Supporting Information

The underlying mechanisms for the modulation of self-assembly and the intrinsic fluorescent properties of amino acid-functionalized gold nanoparticles

Soumya Kanti De, Avijit Maity and Anjan Chakraborty*

Indian Institute of Technology Indore, Discipline of Chemistry, Indore-452020, Madhya Pradesh, India. E-mail: anjanc@iiti.ac.in

Calculation of local concentration of amino acid on Au NPs surface:

In *5 mL* solution, concentration of amino acid is *1mM.*

Moles of amino acid = Concentration of amino acid × Volume of the solution

$= 1 \times 10^{-3}\ M \times 5 \times 10^{-3}\ L$

$= 5 \times 10^{-6}\ mol$

Number of amino acid molecules =Moles of amino acid × Avogadro number

$= 5 \times 10^{-6}\ mol \times 6.023 \times 10^{23}\ mol^{-1}$

$= 3.0115 \times 10^{18}$

In *5 mL*, concentration of $HAuCl_4.4H_2O$ is *0.75mM*

Moles of gold salt = $0.75 \times 10^{-3}\ M \times 5 \times 10^{-3}\ L$

$= 3.75 \times 10^{-6}\ mol$

Molar mass of $HAuCl_4.4H_2O$ is $411.945\ g.mol^{-1}$

Mass of gold salt = Moles of gold salt × Molar mass

$= 3.75 \times 10^{-6}\ mol \times 411.945\ g.mol^{-1}$

$= 1.55\ mg$

So, the mass of gold taken for NP synthesis (Gold only, not gold salt) = $\frac{196.96}{411.945} \times 1.55\ mg =$ *0.741 mg*

Density of gold = $19.3\ g.cm^{-3}$

Volume of Gold taken = $\frac{0.741 \times 10^{-3}\ \text{g}}{19.3\ g\ cm^{-3}} = 3.84 \times 10^{-5}\ cm^3$

For this calculation the average size of the Au NPs was taken (d) = *8 nm.*

Volume of single Au NP $= \frac{4}{3}\pi(4 \times 10^{-7})^3 = 2.68 \times 10^{-19}\ cm^3 = 2.68 \times 10^{-22}\ L$

Number of nanoparticles in solutions = $\frac{3.84 \times 10^{-5}}{2.68 \times 10^{-19}} = 1.43 \times 10^{14}$

Number of amino acid present in a single nanoparticle = $\frac{3.0115 \times 10^{18}}{1.43 \times 10^{14}} = 2.1059 \times 10^{4}$

Number of moles of amino acid on a single Au NP surface = $\frac{2.1059 \times 10^4}{6.023 \times 10^{23}} = 3.496 \times 10^{-20}\ mol$

The concentration of amino acids in a single Au NP surface = $\frac{3.496 \times 10^{-20}}{2.68 \times 10^{-22}}\ \frac{mol}{L}$ = 131 M.

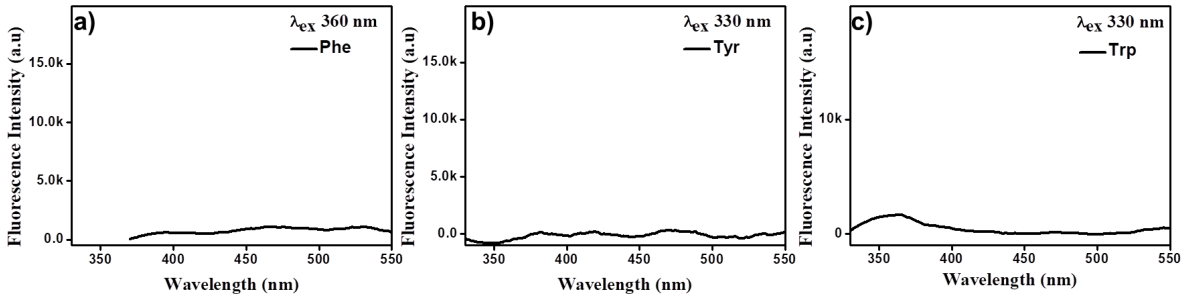

Figure S1: Fluorescence emission spectra of amino acids for a) Phe, b) Tyr, and c) Trp upon excitation at 360 nm (for Phe) and 330 nm (for Tyr and Trp).

