

Supporting Information

Protonation State of Thiols in Self-Assembled Monolayers on Roughened Ag/Au Surfaces and Nanoparticles

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FIGURES

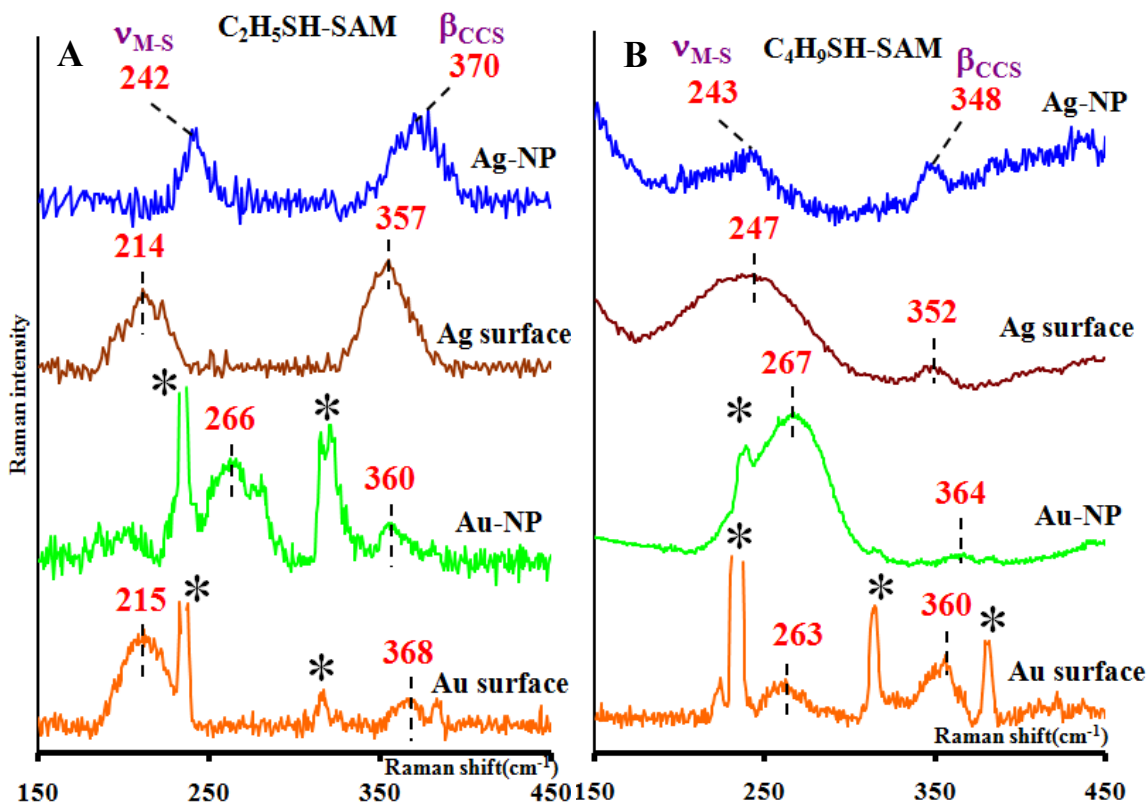


Fig. S1 Low range SER spectra for short chain alkylthiols adsorbed on Ag, Au surfaces and nanoparticles. A) Spectra for C_2SH SAM and B) spectra for C_4SH SAM. * represents plasma lines.

