#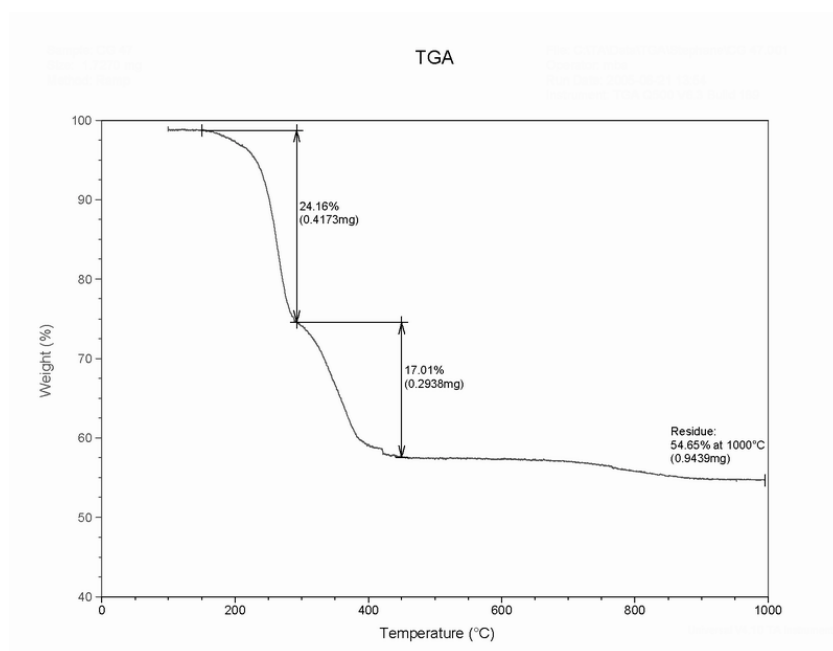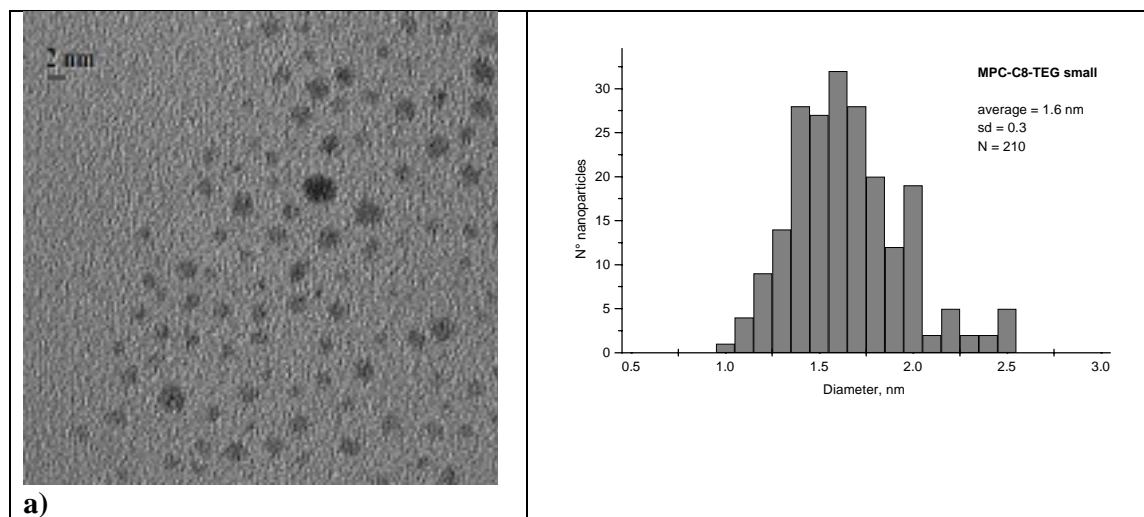 Effect of core size on the partition of organic solutes in the monolayer of water soluble nanoparticles: an ESR investigation

