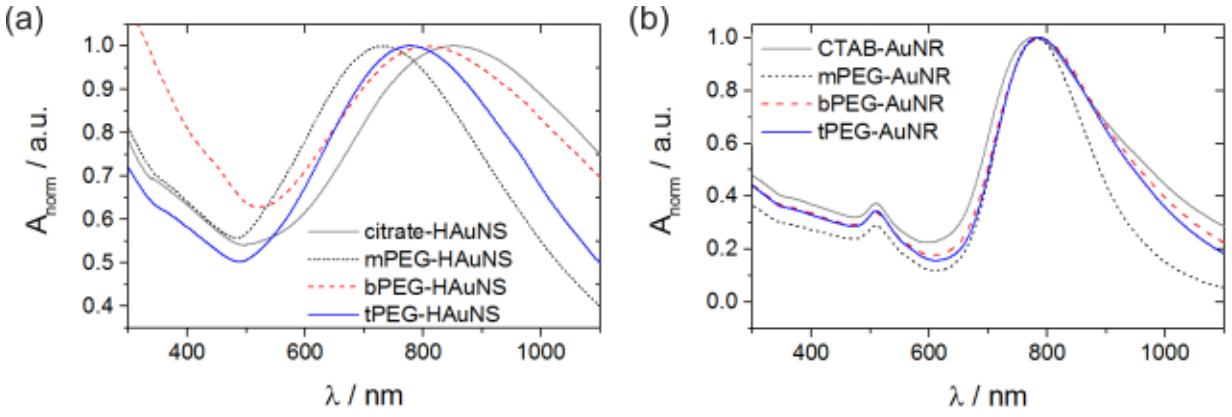

Figure S4. Optical characterization of PEGylated HAuNS and AuNR. (a) Absorbance spectra of HAuNS with a maximum absorbance at 852 nm (citrate-HAuNS), 735 nm (mPEG-HAuNS), 807 nm (bPEG-HAuNS) and 779 nm (tPEG-HAuNS). (b) Absorbance spectra of AuNR with a longitudinal maximum absorbance at 787 nm (CTAB-AuNR), 781 nm (mPEG-AuNR), 789 nm (bPEG-AuNR) and 786 nm (tPEG-AuNR).

