

Water solubilization of hydrophobic nanocrystals by means of poly(maleic anhydride-*alt*-1-octadecene)

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Electronic Supplementary Information

As an example, we report here the calculation of the amounts of polymer and cross-linker needed for spherical iron oxide nanoparticles of 8 nm in diameter (initial concentration was equal to 25 μM). By approximating the shape of the nanocrystal to a sphere, the surface area of one nanoparticle is around 200 nm^2 ($4\pi r^2$). To calculate the amount of polymer (number of polymer monomer units) and number of cross-linker needed per nanoparticle, we first multiply the surface area of the nanoparticle by the ratio to be used, which is 300 and 10 for the polymer and for the cross-linker, respectively:

$$\text{N}^\circ \text{ of polymer monomer units per NP} = 200 \text{ nm}^2 \times 300/\text{nm}^2 = 60000$$

$$\text{N}^\circ \text{ of cross-linker molecules per NP} = 200 \text{ nm}^2 \times 10/\text{nm}^2 = 2000$$

To calculate the volume of polymer and cross-linker needed, we carried on the following calculations. For the first step, we work at a nanoparticle concentration of 0.1 μM and a reaction volume of 25 mL. We use a polymer stock solution with a concentration of polymer monomer units equal to 0.137 M and therefore the volume of poly(maleic anhydride)-*alt*-1-octadecene solution needed is given by:

$$\text{volume of polymer solution} = (60000 \times 0.1 \mu\text{M} \times 25 \text{ mL})/137000 \mu\text{M} = 1.095 \text{ mL}$$

That is, to 0.1 mL of a 25 μM solution of nanoparticles, we add 1.095 mL of a polymer stock solution 0.137 M, we top up the reaction volume to 25 mL with chloroform, and then the solvent is removed under reduced pressure.

For the second step, we work at a nanoparticle concentration of 0.5 μM , a reaction volume of 5 mL, and we use a 0.02 M cross-linker stock solution. Therefore, the volume of cross-linker bis(hexamethylene)tri-amine needed is given by:

$$\text{volume of cross-linker solution} = (2000 \times 0.5 \mu\text{M} \times 5 \text{ mL})/20000 \mu\text{M} = 0.25 \text{ mL}$$

To the flask containing the nanoparticles with the adsorbed polymer, we add 0.25 mL of a solution of bis(hexamethylene)tri-amine in chloroform (concentration of the amine equal to 0.02 M) and then we add additional chloroform so as to bring the total volume to 5 mL. The solvent is removed under reduced pressure and the remaining solid is dissolved in borate buffer.

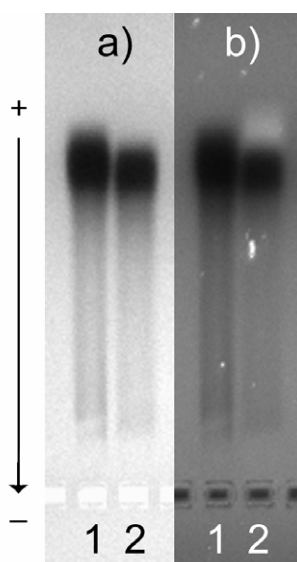


Figure 1s. Electrophoretic analysis on 2% agarose gel of gold nanoparticles coated with C₁₄-P (line 1) and C₁₈-P (line 2) after purification on a gel permeation chromatography column (Sephacryl S-500, GE Healthcare). The lines in panel a) are detected under visible light; while the lines in panel b) are detected under a UV blue filter. It can be noticed that the gel permeation chromatography is not able to completely remove the excess of C₁₈-P, as can be observed by the top band in line 2 panel b). We should point out that the colloidal stability of the C₁₈-P coated nanoparticles purified on size exclusion column is not compromised by the free excess of polymer, for the nanoparticles still migrate on the agarose gel. There are however some drawbacks associated with such nanoparticles. First, a concentration of nanoparticles higher than 2-5 μ M leads to the formation of a gel, most likely due to the presence of the free excess polymer. In addition, any further surface functionalization of such nanoparticles yielded poorly reproducible results, and an excess of reactants were needed, most likely because part of them reacted with the excess free polymer.

