Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information For

Enhancing Near IR Luminescence of Thiolate Au Nanoclusters by Thermo Treatments and Heterogeneous Subcellular Distributions

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Table SI-1. Summary of quantum efficiency enhancements of different gold nanoclusters. The varied parameter is highlighted in bold.

Ligand	Ligand:Au synthesis ratio	Excess ligand added for etching	QE before etching (%)	QE after multi-step etching (%)	Enhancement factor after multi-step etching	Temperature & Duration
The impacts of different temperatures, three-day duration						
MSA	10	10x	0.7	2.8, 3.2, 2.7	4.0, 4.6, 3.9	**50 °C** for 2 days, **60 °C** for 3rd day
MSA	10	10x	0.8	2.2	2.8	**Room temperature** 3 days
The impacts of different thiol:nanocluster ratio, two-day duration (**Fig. SI-1**)						
MSA	3	**5x**	0.6	3.8, 4.1	6.3, 6.8	50 °C 24hrs, 48 hrs
MSA	3	**10x**	0.6	4.1, 5.1	6.8, 8.5	50 °C 24hrs, 48 hrs
MSA	3	**50x**	0.6	3.6, 3.4	6.0, 5.7	50 °C 24hrs, 48 hrs

Ligand	Ligand:Au synthesis ratio	Excess ligand added for etching	QE before etching (%)	QE after etching (%)	Enhancement factor	Temperature & Duration
Different Au nanoclusters from different thiol:Au synthetic ratio						
MSA	**3**	10x	0.3	1.6	5.3	50 °C 24 hours
MSA	**10**	10x	0.3	1.5	5.0	50 °C 24 hours
MSA	**15**	10x	0.4	3.3	8.2	50 °C 24 hours
Reproducibility from different batches						
MSA	15	10x	**0.8**	4.5	5.6	50 °C 24 hours
MSA	15	10x	**0.6**	4.0	6.7	50 °C 24 hours
MSA	15	10x	**1.7**	7.8	4.6	50 °C 24 hours
Different ligand						
Tiopronin	3	10x	**1.8**	6.6	3.7	50 °C 24 hours
Tiopronin	3	10x	**0.7**	4.1	5.9	50 °C 24 hours
Tiopronin	3	10x	**3.2**	5.4	1.7	50 °C 24 hours
Tiopronin	3.4	10x	**4.6**	9.8	2.1	50 °C 24 hours
Average enhancement factor					**4.9**	