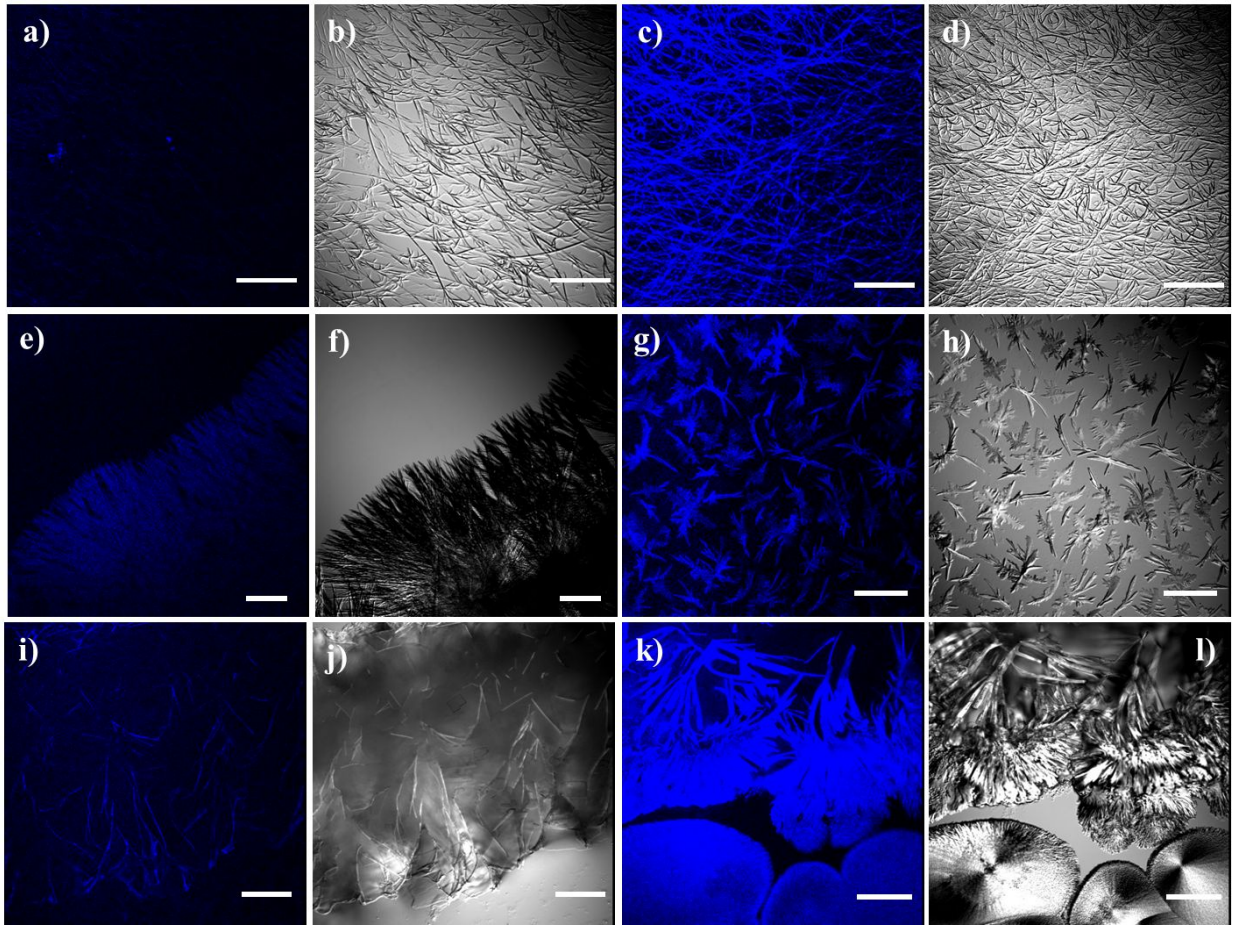

Figure S2: CLSM and bright-field images of a,b) Phe, e,f) Tyr and i,j) Trp and amyloid-like fibril (F_{AA}) of c, d) F_{Phe}, g, h) F_{Tyr} and k, l) F_{Trp}. The F_{AA}s assemblies show intense fluorescence signal specifically from the amyloid structure compared to the blank amino acids. (Scale bar 10 μm).

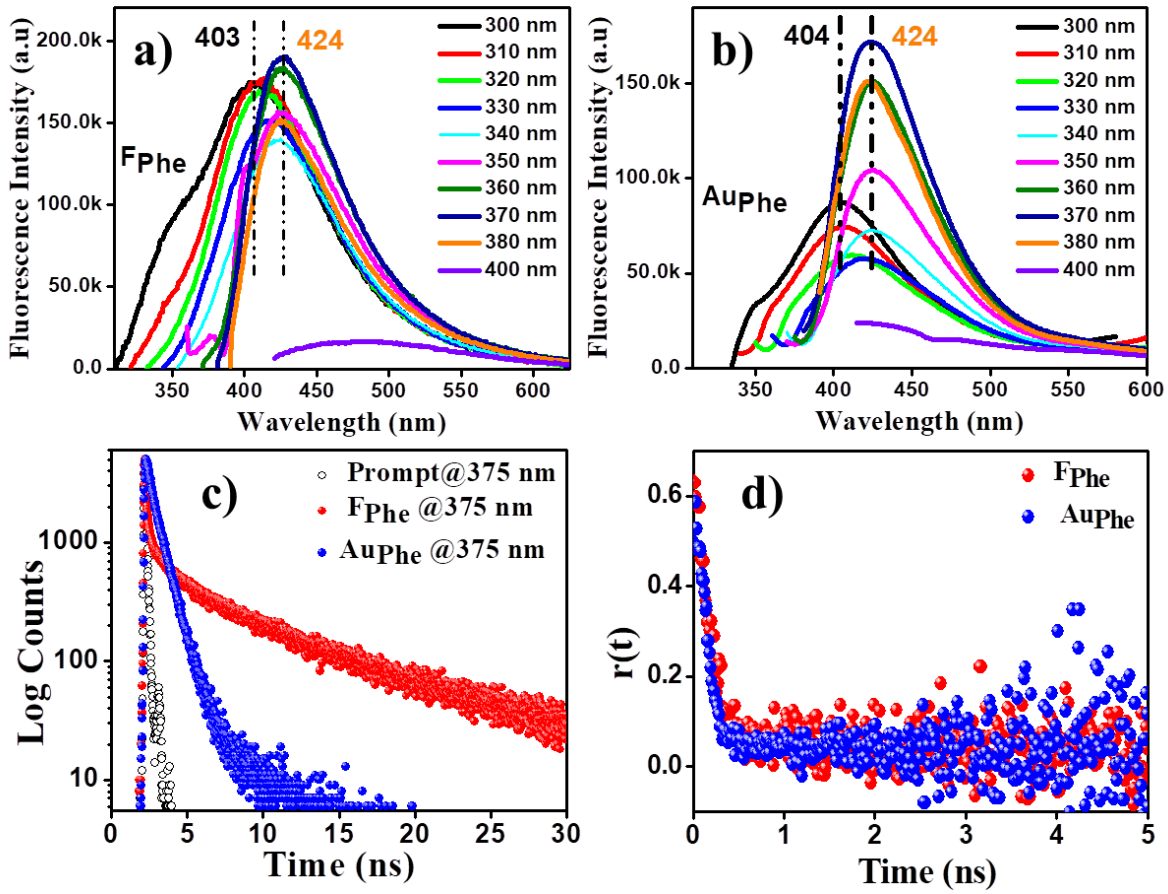

Figure S3: Excitation dependent emission spectra of a) F_{Phe} and b) Au_{Phe} at different λ_{ex} values. Time-resolved decay curves c) and anisotropy decay of F_{Phe} and Au_{Phe} at 424 nm (λ_{ex} = 375 nm).

