Supporting Information

Centrone *et al.* **10.1073/pnas.0803929105**

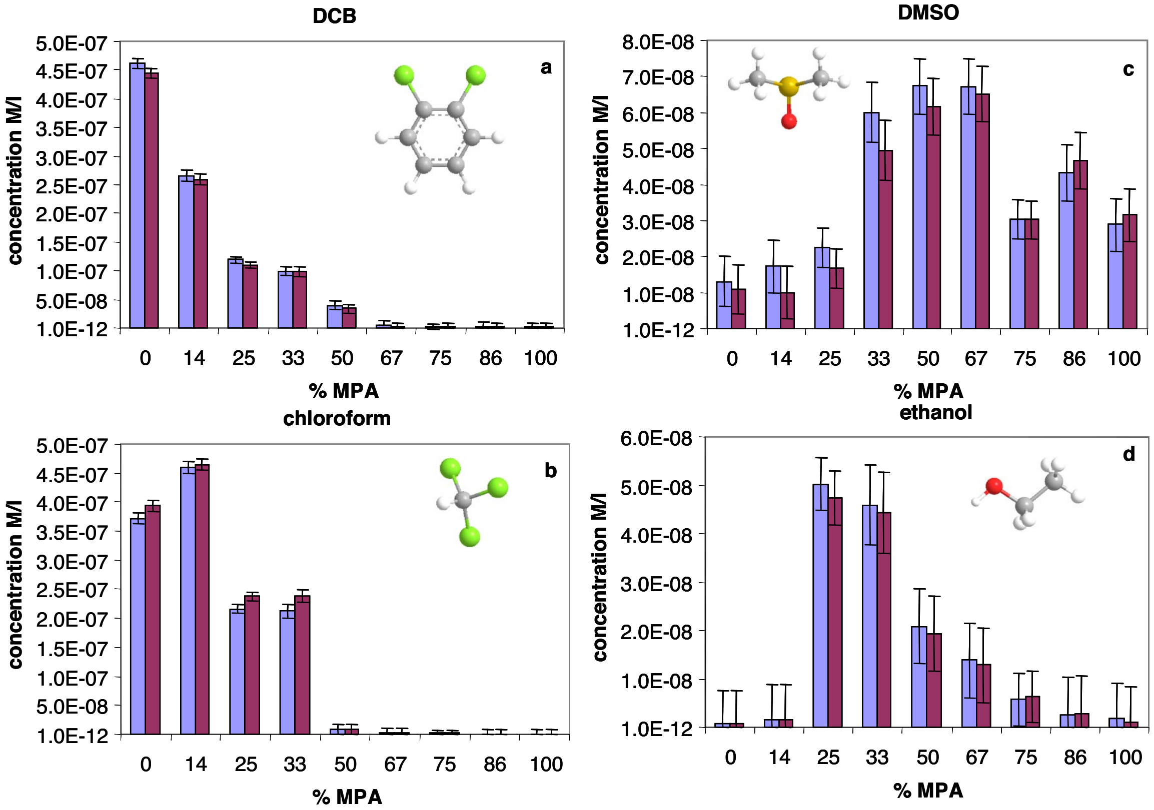

Fig. S1. The blue bars are the concentrations in M × l^{-1} for OT/MPA NPs dissolved in different solvents obtained after a week of decanting; the red bars are the concentration obtained after decanting the samples respectively for 13 days (*a*, DCB), 12 days (*b*, chloroform), 24 days (*c*, DMSO), and 12 days (*d*, ethanol). Error bars are the largest variation in concentration observed for different spectra on the same sample (they account for instrumental, dilution, and sample-preparation uncertainties). The molecular structures of the solvent used have the following color code: carbon (gray), hydrogen (white), oxygen (red), sulfur (yellow), and chlorine (green).