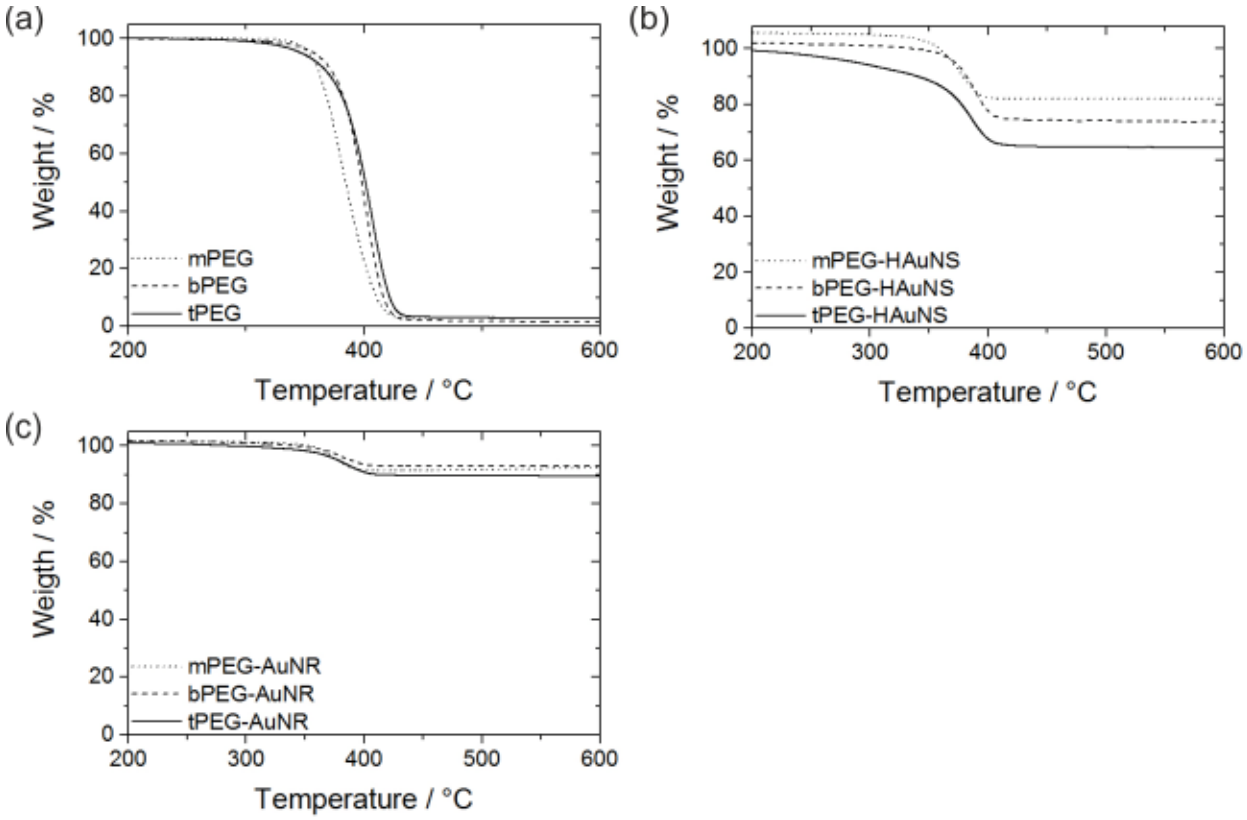

Figure S5. TGA of pure ligands and PEGylated AuNP. TGA of (a) the pure ligands HS-PEG_{5000}-OCH_3, HS_2-PEG_{5000}-OCH_3 and HS_3-PEG_{5000}-OCH_3; the PEGylated particles (b) mPEG-HAuNS, bPEG-HAuNS, tPEG-HAuNS and (c) mPEG-AuNR, bPEG-AuNR and tPEG-AuNR are presented.

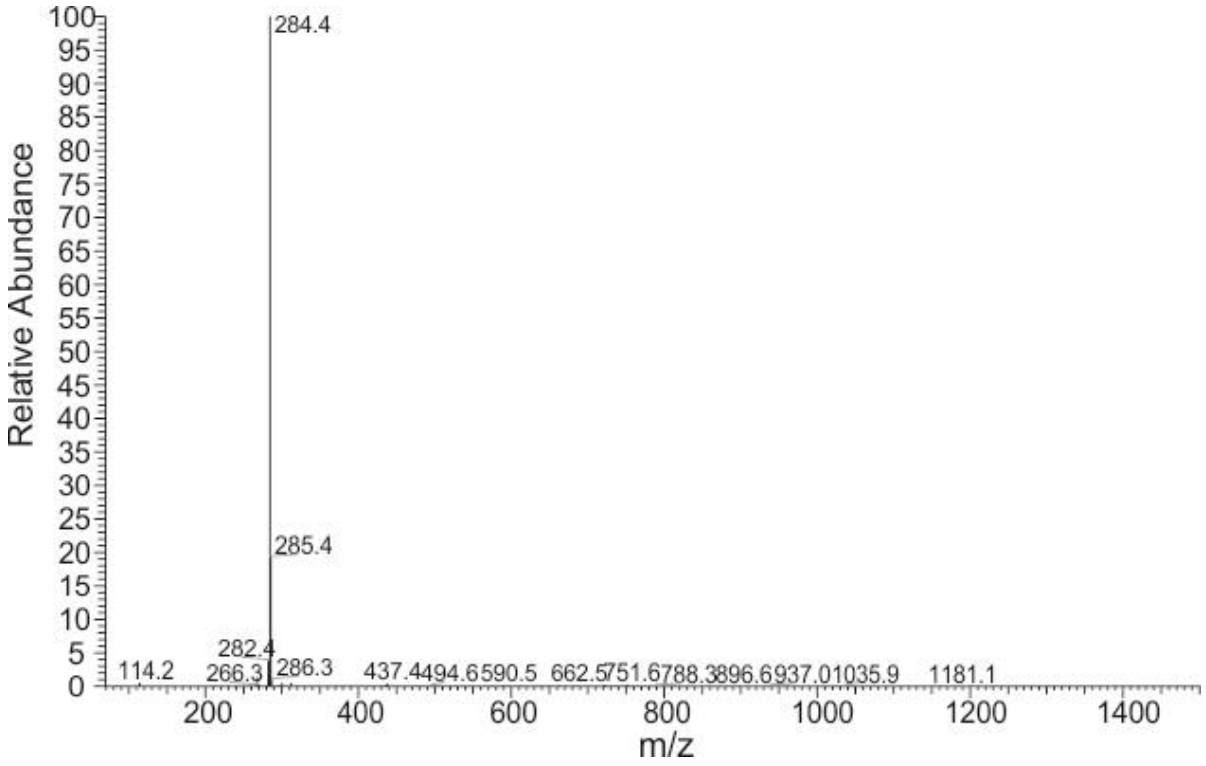

Figure S6a. SIMS spectrum of CTAB-AuNR. The mass peak of m/z = 284 can be attributed to the cetyltrimethylammonium cation ($C_{19}H_{42}N^+$).