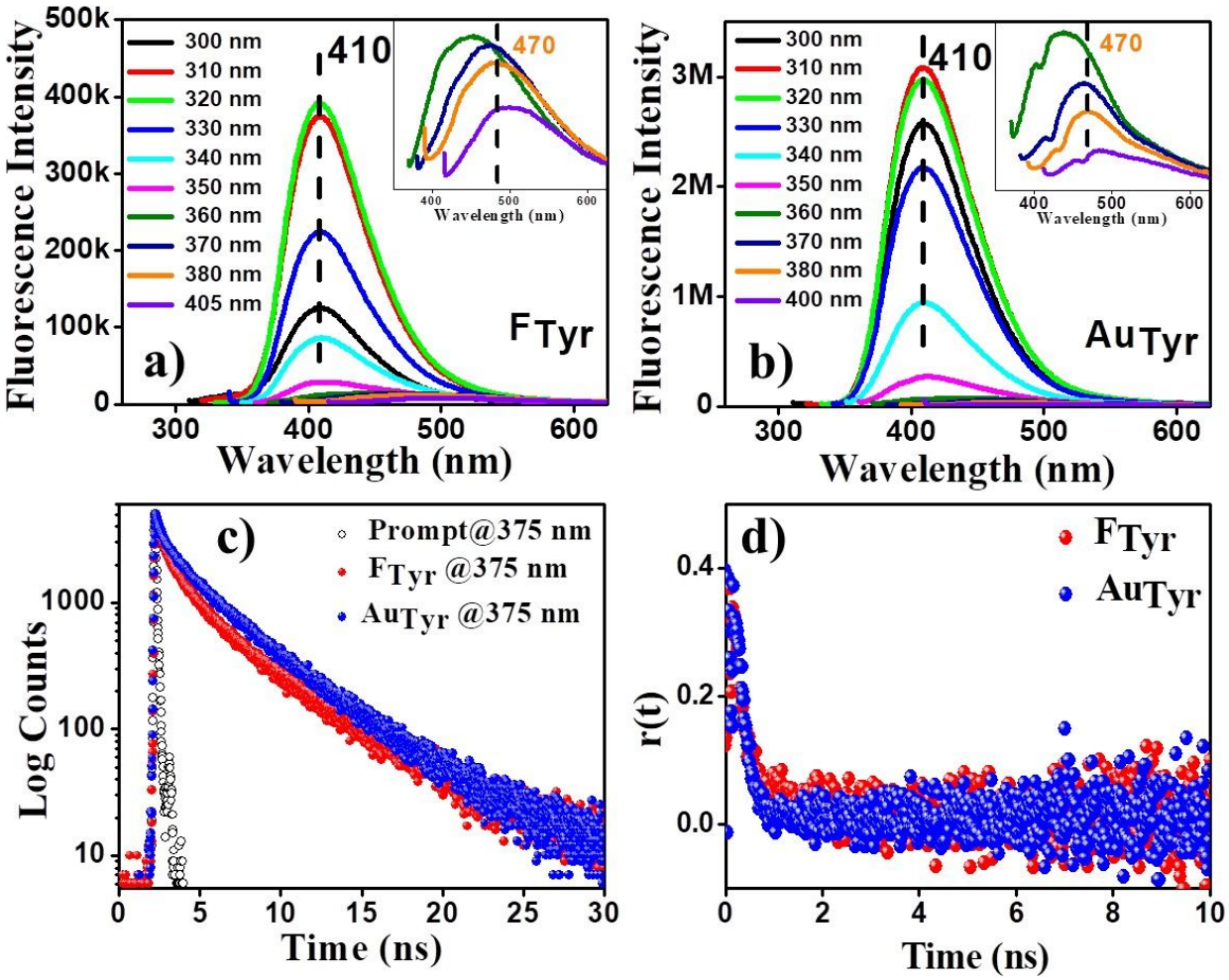

Figure S4: Excitation dependent emission spectra of a) F_{Tyr} and b) Au_{Tyr} at different λ_{ex} values. Time-resolved decay curves c) and anisotropy decay of F_{Tyr} and Au_{Tyr} at 460 nm (λ_{ex} = 375 nm).

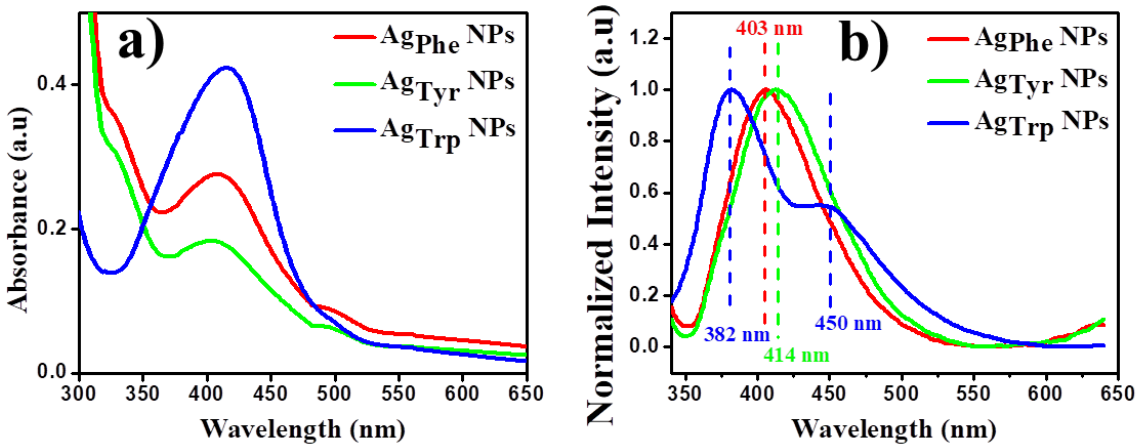

Figure S5: a) UV-Vis spectra and b) normalized emission spectra of aromatic amino acid functionalized silver nanoparticles (Ag_{AA} NPs).

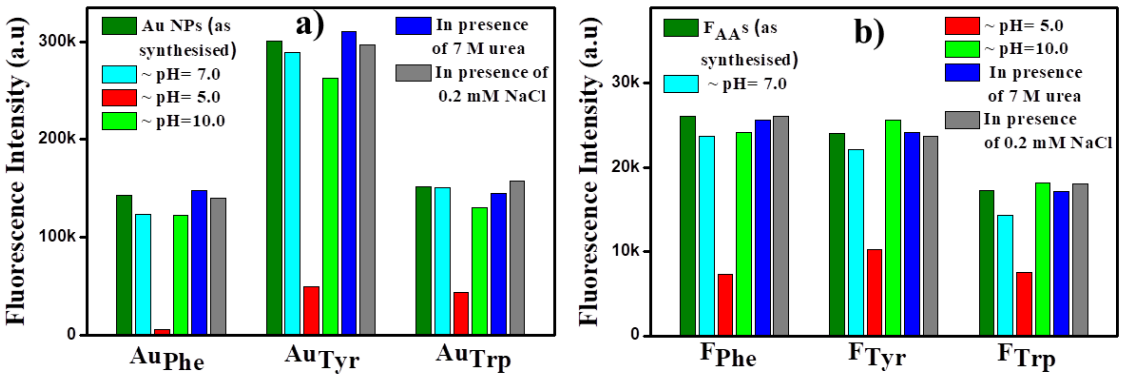

Figure S6: Effect of external stimuli on fluorescence intensity of amino acid-functionalized gold nanoparticles (Au_{AA} NPs) and amyloid-like fibril of amino acids (F_{AA}s). Fluorescence intensity of as-synthesized Au_{AA} NPs and F_{AA}s (Olive), the addition of HCl to as-synthesized Au_{AA} NPs and F_{AA}s to shift the pH of the solution from basic to acidic pH~7.0 (Cyan), pH~5.0 (Red) and addition of NaOH to the same set up to shift the pH of the solution from acidic to basic (Green), effect of urea (blue) and effect of 200 mM NaCl on the synthesized Au_{AA} NPs and F_{AA}s (Gray).

Table S1: Quantum yield of the aromatic amino acid functionalized Au NPs and amyloid-like fibrils.

