SUPPORTING INFORMATION

Hydrophilic Metal Nanoparticles Functionalized by 2-Diethylaminoethane Thiol: A Close Look on the Metal-Ligand Interaction and Interface Chemical Structure

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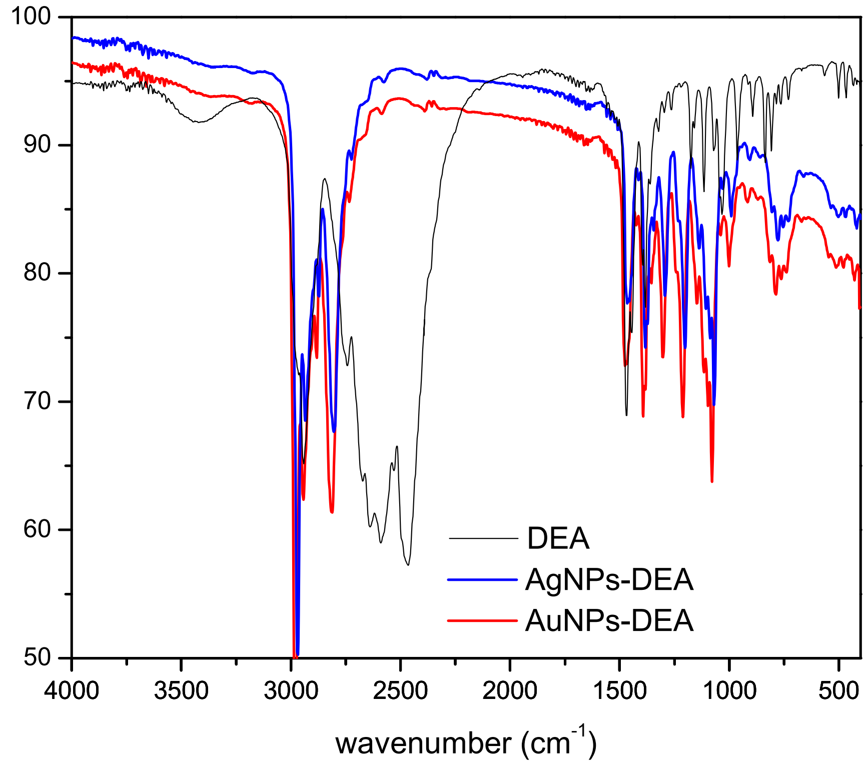


Figure SI-1: FT-IR spectra (film) of AuNPs-DEA and AgNPs-DEA samples at pH 7; compared with DEA thiol.

