Supporting Information for

Atomistic Simulations of the Surface Coverage of Large Gold Nanocrystals

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Table S1. Interaction and geometric parameters of the simulations.

Force Field Parameters for the LJ Interactions

σ_{ij}[Å]	CH_3	CH_2	SH	$Au_{T=300K}$
CH_3	3.76	3.86	4.11	3.54
CH_2	3.86	3.96	4.21	3.54
SH	4.11	4.21	4.45	2.65
$Au_{T=300K}$	3.54	3.54	2.65	

ε_{ij}/k_B[K]	CH_3	CH_2	SH	$Au_{T=300K}$
CH_3	108	78	117	108
CH_2	78	56	84	88
SH	117	84	126	2795
$Au_{T=300K}$	108	88	2795	

R. Pool et al. J. Phys. Chem. C 2007. 111. 10201-10212

Intramolecular interaction parameters for thiols

$$U^{bond} = \sum_{bonds} \frac{1}{2} k_1 (r - r_0)^2$$

For all bonds: k_1 / k_b = 96500 K/Å

r_0(C-C) = 1.54 Å r_0(C-S) = 1.85 Å

$$U^{bend} = \sum_{bends} \frac{1}{2} k_1 (\cos\theta - \cos\theta_0)^2$$

for all bends: k_2 / k_b = 62500 K / rad^2. θ_0 = 114°

$$U^{torsion} = \sum_{torsion} \sum_{n=0}^{5} \eta_n \cos^n \phi$$

η_n / k_b in K

for Cx-CH2-CH2-Cx and HS-CH-CH2-Cx :

η_0	η_1	η_2	η_3	η_4	η_5
1204.654	1947.740	357.845	1944.666	715.690	1565.572

D. Dubbeldam et al. J. Phys. Chem. B 2004. 108. 12301-12313

Table S2. Characteristics of simulations systems: nanocrystal diameter, thiol type, gold atom number, thiol molecule number, total atoms number, simulation box size and simulation time.

NC diameter (nm)	Thiol type	Au number	thiols number	total atom number	Simulation box size (nm)	simulation time (ns)
0.84	eth	13	100	313	3	30
0.84	but	13	100	513	3	30
1.27	eth	55	170	565	3.5	30
1.27	but	55	170	905	3.5	30
1.72	eth	147	150	597	4.7	30
1.72	but	147	150	897	6.2	30
1.72	oct	147	150	1497	7.3	30
1.72	doc	147	150	2097	8.3	30
1.72	hey	147	150	2697	9.3	30
2.17	eth	309	250	1059	4.5	30
2.17	but	309	250	1559	4.5	30
2.63	eth	561	220	1221	5.6	30
2.63	but	561	220	1661	7.1	30
2.63	oct	561	220	2541	8.2	30
2.63	doc	561	220	3421	9.2	30
2.63	hey	561	220	4301	10.2	30
3.1	eth	923	350	1973	5.5	30
3.1	but	923	350	2673	5.5	30
3.56	eth	1415	400	2615	6	30
3.56	but	1415	400	3415	6	30
3.56	oct	1415	400	5015	8	30
3.56	doc	1415	400	6615	9	30
4.02	eth	2057	450	3407	6.5	30
4.02	but	2057	450	3807	6.5	30
4.49	eth	2869	500	4369	6.75	30
4.49	but	2869	500	5369	6.75	30
4.95	eth	3871	600	5671	8	60
4.95	but	3871	600	6871	9.5	60
4.95	oct	3871	600	9271	10.5	60
4.95	doc	3871	600	11671	11.5	60
4.95	hey	3871	600	14071	12.5	60

NC diameter (nm)	Thiol type	Au number	thiols number	total atom number	Simulation box size (nm)	simulation time (ns)
5.42	eth	5083	700	7183	7.5	30
5.42	but	5083	700	8583	7.5	30
5.88	eth	6525	800	8925	8	30
5.88	but	6525	800	10525	8	30
6.35	eth	8217	900	10917	8.5	30
6.35	but	8217	900	12717	8.5	30
6.81	eth	10179	1000	13179	9.8	90
6.81	but	10179	1000	15179	11.3	90
6.81	oct	10179	1000	19179	12.3	90
6.81	doc	10179	1000	23179	13.4	180
6.81	hey	10179	1000	27179	14.4	90
7.28	eth	12431	1100	15731	9.5	30
7.28	but	12431	1100	17931	9.5	30
7.75	eth	14993	1300	18893	12.3	30
7.75	but	14993	1300	21493	12.3	30
8.21	eth	17885	1400	22085	12.7	30
8.21	but	17885	1400	24885	12.7	30
8.68	eth	21127	1600	25927	13.2	30
8.68	but	21127	1600	29129	13.2	30
9.14	eth	24739	1700	29839	13.7	30
9.14	but	24739	1700	33239	13.7	30
9.61	eth	28741	1900	34441	14.1	30
9.61	but	28741	1900	38241	14.1	30
10.07	eth	33153	2100	39453	14.6	30
10.07	but	33153	2100	43653	14.6	30
10.07	oct	33153	2100	52053	15.6	90
10.07	doc	33153	2100	60453	16.6	110

Suite Table S2

Table S3. Results of simulations: number of adsorbed thiols and ratios between the numbers of adsorption sites and adsorbed thiols. Are shown here the results for the total surface and both the center and edge surfaces of the NC facets.