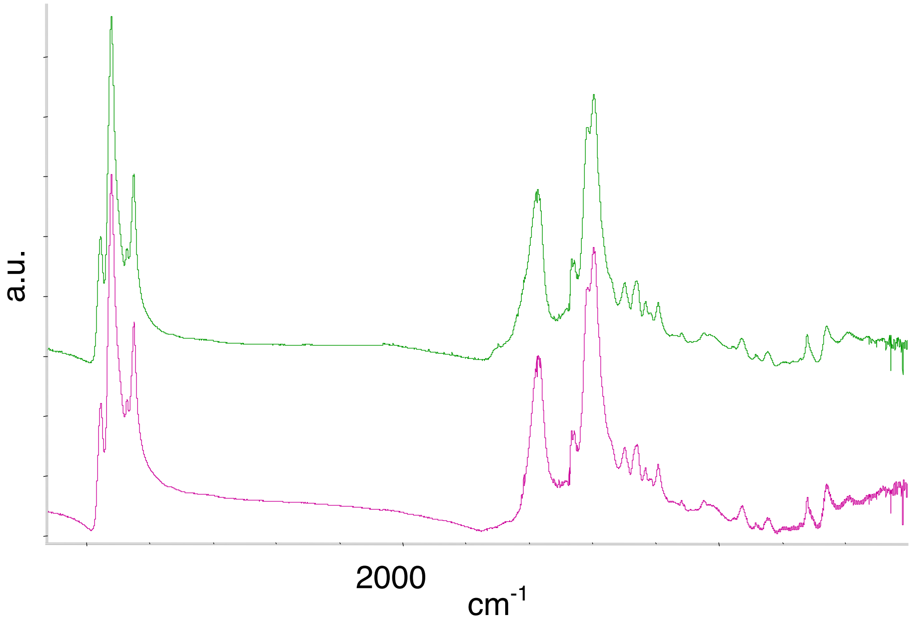

Fig. S2. Comparison of OT-MPA 2–1 NPs FTIR spectra obtained on the pristine material (purple) and after 14 days in chloroform solution (green).

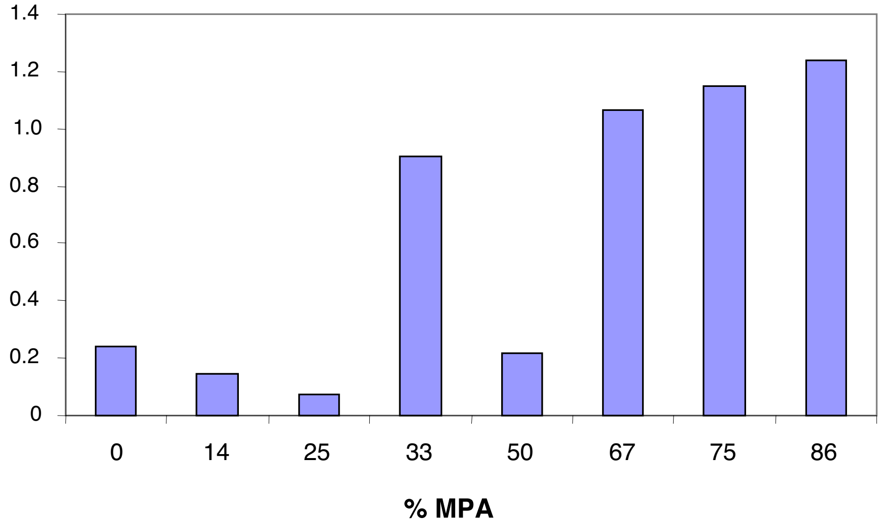

Fig. S3. Partition function of HT-MPA NPs in DMSO as a function of MPA composition. The partition function is defined by the ratio of the optical density in DMSO obtained after mixing the DMSO solution with hexane with respect to the optical density of the original DMSO solution. DMSO solutions of OT-MPA NPs were prepared as described in the main text. After a week of decanting, solutions with an optical density of 0.15 at the plasmon peak were prepared for all of the NPs' compositions. An equal amount of hexane was added, and the solutions were stirred for 1 h. After the stirring, the solvents were allowed to separate, and the optical density at the plasmon peak was determined from the DMSO fraction.