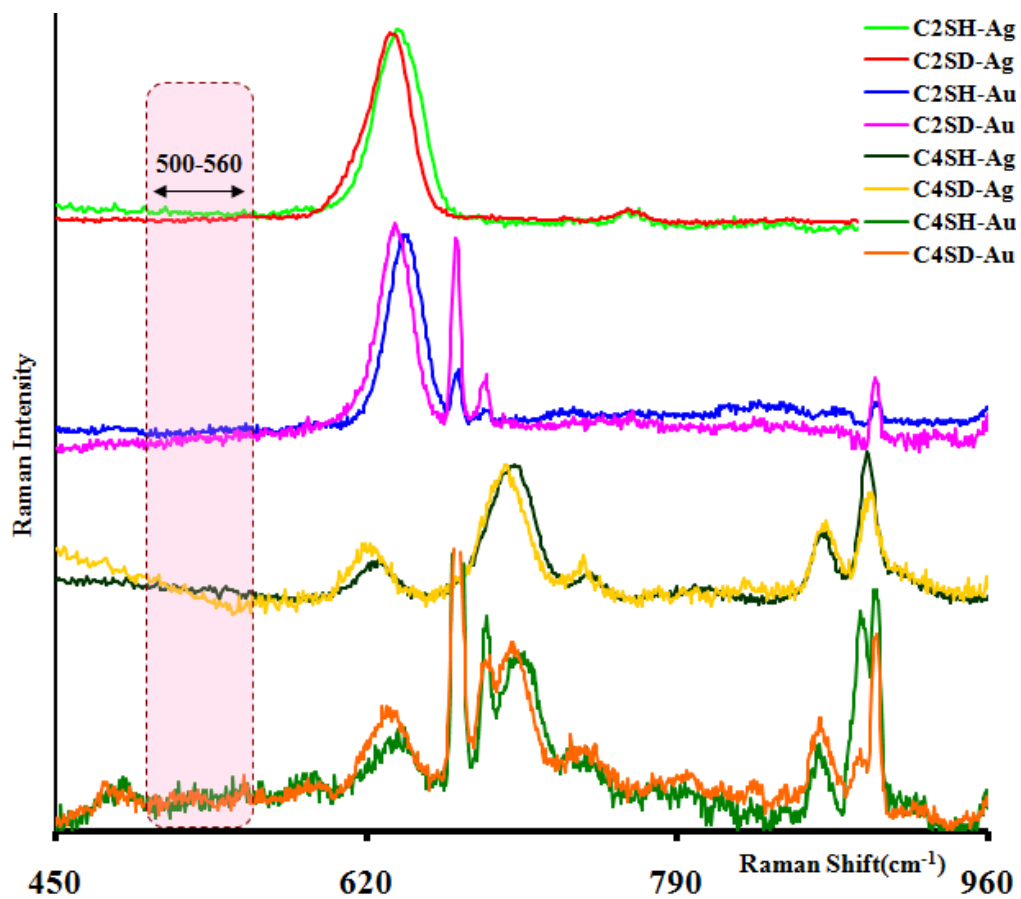


Fig. S2 SER spectra for alkylthiols adsorbed on Ag and Au surfaces. The highlighted region indicates that any peak for S-S stretching frequency is absent for these surface adsorbed molecules.

