Supporting information

Bio-inspired Janus Gold Nanoclusters with Lipid and Amino Acid Functional Capping Ligands: Micro-voltammetry and In-situ Electron Transfer in a Biogenic Environment

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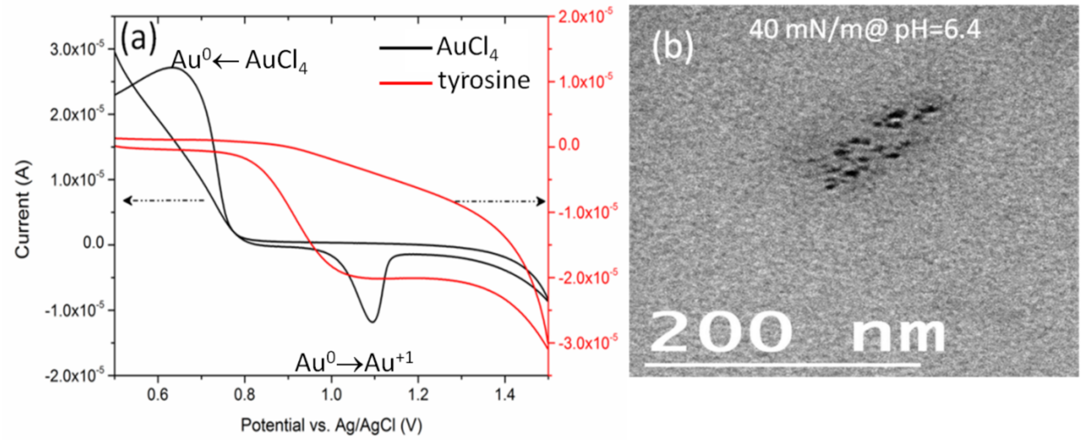

Figure S1. Redox behaviour of $1x10^{-3}$ M aqueous solutions of $HAuCl_4$ (solid black line) and L-tyrosine (solid red line) at pH=10 in 0.1 M $LiClO_4$ electrolyte. Pt disc: working electrode, Pt wire: counter electrode, Ag/AgCl: reference electrode. (b) TEM image of LS film transferred from tyrosine modified subphase at pH=6.4.

The irreversible redox behavior of both $AuCl_4$ as well as tyrosine in basic pH and the magnitude of redox potential imply the potential of tyrosine to fall in a range between the oxidation and reduction of Au.