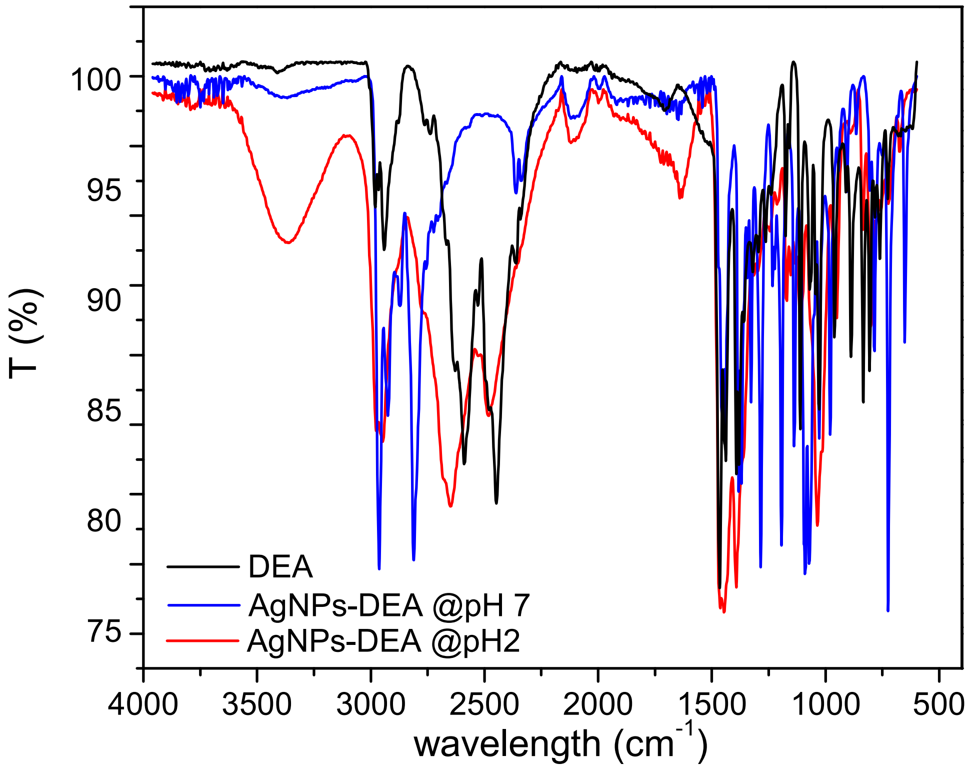
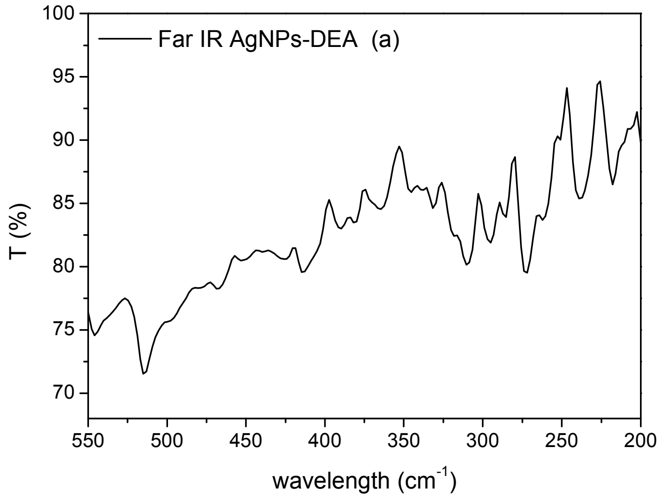


Figure SI-2:ATR spectra of AgNPs-DEA film from water at pH 2 and 7 compared with DEA powder.



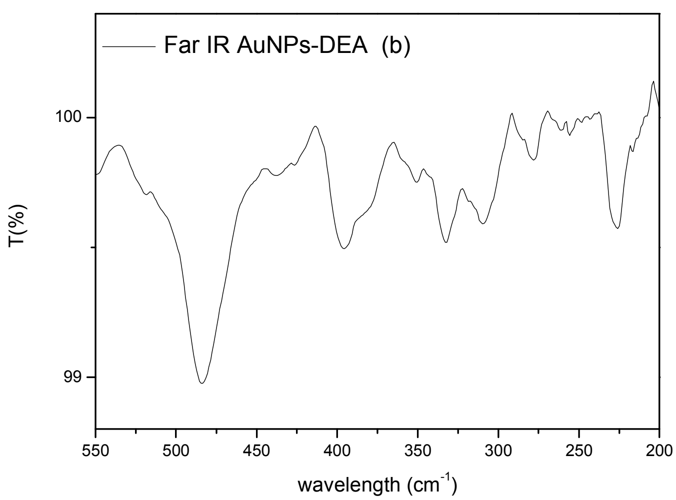


Figure SI-3: Far-IR spectrum (film from chloroform) of AgNPs-DEA (a) and AuNPs-DEA (b)

