Supporting Information

Effect of Ligand Charge on Electron Transfer Rates of Water Soluble Gold Nanoparticles

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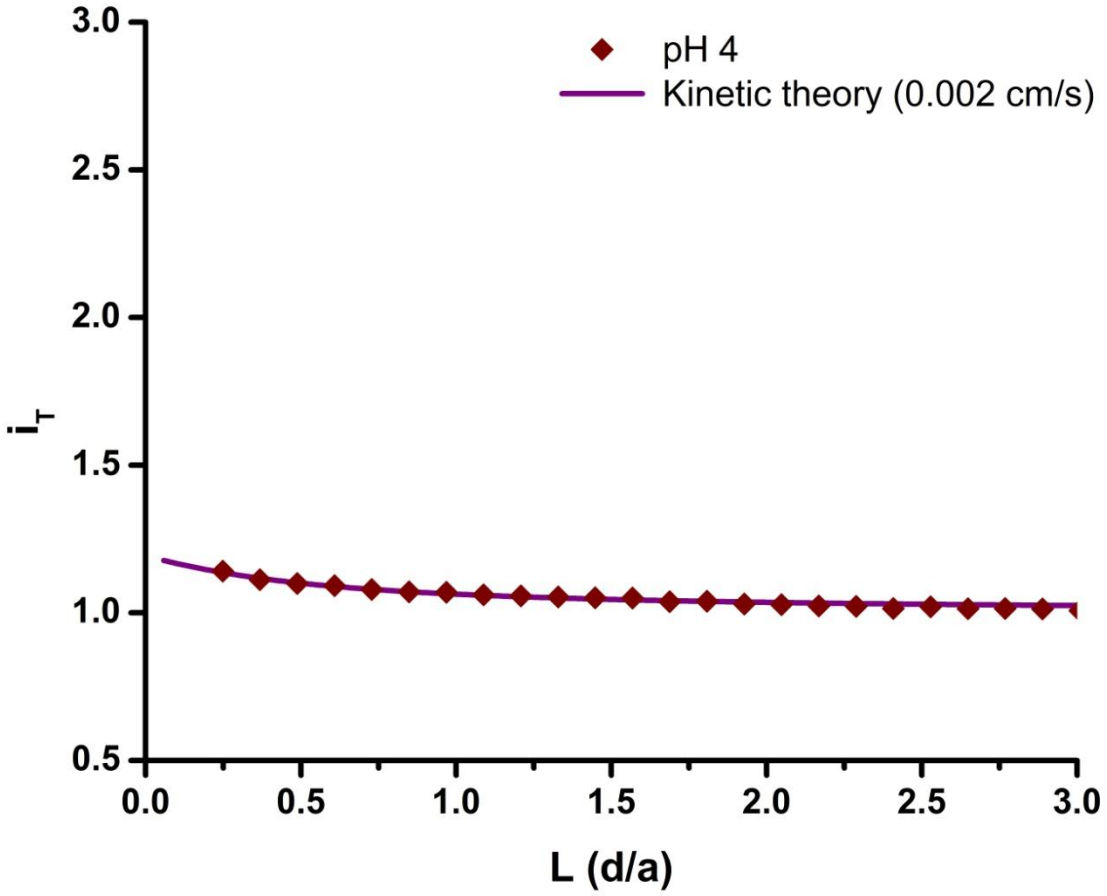
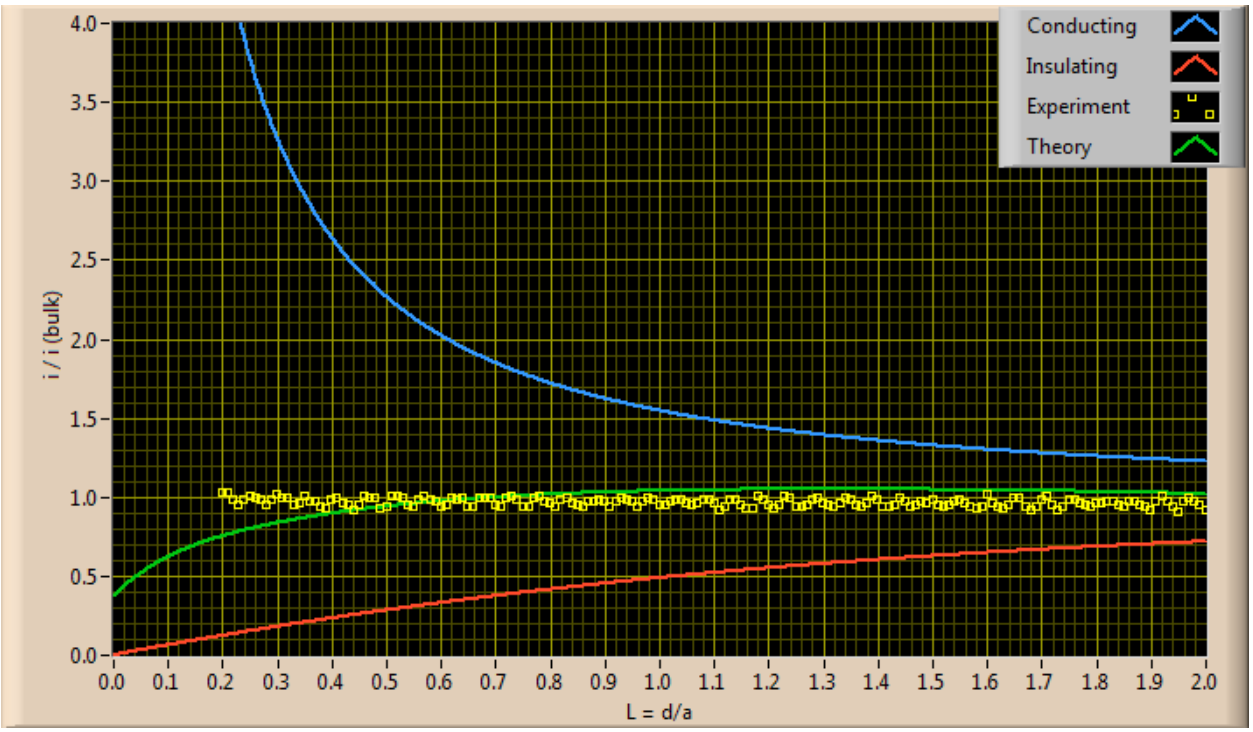
SI-Table 1. k_f Values versus pH for Tiopronin, Gluathione, and TMA-protected AuNPs

