Electronic Supplementary Information (ESI)

Characterization of Mixed-Ligand Shells on Gold Nanoparticles by Transition Metal and Supramolecular Surface Probes

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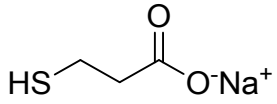
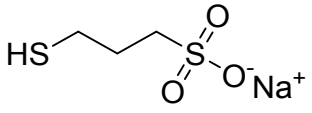
Abbreviations

AMADA-Put: *N*-adamantylmethylbutane-1,4-diamine; AO: acridine orange; AuNPs: gold nanoparticles; CB7: cucurbit[7]uril; DTNB: 5,5′-dithio-*bis*-(2-nitrobenzoic acid) (Ellman's reagent); EDC: 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride salt; Hepes: 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid; MES: 2-(*N*-morpholino)ethanesulfonic acid; MPA: sodium 3-mercaptopropionate; MPS: sodium 3-mercapto-1-propanesulfonate; MUA: sodium 11-mercaptoundecanoate; PV: pyrocatechol violet; TEG: triethylene glycol mono-11-mercaptoundecyl ether.

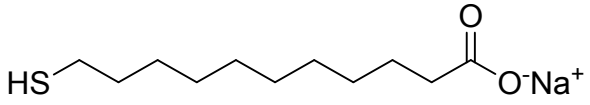
Molecular Structure of Ligands



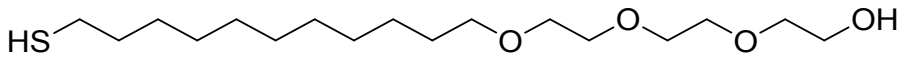
Sodium 3-mercaptopropanoate (MPA)



Sodium 3-mercapto-1-propanesulfonate (MPS)



Sodium 11-mercaptoundecanoate (MUA)



Triethylene glycol mono-11-mercaptoundecyl ether (TEG)

Chart S1. Molecular structures of ligands.

DTNB Assay

Stock solutions of DTNB and MPA were prepared in 0.1 M NaH_2PO_4, 1 mM EDTA, pH 8.0. Varying concentrations of MPA (5-25 µM) and 40 µM DTNB were added to each solution. Solutions were mixed and incubated at room temperature for 5 minutes, and then absorption spectra were recorded. The prepared stock solutions of the AuNPs (ca. 1.5 µM AuNPs) were centrifuged for 25 min at 16400 rcf, and then, 40 µM DTNB was added to the supernatant and absorption spectra were recorded.