NC diameter (nm)	Thiol type	adsorbed thiols			void ratio		
		total	center	edge	total	center	edge
0.84	eth	13.984	0.000	13.984	1.43022	0.00000	1.43022
0.84	but	13.984	0.000	13.984	1.43022	0.00000	1.43022
1.27	eth	35.959	0.000	35.959	2.22494	0.00000	2.22494
1.27	but	36.043	0.000	36.043	2.22011	0.00000	2.22011
1.72	eth	61.708	0.000	61.708	2.91698	0.00000	2.91698
1.72	but	61.720	0.000	61.720	2.91641	0.00000	2.91641
1.72	oct	61.754	0.000	61.754	2.91481	0.00000	2.91481
1.72	doc	61.772	0.000	61.772	2.91395	0.00000	2.91395
1.72	hey	60.750	0.000	60.750	2.96298	0.00000	2.96298
2.17	eth	98.943	0.002	98.941	3.23418	4.00000	3.03211
2.17	but	99.768	0.002	99.766	3.20750	4.00000	3.00709
2.63	eth	136.977	0.005	136.972	3.65025	40.00000	3.06632
2.63	but	139.934	0.005	139.929	3.57311	40.00000	3.00152
2.63	oct	139.933	0.003	139.930	3.57314	24.00000	3.00150
2.63	doc	140.066	0.068	139.998	3.56976	7.92063	3.00005
2.63	hey	136.394	0.052	136.342	3.66589	66.60952	3.08053
3.1	eth	195.973	20.004	175.969	3.67398	8.99821	3.06872
3.1	but	195.864	20.004	175.860	3.67603	8.99823	3.07063
3.56	eth	247.266	39.864	207.402	3.96336	8.03111	3.18227
3.56	but	249.938	42.844	207.094	3.92098	7.47062	3.18700
3.56	oct	252.356	39.755	212.601	3.88342	8.05635	3.10454
3.56	doc	246.396	38.718	207.678	3.97735	8.26665	3.17802
4.02	eth	311.355	60.335	251.020	4.11108	8.28715	3.10734
4.02	but	318.082	60.164	257.918	4.02413	8.31074	3.02424
4.49	eth	381.937	101.154	280.783	4.24154	7.11825	3.20535
4.49	but	391.980	106.019	285.961	4.13286	6.79134	3.14729
4.95	eth	463.708	142.881	320.827	4.31306	6.85902	3.17931
4.95	but	472.569	147.649	324.920	4.23219	6.63777	3.13928
4.95	oct	481.348	157.416	323.932	4.15500	6.22597	3.14888
4.95	doc	468.428	146.993	321.435	4.26961	6.66729	3.17329
4.95	hey	422.970	121.493	301.477	4.72847	8.06643	3.38335

NC diameter (nm)	Thiol type	attached thiols			void ratio		
		total	center	edge	total	center	edge
5.42	eth	554.812	197.521	357.291	4.36185	6.48064	3.19071
5.42	but	559.273	196.143	363.130	4.32705	6.52599	3.13941
5.88	eth	640.627	250.671	389.956	4.49560	6.4628	3.23118
5.88	but	654.754	265.776	388.978	4.39861	6.09546	3.23929
6.35	eth	746.528	323.086	423.442	4.52763	6.19040	3.25904
6.35	but	755.863	327.941	427.922	4.47171	6.09880	3.22493
6.81	eth	863.546	392.010	471.536	4.53943	6.17336	3.18111
6.81	but	876.897	410.199	466.698	4.47031	5.89962	3.21409
6.81	oct	903.987	427.122	476.865	4.33635	5.66587	3.14557
6.81	doc	888.489	436.171	452.318	4.41199	5.54832	3.31628
6.81	hey	718.654	391.829	326.825	5.45470	6.17629	4.58995
7.28	eth	977.453	478.216	499.237	4.60381	6.02243	3.24498
7.28	but	988.475	482.257	506.218	4.55247	5.97197	3.20023
7.75	eth	1100.744	562.675	538.069	4.65140	6.00707	3.23383
7.75	but	1130.113	588.519	541.594	4.53052	5.74326	3.21276
8.21	eth	1224.283	655.152	569.131	4.72113	5.98338	3.26817
8.21	but	1258.447	687.832	570.615	4.59296	5.69910	3.25967
8.68	eth	1370.384	759.950	610.434	4.72860	5.92148	3.24362
8.68	but	1401.316	789.337	611.979	4.62423	5.70101	3.23543
9.14	eth	1519.183	879.693	639.490	4.75256	5.82024	3.28390
9.14	but	1541.198	896.125	645.073	4.68467	5.71350	3.25546
9.61	eth	1671.239	1006.939	664.300	4.78687	5.74018	3.34189
9.61	but	1693.694	1011.284	682.410	4.72341	5.71552	3.25320
10.07	eth	1830.583	1120.349	710.234	4.81814	5.78393	3.29472
10.07	but	1859.349	1151.633	707.716	4.74360	5.62682	3.30644
10.07	oct	1927.909	1209.671	718.238	4.57490	5.35684	3.25800