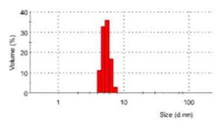
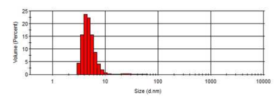
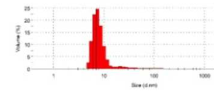
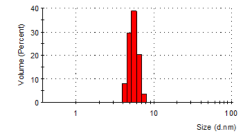
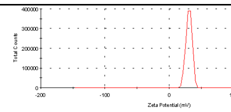
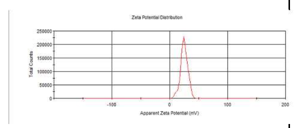
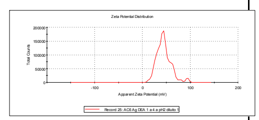
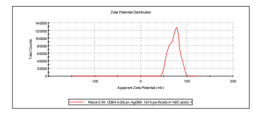
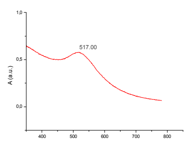
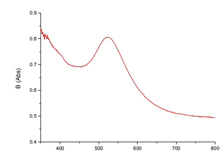
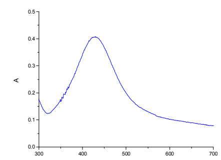
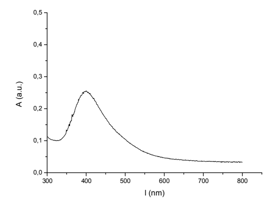
	AuNPs-DEA-4	AuNPs-DEA-10	AgNPs-DEA-4	AgNPs-DEA-10
DLS in H_2O at pH 2				
Hydrodynamic mean diameter value (nm)	5± 1	5± 2	8± 3	5± 1
Zeta potential in H_2O at pH 2				
Zeta potential value (mV)	+30 ± 5	+30 ± 10	+40 ± 10	+70 ± 6
UV-vis in H_2O at pH 2				
Lambda max value (nm)	517	521	423	405

Figure SI-4: DLS spectra and Z potential measurements of AuNPs-DEA and AgNPs-DEA in water at pH 2.

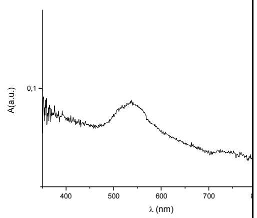
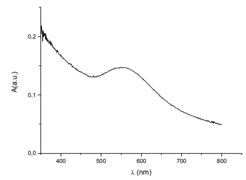
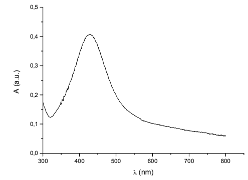
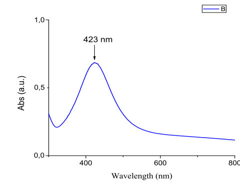
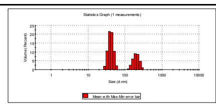
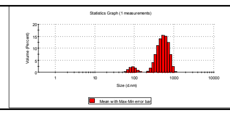
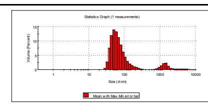
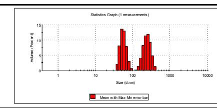
	AuNPs-DEA-4	AuNPs-DEA-10	AgNPs-DEA-4	AgNPs-DEA-10
UV-vis in H_2O at pH 7				
Lambda max value (nm)	550	560	440	423
DLS in H_2O at pH 7				
Hydrodynamic mean diameter value (nm)	40 ± 8 200 ±20	90 ± 10 550 ±30	60 ± 30 > 1000	50 ± 10 250 ± 20

Figure SI-5: UV-vis spectra and DLS data of AuNPs-DEA and AgNPs-DEA in water at pH 7.