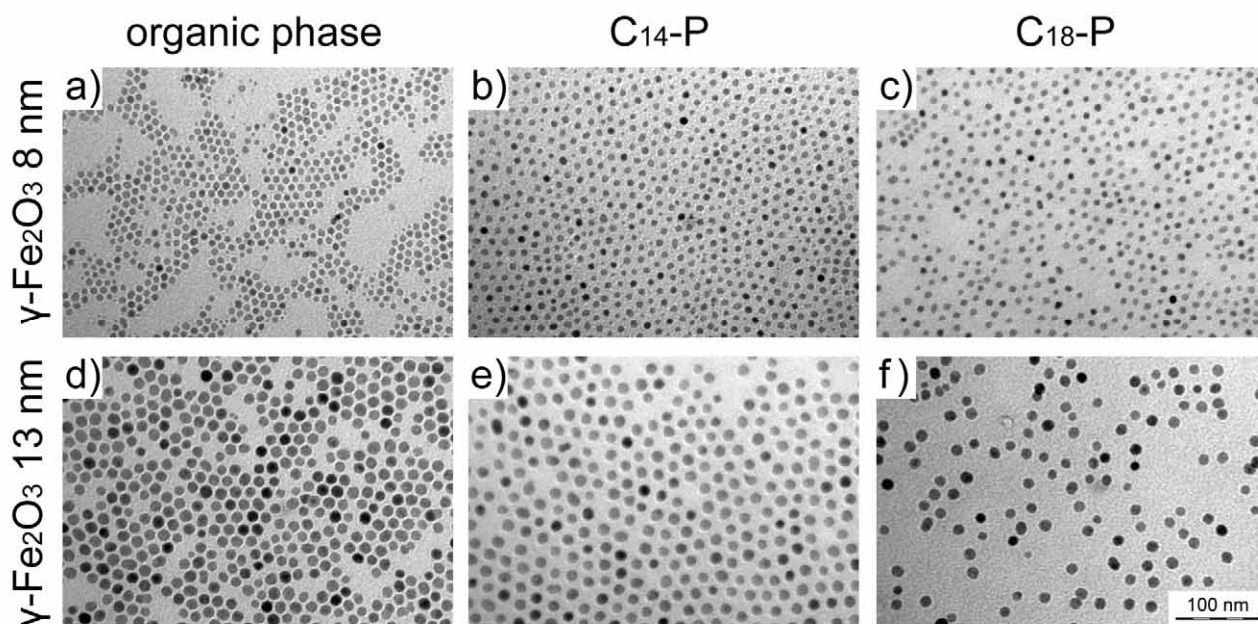


Figure 2s. TEM images of spherical $\gamma\text{-Fe}_2\text{O}_3$ of 8 nm (a, b, and c) and 13 nm (d, e, and f) deposited from toluene (a and d) and from aqueous phase, coated respectively with $\text{C}_{14}\text{-P}$ (b and e) and $\text{C}_{18}\text{-P}$ (c and f). In all cases, a monolayer of nanoparticles is detected and no aggregates can be seen. In addition, as observed by the distribution patterns on the grids, the inter-particle distance in the various samples increases in the following order: surfactant-coated nanoparticle < $\text{C}_{14}\text{-P}$ -coated nanoparticle < $\text{C}_{18}\text{-P}$ -coated nanoparticle, suggesting an increasing thickness of the organic coating around the nanoparticles.