SN	Sample	Quantum Yield (%)
1	Au_{Phe}	0.6
2	Au_{Tyr}	4.2
3	Au_{Trp}	1.1
4	F_{Phe}	0.2
5	F_{Tyr}	0.5
6	F_{Trp}	0.3

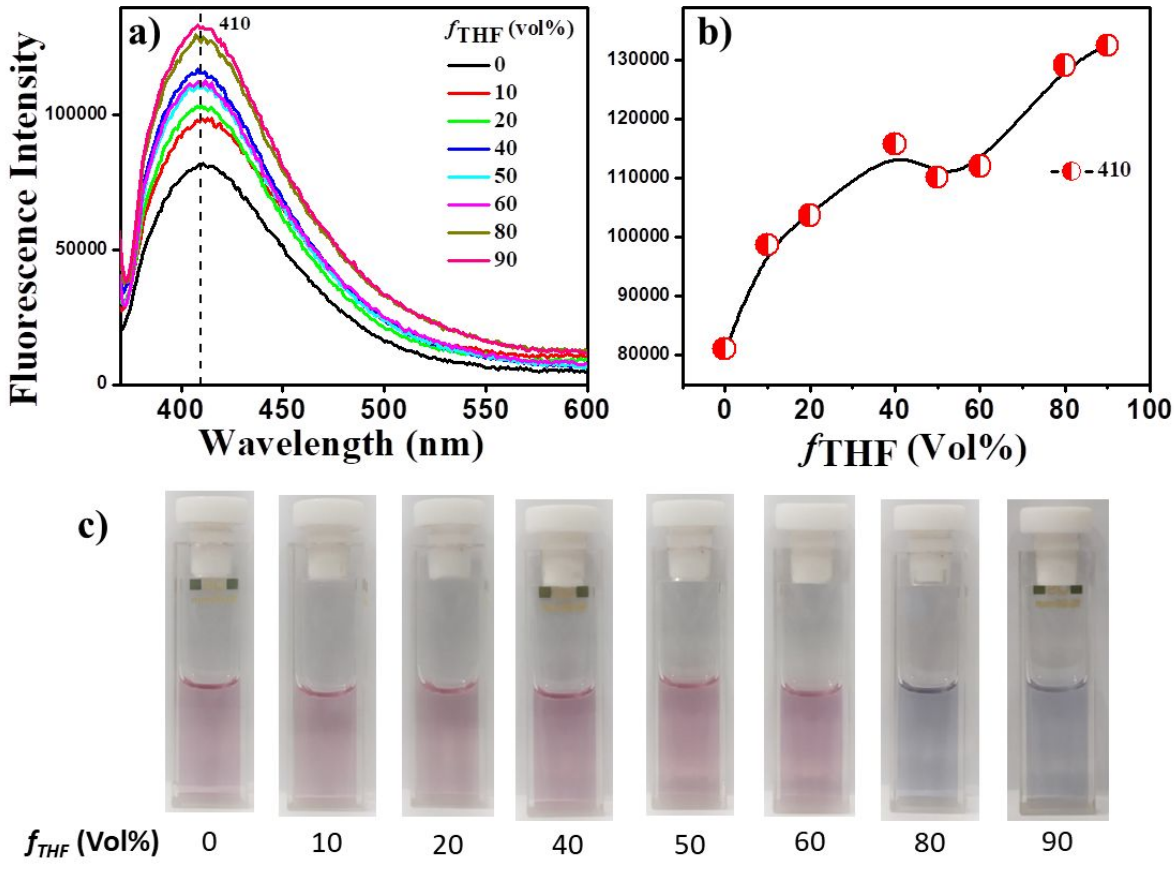

Figure S7: a) fluorescence emission spectra (λ_{ex} 330 nm), b) peak intensities, and c) photographs of Au_{Phe} NPs in water and water/THF mixtures (f_{THF}).

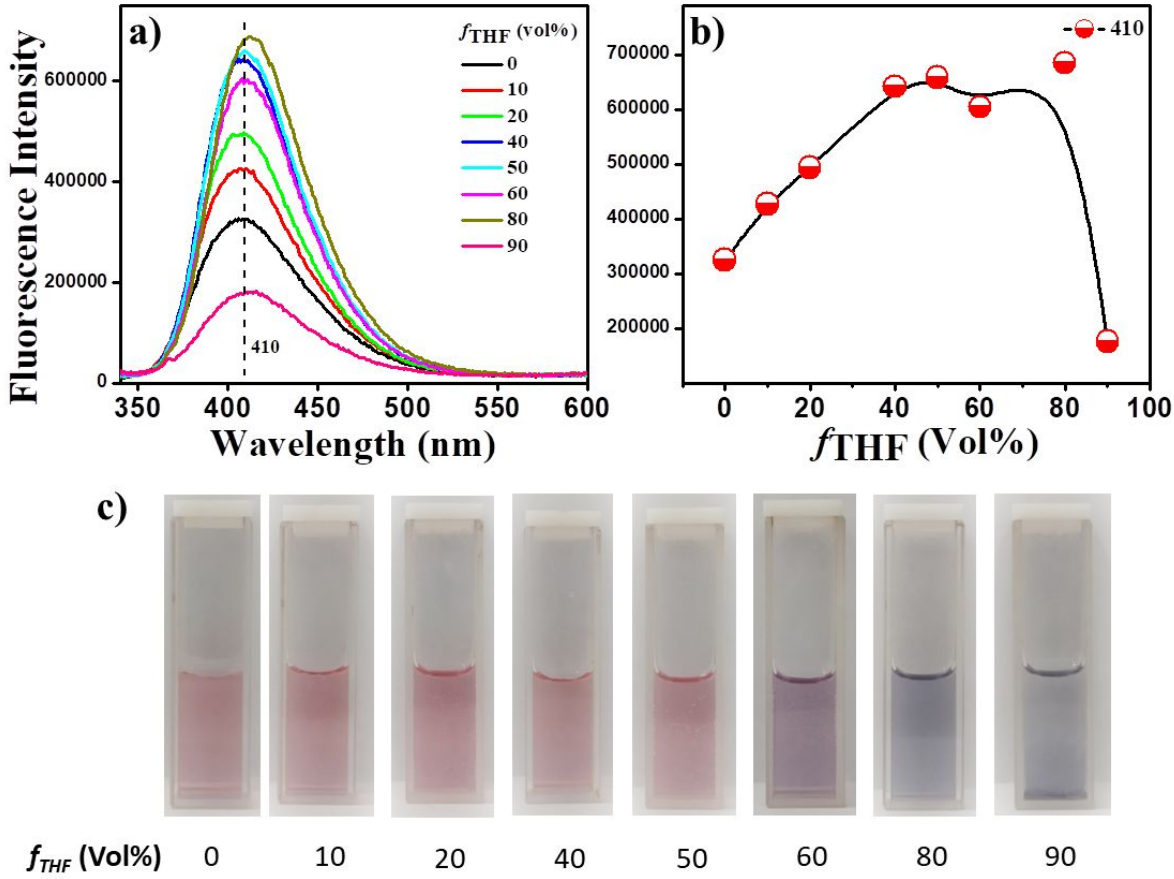

Figure S8: a) fluorescence emission spectra (λ_{ex} 330 nm), b) peak intensities, and c) photographs of Au_{Tyr} NPs in water and water/THF mixtures (f_{THF}).