Ligand	**pH**	k_f **(cm/s)** (n=5)
Tiopronin	3	0.021±0.001
	4	0.018±0.002
	5	0.0036±0.0004
	6	0.0045±0.0009
	7	0.0012±0.0003
	9	0.0003±0.0002
Glutathione	3	0.002±0.001
	4	0.0028±0.0003*
TMA	3	0.0047±0.0003*
	4	0.0046±0.0002*

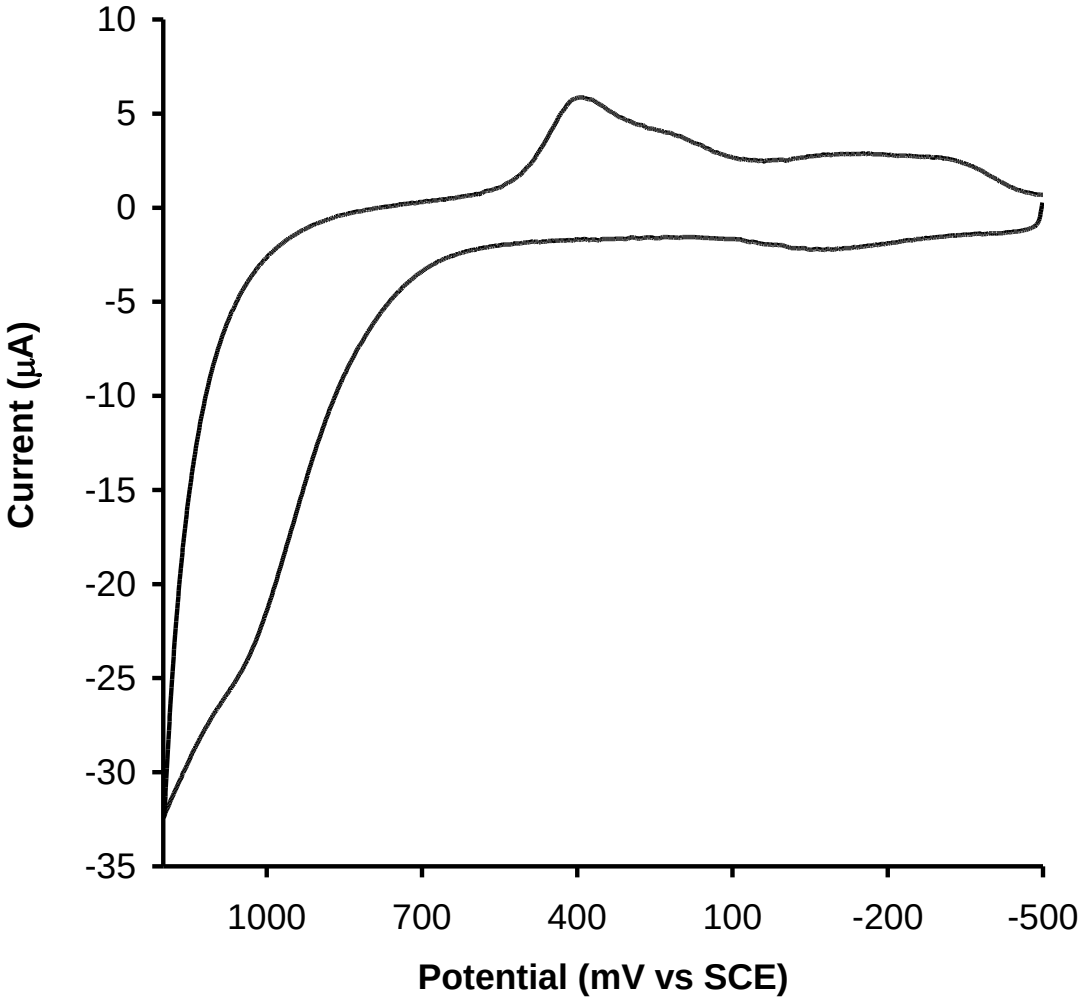
*These values for k_f were calculated using the LabView program PAC_Fit.VI (see SI-Figure 3).[29] The model used for the Tiopronin AuNPs only works on pure positive feedback. The electron transfer rate for these protecting ligands is so slow that a positive feedback is not generated (see SI-Figure 1 and 2).