Suite Table S3

Table S4. Results of simulations: percentage of SAMs with more than 10 and 3 members for the total surface and both the center and edge surfaces of the NC facets. and percentage of zigzag SAM formation.

NC diameter (nm)	Thiol type	% SAM >10 members	% SAM > 3 members			% zigzag SAM
			total	center	edge	
0.84	eth	0.00000	55.97582	0.00000	55.96071	10.15907
0.84	but	0.00000	54.94670	0.00000	54.92006	10.32747
1.27	eth	0.00000	53.55069	0.00000	53.57967	99.60777
1.27	but	0.00000	54.52257	0.00000	54.50178	99.47951
1.72	eth	0.00000	10.83330	0.00000	10.68404	16.89873
1.72	but	0.00000	10.12760	0.00000	9.96842	17.23860
1.72	oct	0.00000	10.45762	0.00000	10.32333	17.15183
1.72	doc	0.00000	10.27200	0.00000	10.15198	16.60652
1.72	hey	0.00000	10.99356	0.00000	10.86561	17.58801
2.17	eth	0.00000	12.92266	0.00000	12.91292	71.10939
2.17	but	0.00000	13.40580	0.00000	13.40177	73.51742
2.63	eth	0.00000	30.78706	0.30000	30.79386	82.44026
2.63	but	0.00000	33.29915	0.30000	33.29868	84.44957
2.63	oct	0.00000	33.07886	0.30000	33.07953	82.42796
2.63	doc	0.00000	33.63051	0.40000	33.64959	81.84529
2.63	hey	0.00000	28.28038	0.35000	28.30011	79.29302
3.1	eth	0.00000	31.74790	56.27935	28.96088	81.93310
3.1	but	0.00000	31.51805	52.75128	29.10428	79.79353
3.56	eth	0.10249	47.11279	60.79189	44.50930	79.12221
3.56	but	0.06579	46.31027	62.96081	42.87748	77.10486
3.56	oct	0.00871	38.12523	53.12191	35.31329	80.91274
3.56	doc	0.04461	39.51820	60.02194	35.69663	76.53585
4.02	eth	3.35460	45.02036	64.89505	40.25394	89.02230
4.02	but	1.26811	43.98331	59.65538	40.33152	90.31107
4.49	eth	5.71564	49.18676	67.61807	42.54541	80.44554
4.49	but	6.85565	48.48865	65.80033	42.06975	84.47650
4.95	eth	13.81157	52.47398	70.66782	44.42387	87.31958
4.95	but	15.15110	53.48224	72.44942	44.88688	83.01508
4.95	oct	15.30121	58.34667	76.83048	49.40176	80.31013
4.95	doc	13.67796	56.12613	71.97273	48.88056	83.88382
4.95	hey	3.53609	46.76264	63.83491	39.88457	78.74681

NC diameter (nm)	Thiol type	SAM >10 members	SAM >3 members			zigzag SAM
			total	center	edge	
5.42	eth	24.35116	56.41892	73.94836	46.76836	88.00961
5.42	but	20.15076	54.97103	72.83280	45.35992	88.21437
5.88	eth	29.60575	60.25411	78.57795	48.48698	86.29300
5.88	but	37.30734	65.17569	82.55694	53.35823	82.71182
6.35	eth	38.22114	63.89715	80.95074	50.95016	84.62338
6.35	but	33.65622	66.14690	81.95352	54.05841	85.07621
6.81	eth	49.09019	69.90956	87.16782	55.58189	90.34443
6.81	but	41.46041	70.01495	86.22559	55.79911	81.56118
6.81	oct	30.08857	69.04472	84.43418	55.28394	83.14174
6.81	doc	28.57655	72.44743	86.27891	59.16662	71.19975
6.81	hey	51.34854	76.68040	88.74862	62.21595	37.06469
7.28	eth	48.91729	70.66597	87.28301	54.75712	86.89099
7.28	but	48.97659	70.87072	86.50634	55.99481	86.57526
7.75	eth	54.05348	72.89799	88.64113	56.46922	87.72570
7.75	but	44.29002	72.04357	86.22469	56.64243	84.97137
8.21	eth	50.84976	72.62749	86.96903	56.13185	88.05031
8.21	but	46.56083	73.78650	87.55898	57.21058	82.46795
8.68	eth	58.87118	75.20759	89.12858	57.92433	88.74596
8.68	but	53.26079	75.63136	89.06559	58.35128	84.69985
9.14	eth	58.17399	75.47278	88.73233	57.24636	85.00374
9.14	but	55.40573	76.25910	88.91473	58.68719	83.74576
9.61	eth	58.68362	76.73341	89.23381	57.79174	81.89078
9.61	but	58.20221	76.87859	89.33269	58.43842	85.38945
10.07	eth	61.65004	77.34685	89.64862	57.97088	85.65024
10.07	but	57.22368	77.43289	88.97446	58.66811	80.77892
10.07	oct	40.78062	76.61690	86.82027	59.46750	74.41269