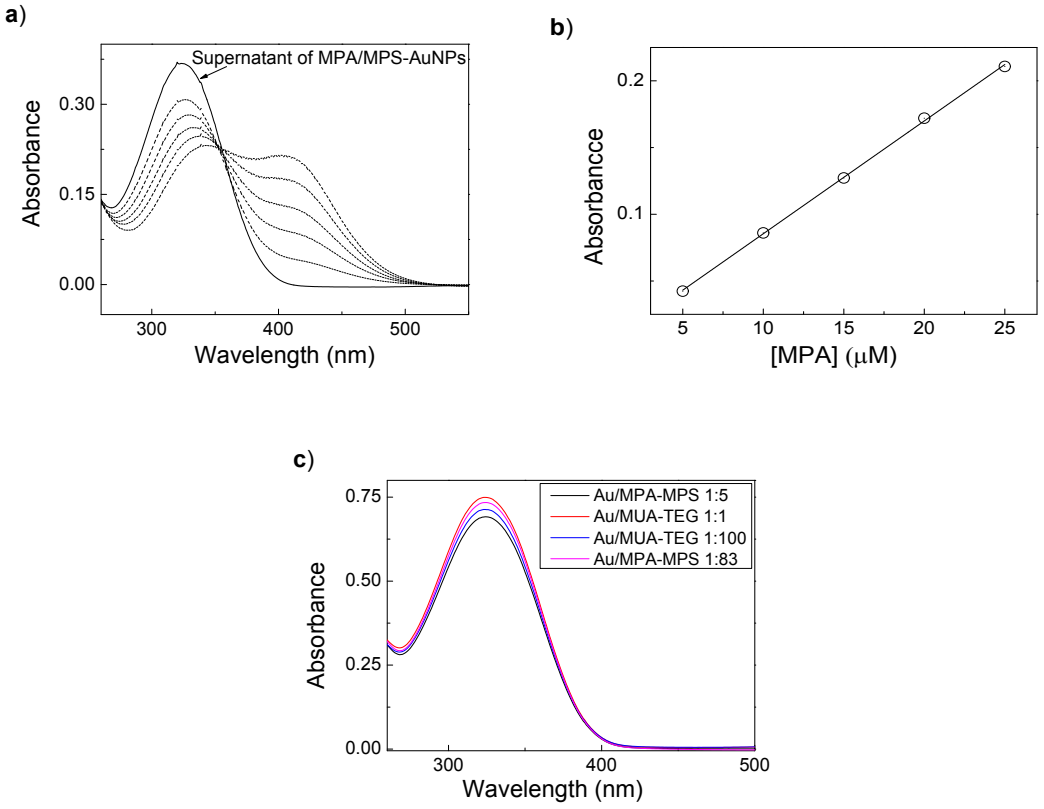


Fig. S1 a) Absorption spectra of 40 µM DTNB with varying concentration of MPA (5-25 µM) and MPA/MPS-AuNPs nanoparticles in 0.1 M NaH_2PO_4, 1 mM EDTA, pH 8.0. b) Corresponding plot of the absorbance at 412 nm against the concentration of MPA. The limit of detection (LOD) of DTNB assay was calculated using the equation; LOD = $3s_a/b$ where, s_a is the standard deviation of the blank and b is the slope of the calibration line. c) Absorption spectra of 80 µM DTNB with different molar ratio of the ligand capped nanoparticles (after five months storage at 4 ˚C) in 0.1 M NaH_2PO_4, 1 mM EDTA, pH 8.0.

Analysis of Particle Size Distribution by TEM

The synthesized mixed-ligand nanoparticles (ca. 1.5 μM) were fivefold diluted with NANOpure water and then deposited onto a carbon film-coated copper net TEM grid (PLANO GmbH). Samples were allowed to air dry and then dried under high vacuum before characterization by TEM at 80 kV. To obtain the size of distribution of the nanoparticles from TEM images, ImageJ 1.47d (National Institute of Health, USA) was used and at least 200 AuNPs from various areas of the grid were considered.