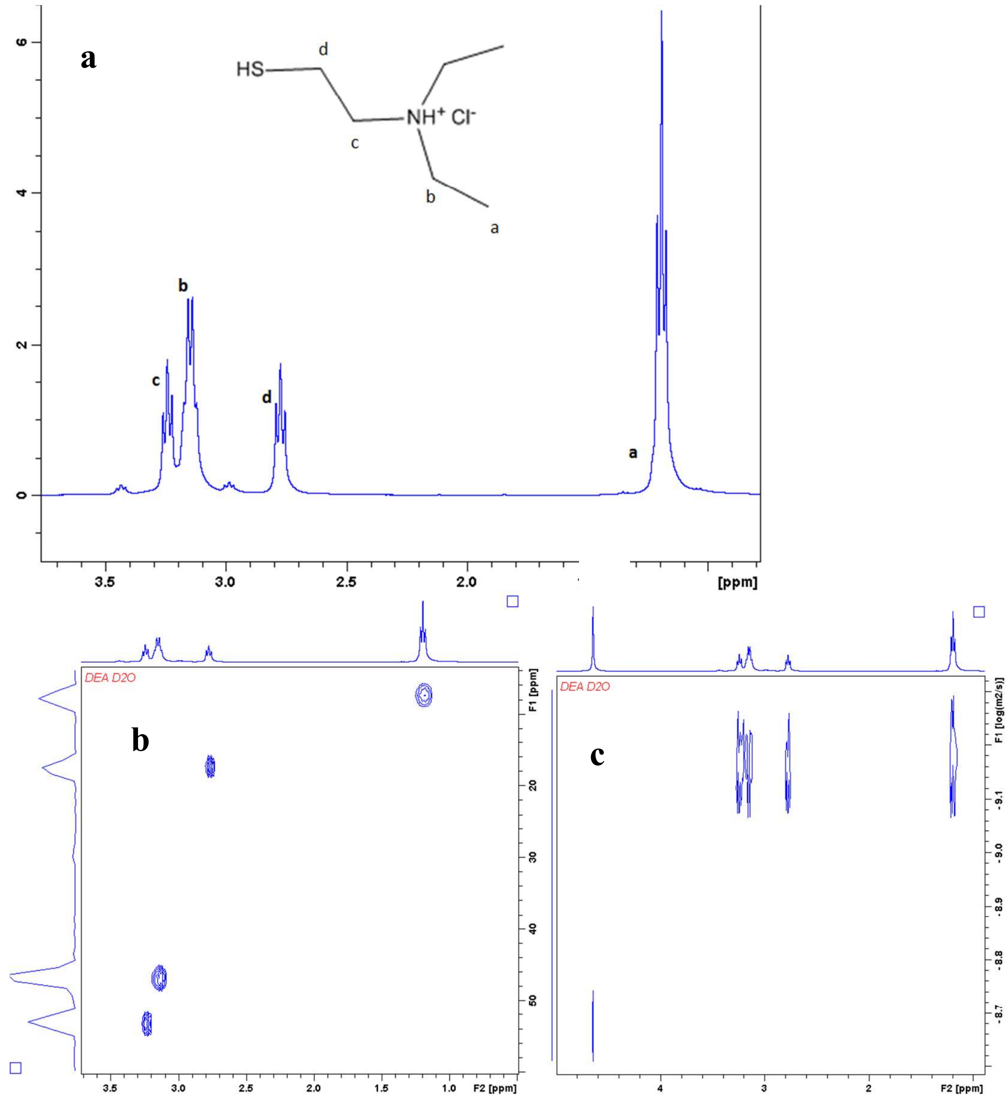


Figure SI-6: NMR spectra of DEA in D_2O: a) ^1H NMR; b) HSQC; c) DOSY.

Moiety	*δ ^{1}H (ppm)*	*Multiplicity*	*δ ^{13}C (ppm)*
-CH_3 (a)	*1,19*	*t (7,4 Hz)*	*8,0*
N-C$\underline{H}_2$-CH_3 (b)	*3,15*	*q (7,4 Hz)*	*47,0*
N-C$\underline{H}_2$-CH_2-S (c)	*3,24*	*t (7,4 Hz)*	*53,9*
N-CH_2-C$\underline{H}_2$-S (d)	*2,78*	*t (7,4 Hz)*	*17,8*