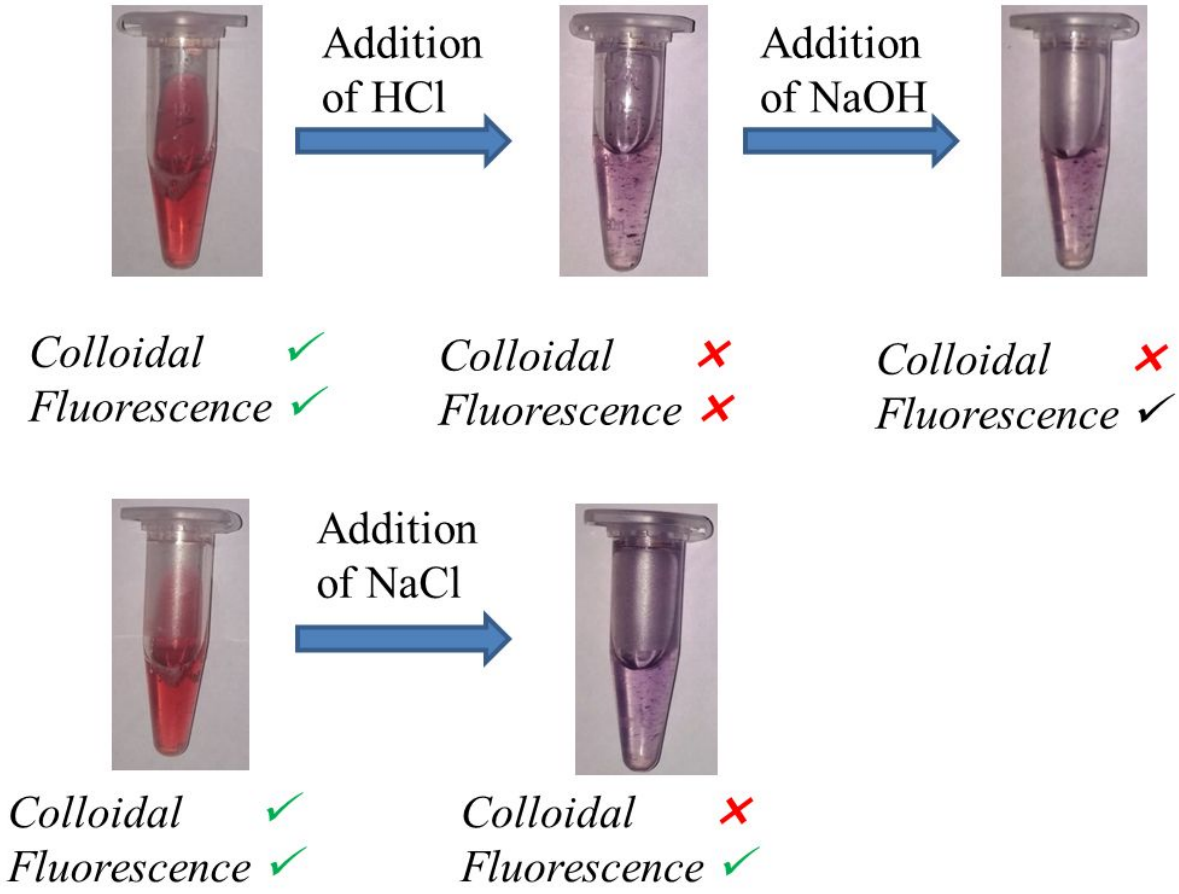

Figure S9: Effect of high concentration of HCl and NaCl on the colloidal stability and fluorescence properties (see Figure S6 also) of Au_{AA} NPs.

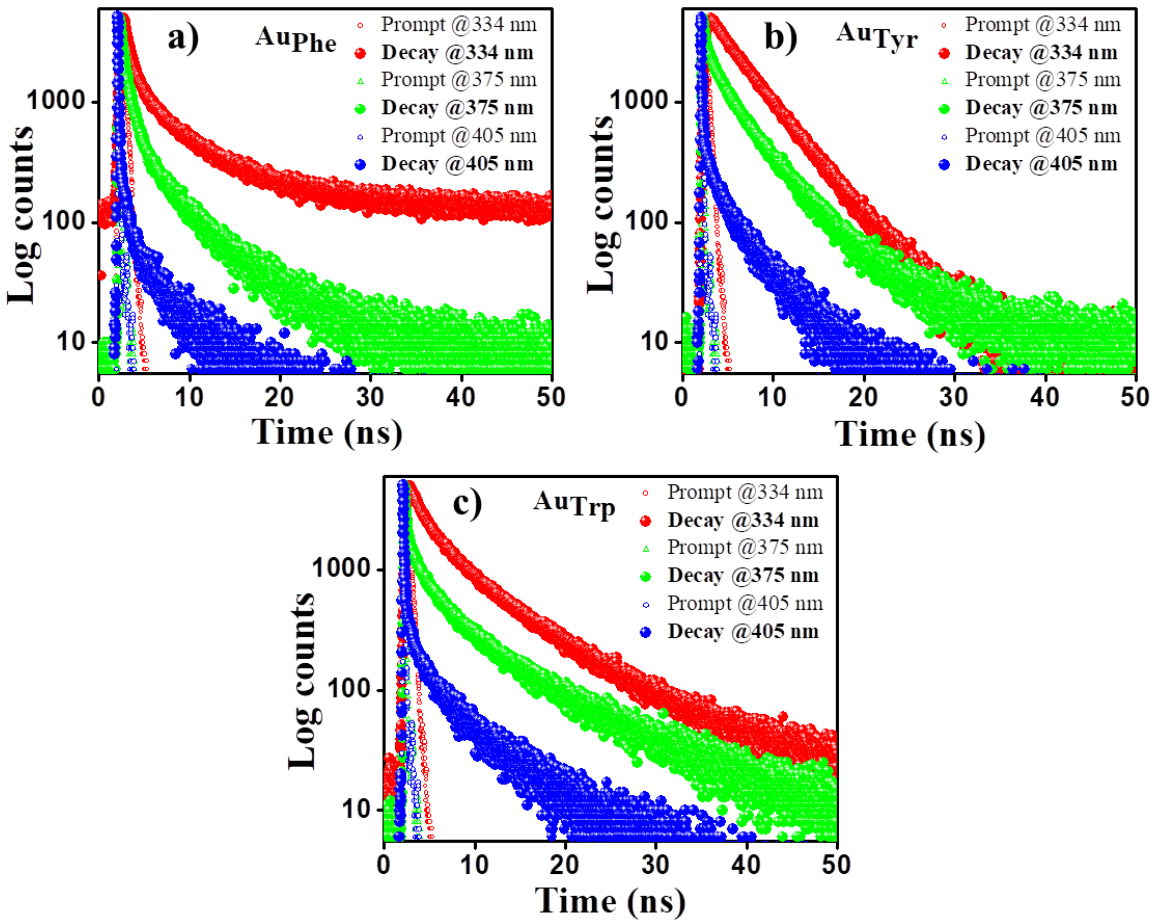

Figure S10: Time-resolved decay curves of a) $Au_{Phe,}$ b) Au_{Tyr} and c) Au_{Trp} solution monitored at 420 nm (λ_{ex} = 334 nm), 460 nm (λ_{ex} = 375 nm), and 480 nm (λ_{ex} = 405 nm).