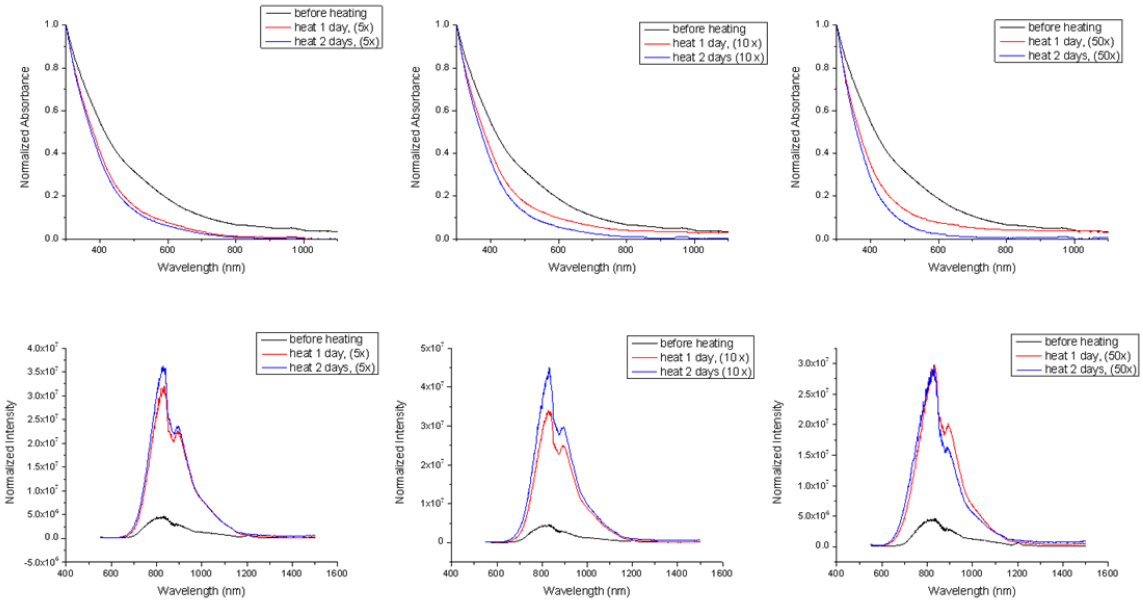

Figure SI-1. Normalized absorbance (300 nm, top) and luminescence (excitation, 450 nm, bottom) spectra of Au-MSA NCs before, during, and after heating at 50 °C in presence of excess thiol. A 5X, 10X or 50X excess thiol was added to a solution containing the same Au-MSA NCs respectively during heating at 50 °C. Data listed in Table SI-1.

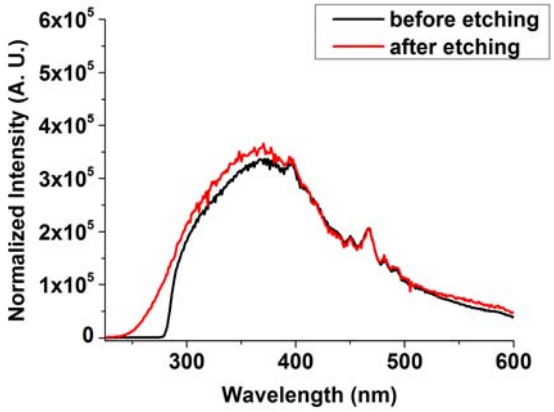

Figure SI-2. Excitation spectra of Au-Tio nanoclusters before and after etching with excess tiopronin at 50 °C for 24 hours. Spectra were normalized at 467 nm to illustrate similarity.

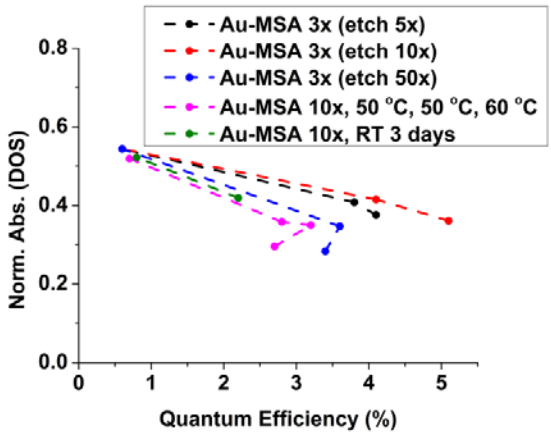

Figure SI-3.The changes in absorption curvature and QE. The absorbance value at 400 nm was used as Norm. Abs. to reflect the curvature, or DOS, by normalizing the absorbance at 300 nm to 1 in each corresponding spectrum. Note the QE decreases at higher concentrations of excess thiol, higher temperatures, or both at longer durations. Data listed in Table SI-1.

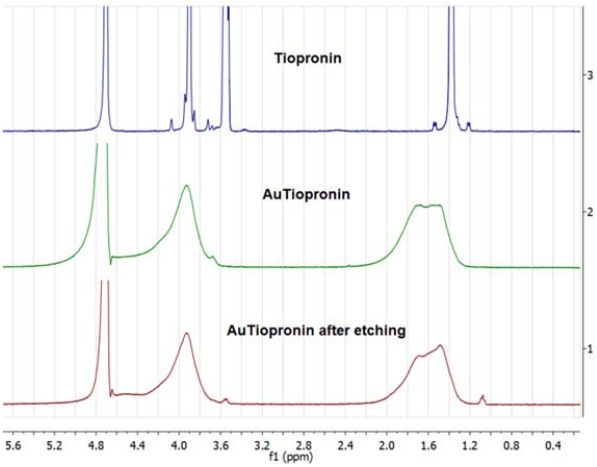

Figure SI-4.^{1}H NMR spectra of tiopronin protected gold nanoclusters before (green) and after (red) etching with excess tiopronin (blue, free tiopronin molecules) at 50 °C for 24 hours.