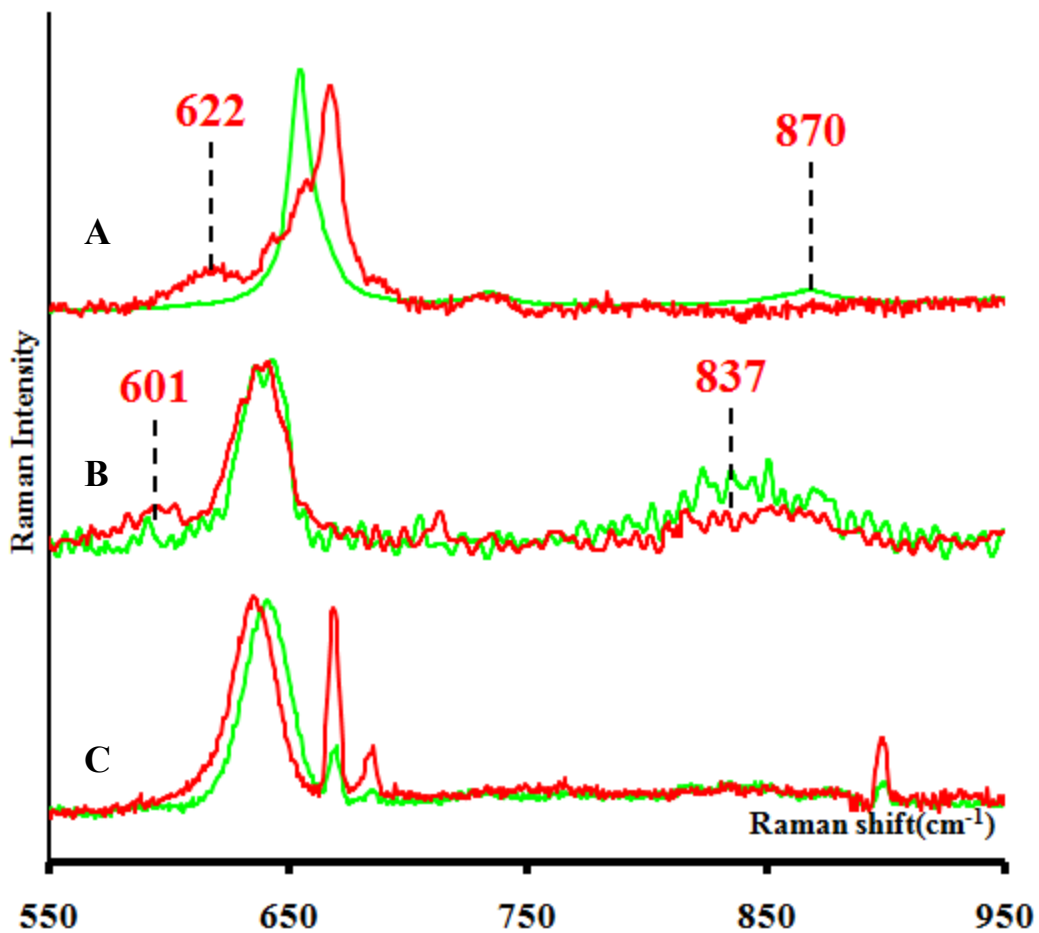


Fig. S3 Raman spectra of C₂H₅SH (green) and C₂H₅SD (red) (A) in solution and (B-C) on Au surfaces (SERS). (B) SERS of physisorbed thiol SAMs (monolayer deposited surfaces without washing by any solvents) (C) SERS of chemisorbed thiol SAMs (monolayer deposited surfaces after thorough washing with EtOH and CHCl₃).