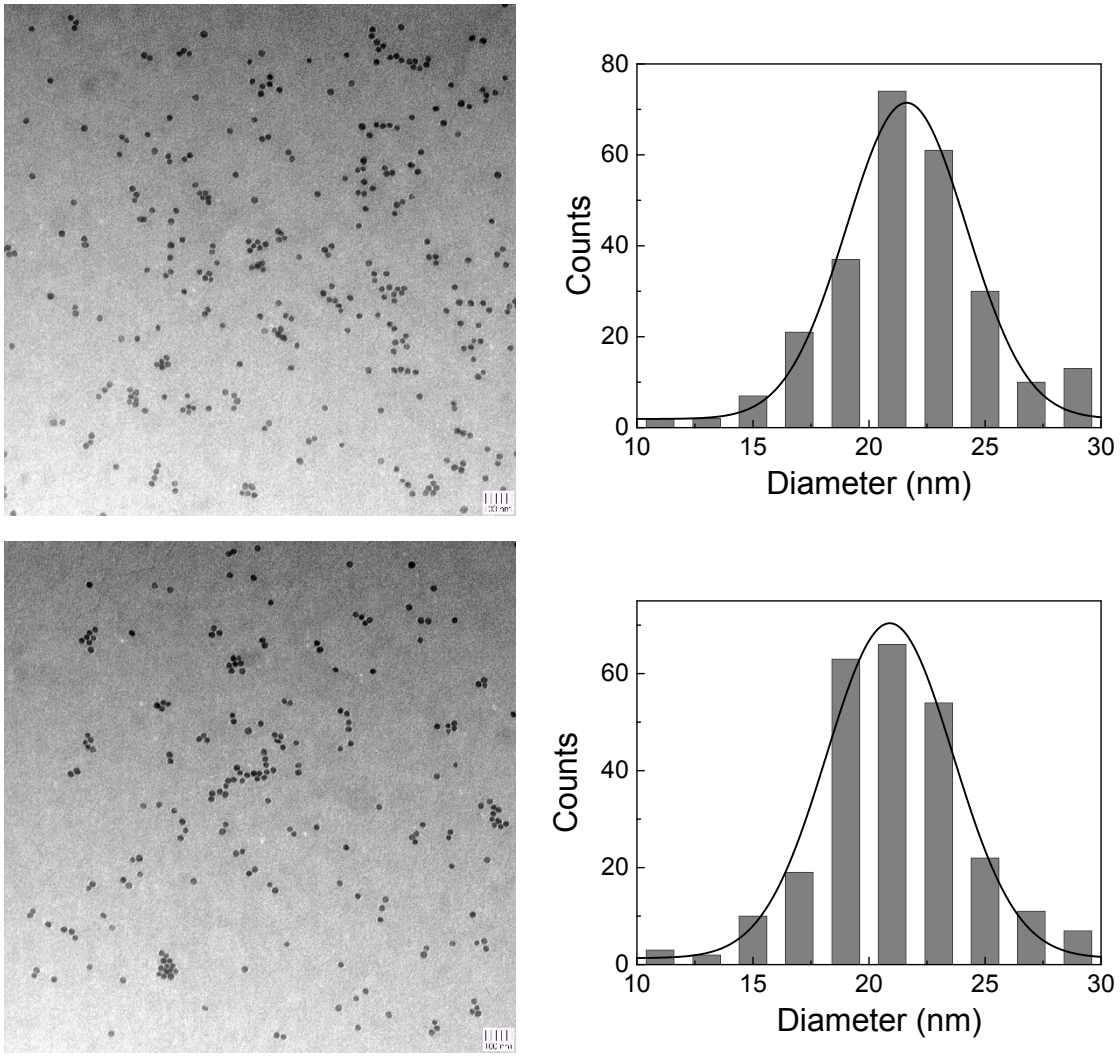


Fig. S2 TEM images of MPA/MPS-AuNPs (top) and MUA/TEG-AuNPs (bottom) and respective size distribution histograms.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a SDT Q600 (TA Instruments). MUA/TEG-AuNP samples (2 - 5 mg) were prepared by drying and the temperature range between 20 ˚C and 700 ˚C was scanned at a rate of 5 ˚C/min under a nitrogen flow of 100 mL/min.

Other Supporting Figures and Tables

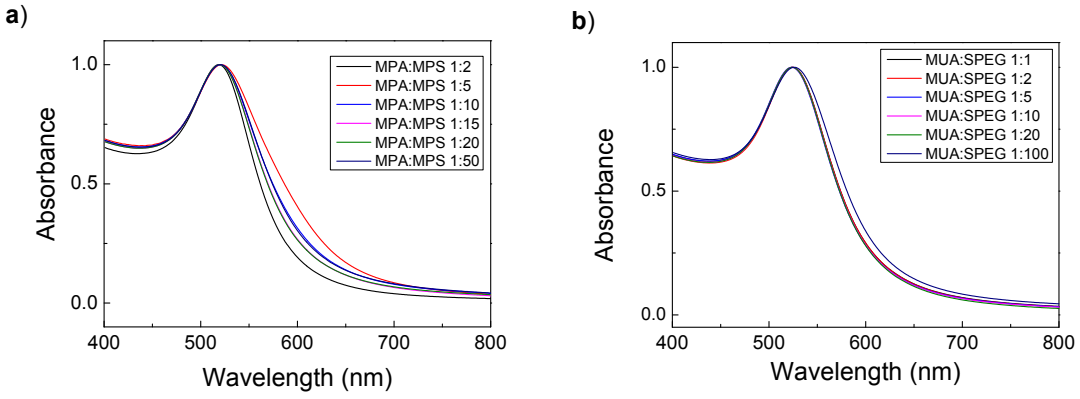


Fig. S3 Normalized absorption spectra of functionalized particles: a) MPA/MPS-AuNPs, b) MUA/TEG-AuNPs.