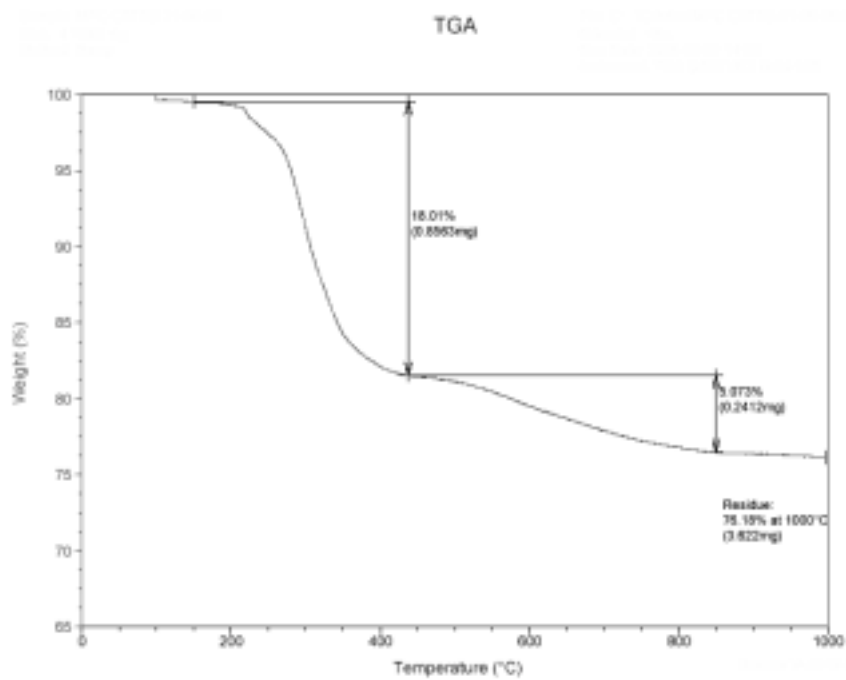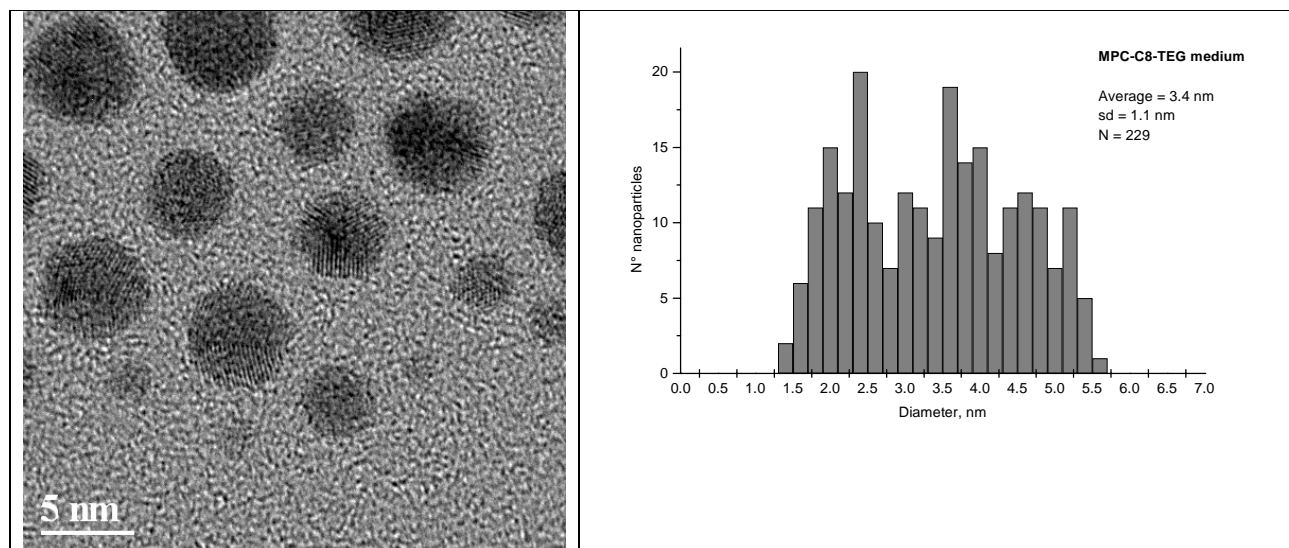Marco Lucarini,*[†] Paola Franchi,[†] Gian Franco Pedulli,[†] Cristina Gentilini,[‡] Stefano Polizzi,[§] Paolo Pengo,[¶] Paolo Scrimin[¶] and Lucia Pasquato*[‡]