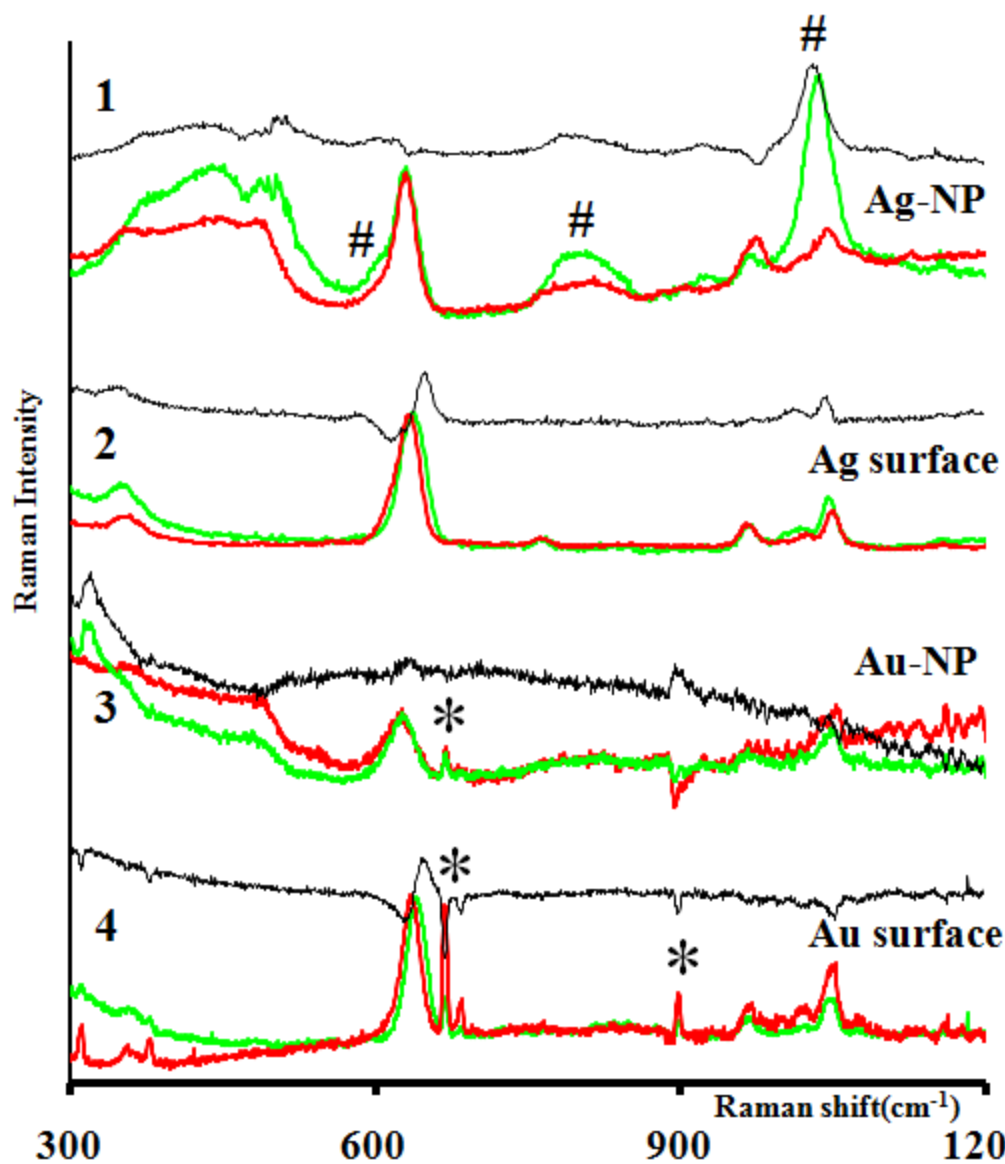


Fig. S4 Full range SER spectra for ethanethiol adsorbed on Ag, Au surfaces and NPs. * represents plasma lines. # represent solvent peaks.