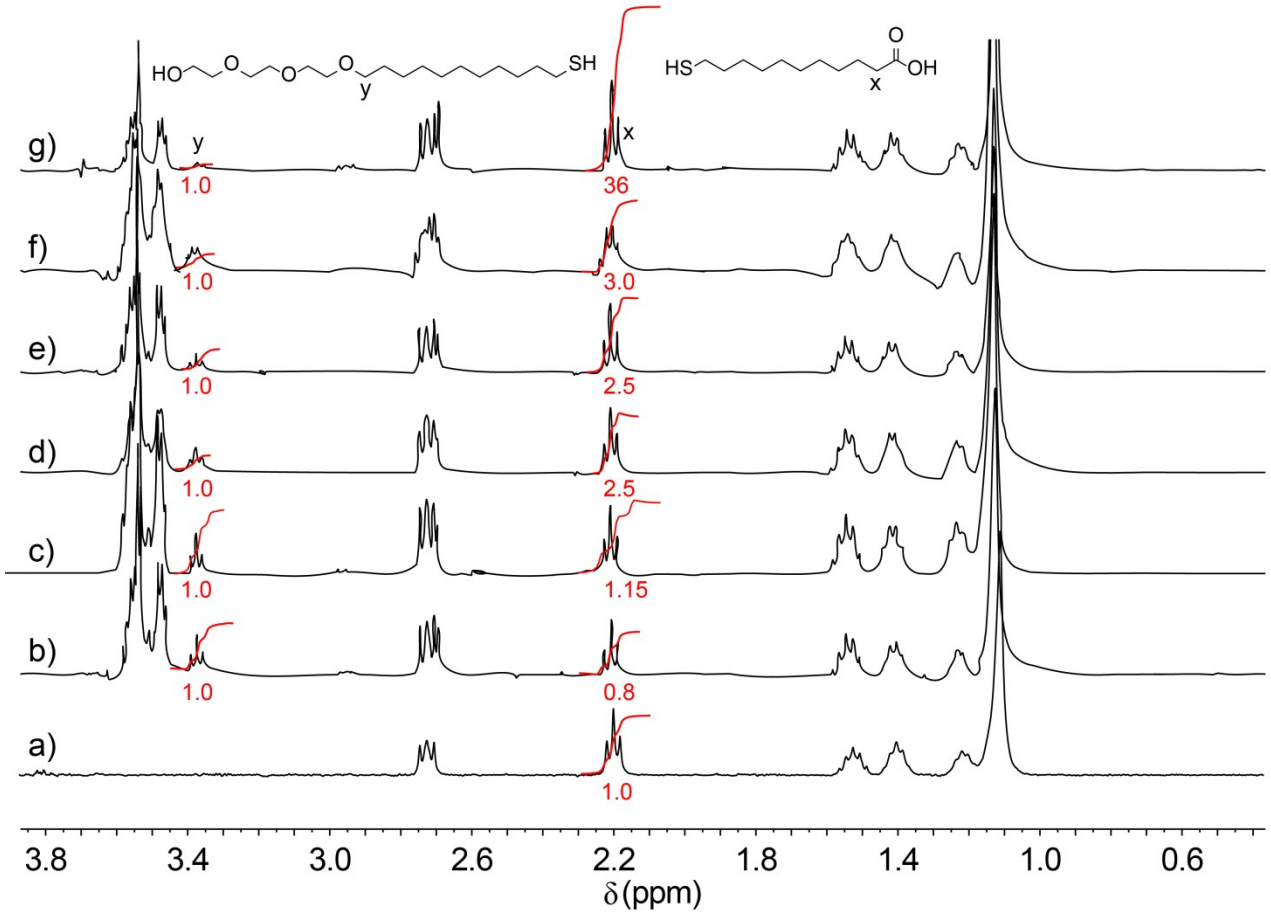


Fig. S4 ^{1}H NMR spectra of MUA/TEG-AuNPs with varying molar ratio of MUA and TEG after digestion with aqua regia and subsequent dilution with D_2O (pD 1.6). a) MUA only and MUA/TEG molar ratio b) 1:1, c) 2:1, d) 5:1, e) 10:1, f) 20:1, g) 100:1.

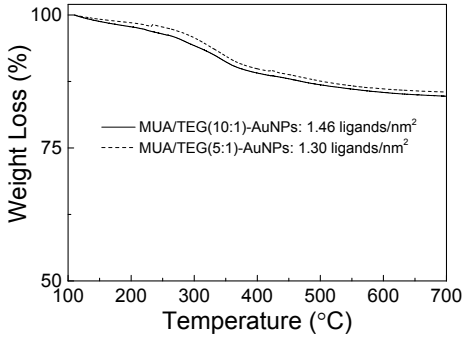


Fig. S5 TGA plots of MUA/TEG-AuNPs coated with different molar ratios of MUA and TEG.