Suite Table S4

Table S5. Results of simulations: Average distance between the SH groups on the center and edge of the NC facets and frequencies of thiol head groups in contact with 1, 2 and 3 gold atoms.

NC diameter (nm)	Thiol type	thiols distance center	thiols distance edge	% Au neighbors per thiol 1	% Au neighbors per thiol 2	% Au neighbors per thiol 3
0.84	eth	0.00000	4.64551	2.53182	45.79480	51.67339
0.84	but	0.00000	4.64531	2.06640	45.75816	52.17545
1.27	eth	0.00000	4.46484	30.35293	24.01756	45.62951
1.27	but	0.00000	4.46525	30.08415	24.15423	45.76161
1.72	eth	0.00000	4.45393	3.68121	29.62699	66.69179
1.72	but	0.00000	4.45378	3.70154	29.47563	66.82283
1.72	oct	0.00000	4.45430	3.79180	29.37326	66.83495
1.72	doc	0.00000	4.45228	3.88161	29.23857	66.87982
1.72	hey	0.00000	4.45672	3.86615	30.76077	65.37308
2.17	eth	0.00000	4.43309	14.89141	23.76313	61.34546
2.17	but	0.00000	4.43164	14.65536	25.64552	59.69912
2.63	eth	0.00000	4.49757	3.10627	21.75403	75.13971
2.63	but	0.00000	4.47930	4.90804	23.75044	71.34152
2.63	oct	0.00000	4.47966	4.88807	23.82204	71.28988
2.63	doc	0.00000	4.48366	5.24063	22.98651	71.77285
2.63	hey	0.00000	4.48872	4.15919	22.71001	73.13079
3.1	eth	0.02175	4.4587	7.73677	21.48160	70.78163
3.1	but	0.02958	4.4545	8.09886	21.13466	70.76647
3.56	eth	4.34705	4.49512	4.78724	25.19464	70.01812
3.56	but	4.40138	4.48880	6.78676	25.06057	68.15267
3.56	oct	4.36720	4.46281	8.28434	23.45298	68.26268
3.56	doc	4.54335	4.48396	8.20371	19.39026	72.40603
4.02	eth	4.42014	4.47343	5.30109	16.95749	77.74142
4.02	but	4.32408	4.44404	5.52441	20.19532	74.28027
4.49	eth	4.52611	4.47985	4.16297	19.92716	75.90987
4.49	but	4.48080	4.46474	5.78882	21.94347	72.26771
4.95	eth	4.52244	4.47243	3.72186	20.92351	75.35463
4.95	but	4.51432	4.46070	5.40957	23.58725	71.00318
4.95	oct	4.52330	4.45811	6.10686	28.86977	65.02337
4.95	doc	4.50849	4.48104	5.31852	22.78914	71.89234
4.95	hey	4.58734	4.50710	1.78736	10.56246	87.65018

NC diameter (nm)	Thiol type	thiols distance center	thiols distance edge	% Au neighbors per thiol 1	% Au neighbors per thiol 2	% Au neighbors per thiol 3
5.42	eth	4.54659	4.48335	5.21013	20.00762	74.78225
5.42	but	4.53999	4.46606	6.81487	19.38139	73.80374
5.88	eth	4.60509	4.47131	1.85678	24.45402	73.68920
5.88	but	4.60712	4.46946	3.96164	27.23880	68.79956
6.35	eth	4.62590	4.47968	2.94065	24.32085	72.73850
6.35	but	4.60340	4.46950	3.31535	26.76193	69.92272
6.81	eth	4.64775	4.48223	1.84338	27.78559	70.37102
6.81	but	4.62147	4.47071	3.50915	29.89122	66.59963
6.81	oct	4.56738	4.45186	5.22397	31.46258	63.31345
6.81	doc	4.59516	4.46588	4.59663	33.84579	61.55758
6.81	hey	4.81976	4.56705	0.10991	11.82125	88.06884
7.28	eth	4.65211	4.48197	1.51463	27.89672	70.58866
7.28	but	4.64744	4.46946	3.01702	28.16037	68.82261
7.75	eth	4.67844	4.47572	2.07551	27.02232	70.90217
7.75	but	4.61499	4.47009	3.46981	29.74978	66.78041
8.21	eth	4.66723	4.48050	1.35866	26.12771	72.51363
8.21	but	4.62663	4.47728	2.88137	30.32946	66.78917
8.68	eth	4.68622	4.48664	1.61128	27.28723	71.10148
8.68	but	4.6473	4.47923	3.05901	29.82372	67.11727
9.14	eth	4.67977	4.48188	1.66173	27.66513	70.67315
9.14	but	4.65585	4.47565	2.52108	29.69637	67.78255
9.61	eth	4.67596	4.48167	1.31925	28.51831	70.16244
9.61	but	4.65992	4.47444	1.96207	29.64992	68.38802
10.07	eth	4.68693	4.48602	1.52523	27.51321	70.96156
10.07	but	4.65657	4.47534	2.13574	29.99012	67.87415
10.07	oct	4.58794	4.45445	4.19231	33.45282	62.35486
10.07	doc	4.61372	4.68708	3.12663	30.41266	66.46071