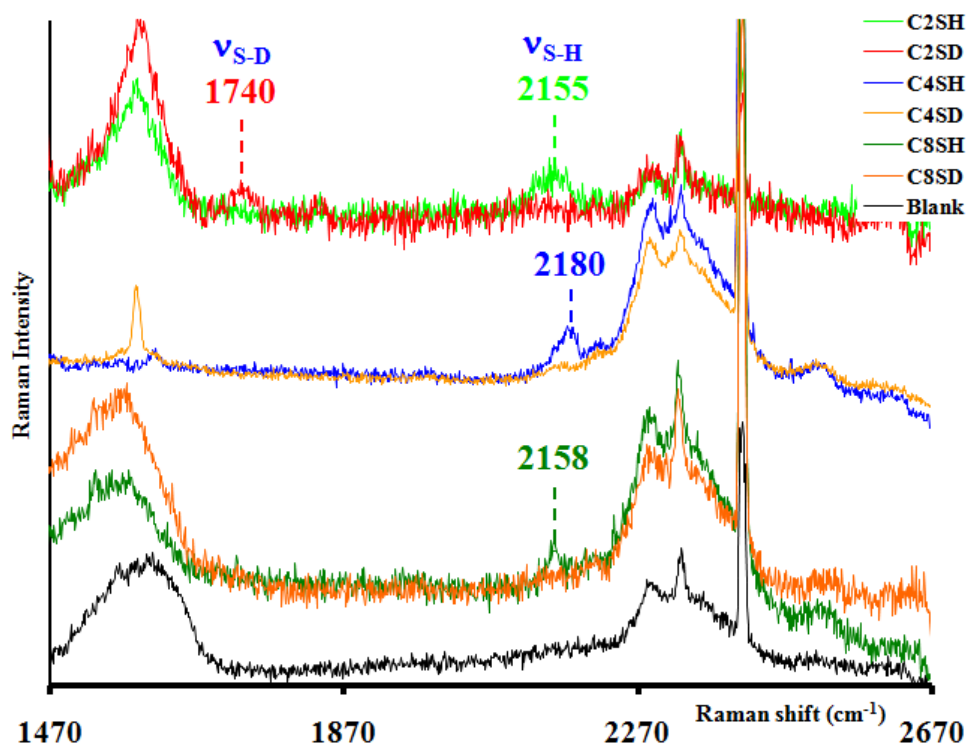


Fig. S5 SER spectra in high range (1470 – 2670 cm⁻¹) for short and moderate chain alkyl thiols adsorbed on Ag surfaces.

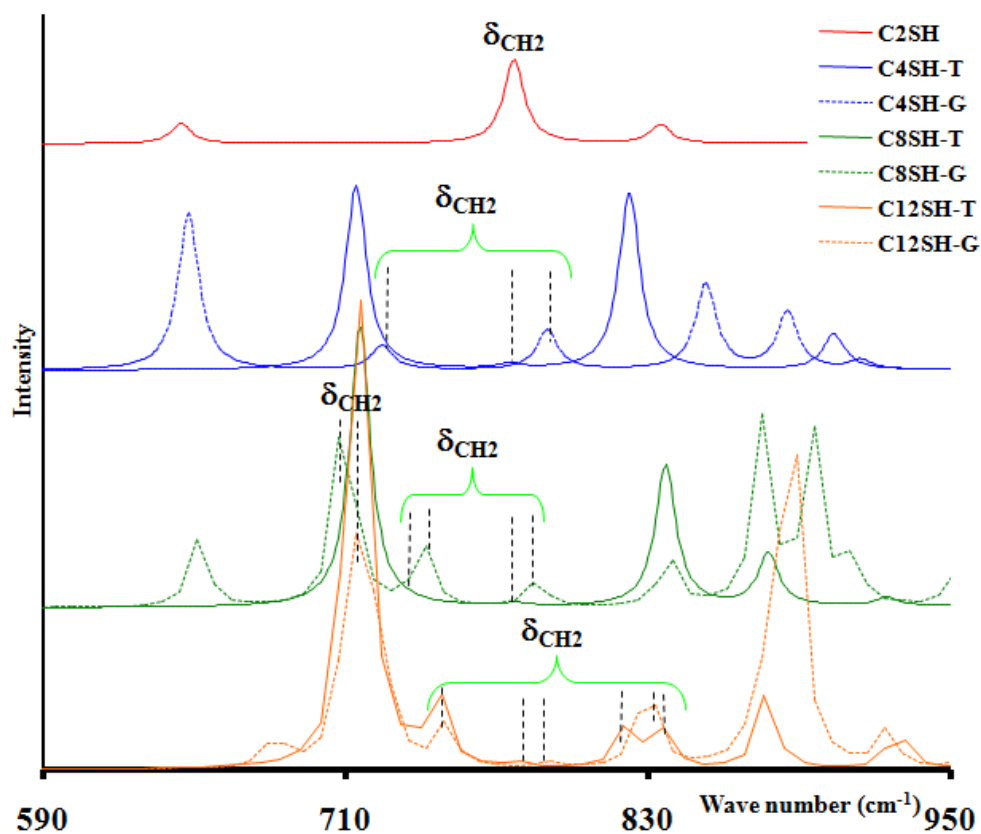


Fig. S6 DFT calculated wave numbers of alkyl thiols. Methylene rocking modes (δ_{CH_2}) are shown here. T and G mean trans and gauche conformations, respectively. The details of DFT calculation and peak assignments are reported in *Analyst*, 2014, **139**, 2118-2121.