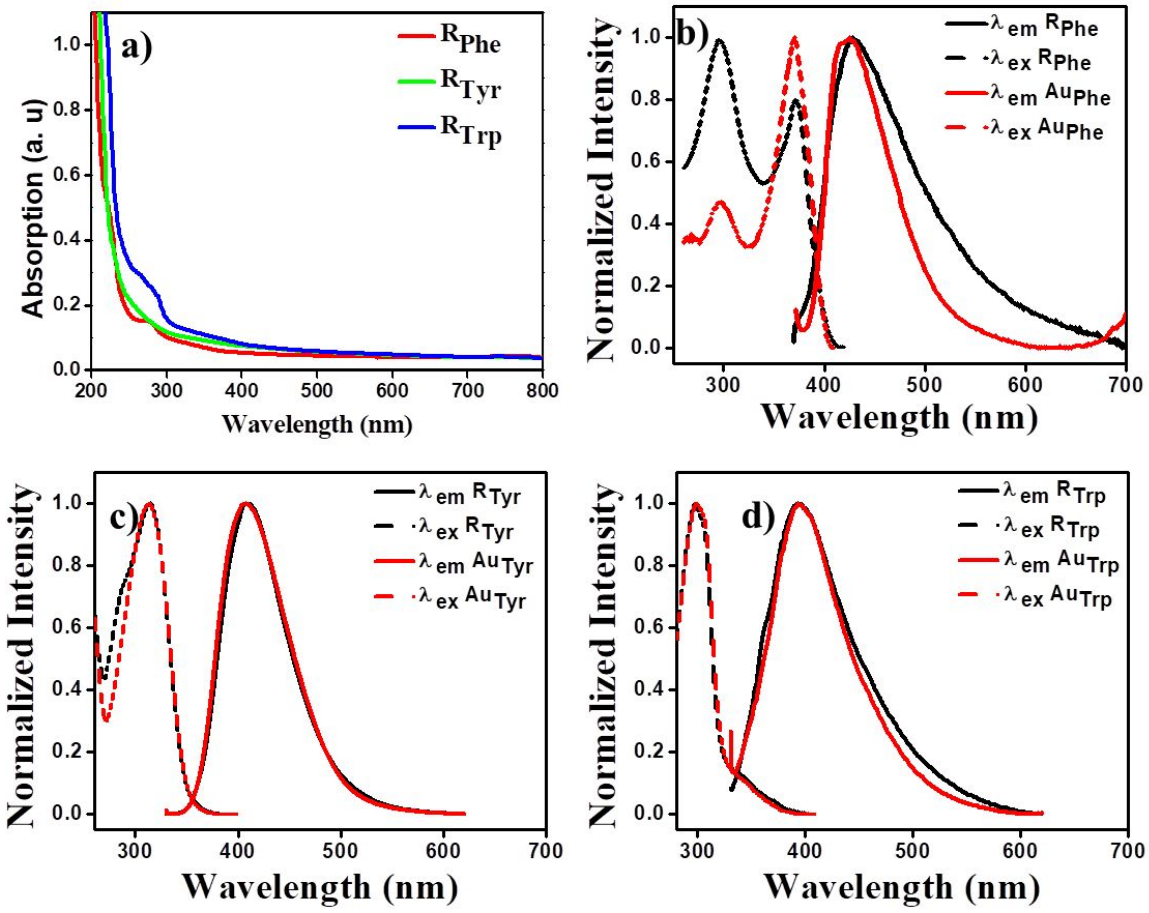

Figure S11: a) UV-Vis spectra and (b-d) normalized excitation and emission spectra of R_{AA} after removal of Au NPs from the Au_{AA} NPs by Ethane-1,2-dithiol (EDT). Absence of SPR peak confirms the removal of maximum Au NPs.

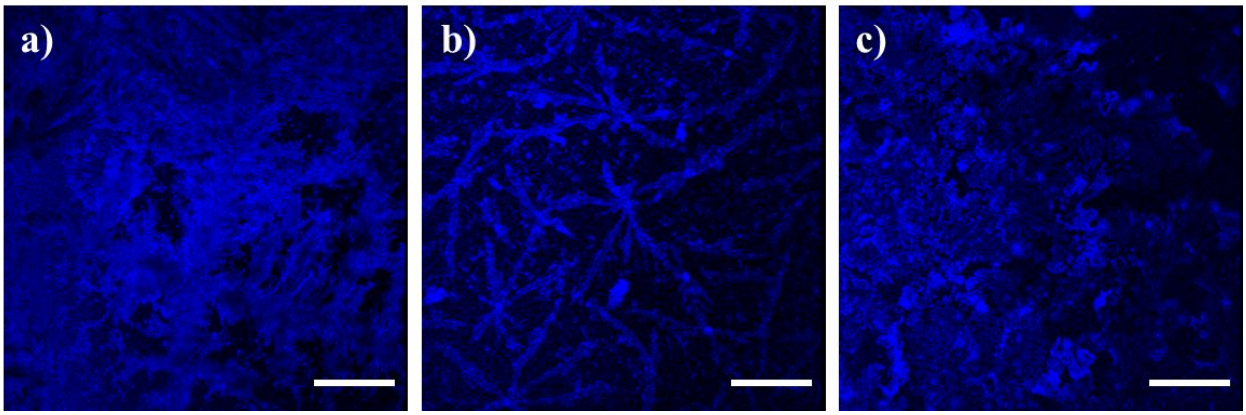

Figure S12: CLSM images of R_{AA} after removal of Au NPs from the Au_{AA} NPs. Scale bar 5 μM.

Table S2: Generalized table of the formation and fluorescence properties of the amino acid-functionalized gold nanoparticles. We purposely avoid the using of thiol-containing amino acids. (a- we also find colloidal and fluorescence properties from 2-hydroxy proline functionalized Au NPs).

Name of the amino Aaid	Formation of colloidal Au_{AA} NPs	Fluorescence properties
Arginine	Yes	Yes
Lysine	Yes	Yes
Histidine	No	No
Aspartic acid	Yes	No
Glutamic acid	Yes	No
Serine	Yes	Yes
Threonine	Yes	Yes
Asparagine	No	No
Glutamine	No	No
Glycine	Yes	Yes
Proline [a]	Yes	Yes
Alanine	Yes	No
Valine	Yes	No
Leucine	Yes	No
Isoleucine	Yes	No
Phenylalanine	Yes	Yes
Tyrosine	Yes	Yes
Tryptophan	Yes	Yes