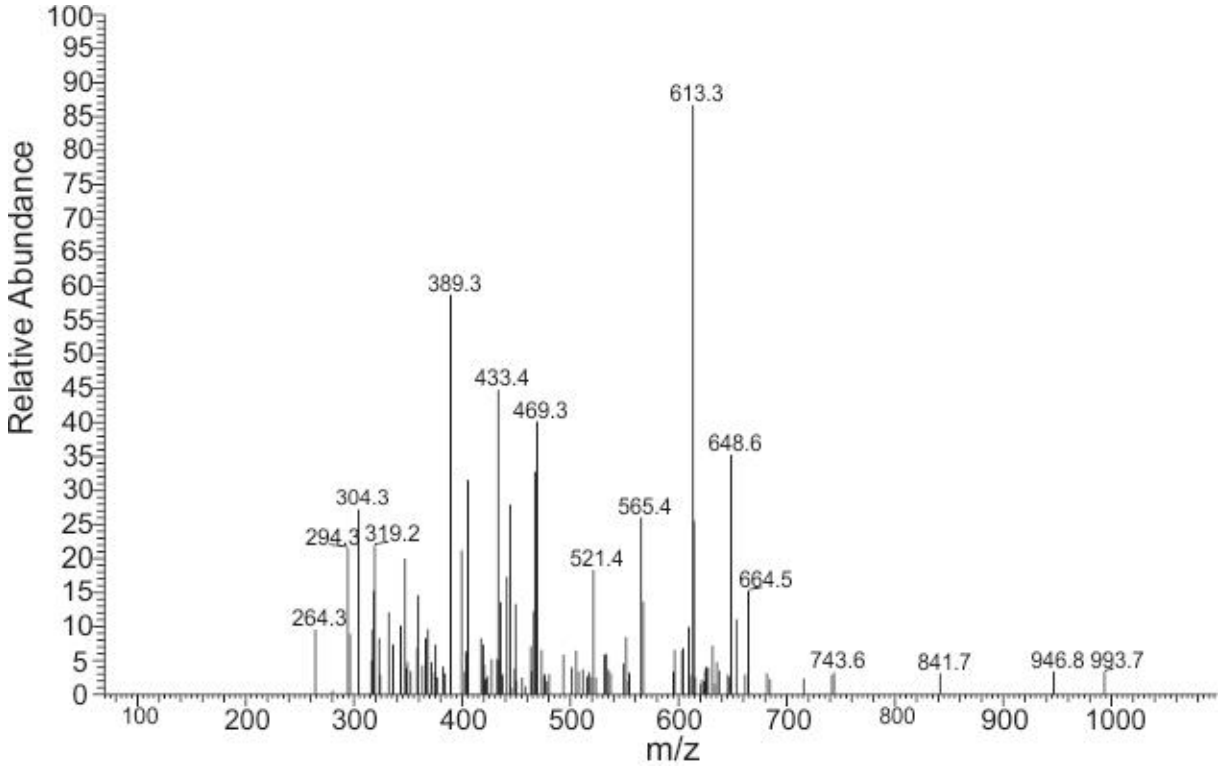

Figure S6b. SIMS spectrum of mPEG-AuNR.