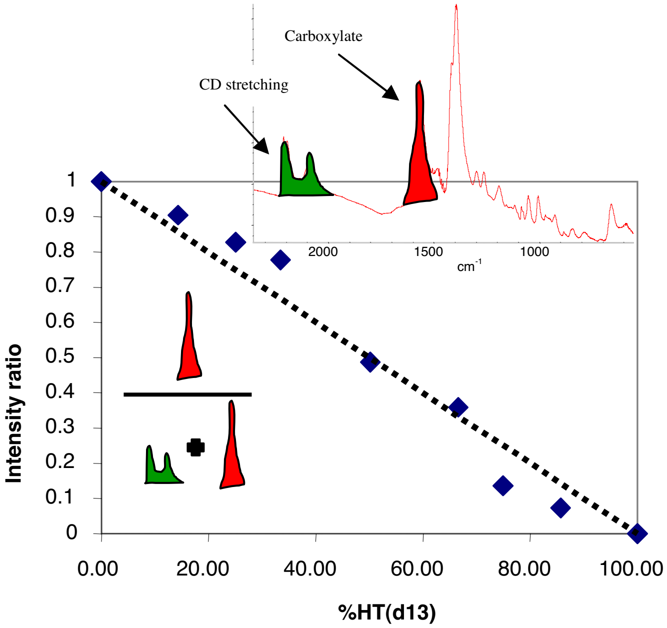

Fig. S4. We synthesized a series of NPs coated with a fully deuterated hexane thiol, HT(d13), and MPA to verify by means of IR spectroscopy that the composition in the ligand shell was close to the ligand stoichiometric ratio used in the synthesis following an already published method (1). Here, we report the plot of the ratio of intensity of the CO stretching peak to the sum of the CO stretching peak and of the CD stretching region as function of stoichiometric fraction of HT(d13) used to synthesize HT(d13)/MPA NPs. The dotted line (perfect correspondence to stoichiometric ratio between ligand) is meant to guide the eye. The *Inset* provides a qualitative cartoon to explain how the peak intensity ratio was calculated.

1. Centrone A, Hu Y, Jackson AM, Zerbi G, Stellacci F (2007) Phase separation on mixed-monolayer-protected metal nanoparticles: A study by infrared spectroscopy and scanning tunneling microscopy. *Small* 3:814–817.