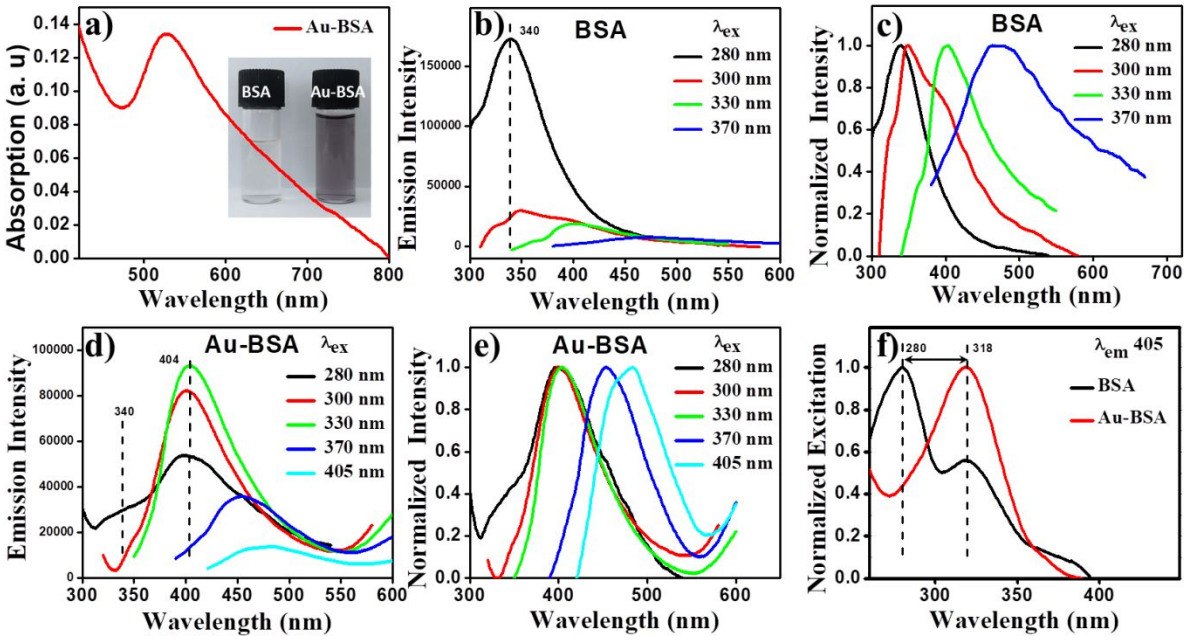

Figure S13: Formation of BSA functionalized gold nanoparticles and their fluorescence excitation and emission spectra. a) UV-Vis spectra of BSA functionalized Au NPs (Au-BSA NPs). b) Emission spectra and c) normalized emission spectra of BSA solution (1mg/ml) at different λ_{ex} values. d) Emission spectra and e) normalized emission spectra of Au-BSA NPs at different λ_{ex} values. f) Normalized excitation spectra of 1 mg/ml BSA solutions and Au-BSA NPs at λ_{em} 405.

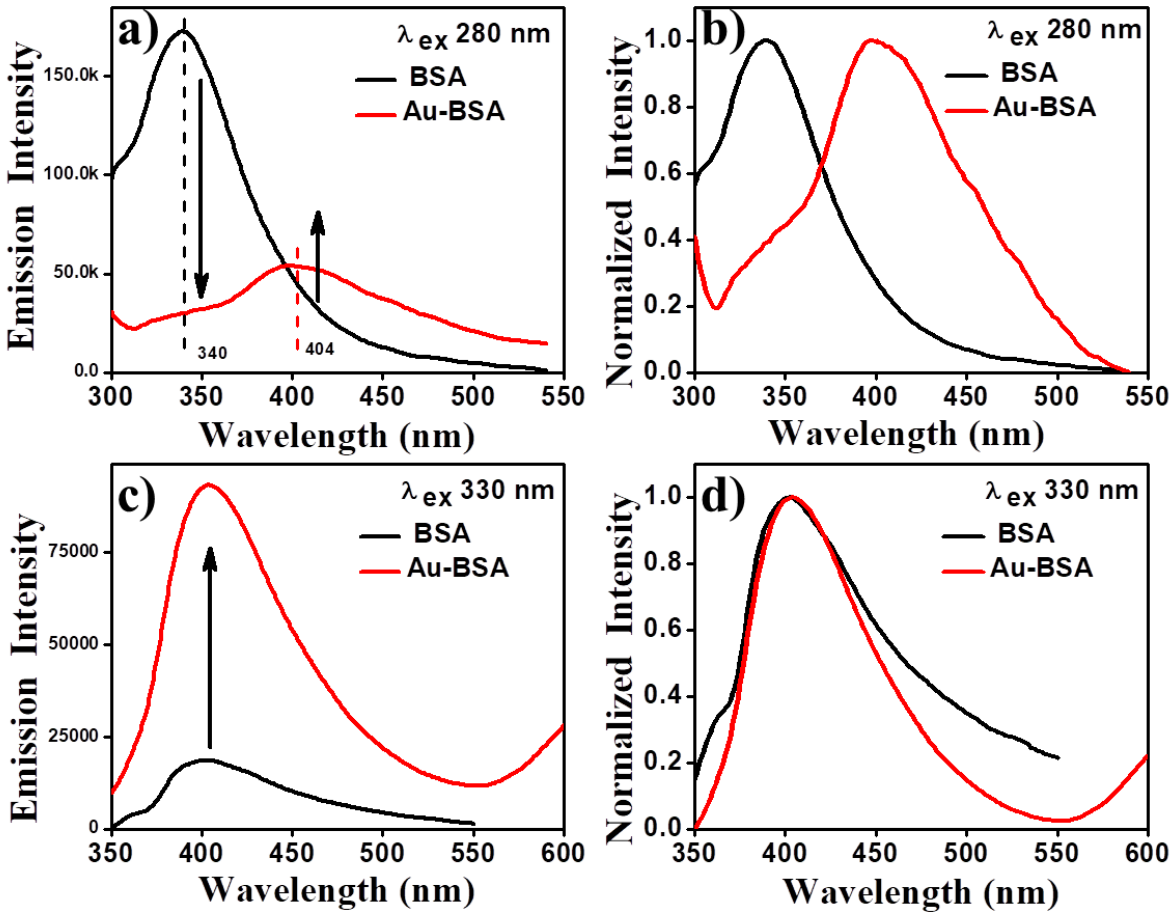

Figure S14: Emission intensity (a, c) and normalized emission intensity (b, d) of BSA and Au-BSA at λ_{ex} 280 nm (a, b) and λ_{ex} 330 nm (c, d) respectively.