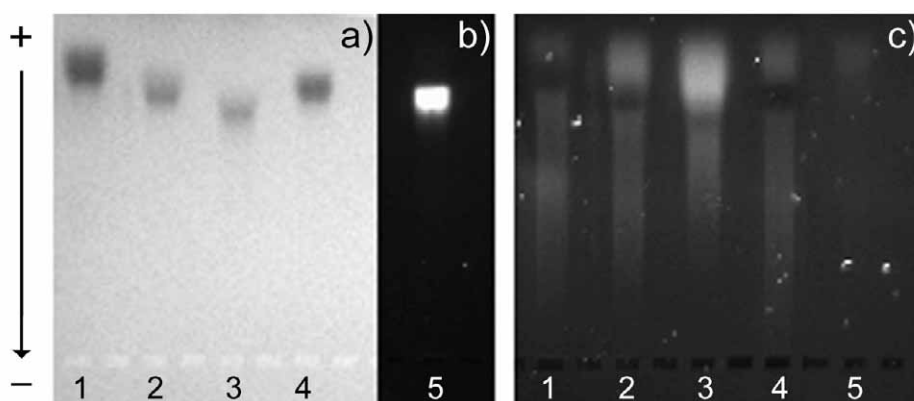


Figure 3s. Electrophoretic mobility on 1% agarose gel of different types of nanocrystals coated with $\text{C}_{18}\text{-P}$ before purification by ultracentrifugation. Au spheres, 6 nm (line 1), $\gamma\text{-Fe}_2\text{O}_3$ spheres of 8 nm (line 2) and 13 nm average diameter (line 3), and FePt- Fe_xO_y heterodimers of 9 nm total length (line 4) are detected under visible light (panel a); CdSe/CdS nanorods of 5 nm diameter \times 38 nm length (line 5) are detected under UV orange filter (panel b). An high excess of free polymer is observed in all the samples after the polymer coating procedure and before the purification, as can be clearly observed by the presence of the fast running top band detected under a UV blue filter (panel c), and that corresponds to the fluorescence from the excess unbound polymer.

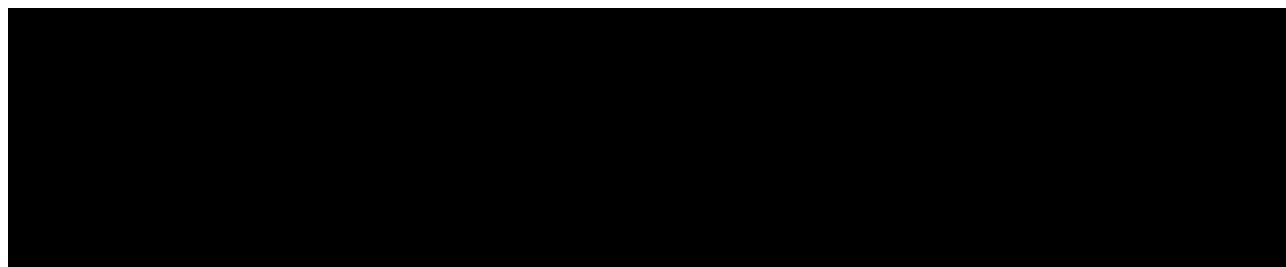


Figure 4s. Dynamic light scattering measurements plotted in arbitrary units of intensity, showing the size distribution of Au (6 nm) and γ -Fe₂O₃ (8 and 13 nm in diameter) nanoparticles, surfactant-coated in toluene and C₁₄-P- and C₁₈-P-coated in borate buffer. The graphs show the clear shift in size due to the additional polymer coating shells as compared to bare surfactant-coated nanoparticles in the organic phase. The shift in size for the C₁₈-P coated nanoparticles is always larger compared to that of the C₁₄-P coated ones.