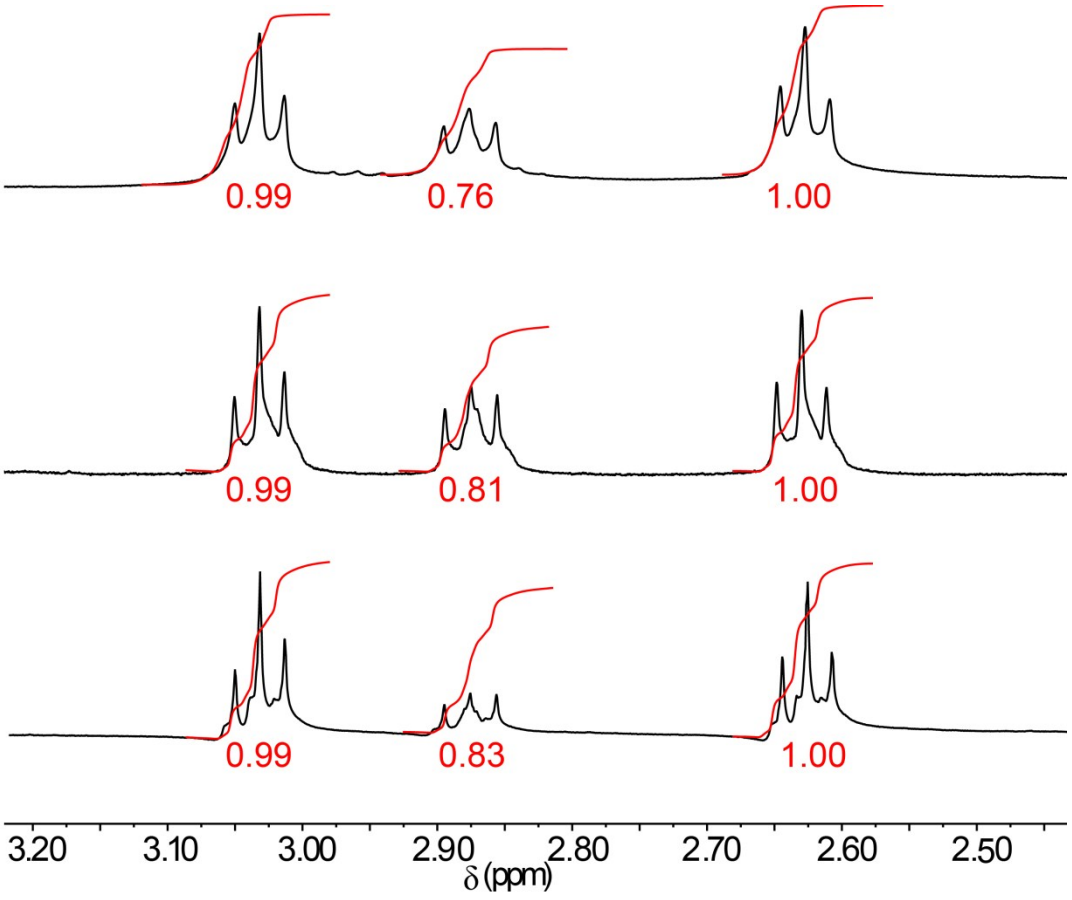


Fig. S6 Reproducibility measurements of different batches of MPA/MPS(1:5)-AuNPs by ^{1}H NMR spectroscopy of after digestion with aqua regia and subsequent dilution with D_2O (pD 1.6).