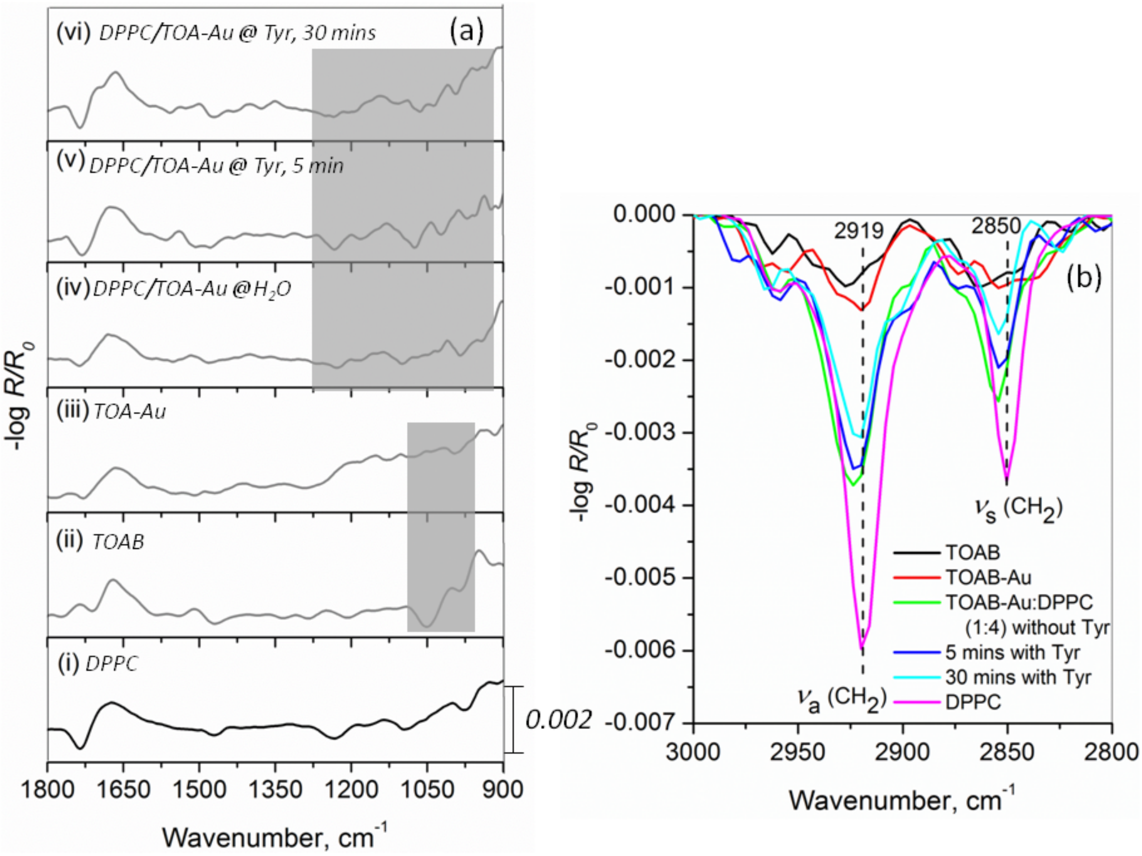

Figure S2. (a) *p*-Polarized IRRAS spectra in the region 1800-900 cm^{-1} for (i) DPPC, (ii) TOAB, (iii) TOA^{+}-Au^{3+} over pure water subphase, (iv) DPPC/TOA^{+}-Au^{3+} over pure water subphase, (iv) and (v) DPPC/TOA^{+}-Au^{3+} over tyrosine modified subphase at pH =10 after 5 and 10 mins respectively at a constant surface pressure 20 mN/m. (b) p-Polarized IRRAS spectra in the alkyl chain stretching vibrational region (3000-2800 cm^{-1}) under varied experimental conditions.

At low surface pressure, no significant shift in DPPC functional groups (data not shown) was witnessed. However, at higher surface pressure, above ~20 mN/m and with increasing reaction time (30 mins), the choline as well as the phosphate group vibrations of DPPC engage through electrostatic interaction with TOA-Au complex as evidenced from Fig. S2a. In presence of tyrosine and with time, evolution of increasing order in the alkyl chains is evident from the observed all-trans conformation of the ν_a (CH$_2$) stretching frequency (shifts from 2921 to 2918 cm^{-1}) in Figure S2b. Surface pressure induced hydrophobic interactions between the -CH_2 alkyl chains of DPPC and TOA and typical head-group interactions provide a suitable environment for the templated assembly and nucleation site for Janus NP formation.

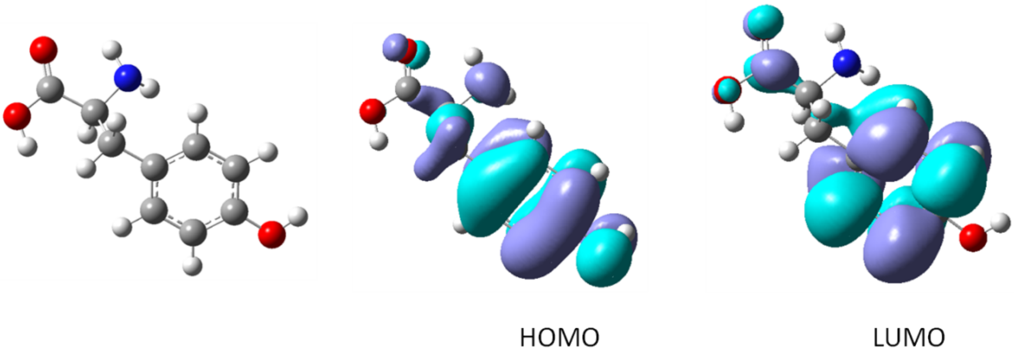

Figure S3. DFT (b3lyp/6-31g(d)) energy minimized structure of tyrosine along with its frontier orbitals HOMO and LUMO.