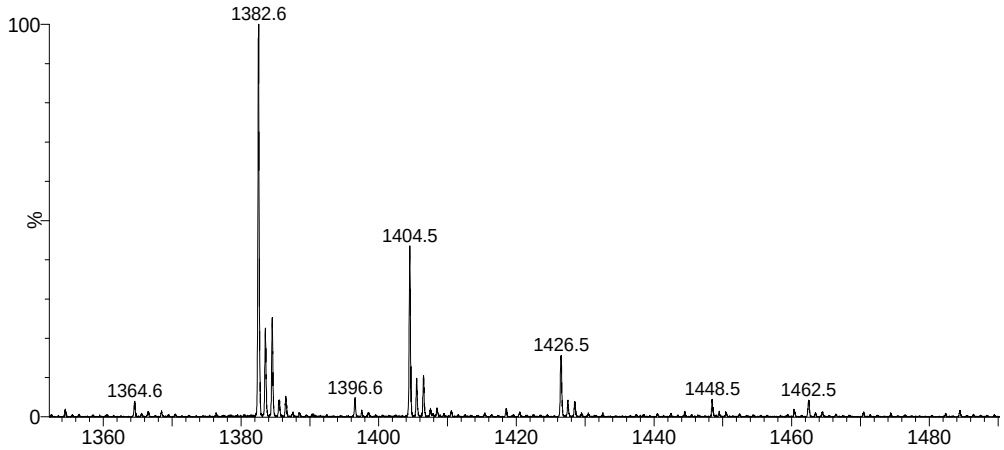

Figure SI-5. ESI-Q-TOF mass spectrum of Au-MSA nanoclusters under negative mode. Peak at 1383 m/z corresponds to Au_4MSA_4 fragment with visible H^+-Na^+ ion exchange patterns (+/- 22 m/z).