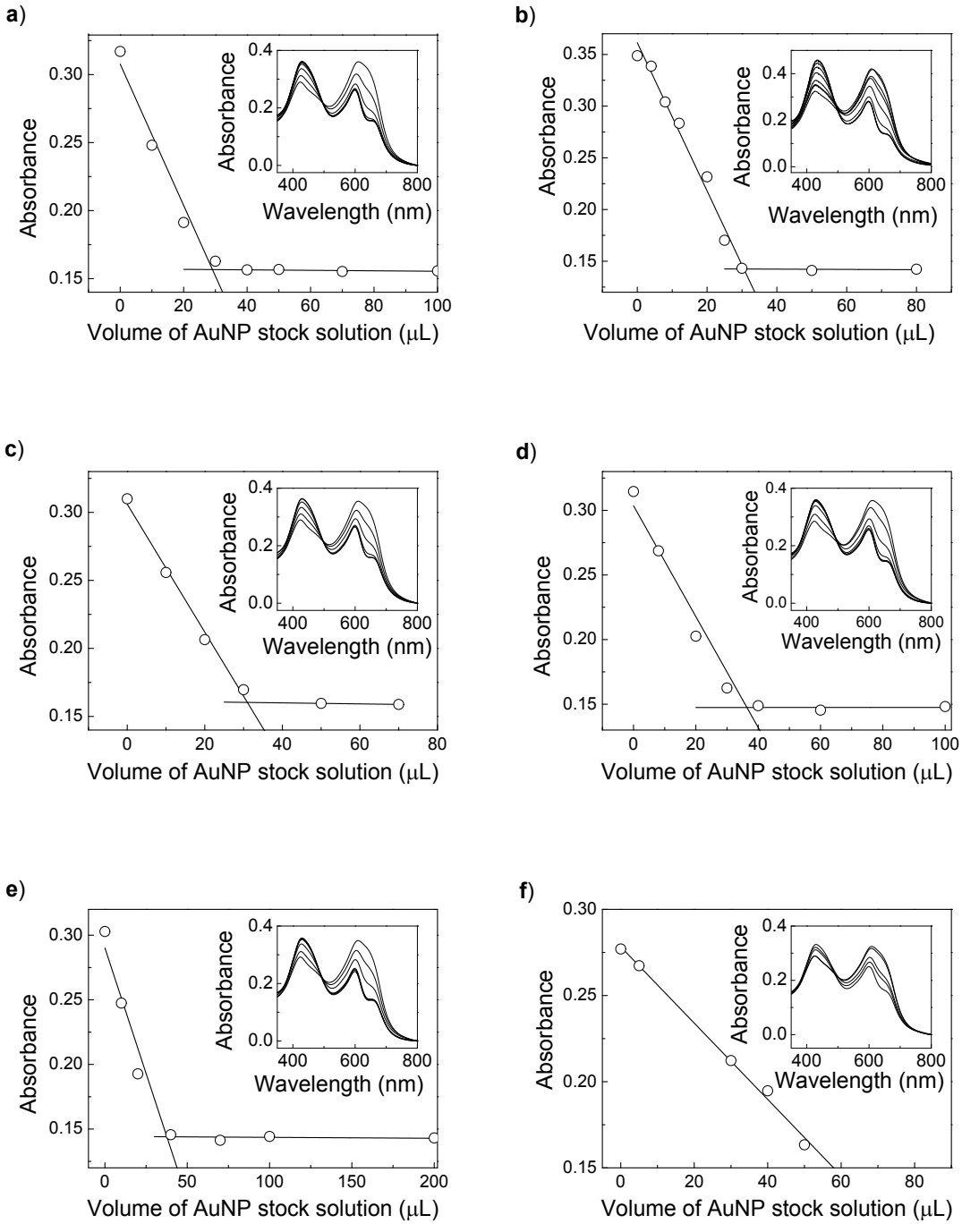


Fig. S7 Results of NiPV assay for quantification of negatively charged surface functional groups on AuNPs. Dependence of the absorbance at 650 nm versus the volume of particles a) MPA only and MPA/MPS molar ratio b) 1:5, c) 1:10, d) 1:30, e) 1:50, f) 1: 83.

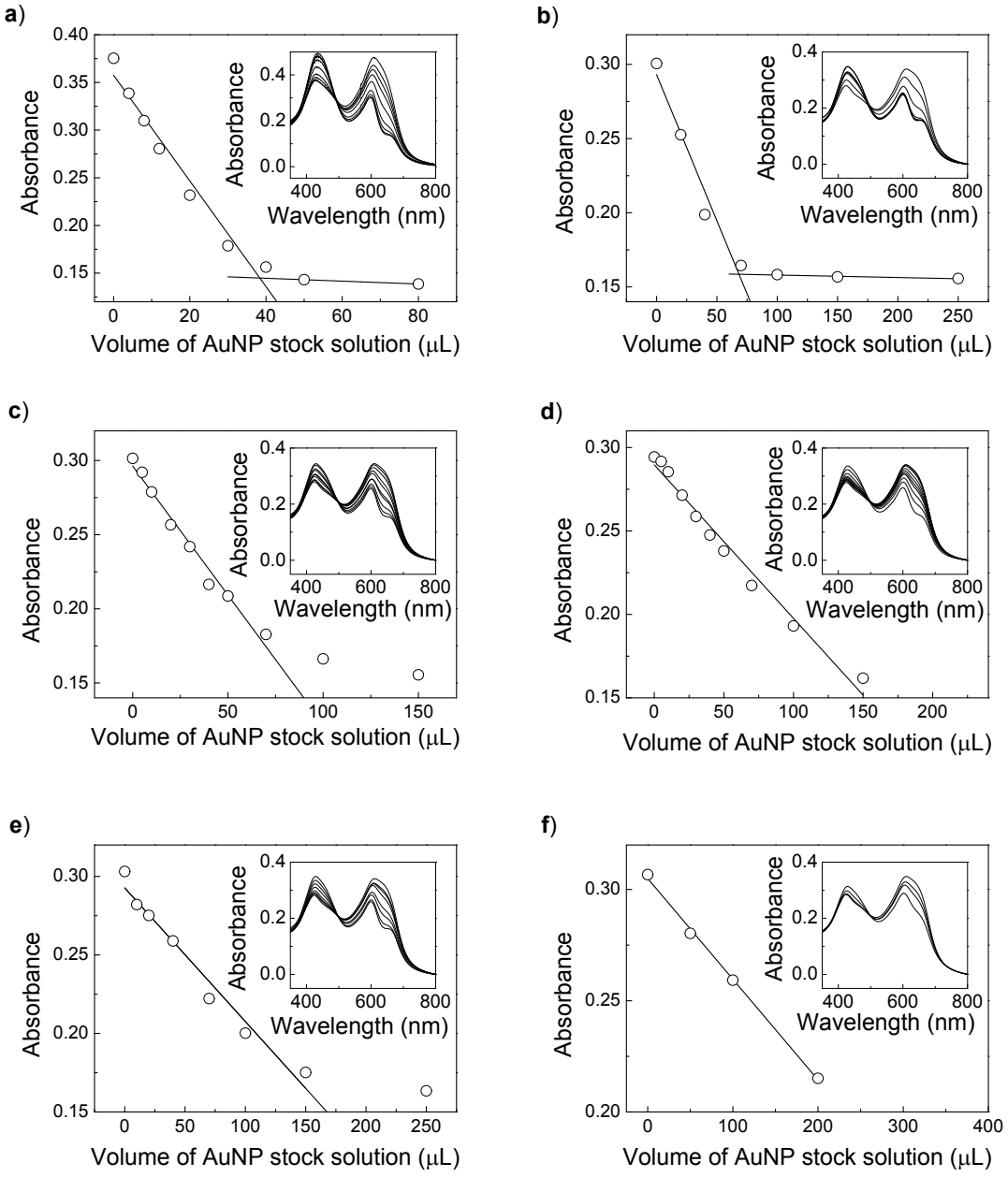


Fig. S8 Results of NiPV assay for quantification of negatively charged surface functional groups on AuNPs. Dependence of the absorbance at 650 nm versus the volume of particles a) MUA only and MUA/TEG molar ratio b) 100:1, c) 20:1, d) 10:1, e) 5:1, f) 2:1.