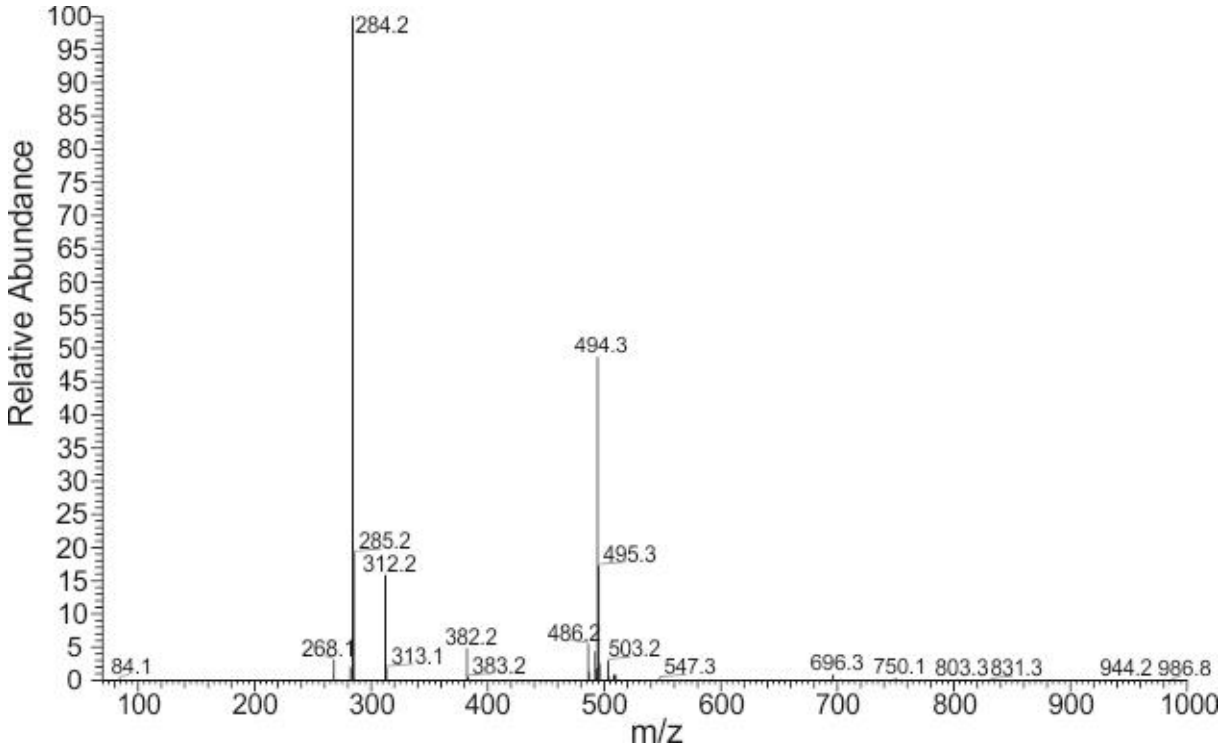

Figure S6c. SIMS spectrum of bPEG-AuNR.

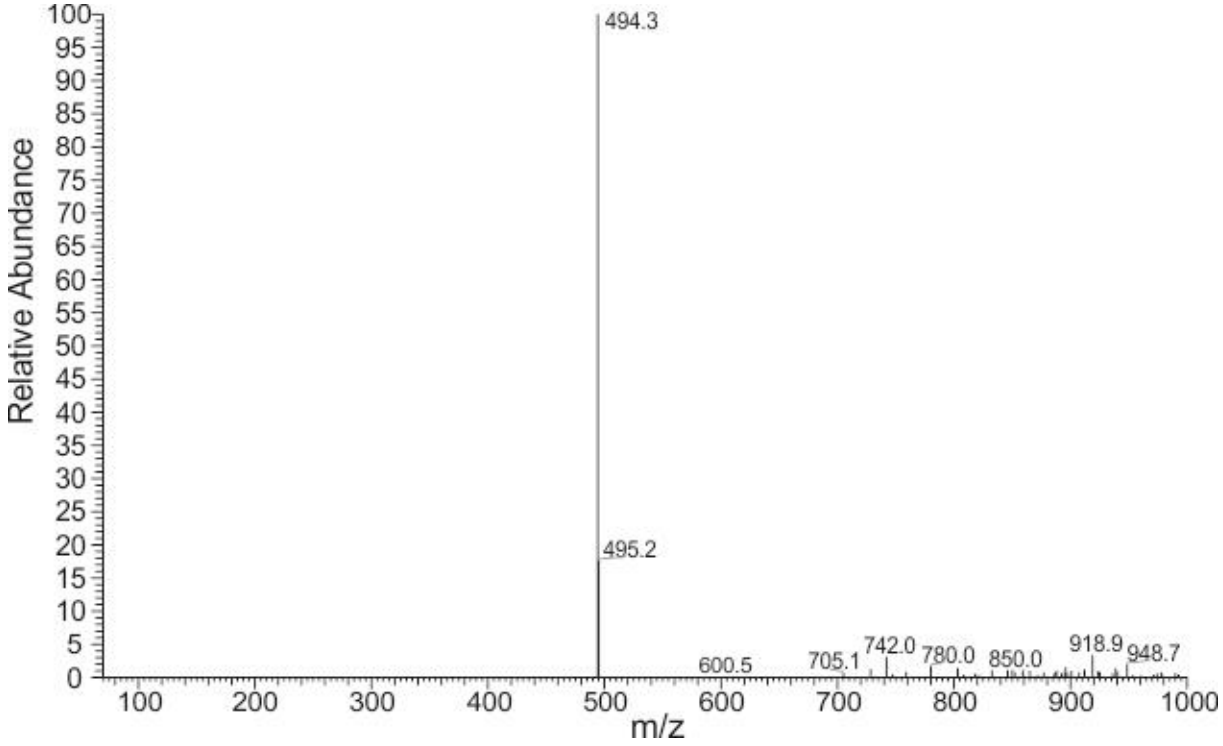

Figure S6d. SIMS spectrum of tPEG-AuNR.