Mulliken charge analysis	DPPC	Au3	Tyr	Janus NP
Au$_1$	-	-0.020	-	-0.126
Au$_2$	-	0.041	-	0.0
Au$_3$	-	0.067	-	0.0281
PO_2^- (O$_1$)	-0.585	-	-	-0.623
PO_2^- (P)	1.224	-	-	1.371
Tyr (N$_2$)	-	-	-0.558	-0.751
Tyr (O$_5$)	-	-	-0.298	-0.525
Tyr (O$_6$)	-	-	-0.416	-0.518

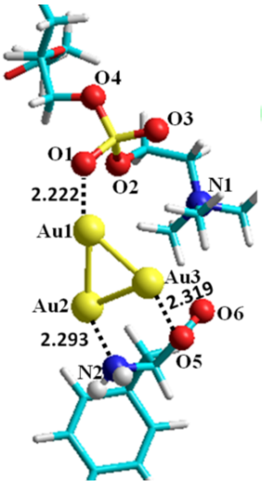

Figure S4. Mulliken charge analysis for pristine DPPC, Au3, tyrosine and the Janus cluster.

Experimental procedures for the syntheses of pristine DPPC and tyrosine capped Au clusters:

The synthesis of DPPC-capped Au clusters was done by slight modification of the reported procedure.[1] In short, 0.9 mg of DPPC was dissolved in 2 ml of $CHCl_3$ taken in a round bottom flask and stirred vigorously for 10 min. 1 ml of 1 mM aqueous solution of $HAuCl_4$ was then added followed by 10 mM sodium citrate aqueous solution into the stirred $CHCl_3$ solution. The reactants were continuously stirred for 12 h. The lower organic phase turned from clear solution to faint pink (cf. Figure S5a, inset).