Suite Table S5

Table S6. Influence of the SH-Au and SH-SH interactions. In the first column, we give the factor with which $\varepsilon_{Au,SH}$ is multiplied. Here we show the results for 7 nm NC coated with butanethiol.

First table: number of adsorbed thiols and ratios between the numbers of adsorption sites and adsorbed thiols. Are shown here the results for the total surface and both the center and edge surfaces of the NC facets.

Factor for $\varepsilon_{Au,SH}$	**$\sigma_{SH,SH}$[Å]**	**adsorbed thiols**			**void ratio**		
		total	**center**	**edge**	**total**	**center**	**edge**
1/100	4.45	125.4	068.0	057.4	31.29	35.64	26.19
1/10	4.45	356.4	188.7	167.8	11.0	12.83	8.95
1/5	4.45	611.5	319.1	292.4	6.41	7.59	5.13
1/2	4.45	816.0	419.0	397.0	4.80	5.78	3.78
1/1.5	4.45	842.0	403.0	439.0	4.66	6.00	3.42
1	4.45	877.0	409.0	468.0	4.47	5.92	3.21
1.5	4.45	907.0	418.0	489.0	4.32	5.79	3.07
2	4.45	921.0	427.0	494.0	4.26	5.67	3.04
5	4.45	991.7	467.9	523.8	3.95	5.17	2.86
10	4.45	1000.0	488.0	512.0	3.92	4.96	2.93
100	4.45	989.3	588.0	401.3	3.96	4.12	3.74
1	4.97	710.2	424.3	285.8	5.52	5.70	5.25
5	4.97	798.5	367.0	431.5	4.91	6.59	3.48

Second table: percentage of SAMs with more than 10 and 3 members for the total surface and both the center and edge surfaces of the NC facets, and percentage of zigzag SAM formation.

Factor for $\varepsilon_{Au,SH}$	**$\sigma_{SH,SH}$[Å]**	**% SAM >10 members**	**% SAM > 3 members**			**% zigzag SAM**
			total	**center**	**edge**	
1/100	4.45	00.0	07.4	11.4	05.8	00.1
1/10	4.45	00.1	32.2	43.2	27.0	01.6
1/5	4.45	26.7	68.2	78.9	58.5	11.5
1/2	4.45	65.1	80.8	90.5	70.5	43.6
1/1.5	4.45	60.7	75.8	91.3	61.5	76.5
1	4.45	42.5	70.9	87.3	56.6	81.2
1.5	4.45	24.9	63.4	77.8	51.1	85.9
2	4.45	18.7	65.0	78.5	53.4	87.4
5	4.45	06.9	57.7	76.3	41.1	48.9
10	4.45	04.3	55.4	74.2	37.5	39.4
100	4.45	00.5	45.5	53.3	34.2	19.2
1	4.97	94.3	97.4	99.9	93.9	05.2
5	4.97	14.8	50.8	66.6	37.2	74.0

Third table: Average distance between the SH groups on the center and edge of the NC facets and frequencies of thiol head groups in contact with 1, 2 and 3 gold atoms.

Factor for $\varepsilon_{Au,SH}$	**$\sigma_{SH,SH}$[Å]**	**thiols distance**		**% Au neighbors per thiol**		
		center	**edge**	**1**	**2**	**3**
1/100	4.45	4.91	0.00	41.5	26.5	31.3
1/10	4.45	4.88	4.87	29.9	35.2	34.9
1/5	4.45	4.85	4.81	14.3	35.6	50.1
1/2	4.45	4.75	4.64	6.60	35.4	58.0
1/1.5	4.45	4.72	4.56	3.20	32.8	64.0
1	4.45	4.62	4.47	3.00	30.6	66.5
1.5	4.45	4.51	4.40	3.30	24.8	71.9
2	4.45	4.47	4.39	2.80	23.6	73.6
5	4.45	4.33	4.14	1.00	20.1	78.9
10	4.45	4.27	4.04	0.40	15.2	84.4
100	4.45	3.90	3.69	0.30	01.5	98.2
1	4.97	4.99	4.85	0.70	06.2	93.1
5	4.97	4.62	4.47	1.30	09.0	89.6

Table S7. Influence of the temperature. Here we show the results for 7 nm NC coated with butanethiol.