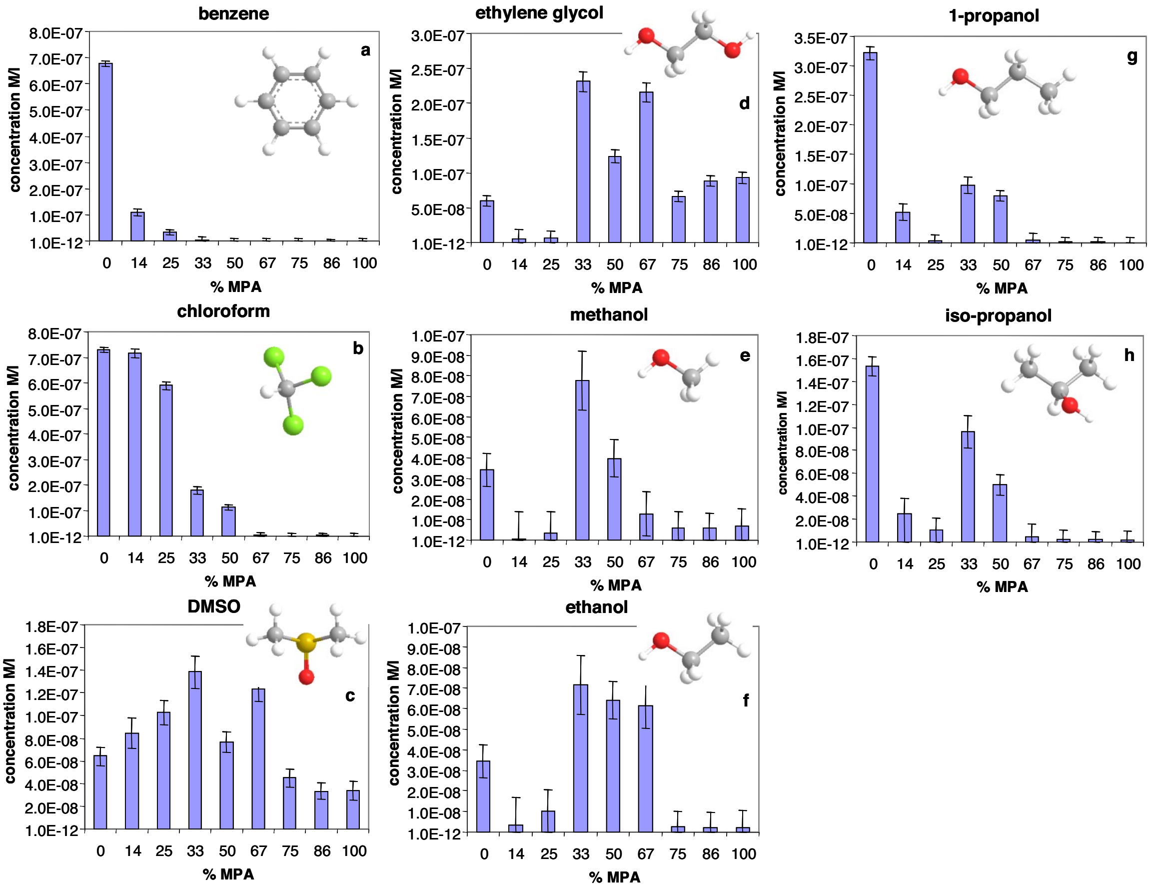

Fig. S5. Concentrations in M × l^{-1} for HT/MPA NPs dissolved in various solvents: benzene (*a*), chloroform (*b*), DMSO (*c*), ethylene glycol (*d*), methanol (*e*), ethanol (*f*), 1-propanol (*g*), and iso-propanol (*h*). Error bars are the largest variation in concentration observed for different spectra on the same sample and/or on samples with the same composition prepared on different occasions (they account for instrumental, dilution, and sample-preparation uncertainties). The molecular structures of the solvents used have the following color code: carbon (gray), hydrogen (white), oxygen (red), sulfur (yellow), and chlorine (green).

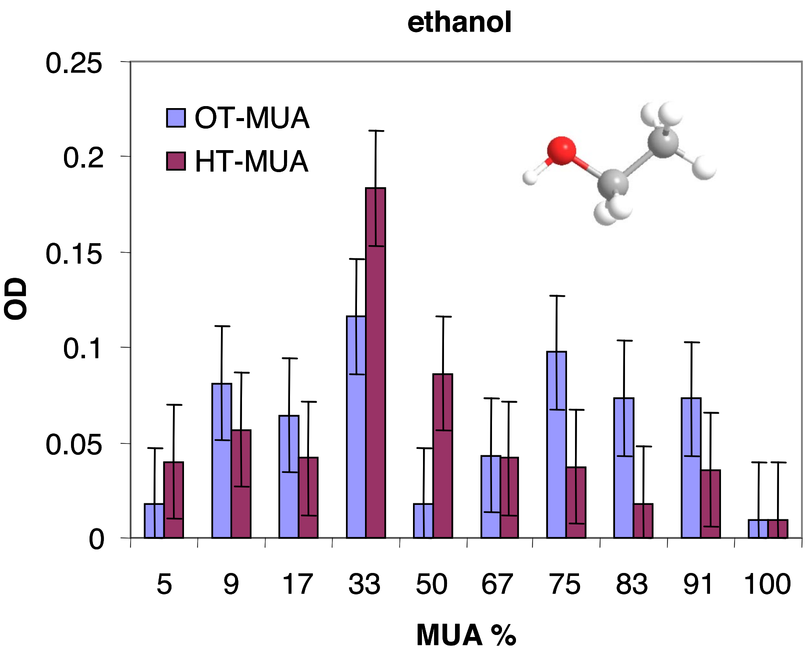

Fig. S6. Optical density at the plasmon resonance peak (≈520 nm) for OT/MUA (blue) and HT-MUA (purple) NPs dissolved in ethanol. Error bars are the largest variation in concentration observed for different spectra on the same sample and on samples with the same composition prepared on different occasions (they account for instrumental, dilution, and sample-preparation uncertainties). The molecular structures of the solvents used have the following color code: carbon (gray), hydrogen (white), oxygen (red). These NPs were not analyzed as synthesized, but we tried to protonate the carboxylate groups. Briefly 1 mg of nanoparticles was suspended in ethanol (≈2 ml) via sonication. One drop of hydrochloric acid was added to form sodium chloride and reduce the sodium carboxylate end groups into carboxylic acid. The nanoparticle solution was quickly dried and than washed extensively with deionized water to remove salt precipitates. After removal of water, 10 ml of ethanol was added. The new solution was sonicated for 15 min and stirred for 3 h. After stirring, the solution was given 1 week to settle before further use.

