Electronic Supplementary Information

for

Impact of the lipid head-groups in GUVs on electron transfer by the surface-adsorbed fluorescent gold nanoclusters

Materials and Reagents. All the chemicals and reagents used in the experiments were of high purity (>98%). Glutathione (GSH), $HAuCl_4$, 1,2-dimyristoyl-3-trimethylammonium-propane (DMTAP), dipalmitoylphosphatidylcholine (DPPC), methyl viologen and tris buffer tablets were procured from Sigma-Aldrich. The solvents, chloroform and methanol, were also obtained from Sigma-Aldrich in pure form and used as received. HPLC grade water was used to prepare the solutions. The experiments were done at 23^{o}C and pH 7.4.

Methods. A JEM-2100F, JEOL field emission gun (FEG) electron microscope was used for taking the transmission electron microscopy (TEM) images using a 200kV electron source. The instrument is available at the DST-FIST facility in IISER Kolkata. An aqueous solution of GSH-AuNCs was drop-casted on a carbon-coated copper grid and dried. The zeta-potential measurements were performed in a Malvern Zetasizer Nano ZS, Malvern Instruments Ltd., UK equipped with a He−Ne laser beam operating at 633 nm and a Nanoparticle Analyser SZ-100 from Horiba Scientific using He−Ne laser beam at 633 nm in aqueous solutions. For each sample the instrument performed 20 scans (70 runs each). The microscopic images were taken using a confocal laser scanning inverted microscope (Axio Observer A1) from Zeiss was coupled with DCS-120 system from Becker & Hickl GmbH. A picosecond diode laser (BDL-488-SMC, BH and λ_{ex} = 488 nm) was used as the excitation source. The scanning was controlled by a BH GVD-120 scan controller. The BH HPM-100-40 hybrid detector module in DCS-120 system was controlled by the DCC-100 software. A long pass filter (HQ495LP) was placed to block the excitation light and two narrow band pass filters of 550 nm and 650 nm (FKB-Vis-10, FWHM = 10 nm, Thorlabs) were used to monitor the emission wavelengths. A Hitachi U-2900 spectrophotometer and a QM 40 spectrofluorimeter from PTI, Inc. were used to collect the absorption and emission spectra. The time-resolved fluorescence decay studies were done using the method of time correlated single photon counting (TCSPC) using a picosecond spectrofluorimeter from Horiba Jobin Yvon IBH equipped with a FluoroHub single photon counting controller. The samples were excited by a 375 nm diode laser (temporal resolution < 200 ps). The

raw data were fitted using a non-linear least-square iteration procedure using IBH DAS6 (version 2.2). The average fluorescence lifetime value, $\langle\tau\rangle$ were calculated using the equation:

$$\langle\tau\rangle = \Sigma_i A_i\tau_i^2 / \Sigma_i A_i\tau_i$$

where, τ_i is the excited-state lifetime component of the decay curve and A_i is the corresponding amplitude of that component. The steady-state fluorescence anisotropy measurements were carried out in the QM-40 spectrofluorimeter using excitation and emission polarizers. Anisotropy (r) was determined using the following equation:

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

where, G is the correction factor ($G = I_{VH}/I_{HH}$) and I is the fluorescence intensity and the suffixes denote the alignment of excitation and emission polarizers, respectively.

The theoretical calculations were done using Gaussian 16 and applying the density functional (DFT) theory with ωB97X-D routine and 631-G basis set.

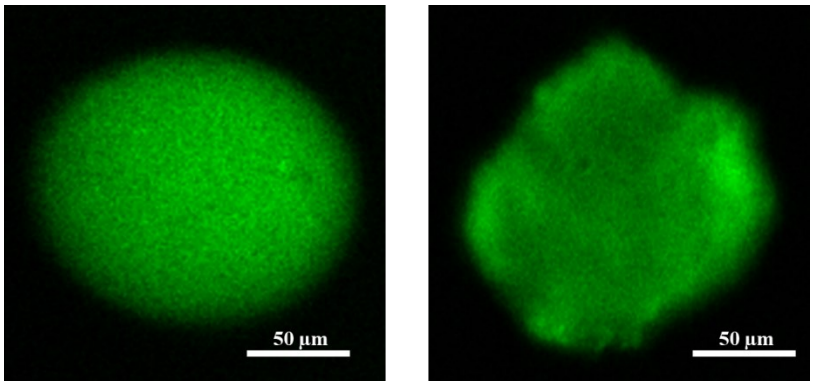

Fig. S1. Confocal images of DMTAP and DPPC lipid vesicles using rhodamine 6G stain.