First table: number of adsorbed thiols and ratios between the numbers of adsorption sites and adsorbed thiols. Are shown here the results for the total surface and both the center and edge surfaces of the NC facets.

Temperature	**adsorbed thiols**			**void ratio**		
	total	**center**	**edge**	**total**	**center**	**edge**
50 K	490	272	218	8	8.9	6.88
100 K	675	357	318	5.81	6.78	4.72
150 K	868	394	474	4.52	6.14	3.16
200 K	897	415	482	4.37	5.83	3.11
250 K	889	421	468	4.41	5.75	3.21
300 K	884	412	472	4.43	5.87	3.18
350 K	863	400	463	4.54	6.05	3.24
400 K	854	397	457	4.59	6.1	3.28
450 K	840	395	445	4.67	6.13	3.37
500 K	826	405	421	4.75	5.98	3.56

Second table: percentage of SAMs with more than 10 and 3 members for the total surface and both the center and edge surfaces of the NC facets, and percentage of zigzag SAM formation.

Temperature	% SAM >10 members	% SAM > 3 members			% zigzag SAM
		total	center	edge	
50 K	4.9	47.1	59.6	31.7	23.9
100 K	19	58.4	73.9	40.9	57.2
150 K	15.4	56.3	69.8	45.1	86.9
200 K	31	64.4	79	51.9	87.3
250 K	35.1	70.9	84.3	58.8	84
300 K	41.9	70	86.4	55.7	83.9
350 K	50.9	70.9	88	56.2	81.9
400 K	56.8	73.7	88.2	61.1	80.1
450 K	51.5	73.5	89.1	59.6	81.6
500 K	51	75.2	89.1	61.8	67.2

Third table: Average distance between the SH groups on the center and edge of the NC facets and frequencies of thiol head groups in contact with 1, 2 and 3 gold atoms.

Temperature	thiols distance		% Au neighbors per thiol		
	center	edge	1	2	3
50 K	4.77	4.01	0.4	1.8	97.8
100 K	4.7	4.25	0.1	6.8	93
150 K	4.53	4.42	3.5	18.8	77.8
200 K	4.55	4.43	4.1	25.8	70.1
250 K	4.58	4.46	3.7	29.2	67
300 K	4.61	4.47	4.1	30.2	65.7
350 K	4.65	4.48	3	29	68
400 K	4.67	4.51	2.8	30.7	66.5
450 K	4.69	4.53	2.5	31.9	65.6
500 K	4.7	4.55	2.1	29.4	68.5