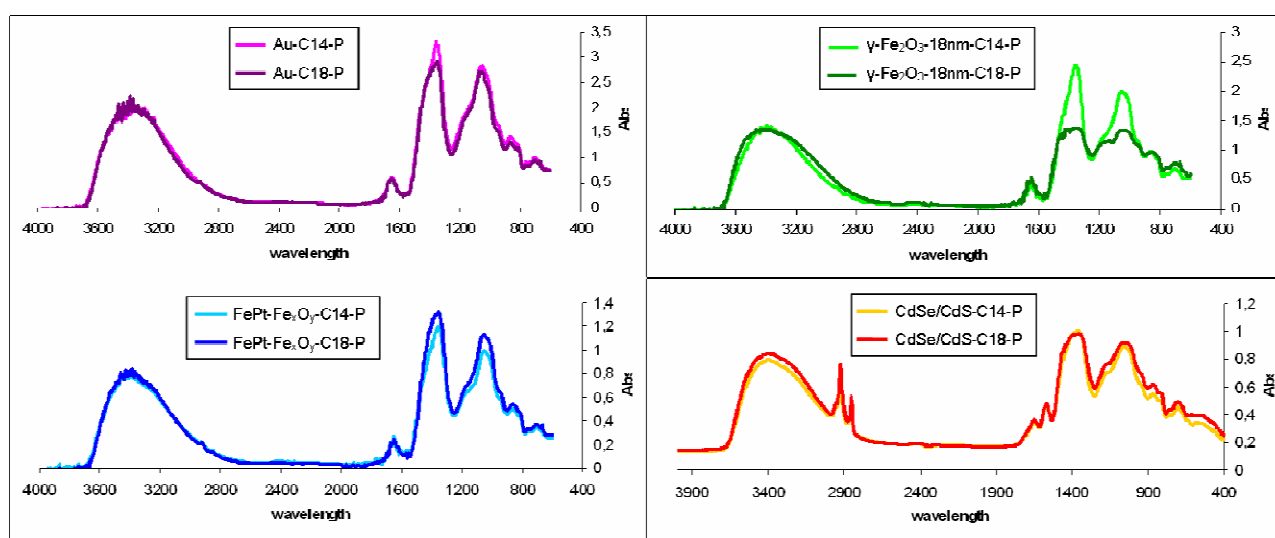


Figure 5s. Comparison of FT-IR spectra of Au, γ -Fe₂O₃, FePt-Fe_xO_y, and CdSe/CdS nanoparticles coated respectively with C₁₄-P and C₁₈-P. The peak profiles are basically the same in the two particles and no significant shift of the positions of the peaks are observed when comparing the C₁₄-P coated particles with the C₁₈-P coated ones.

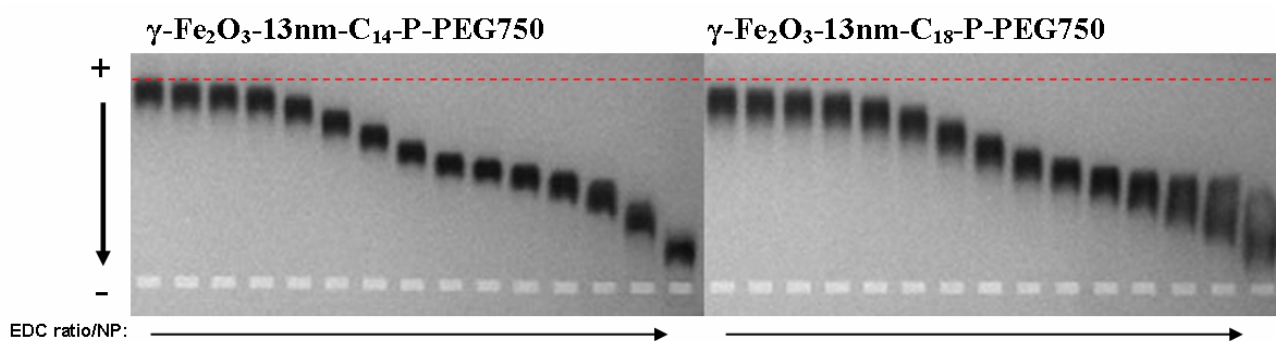


Figure 6s. Electrophoretic migration patterns of $\gamma\text{-Fe}_2\text{O}_3$ NPs, coated with $\text{C}_{14}\text{-P}$ and $\text{C}_{18}\text{-P}$ polymers, respectively, after conjugation to mono amino-PEG750. The conjugation of mono amino-PEG molecules to the carboxylic groups at the nanoparticle surface is mediated by the EDC. The amount of mono amino-PEG molecules attached per $\gamma\text{-Fe}_2\text{O}_3$ NPs, and thus the migration of the conjugates, is adjusted by changing the ratio of EDC/ $\gamma\text{-Fe}_2\text{O}_3$ NPs, which was varied from 0 to 512000. The bands of the $\gamma\text{-Fe}_2\text{O}_3\text{-C}_{14}\text{-P-PEG750}$ NPs are as narrow as those of the $\gamma\text{-Fe}_2\text{O}_3\text{-C}_{18}\text{-P-PEG750}$ NPs for the lower ratio of EDC/NP, while they are slightly more spread for bigger conjugates, therefore indicating similar chemical reactivities for the two types of polymer-coated nanoparticles.