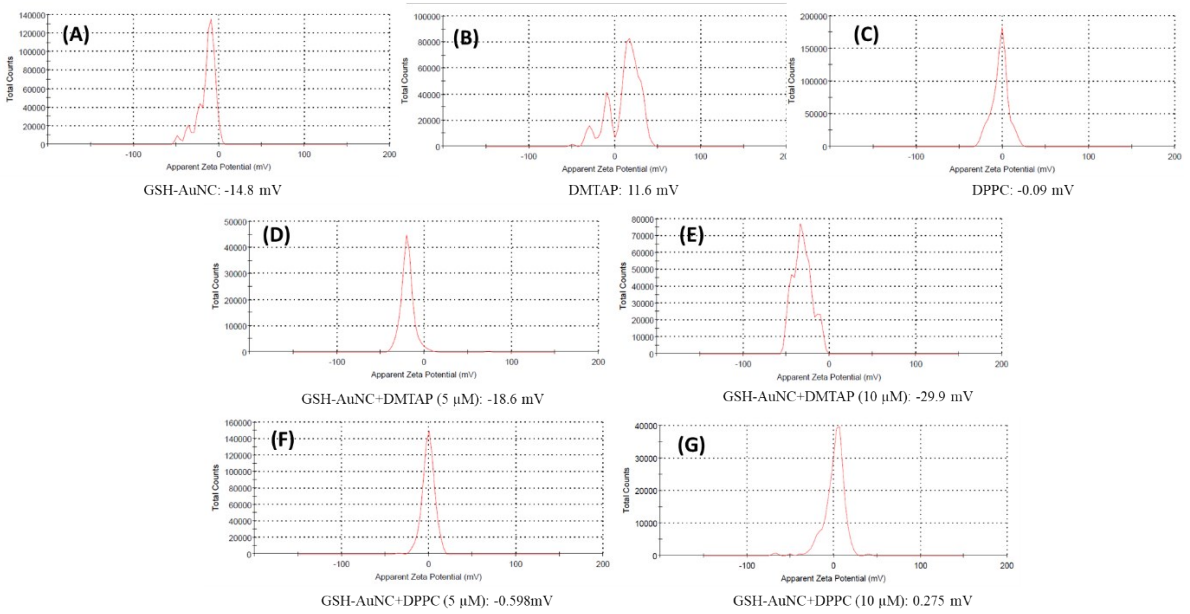

Fig. S2. Change in zeta potential values of GSH-AuNCs on interactions with the DMTAP and DPPC GUVs in tris buffer at 23^{o}C at pH 7.4.

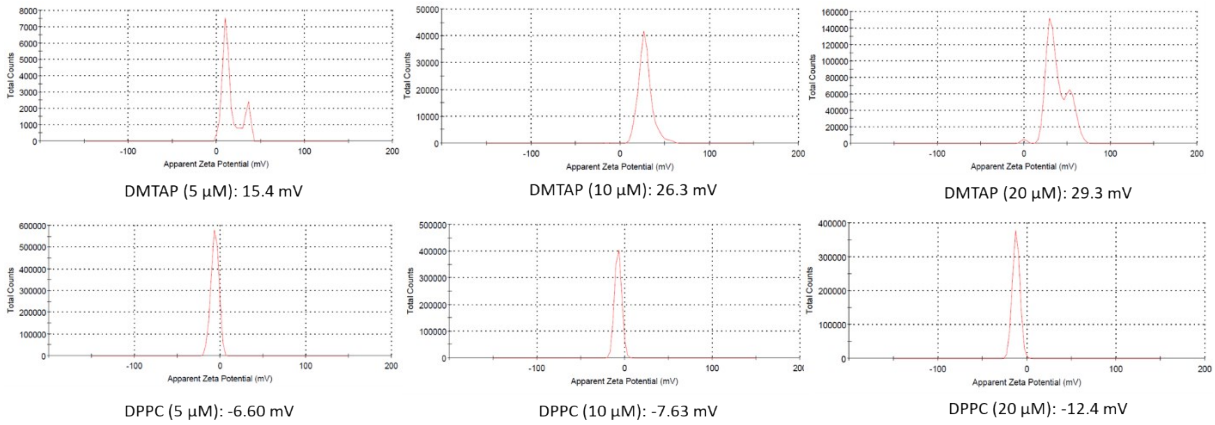

Fig. S3. Change in zeta potential of the DMTAP and DPPC GUVs in tris buffer at 23^{o}C at pH 7.4.