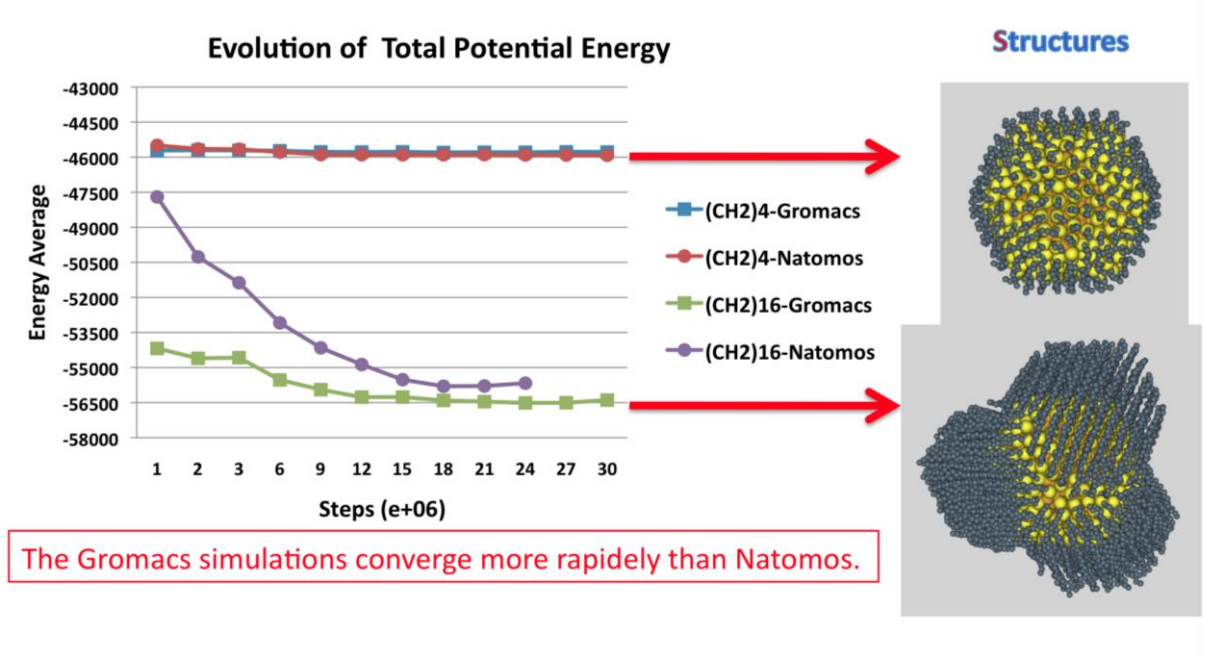

Figure S1. Evolution of the potential total energy with simulation steps for 4.7 nm NCs coated with butane and hexadecane thiol. The corresponding structures obtained by Gromacs are shown on the right.

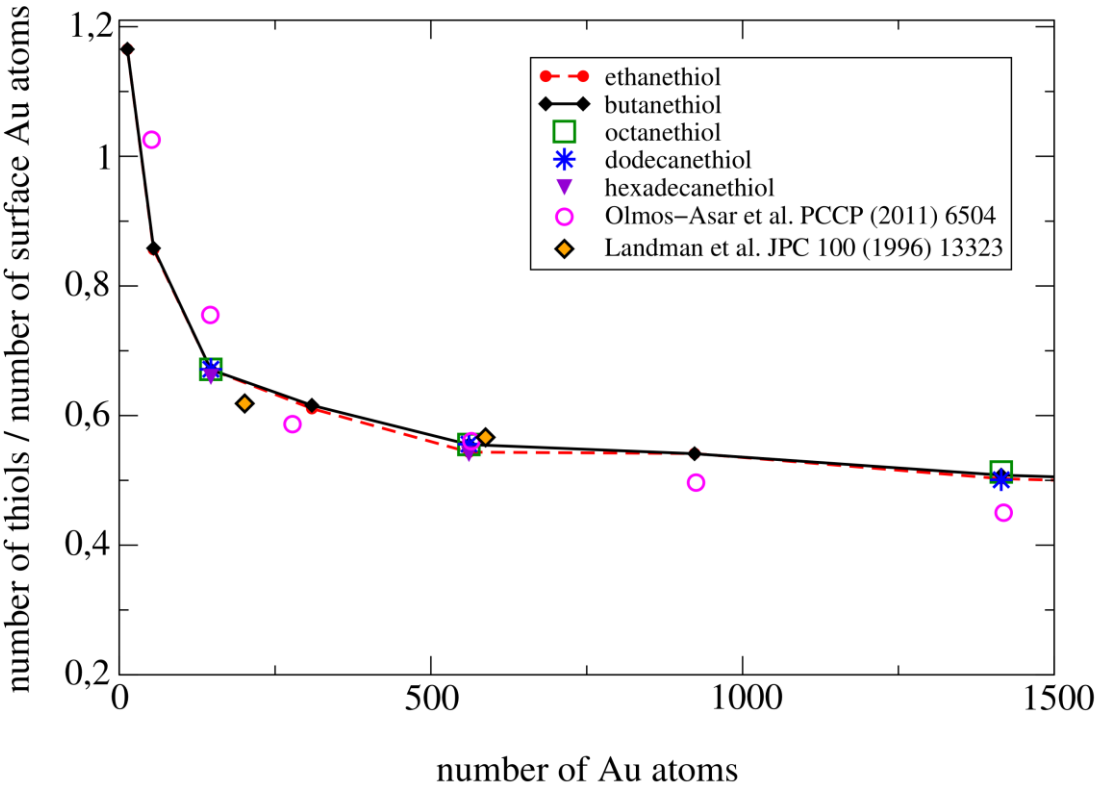

Figure S2. Ratio of the numbers of adsorbed thiols and gold atoms on the NC surface. Our results are compared to those obtained in Refs.(17,24).