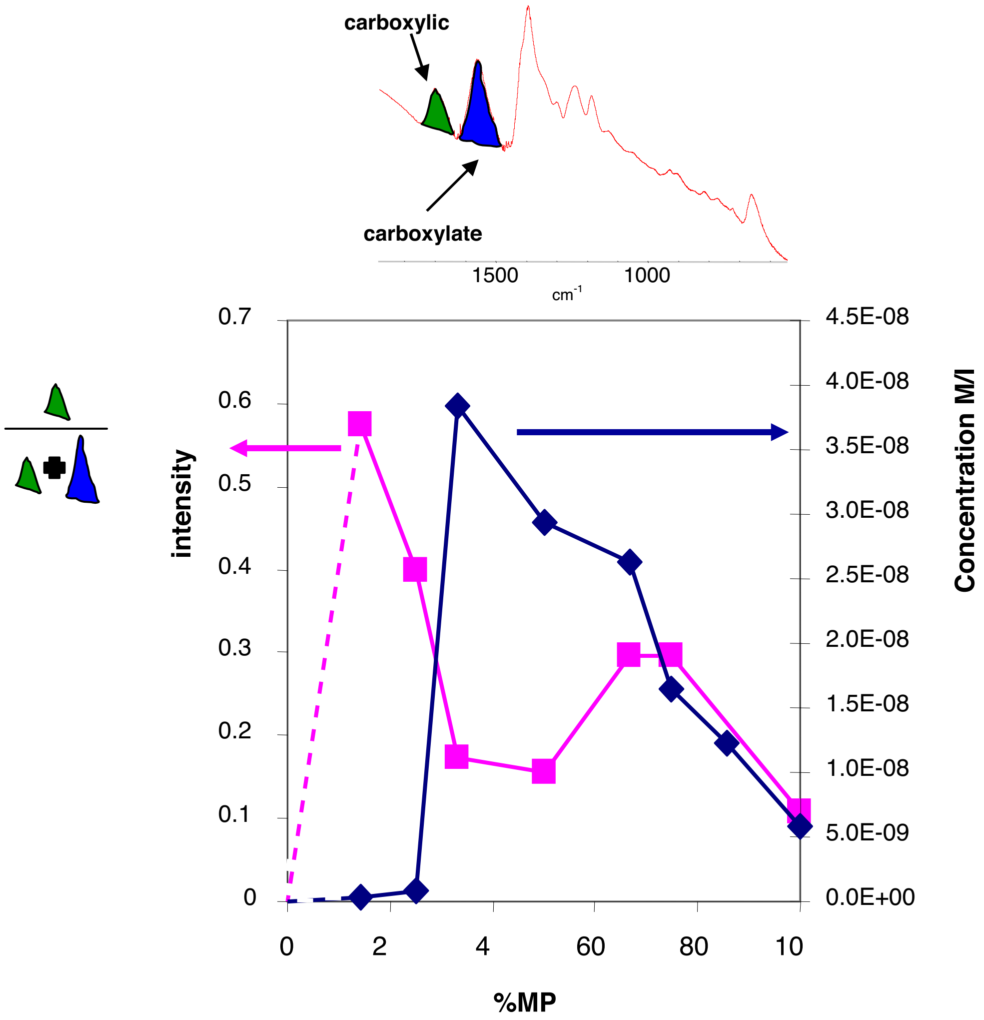

Fig. S7. Plot of saturation concentration for OT-MPA NPs as a function of composition (blue, right scale) compared with the ratio of intensity of the carboxylic C–O stretching peak to the sum of the carboxylic C–O stretching peak and of the asymmetric carboxylate CO peak (purple, left scale); The *Inset* provides a qualitative cartoon to explain how the peak intensity ratio was calculated.