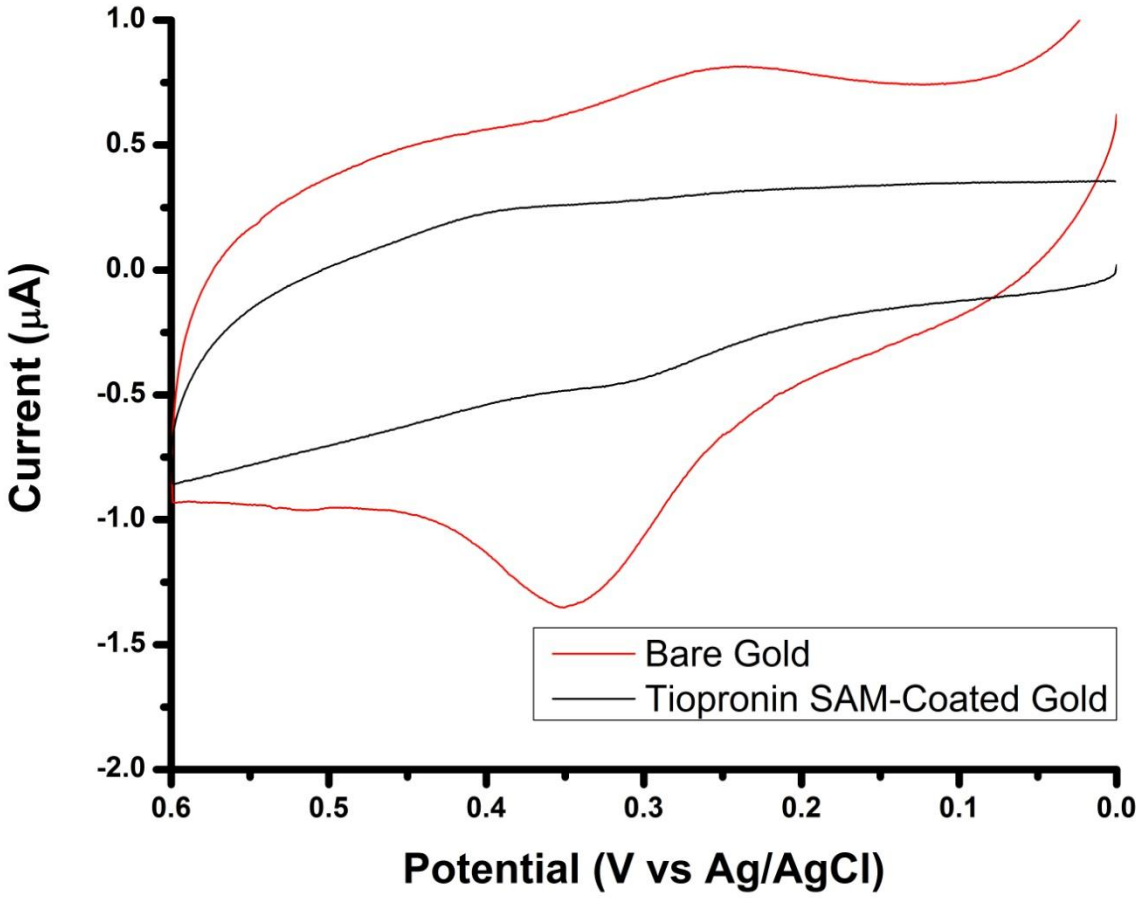
SI-Figure 1. SECM (CHI 900) approach curves, 10 μm Pt UME, unbiased Pt substrate electrode (2 mm), Ag/AgCl (3 M KCl) reference, 20 mg glutathione protected AuNPs in 5 mL of 0.1 M $NaCH_3CO_2$ buffer (pH 3)