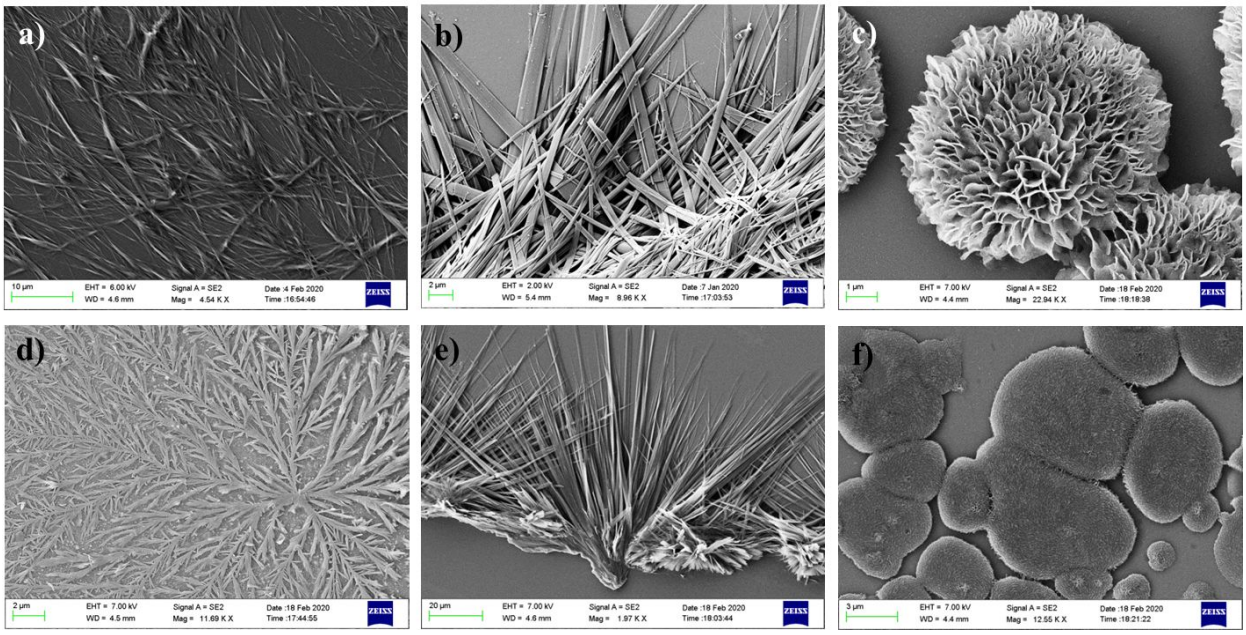

Figure S15: SEM images of S_{AA} a) S_{Phe}, b) S_{Tyr} and c) S_{Trp} and amyloid-like fibril (F_{AA}) of d) F_{Phe}, e) F_{Tyr} and f) F_{Trp} where the concentration of amino acid is 1 mM.

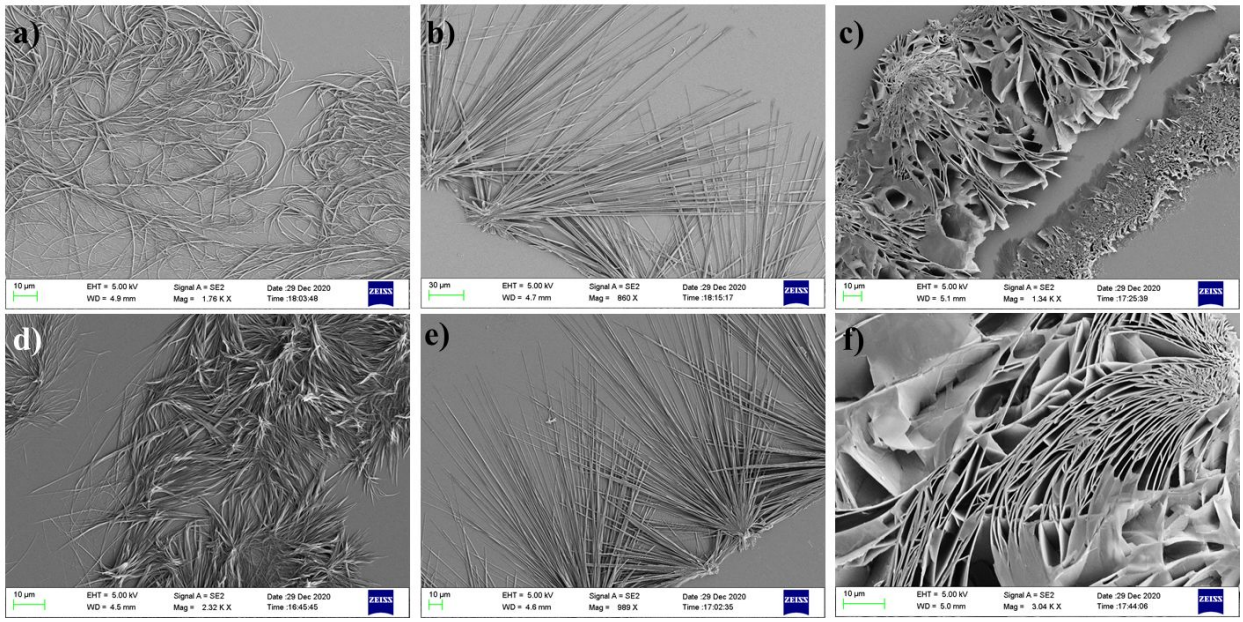

Figure S16: SEM images of S_{AA} a) S_{Phe}, b) S_{Tyr} and c) S_{Trp} and amyloid-like fibril (F_{AA}) of d) F_{Phe}, e) F_{Tyr} and f) F_{Trp} where the concentration of amino acid is 25 mM.

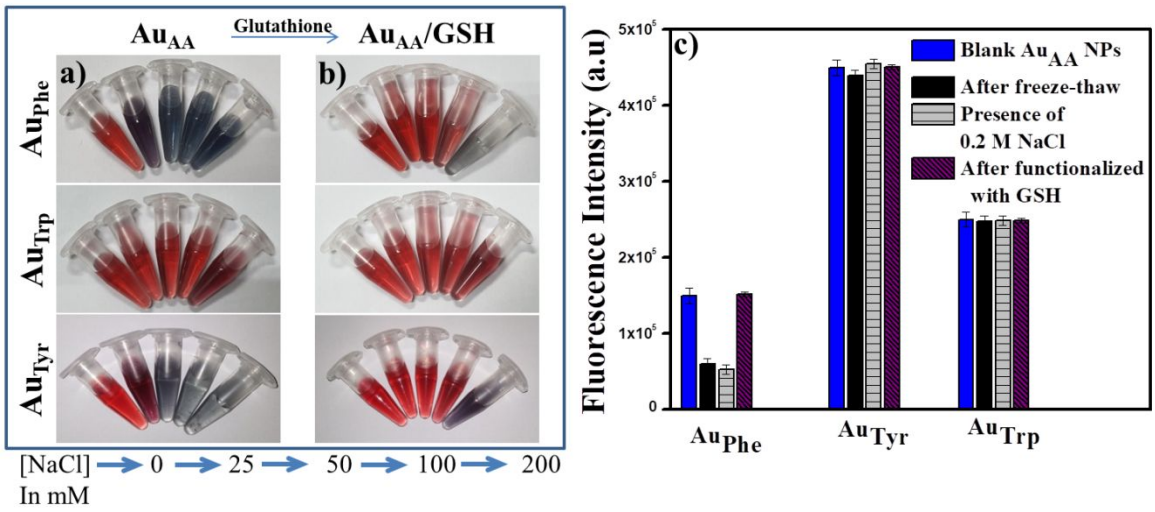

Figure S17: stability of the colloidal gold nanoparticles against external stimuli. Effect of different concentration of NaCl on a) aromatic amino acid-functionalized Au NPs and b) glutathione modified Au_{AA} NPs. c) Fluorescence stability of colloidal Au_{AA} NPs before and after functionalized with glutathione, in presence of 0.2 M NaCl and after a freeze-thaw cycle.