Table SI-1: *resonance assignment of DEA t: triplet, q:quartet*

Moiety	*δ ^{1}H (ppm)*	*Multiplicity*	*δ ^{13}C (ppm)*
$-CH_3$ (a)	0,98	t (7,4 Hz)	11
$N-C\underline{H}_2-CH_3$ (b)	2,48	q (7,4 Hz)	47
$N-C\underline{H}_2-CH_2-S$ (c)	2,71	m	52
$N-CH_2-C\underline{H}_2-S$ (d)	2,71	m	37
$-CH_3$ (a’)	1,08	m	11
$N-C\underline{H}_2-CH_3$ (b’)	2,59	m	47
$N-C\underline{H}_2-CH_2-S$ (c’)	2,84	m	**35**
$N-CH_2-C\underline{H}_2-S$ (d’)	2,84	m	52

Table SI-2. *resonance assignment of AuNPs-DEA t: triplet, q:quartet, m:multiplet*

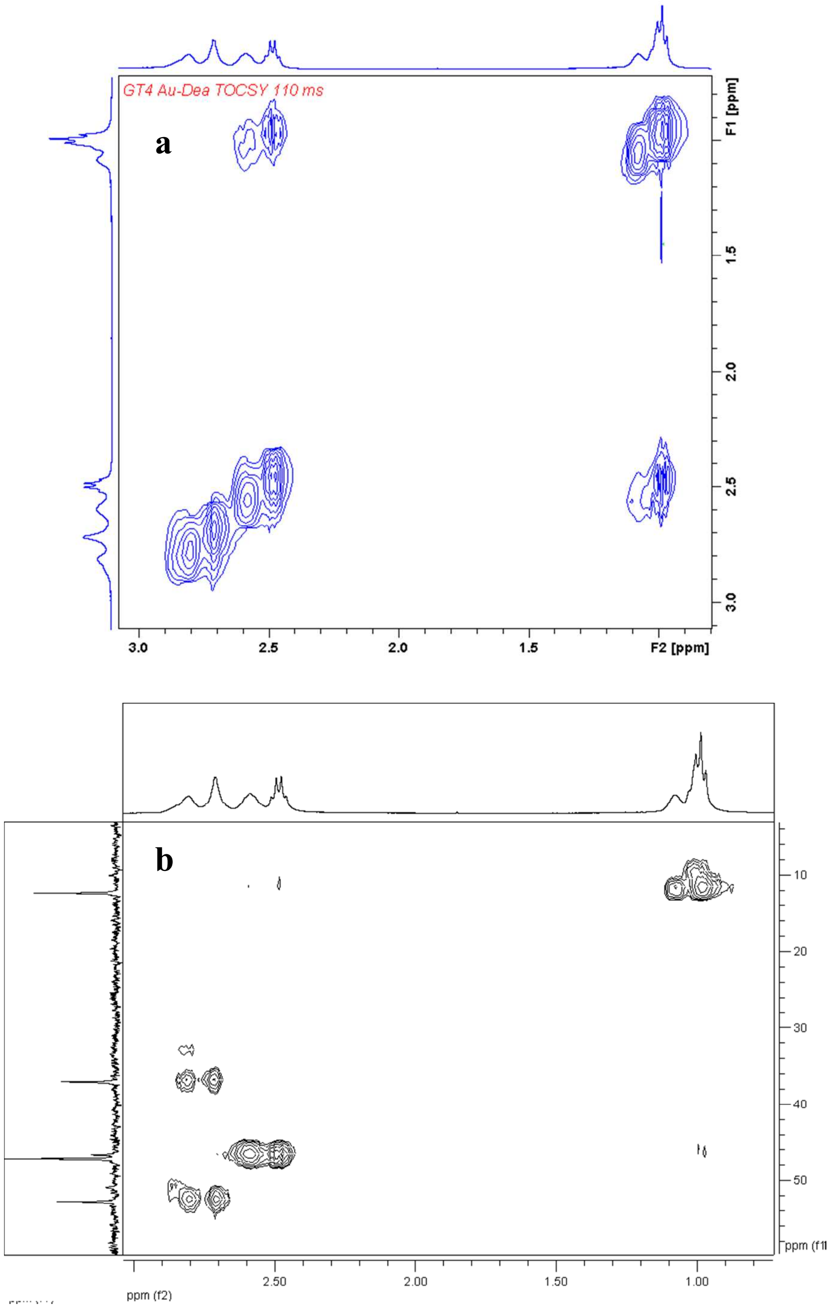


Figure SI-7: NMR spectra of DEA in D_2O: a) TOCSY; b) HSQC.