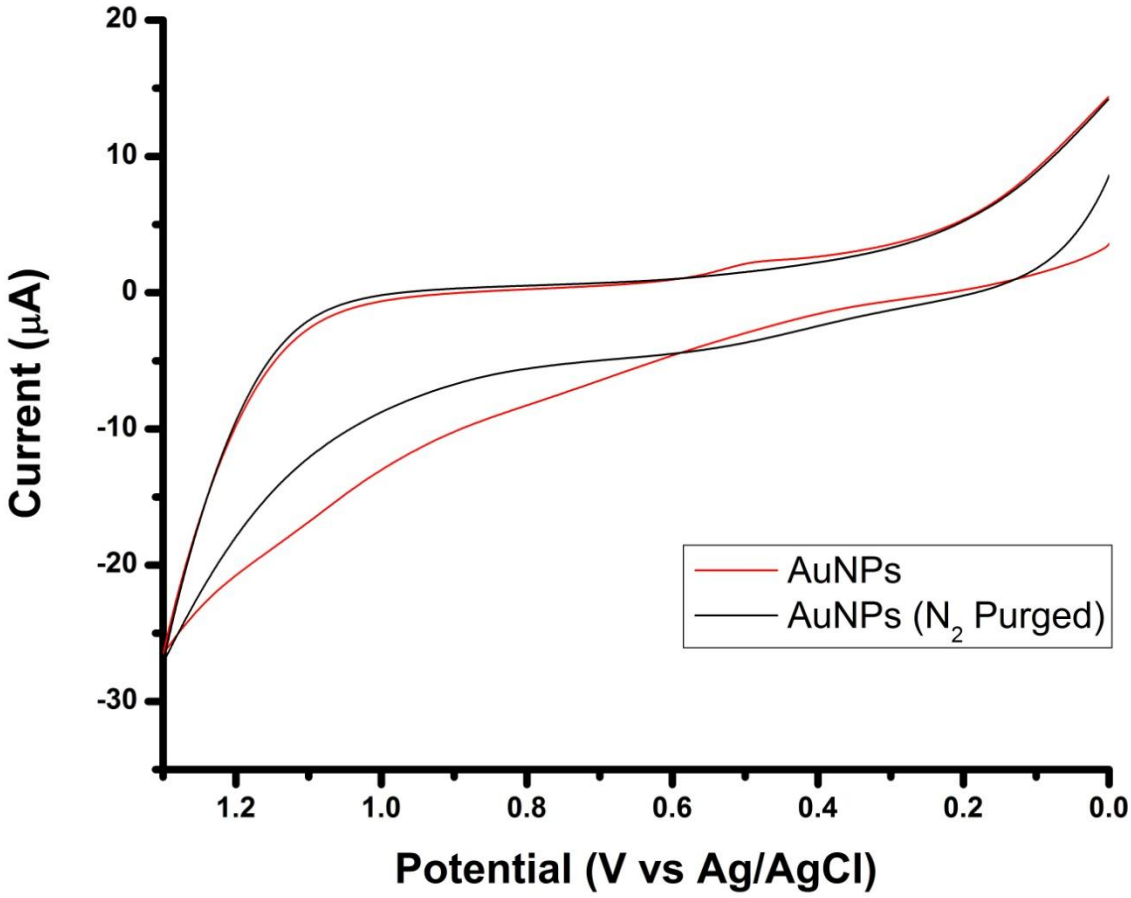
SI-Figure 2. Sample SECM (CHI 900) approach curve, 10 µm Pt UME, unbiased Pt substrate electrode (2 mm), Ag/AgCl (3 M KCl) reference, 20 mg TMA protected AuNPs in 5 mL of 0.1 M $NaCH_3CO_2$ buffer (pH 3) analyzed using the PAC_Fit.VI program. k_f = 0.00683 obtained through the optimization feature of the program.



SI-Figure 3. Oxidation of Tiopronin Au MPC (55 μM TioMPC Cluster= 5 mM Tiopronin) in 0.10 M pH 7.0 phosphate buffer at a GC electrode at 50 mV/s. The oxidation wave as shown is pushed nearly to the solvent window, but the reduction peak of the oxide formed is observed at the expected potential compared to the gold oxide reduction on a bare gold electrode. The oxide reduction peak shape has more diffusive character than that of a typical gold oxide reduction suggesting that reduction of the oxide could be occurring on the surface of MPCs diffusing to the electrode surface. An approximate value of 5 electrons per cluster was obtained by integrating the gold oxide reduction wave and relating it to the concentration of MPC present.



SI-Figure 4. Cyclic voltammogram of a 2 mm Au macroelectrode, Ag/AgCl (Sat. KCl) reference, in 0.1 M $NaCH_3CO_2$ buffer (pH 3). In the bare gold (red line), a gold oxide peak is present between 300-400 mV. This peak is still present after applying a tiopronin self assembled monolayer to the surface of the electrode (20 minutes in a 2 mM tiopronin solution at -0.2 V).



SI-Figure 5. Cyclic voltammogram of tiopronin protected AuNPs (~5 mg/ml) using a 2 mm Pt macroelectrode, Ag/AgCl (Sat. KCl) reference, in 0.1 M $NaCH_3CO_2$ buffer (pH 3) showing the gold oxidation peak shifted to the solvent window. The reduction of the gold oxide peak is still present when performing the experiment in the presence of oxygen. This reduction peak is removed after purging the solution with nitrogen, thus preventing the formation of gold oxide.