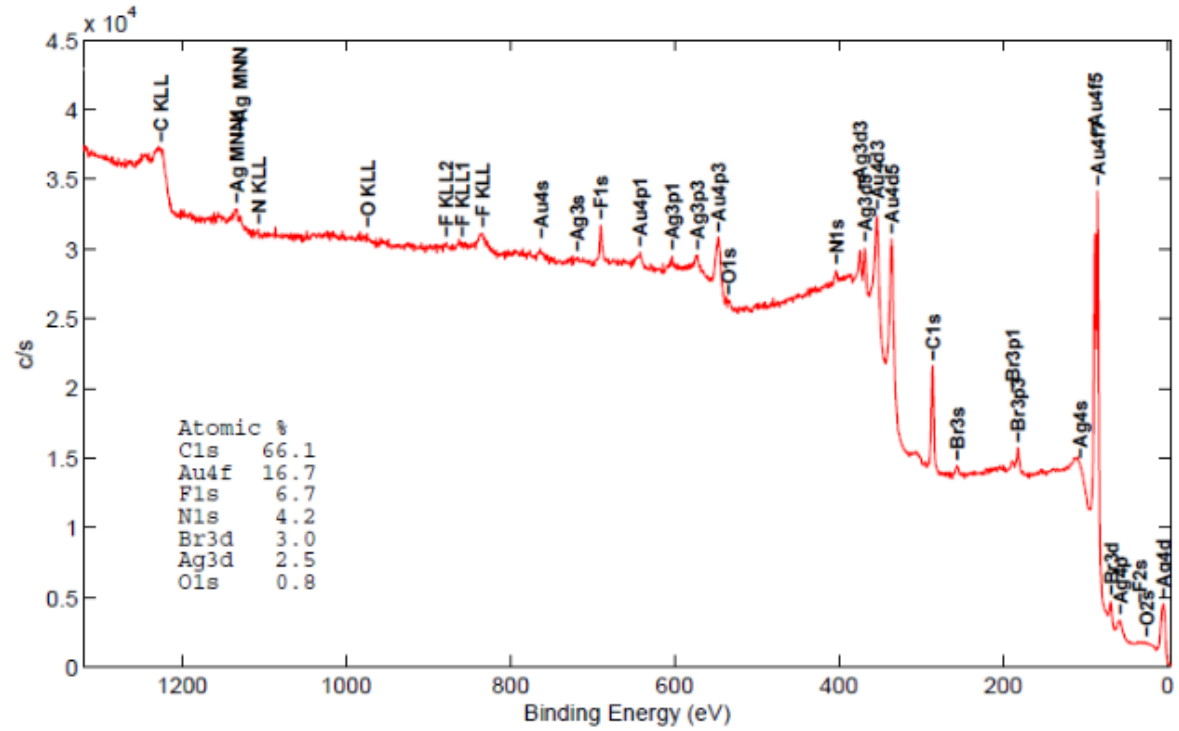

Figure S7a. Overview XPS spectrum of CTAB-AuNR. Spectrum were recorded at 187.5 eV pass energy and a step size of 0.8 eV and evaluated with *Phi MultiPak.*