Sample	SIGNAL	BE (eV)	FWHM (eV)	Atomic %	Atomic ratio I_j/I_i (theor)	Assignment
SAM-DEA						
	C1s	285.00 285.71 286.63 287.39	1.05 1.05 1.05 1.05	55.4 44.6	1.2 (1) 1.0 (1)	C-C + C-S C-N C-O impurities C=O impurities
	$S2p_{3/2}$	161.47 162.22 163.42	1.00 1.00 1.00	30.8 38.3 30.9	1.0 1.2 1.0	RS-Au (S atom sp) RS-Au (S atom sp^3) RS-H
AuNPs-DEA-4						
	C1s	285.00 285.47 286.35 286.96	1.06 1.06 1.06 1.06	51.9 48.1	1.1 (1) 1.0 (1)	C-C + C-S C-N C-O impurities C=O impurities
	$S2p_{3/2}$	161.40 162.44 163.63	1.00 1.00 1.00	28.3 46.6 25.1	1.1 1.8 1.0	RS-Au (S atom sp) RS-Au (S atom sp^3) RS-H
	$Au4f_{7/2}$	83.97 84.73	0.60 0.60	86.37 13.63	6.3 1.0	Au(0) $Au(\delta^+)$
	N1s	399.23 401.28	2.19 2.19	75.06 24.94	3.0 1.0	R_3N (amine) R_3NH^+ (charged amine)
	$Cl2p_{3/2}$	198.42	1.52	100	1.0	Cl^-
AgNPs-DEA-4						
	C1s	285.00 285.62 286.50 287.35	0.91 0.91 0.91 0.91	52.6 47.4	1.1 (1) 1.0 (1)	C-C + C-S C-N C-O impurities C=O impurities
	$S2p_{3/2}$	161.50 162.48 163.49	0.86 0.86 0.86	66.18 19.86 13.96	4.7 1.4 1.0	RS-Ag (S atom sp) RS-Ag (S atom sp^3) RS-H
	$Ag3d_{5/2}$	368.21 369.16	0.78 0.78	96.4 3.6	26.7 1.0	Ag(0) $Ag(\delta^+)$
	N1s	399.37 400.93	2.00 2.00	75.6 24.4	3.1 1.0	R_3N (amine) R_3NH^+ (charged amine)
	$Cl2p_{3/2}$	199.02	2.40	100	1.0	Cl^-

Table SI-3: *SR-XPS data on DEA SAM, AuNPs-DEA-4, AgNPs-DEA-4 samples. The statistic error in semiquantitative XPS analysis is of about 5% of the estimated value*[1].