Table S1. Reproducibility measurements of MPA/MPS(1:5)-AuNPs by the NiPV assay.

Au-MPA/MPS	Ligand density (ligands/nm^2)
Sample 1	5.449
Sample 2	5.374
Sample 3	5.426
Sample 4	5.415
Sample 5	5.578
Sample 6 (different batch)	5.454
Average	5.449 ± 0.070
Coefficient of Variation (%)	1.3

Table S2. Reproducibility measurements of MPA/MPS(1:5)-AuNPs by the CB7 assay.

Au-MPA/MPS	Ligand density (ligands/nm^2)
Sample 1	0.07798
Sample 2	0.07559
Sample 3	0.07902
Sample 4	0.09128
Sample 5	0.08533
Sample 6	0.09279
Average	0.0837 ± 0.0073
Coefficient of Variation (%)	8.6

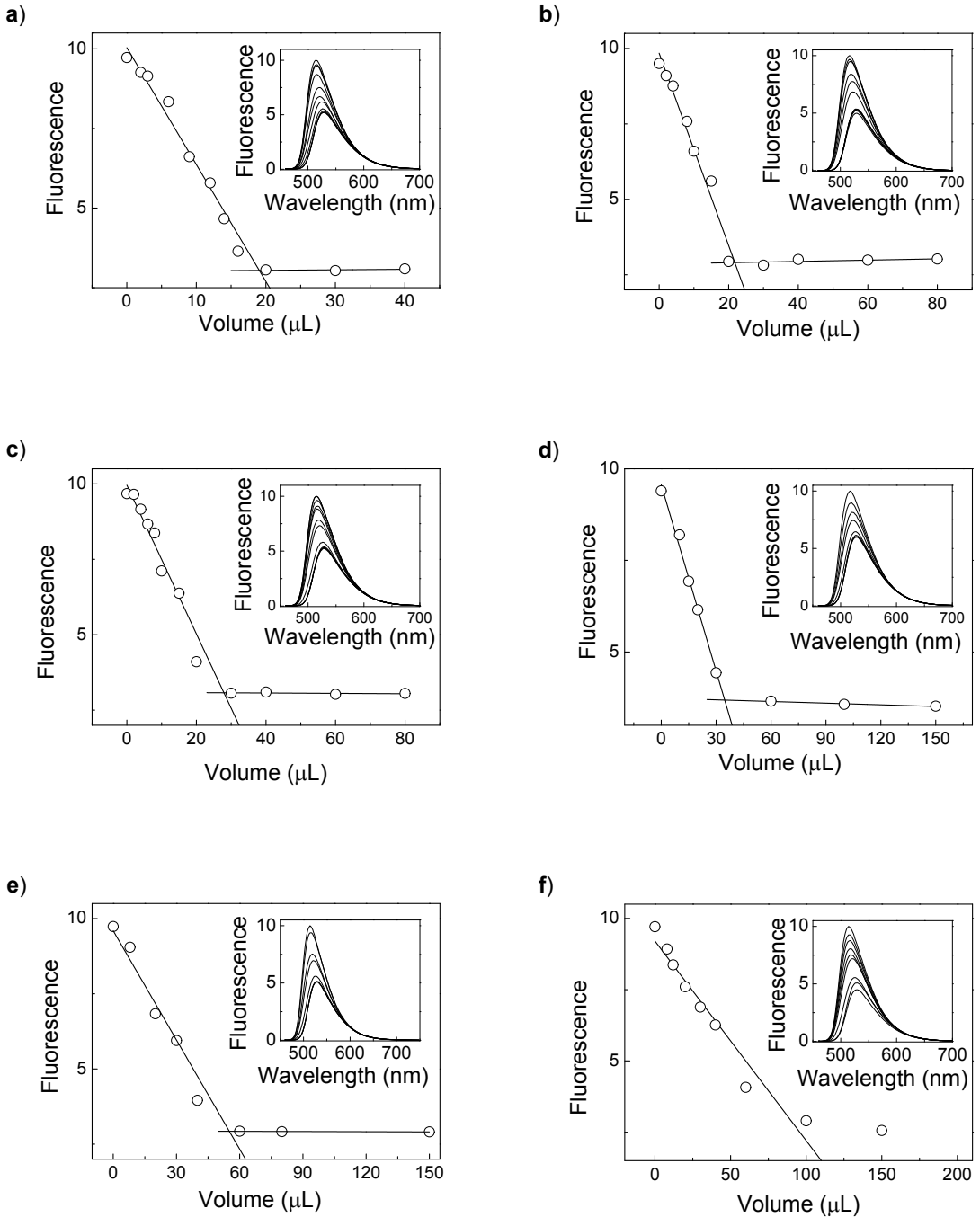


Fig. S9 Results of CB7 assay for quantification of accessible surface functional groups on MPA/MPS-AuNPs a) MPA only and MPA/MPS molar ratio b) 1:5, c) 1:10, d) 1:15, e) 1:30, f) 1:83. Shown is the variation of fluorescence spectra with increasing volume of AuNPs stock solution (see main text for details) (λ_{em} = 510 nm, λ_{exe} = 450 nm).