Table S1. Average core diameter (in nanometers), standard deviation (in nanometers), and ratio of the standard deviation to the average diameter as determined from TEM images or OT-MPA and HT-MPA NPs

OT, %	MPA, %	Avg. diameter, nm	SD, nm	Stdv/(Avg. Diam.)	Extinction coefficient (M^{-1} × cm^{-1})
			OT-MPA NPs		
100.0	0.0	3.84	1.11	0.29	4.313E+06
85.7	14.3	3.78	1.04	0.28	4.093E+06
75.0	25.0	4.13	1.24	0.30	5.494E+06
66.7	33.3	3.65	0.99	0.27	3.614E+06
50.0	50.0	3.72	1.03	0.28	3.878E+06
33.3	66.7	3.73	1.09	0.29	3.885E+06
25.0	75.0	4.16	0.98	0.24	5.605E+06
14.3	85.7	3.72	1.06	0.29	3.857E+06
0.0	100.0	3.78	1.09	0.29	4.091E+06
			HT-MPA NPs		
100.0	0.0	3.68	0.83	0.23	3.731E+06
85.7	14.3	3.15	0.70	0.22	2.226E+06
75.0	25.0	3.39	0.97	0.29	2.841E+06
66.7	33.3	3.10	0.51	0.16	2.111E+06
50.0	50.0	3.55	0.86	0.24	3.311E+06
33.3	66.7	3.38	0.97	0.29	2.813E+06
25.0	75.0	3.71	0.79	0.21	3.833E+06
14.3	85.7	3.78	1.07	0.28	4.078E+06
0.0	100	3.62	0.78	0.21	3.533E+06

The NPs extinction coefficient (M^{-1} × cm^{-1}) was calculated from the average diameters by using the approach developed by Liu and coworkers (1).

1. Liu X, Atwater M, Wang J, Huo Q (2007) Extinction coefficient of gold nanoparticles with different sizes and different-capping ligands. *Colloids Surf B* 58:3–7.

Table S2. Dipole moments (10^{30} C × m), polarity indexes, dielectric constants, and Hildebrand parameters ($MPa^{1/2}$) of the solvents used in this study

Solvent	Dipole moment (10^{30} C × m) (3)	Polarity index*	Dielectric constant*	Hildebrand parameter ($MPa^{1/2}$)*
Methanol	5.54	5.1	32.63	29.6
Ethanol	5.61	4.3	24.30	26.5
1-propanol	5.54	4.0	20.1	24.5
Isopropanol	5.61	3.9	18.3	23.5
Ethylene glycol	7.7	6.9	37.7[†]	32.9
DMSO	14.98 (vapor)	7.2	46.6	26.7
1,2 dichlorobenzene	8.34[‡]	2.7[§]	7.5 (7)	20.5
THF	5.44	4.0	7.61	19.4
Chloroform	3.84	4.1	4.81	19.0
Hexane	0.27	0.1	1.89	14.9
Carbon tetrachloride	0.0	1.6	2.2[¶]	17.8
Benzene	0.0	2.7	2.28	18.6

*The values are obtained from Barton AFM (1983) *Handbook of Solubility Parameters and Other Cohesion Parameters* (CRC, Boca Raton, FL) unless otherwise noted.

[†] Value obtained from http://organicdivision.org/organic_solvents.html.

[‡] Value obtained from Lide DR (1995) *Handbook of Organic Solvents* (CRC, Boca Raton, FL).

[§] Value obtained from http://macro.lsu.edu/howto/solvents/Polarity%20index.htm.

[¶] Value obtained from www.knovel.com/knovel2/Show_Table.jsp.

Table S3. Relative changes in the interfacial free energy induced from changes in the solvent pressure after surface ordering

Surface	$\langle P_z \rangle$, kbar	$\Delta I_{1,N}$, cal/mol/Å^2
1 × 1	−0.05	0.0
2 × 2	−0.16	−17.0
3 × 3	−0.19	−22.0
4 × 4	−0.25	−31.5
6 × 6	−0.37	−51.1
12 × 12	−0.62	−91.2