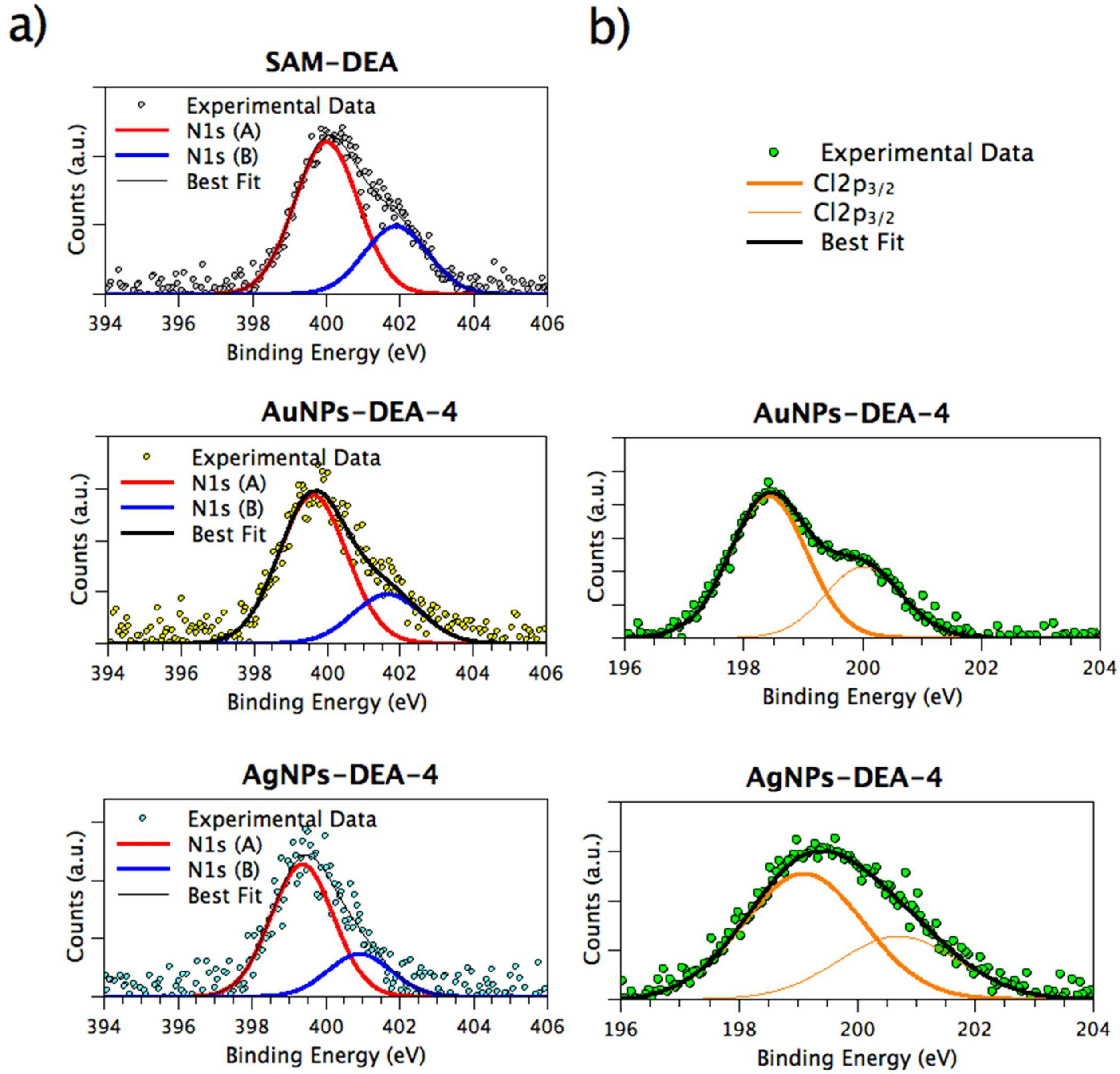


Figure SI-8. *XPS a) N1s and b) Cl2p spectra collected on SAM-DEA, AuNPs-DEA-4 and AgNPs-DEA-4 samples.*

	a_{Au}	σ^2_{I}	σ^2_{II}	σ^2_{MS}	σ^2_{III}	σ^2_{IV}	x	D	R_{AuS}	
	(Å)	(x10^3Å^2)	(x10^3Å^2)	(x10^3Å^2)	(x10^3Å^2)	(x10^3Å^2)		(nm)	(Å)	(x10^3Å^2)
Au	4.061(3)	1.7(1)	2.4(2)	5(2)	2.7(3)	5.5(2)	1	-	-	-
AuNPS-DEA-4	4.055(3)	2.2(1)	3.9(3)	3(1)	3.9(3)	8.4(4)	0.88(7)	9(1)	2.34(1)	5.6(5)
AuNPS-DEA-10	4.054(3)	3.6(2)	5.5(4)	2(1)	5.5(4)	14(1)	0.75(6)	3.6(4)	2.31(2)	3.8(4)

Table SI-4: results of the EXAFS data analysis on Au-foil (Au) and AuNPS-DEA-4 (large NP) and AuNPS-DEA-10 (small NP). The Au bulk lattice parameter (a_{Au}) has been refined while the other coordination distances are calculated applying crystallographic constraints based on fcc structure. Mean square relative displacement (σ^2) parameters were refined independently. The fraction of Au in NP core (x) and the NPs size calculated from the data (see text and ref [2] are reported.