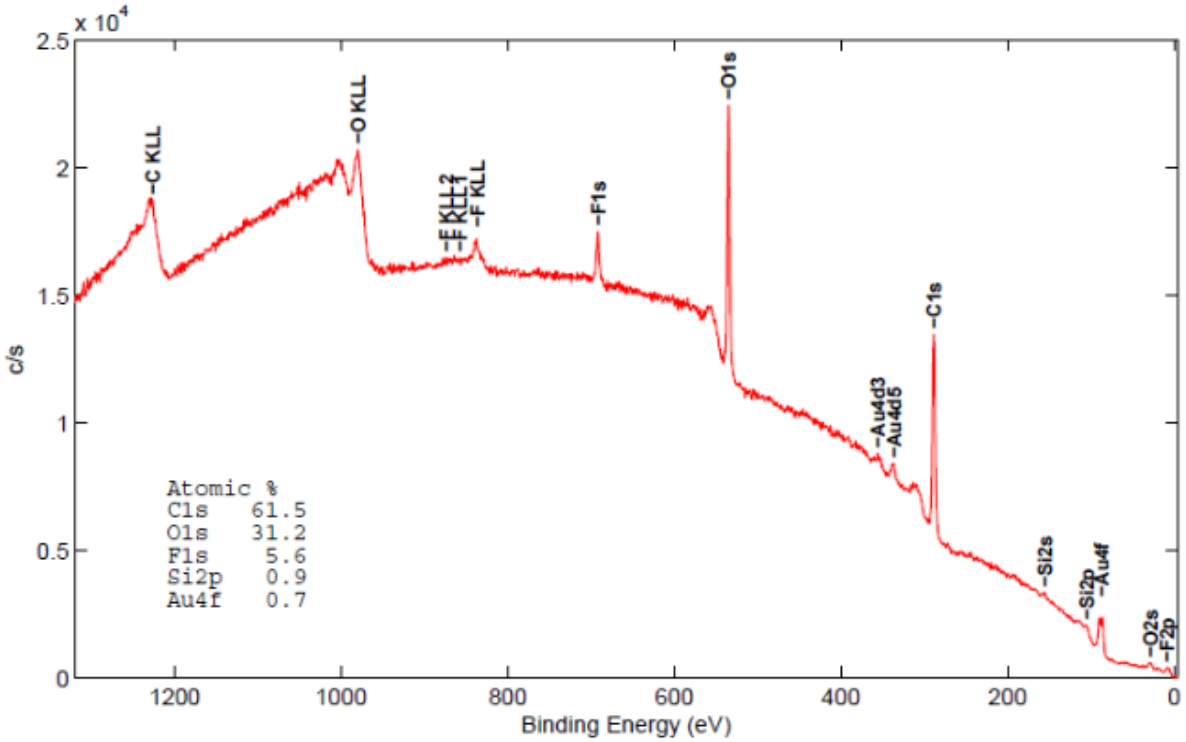

Figure S7b. Overview XPS spectrum of mPEG-AuNR. Spectrum were recorded at 187.5 eV pass energy and a step size of 0.8 eV and evaluated with *Phi MultiPak.*

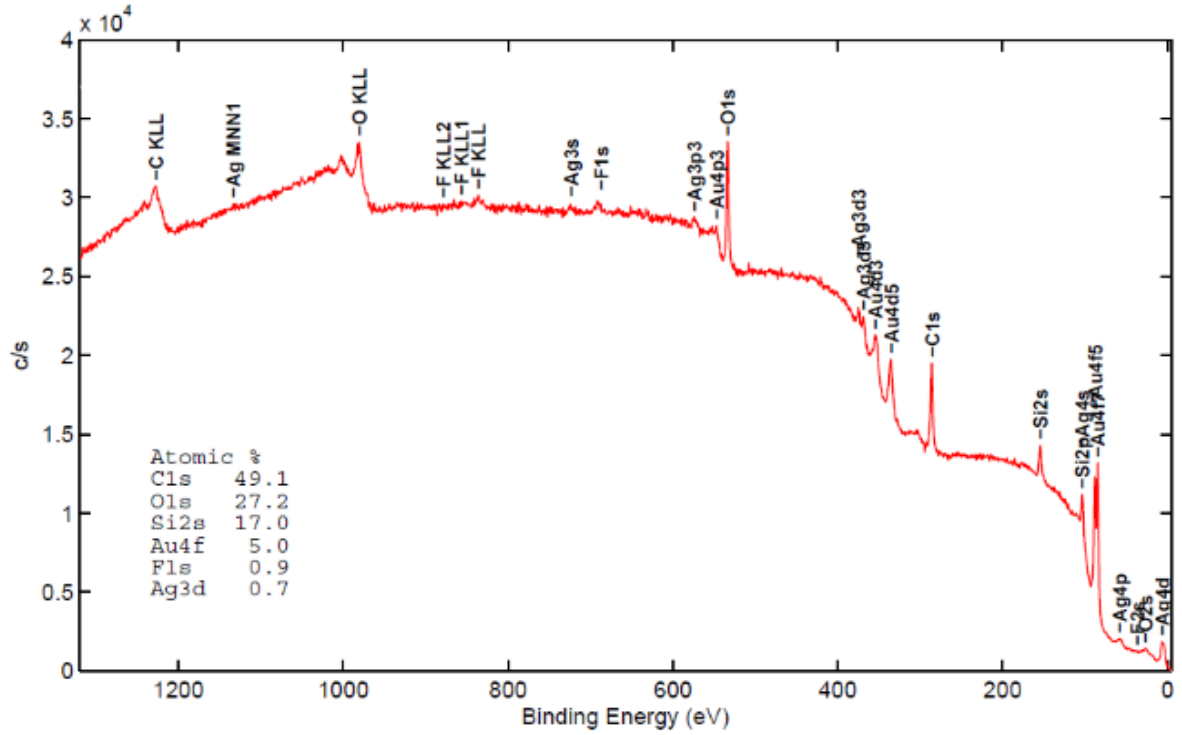

Figure S7c. Overview XPS spectrum of bPEG-AuNR. Spectrum were recorded at 187.5 eV pass energy and a step size of 0.8 eV and evaluated with *Phi MultiPak.*