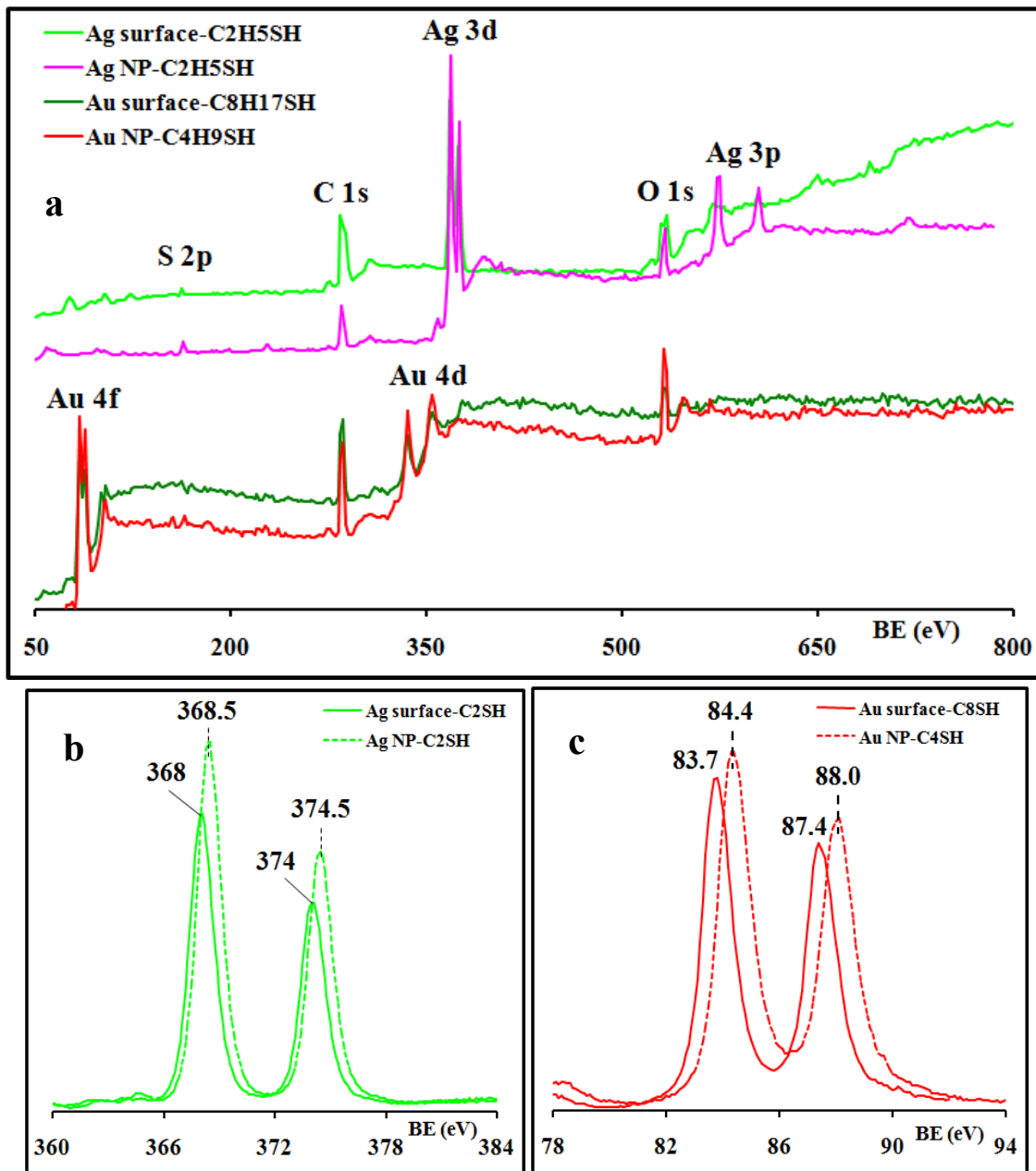


Fig. S7 (a) Full range XP spectra for C₂H₅SH bound Ag surfaces and NPs (top) and C₈H₁₇SH bound Au surfaces and C₄H₉SH bound Au NPs (bottom). (b) High-resolution XP spectra of Ag for C₂H₅SH bound Ag surfaces and NPs and (c) same of Au for C₈H₁₇SH bound Au surfaces and C₄H₉SH bound Au NPs.

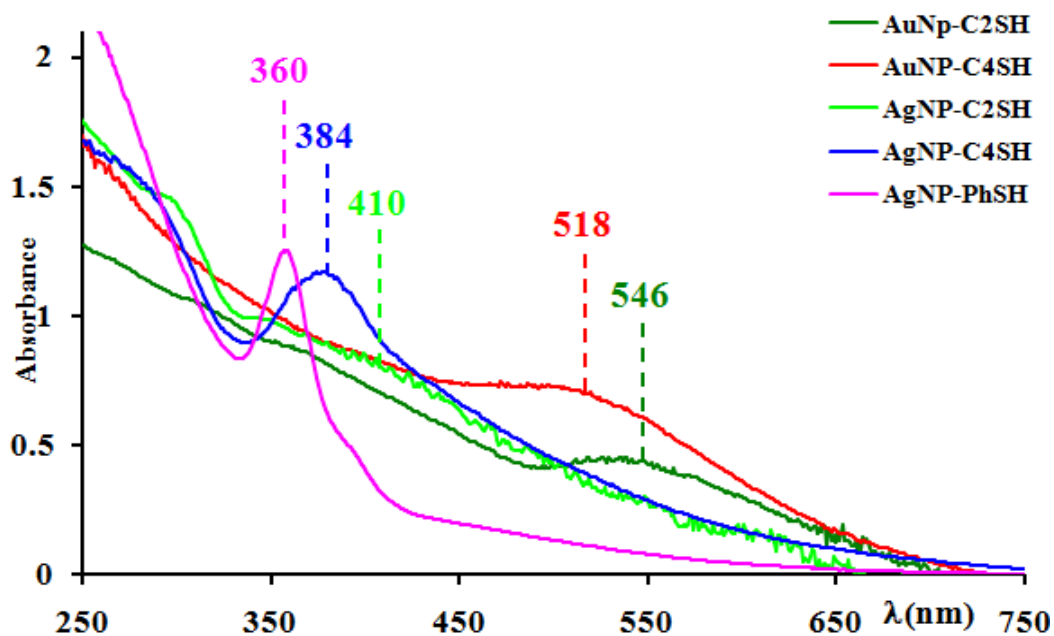


Fig. S8 Absorbance spectra of aromatic and alkyl thiol capped Ag and Au nanoparticles solubilized in MeOH.

Table S1. Ordinary Raman and Surface Enhanced Raman vibrational assignments of an aromatic thiol and some aliphatic thiols adsorbing them on Ag and Au nanoparticles.

	Solution	Ag-NP	Au-NP	Assignment
C ₂ SH(D)	654 (671)	631 (631)	628 (628)	ν_{CS}
	870 (622)			$\beta_{CSH/CSD}$
PhSH(D)	284 (275)	336 (336)		β_{CS}
	414 (414)	425 (425)		ν_{CS}
	617 (617)	616 (616)		ν_{CS}
	698 (703)	695 (695)		ν_{CS}
	918 (680)	-		$\beta_{CSH/CSD}$
	1094 (1094)	1078 (1078)		ν_{CS}
C ₄ SH(D)	654 (661)	610 (610)	627 (627)	ν_{CS-G}
	732 (745)	702 (702)	698 (698)	ν_{CS-T}
	846 (614)	-		$\beta_{CSH/CSD}$