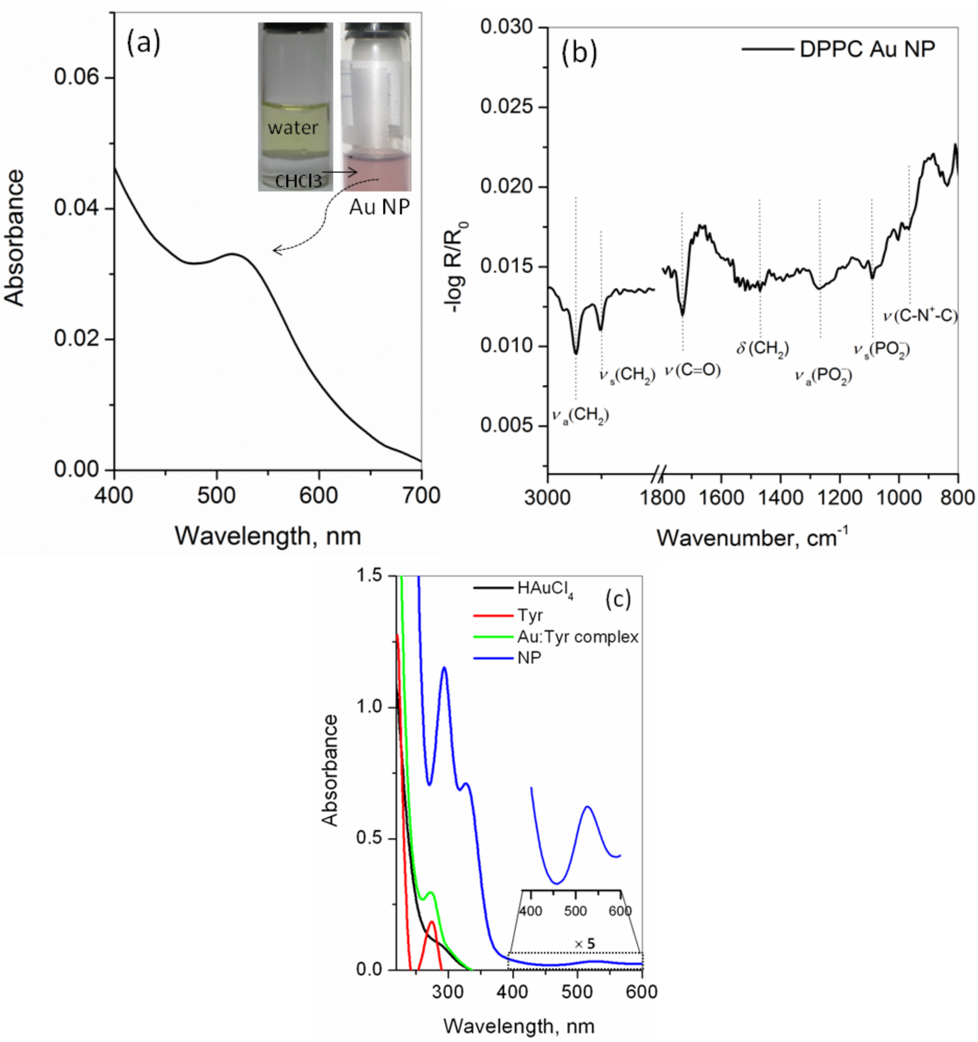

Figure S5. (a) UV-Vis spectrum of pristine DPPC capped Au NP extracted into chloroform phase showing the surface plasmon band at 522 nm. (b) p-polarized FT-IRRAS spectral analysis of DPPC protected Au NP at air/water interface evidencing the binding of DPPC to Au through electrostatic interaction, acquired at a holding surface pressure of 30 mN/m. (c) UV-Vis absorption spectral characteristics of tyrosine protected gold nanoclusters and their precursors; the surface plasmon band at ~ 530 nm is observed.

For the tyrosine capped Au NPs, 10 ml of 0.1 mM aqueous $HAuCl_4$ and 1 mM of tyrosine was stirred for 30 min. 1 ml of KOH (pH=10) aqueous solution was then drop wise added to the reaction flask over a period of 5 min. The colour of the reactant turned yellow to black confirming the feasibility of reduction process. The prepared solutions were then subjected to UV-Vis spectral acquisition.

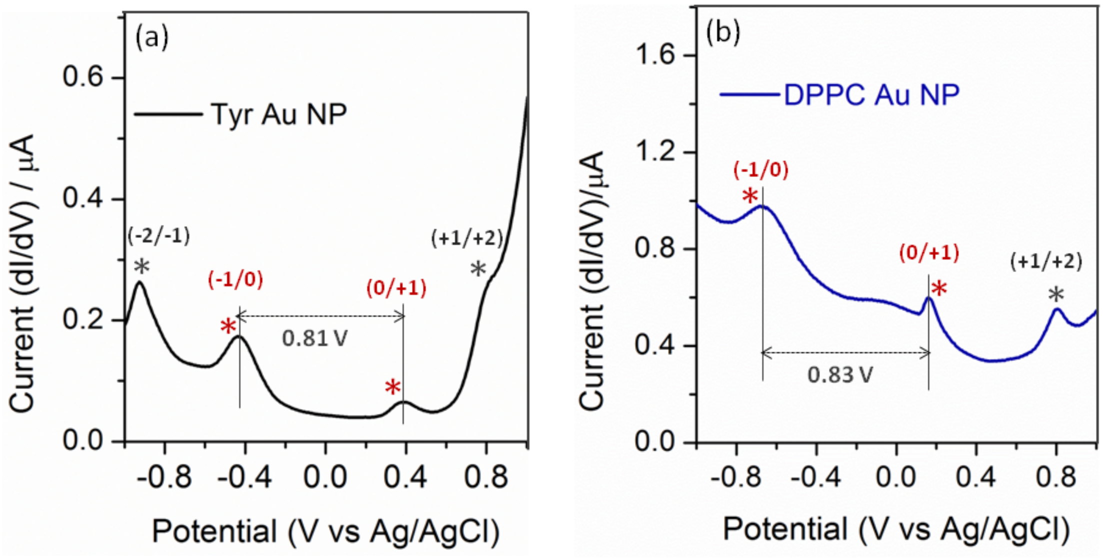

Figure S6. Differential pulse voltammetry of pristine (a) tyrosine and (b) DPPC capped Au nanoclusters at Pt UME (25 µm) showing quantized redox behaviour. The HOMO-LUMO gaps were estimated to be 0.81 and 0.83 V respectively.

Laviron Equation:

$$\log k_{app} = \alpha \log(1-\alpha) + (1-\alpha)\log\alpha - \log(RT/nF\nu) - \alpha(1-\alpha)nF\Delta E_p / 2.3RT$$

References:

1. H. Zhu, C. Tao, S. Zheng and J. Li. *Colloid and Surface A: Physiochem. Eng. Aspects* 2005, **257-258**, 411-414.