[†] University of Bologna
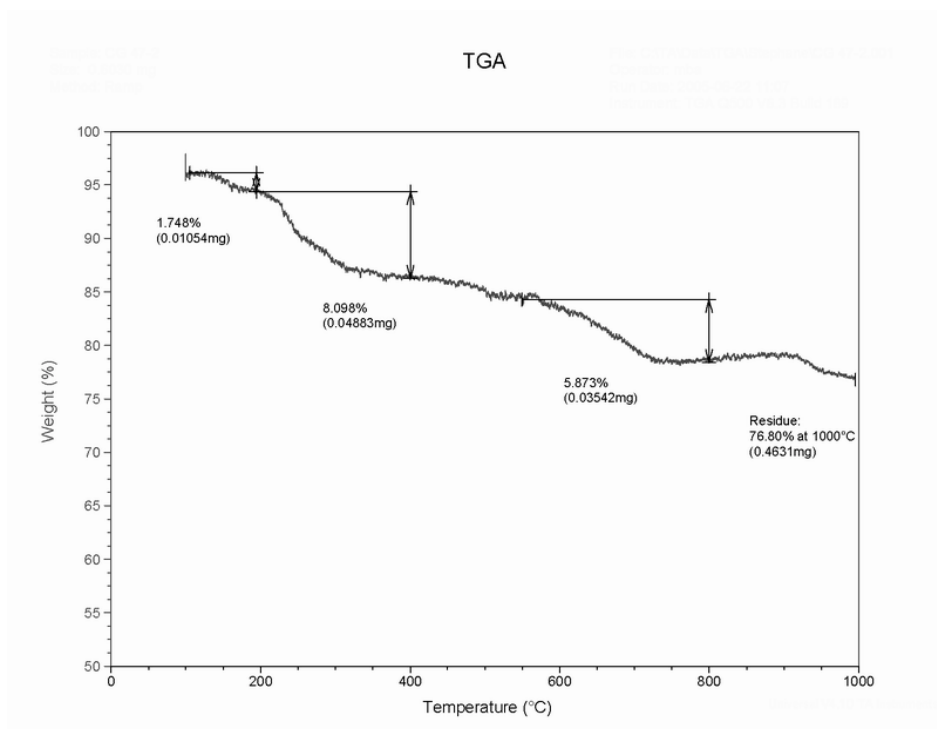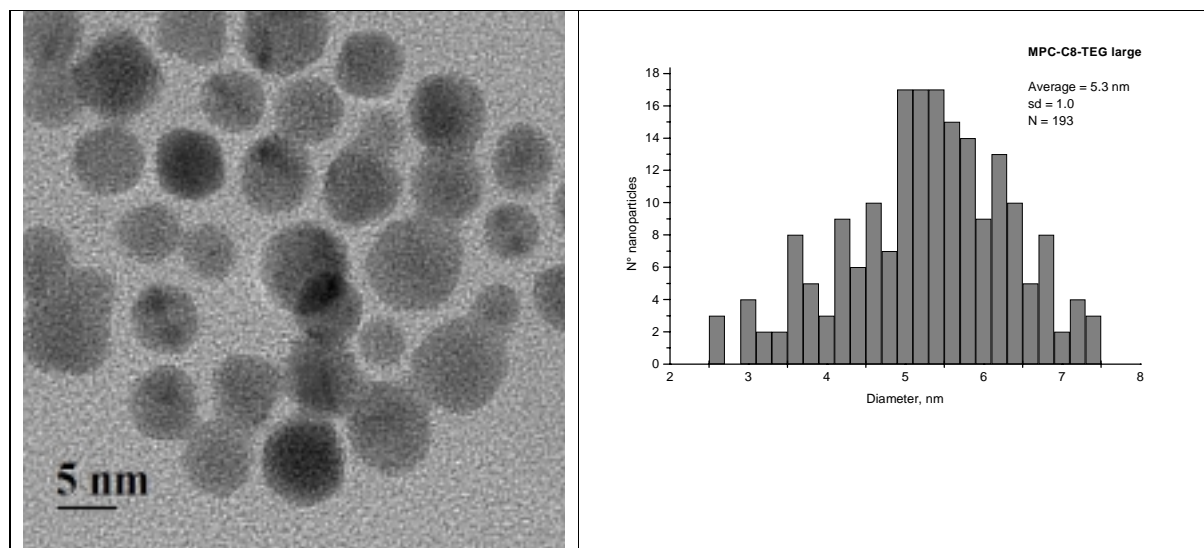[‡] University of Trieste
[§] University of Venice
[¶] University of Padova

Figure S1. TEM image, histogram and TGA analysis of MPC-C8-TEG with an average core diameter of 1.6 nm.

Figure S2. TEM image, histogram and TGA analysis of MPC-C8-TEG with an average core diameter of 3.4 nm.

Figure S3. TEM image, histogram and TGA analysis of MPC-C8-TEG with an average core diameter of 5.3 nm.

***Table S1.*** Detailed radical ratios determined by ESR measurements of equilibrium constant K_{eq}.

Average size (nm)	[MPC-C8-TEG] (mg/mL)	[HS-C8-TEG]^a (mM)	$\dfrac{[\,2\,]_{\text{MPC-C8-TEG}}}{[\,2\,]_{\text{water}}}$	K_{eq} (M^{-1})
1.6	26.1	33.6	3.2	104.0 ± 7.4
Au$_{116}$(SR)$_{50}$	40.9	52.6	5.8	
(MW=38,852)	53.8	69.2	7.0	
	76.9	98.9	10.2	
3.4	48.7	33.5	2.3	77.6 ± 9.0
Au$_{1415}$(SR)$_{246}$	97.5	67.0	4.2	
(MW=357,475)	151.7	104.3	8.0	
	167.9	115.5	8.9	
5.3	126.7	55.4	1.8	34.4 ± 1.5
Au$_{5093}$(SR)$_{510}$	221.3	96.8	3.3	
(MW=1,166,521)	307.7	134.5	4.5	
	531.2	232.2	6.0	

^{a} The molar concentration of thiols present on the monolayer has been calculated by multipling the molar concentration of gold nanoparticles by the average number of thiol chains present on the monolayer of the gold nanoparticles (see column 1 and note 9 of the manuscript).