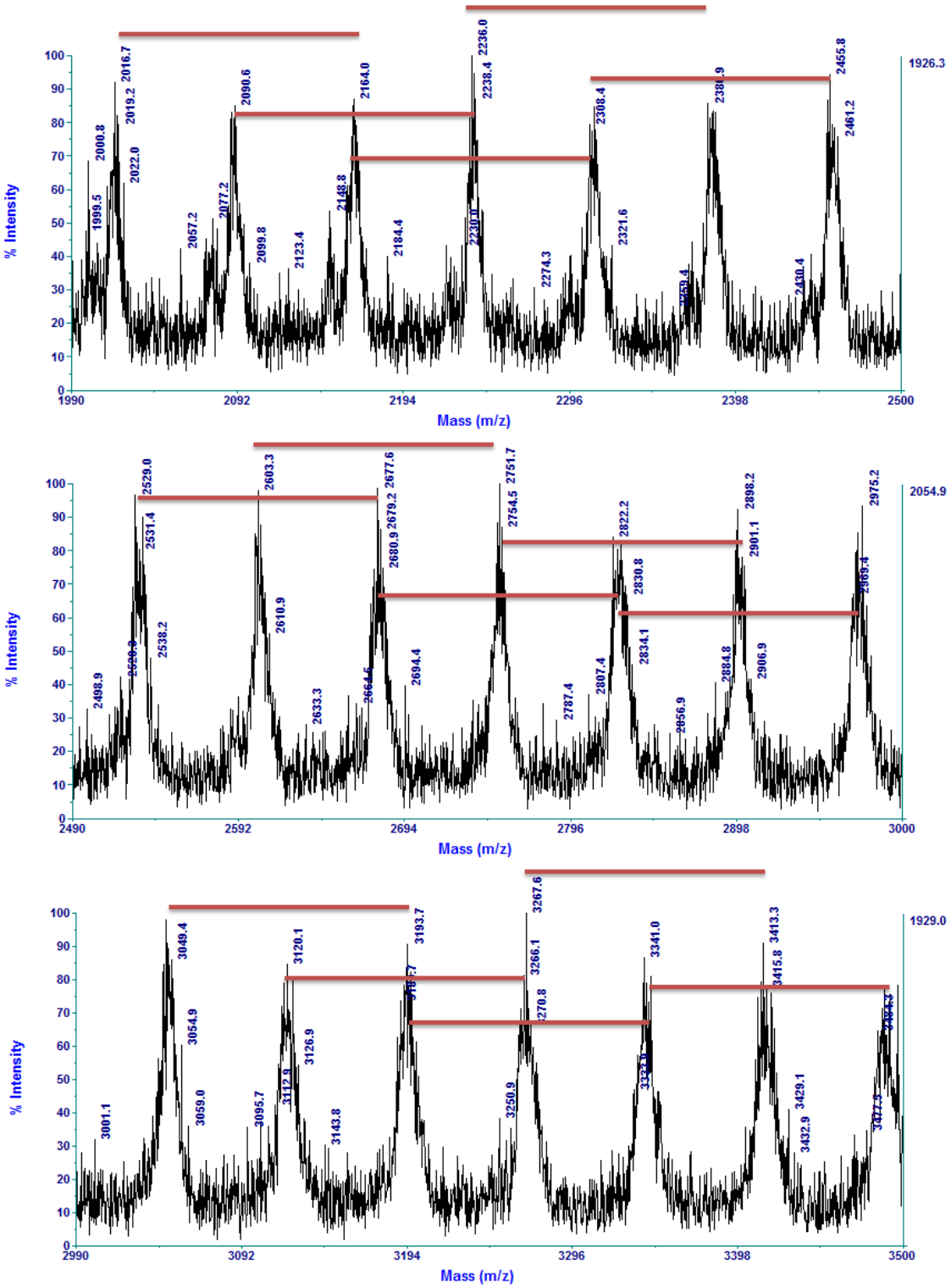

Figure SI-6. MALDI mass spectra of Au-MSA NCs. Note the red bars illustrate uniform spacing at ca. 149 m/z between peaks that corresponds to a difference of the MSA ligand. Data collected under linear negative mode using CHCA as matrix.

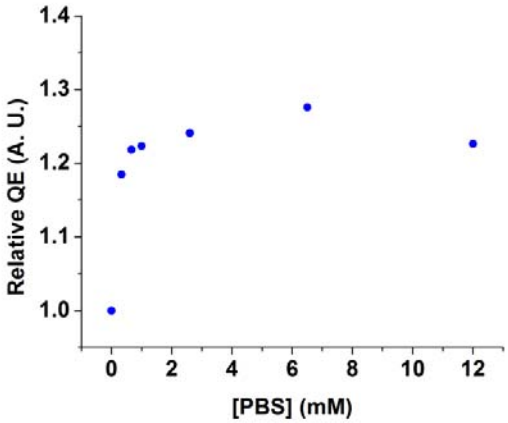

Figure SI-7. Relative QE of Au-MSA nanoclusters dissolved in water and titrated with PBS.

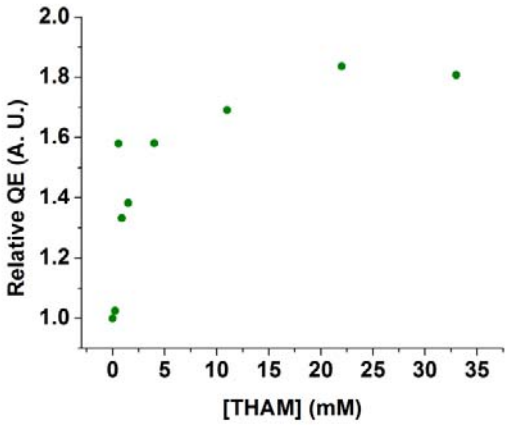

Figure SI-8. Relative QE of Au-MSA nanoclusters dissolved in water and titrated with THAM.