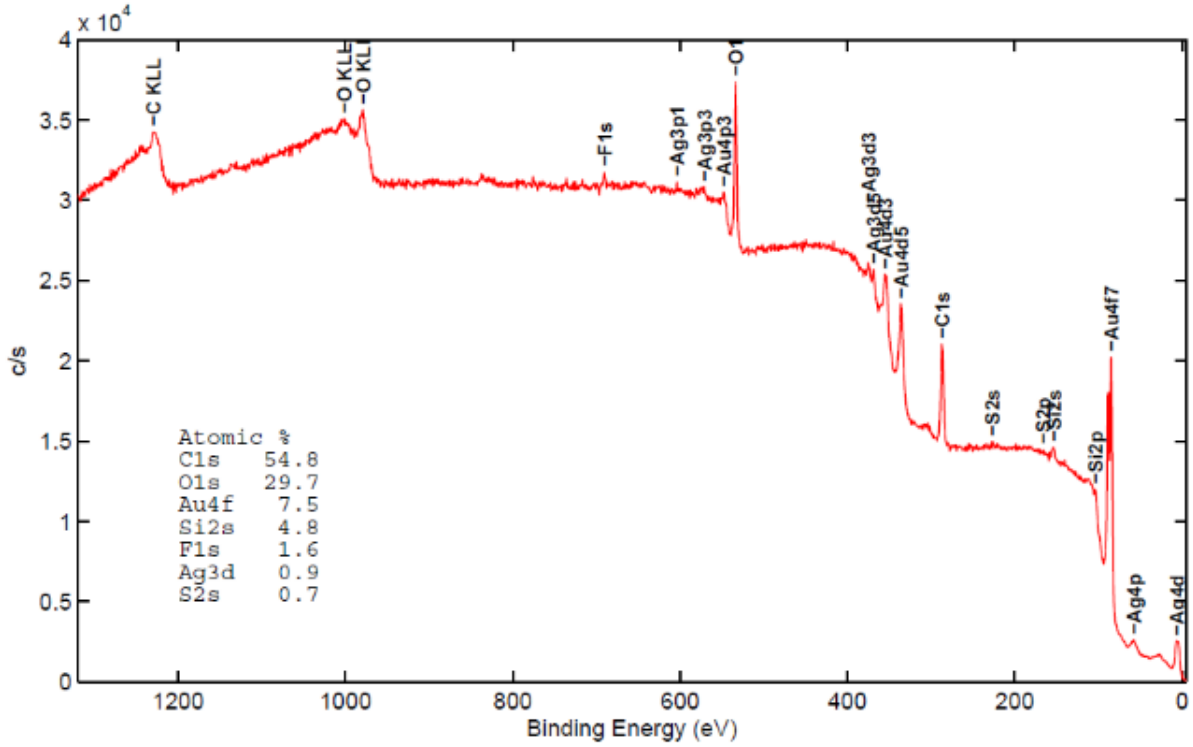

Figure S7d. Overview XPS spectrum of tPEG-AuNR. Spectrum were recorded at 187.5 eV pass energy and a step size of 0.8 eV and evaluated with *Phi MultiPak*.

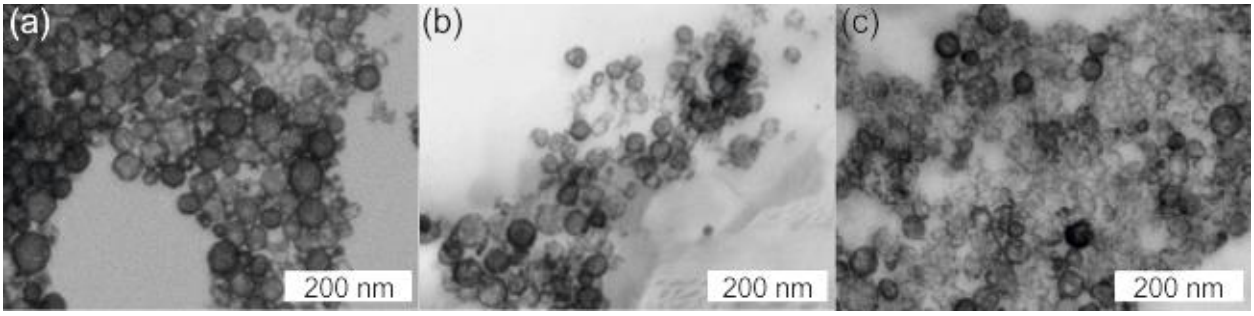

Figure S8. Etching process of HAuNS. SEM-T imaged of mPEG-HAuNS (a) before the addition of KCN, (b) 15 min after the addition of KCN and (c) 60 min after the addition of KCN.