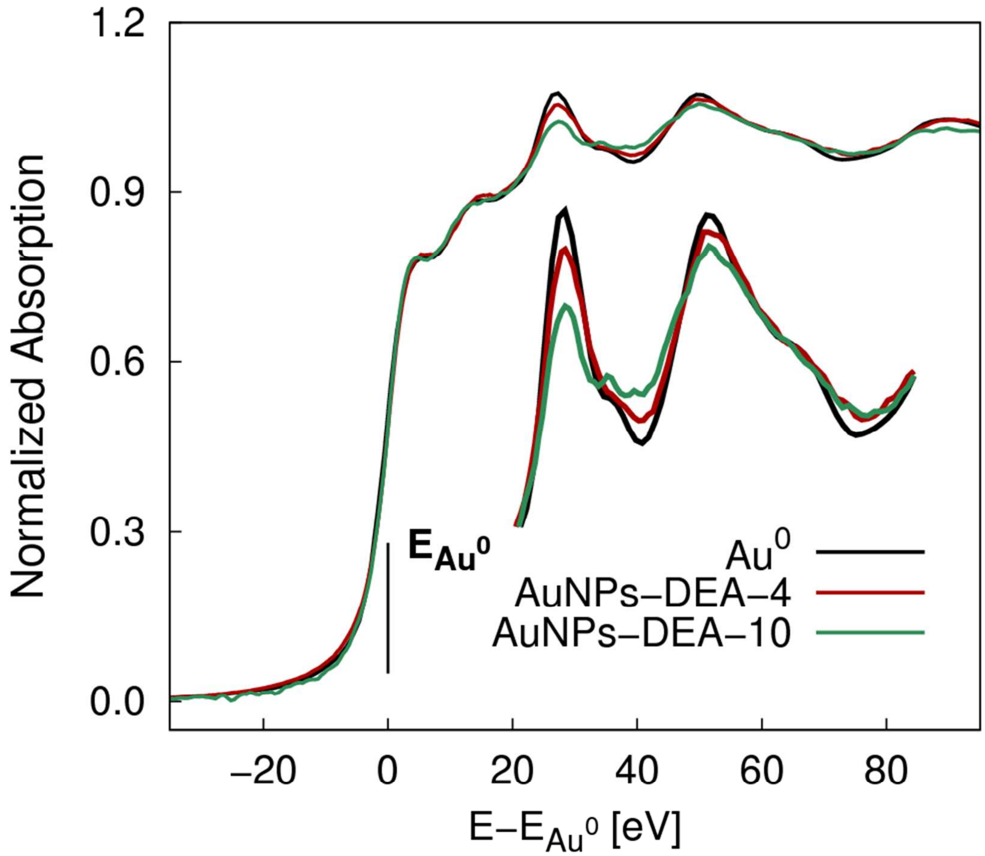


Fig.SI 9.: The Au-LIII normalized absorption spectra for Au-reference foil (black) and AuNPs-DEA samples (red and green curves). The fine structure oscillations progressively decrease (see inset curves) accordingly to the decreasing NPs size.

References

[1] G. Beamson, D. Briggs, High resolution XPS of organic polymers : the Scienta ESCA300 Database, John Wiley & Sons, Chichester, 1992.

[2] Battocchio, C.; Meneghini, C.; Fratoddi, I.; Venditti, I.; Russo, M.V.; Aquilanti, G.; Maurizio, C.; Bondino, F.; Matassa, R.; Rossi, M.; Mobilio, S.; Polzonetti, G. Silver Nanoparticles Stabilized with Thiols: a Close Look to the Local Chemistry and Chemical Structure. *J. Phys. Chem. C* **2012**, 116, 19571–19578