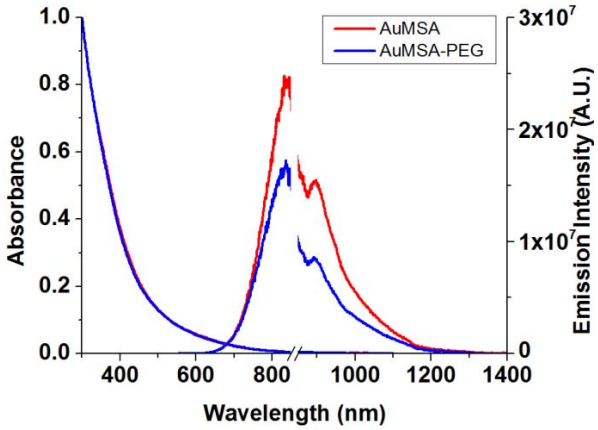

Figure SI-9. UV-vis absorbance and emission spectra of Au-MSA NCs before and after coupling reaction with methoxypolyethylene glycol amine. Break in wavelength axis indicates the data from two different detectors.

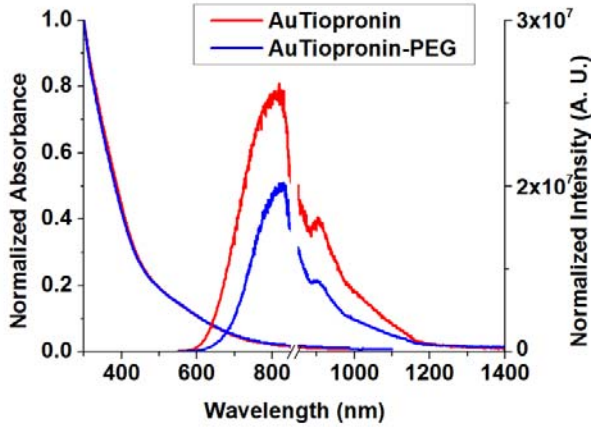

Figure SI-10. UV-vis absorbance and emission spectra of Au-Tio NCs before and after coupling reaction with methoxypolyethylene glycol amine. Break in wavelength axis indicates joining data from two different detectors.

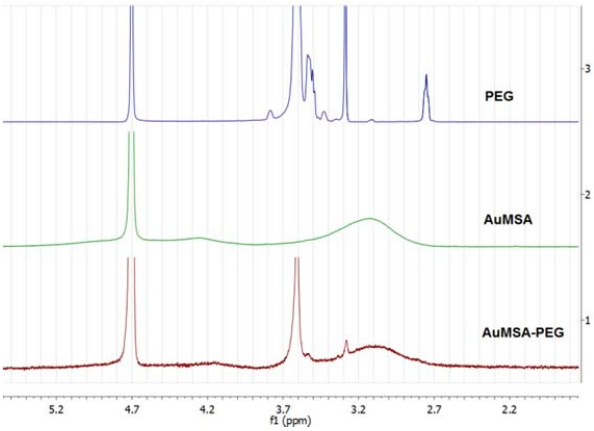

Figure SI-11. ^{1}H NMR spectra of Au-MSA nanoclusters before (green) and after (red) coupling with methoxypolyethylene glycol amine (blue).

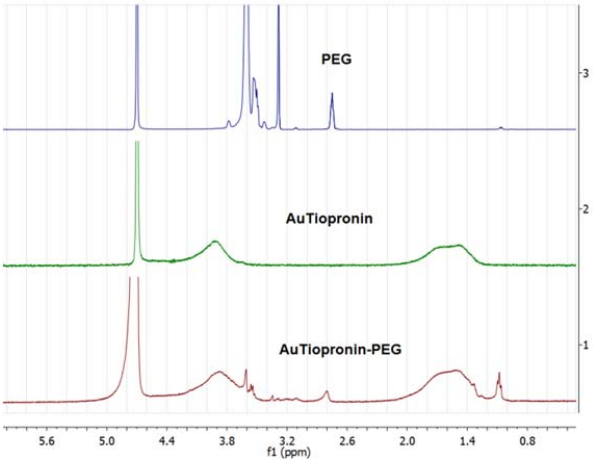

Figure SI-12. ^{1}H NMR spectra of Au-Tio nanoclusters before (green) and after (red) coupling with methoxypolyethylene glycol amine (blue).