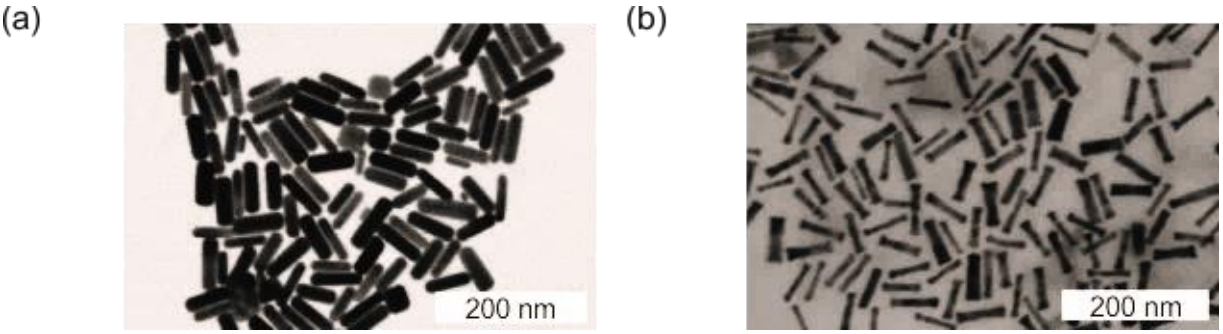

Figure S9. Etching process of AuNR. SEM-T imaged of mPEG-AuNR (a) before the addition of KCN and (b) 90 min after the addition of KCN.

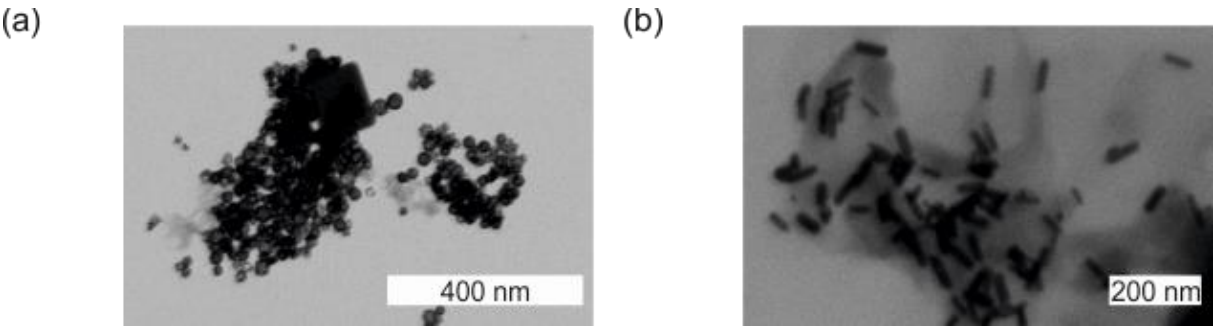

Figure S10. Morphological stability of (a) mPEG-HAuNS and (b) mPEG-AuNR after aggregation in 1 M NaCl solution.

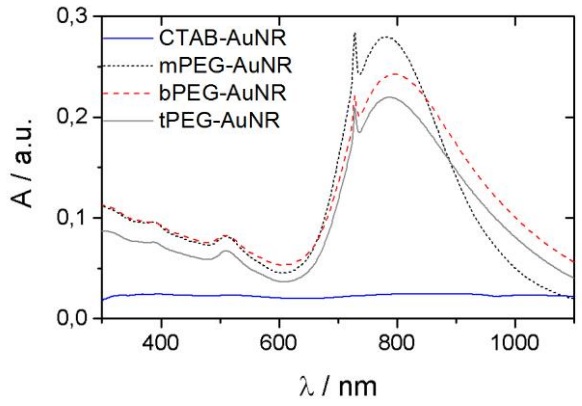

Figure S11. CTAB-AuNR and mPEG-, bPEG- and tPEG-AuNR in cell culture medium DMEM after 96 h.