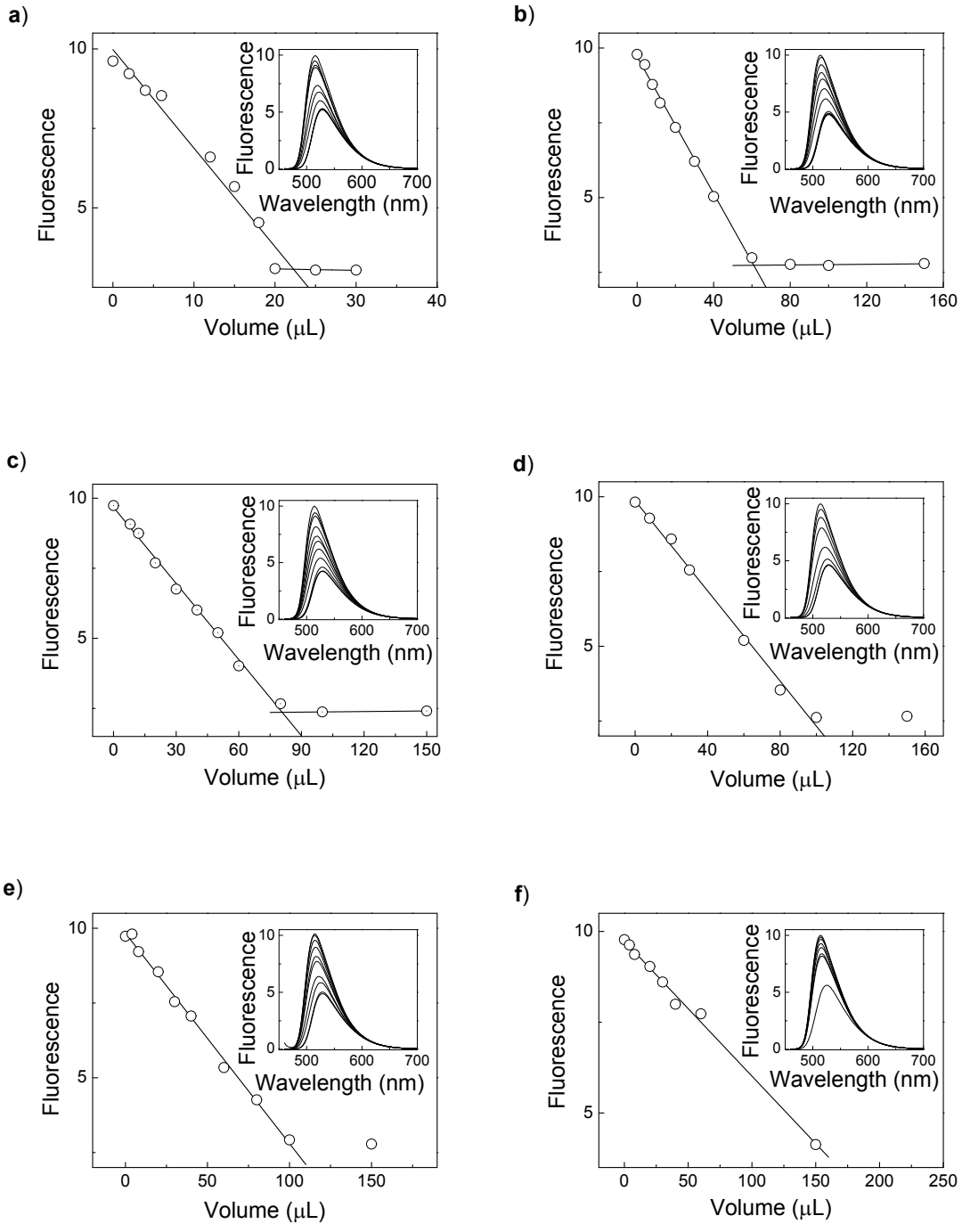


Fig. S10 Results of CB7 assay for quantification of accessible surface functional groups on MUA/TEG-AuNPs a) MUA only and MUA/TEG molar ratio b) 100:1, c) 20:1, d) 10:1, e) 5:1, f) 2:1. Shown is the variation of fluorescence spectra with increasing volume of AuNPs stock solution (λ_{em} = 510 nm, λ_{exe} = 450 nm).