ESR spectra were obtained using a Bruker ESP300 spectrometer equipped with an NMR gaussmeter for field calibration and a Hewlett Packard 5350B microwave frequency counter for the determination of the *g*-factors, which were referenced to that of the perylene radical cation in concentrated H_2SO_4 (g = 2.00258). The sample temperature was controlled with a standard variable temperature accessory and was monitored before and after each run using a copper-constantan thermocouple. The instrument settings were as follows: microwave power 5.0 mW, modulation amplitude 0.05 mT, modulation frequency 100 kHz, scan time 180 s. Digitised EPR spectra were transferred to a personal computer for analysis using digital simulations carried out with a program developed in our laboratory and based on a Monte Carlo procedure (B. Kirste, *J. Magn. Reson.* **1987**, *73*, 213). The input data for the program are the number of non-equivalent nuclei, the hyperfine splitting constants of the free species and of the nitroxide partitioned in the monolayer, the central field difference and their relative amount. The signals of the nitroxide solubilized in the monolayer were correctly reproduced by assuming an asymmetric line brodening for the lines corresponding to $M_I(N)$ =0,±1 according to the formula $1/T_2 = A + BM_I + CM_I^2$.
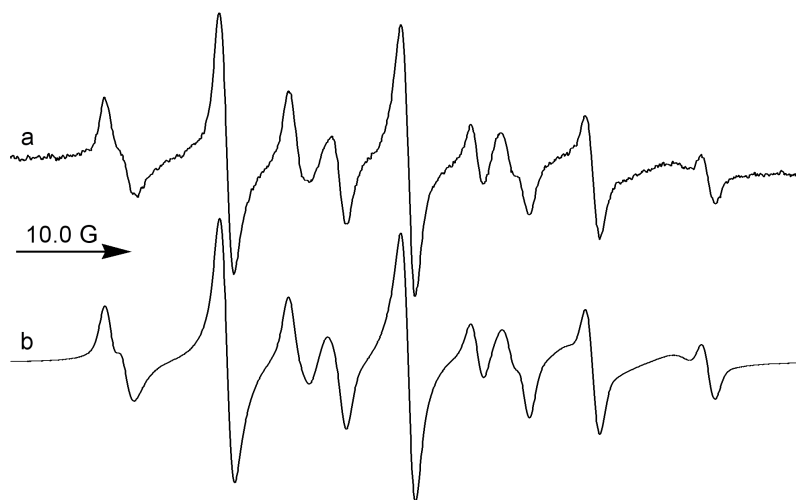
Figure S4. ESR spectrum of nitroxide **2** recorded in the presence of MPC-C8-TEG (3.4 nm average diameter, 0.097 mg/μL) at 298 K (a) and the corresponding theoretical simulation (b).
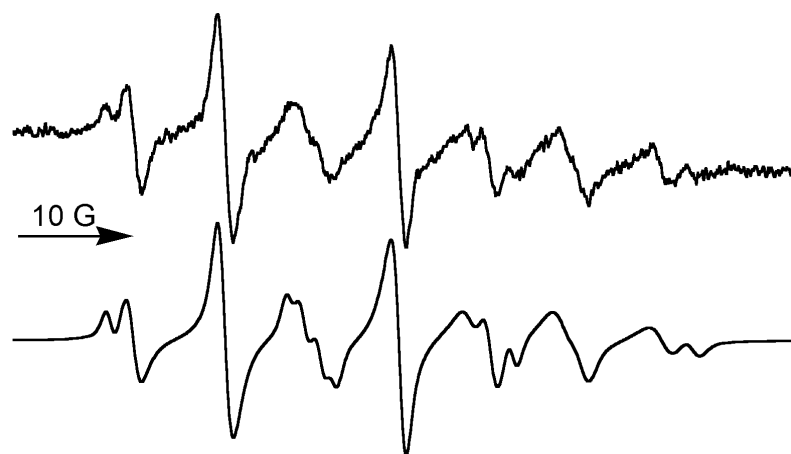
Figure S5. ESR spectrum of nitroxide **2** recorded in the presence of MPC-C8-TEG (5.3 nm average diameter, 0.53 mg/μL) at 320 K (up) and the corresponding theoretical simulation (bottom).