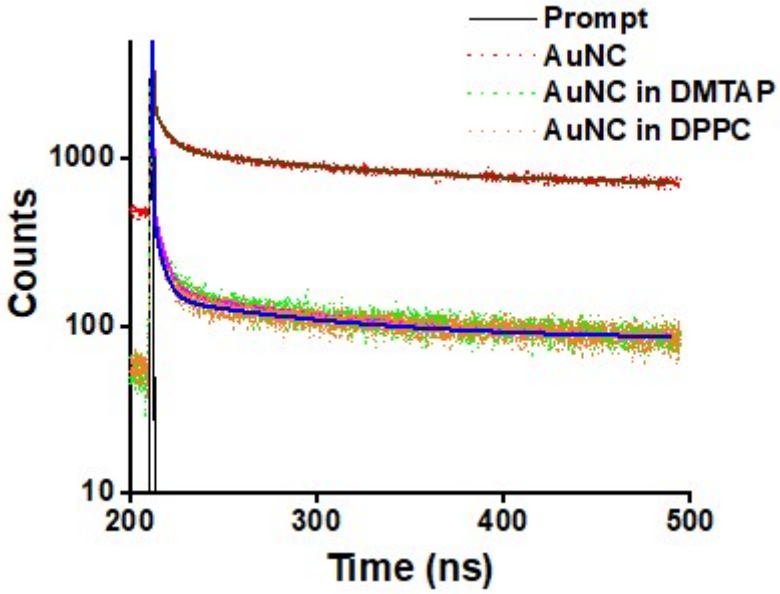

Fig. S4. The time-resolved fluorescence decay traces of GSH-AuNCs in absence and presence of the DMTAP and DPPC GUVs.

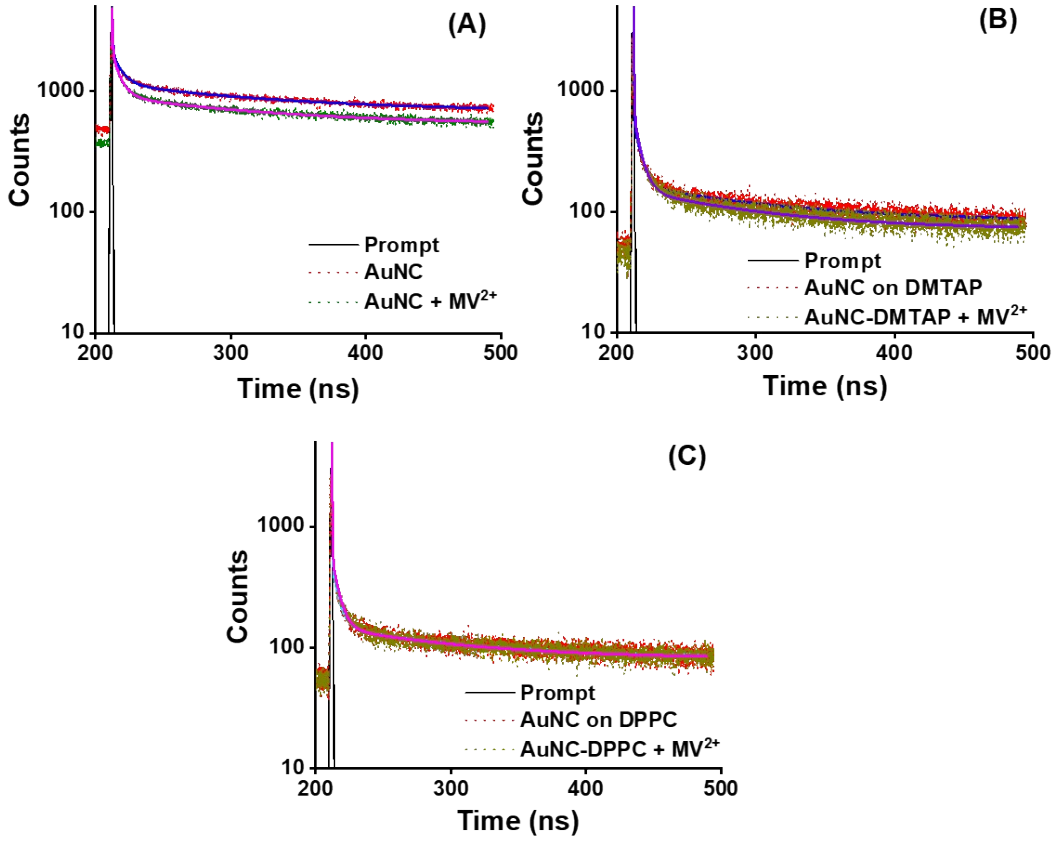

Fig. S5. The time-resolved fluorescence decay traces of the interaction of the GSH-AuNCs with MV^{2+} in (A) absence and presence of the (B) DMTAP and (C) DPPC GUVs.