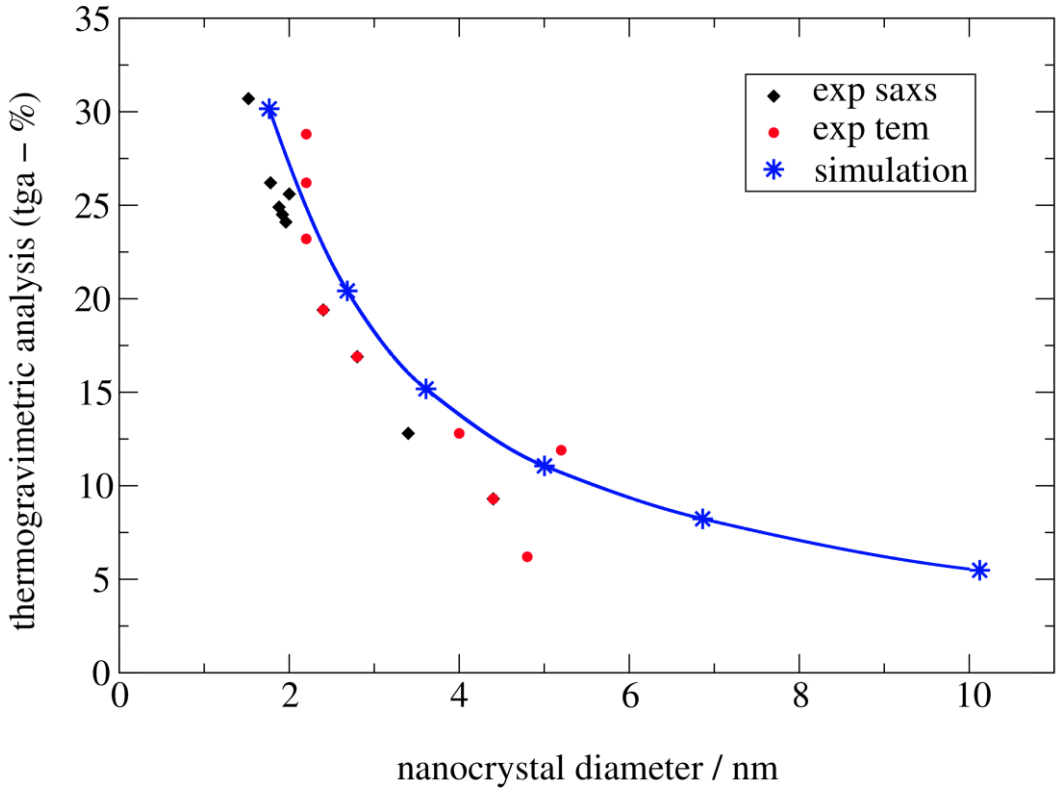

Figure S3. The mass percentage of the organic ligand with respect to the total mass of dodecanethiol coated NCs obtained by simulations and experiments (exp). A spline fit connects the theoretical data. The experimental data are taken from table 1 in Ref. 14 where the radius is obtained either by HRTEM or from SAXS using Porod plot.

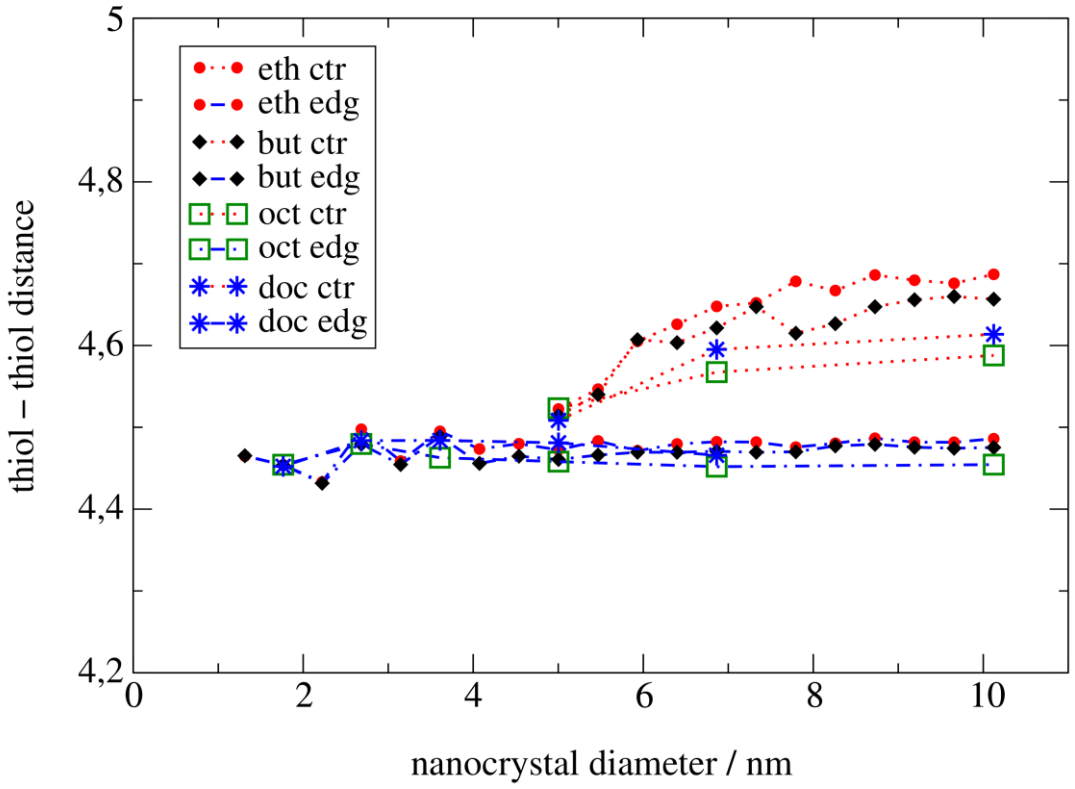

Figure S4. Average distance between neighboring SH groups on the edge and center of the facets.