Supporting Information

Effect of nanoparticles on spontaneous « Ouzo » emulsification

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A. Characterization of the nanoparticles

CdSe@ZnS Quantum Dots. The core-shell CdSe@ZnS QD purchased from CytodiagnosticS Inc. were characterized by HRTEM and EDX.

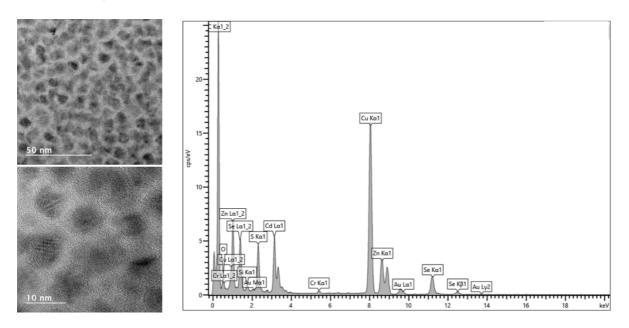


Figure SI-1: HRTEM (left) and EDX (right) analysis of the commercial Quantum Dots.

HRTEM analysis (Figure SI- 1) of the quantum dots purchased from CytodiagnosticS Inc. reveals faceted nanocrystals of fairly irregular shape, which do not allow their size to be defined in an unambiguous way. If we adopt as size definition the radius of the smallest circle inscribing the particle, we obtain a rough estimate of the average of 7.8 (1.2) nm (measurement of 70 particles, the number in brackets represents the standard deviation). Analysis by EDX spectroscopy confirms the presence of the elements Cd, Se, S and Zn. As we found the presence Zn even outside areas where the QDs are present (perhaps due to the residual presence of zinc salts), we subsequently relied on the presence of the elements Cd and Se to characterize the presence of the QDs.

InP@ZnS Quantum Dots. The core-shell InP@ZnS QD were characterized by TEM, XRD and ¹³C MAS NMR. The size of the particles is 4.5 (0.4) nm (measurement of 150 particles).

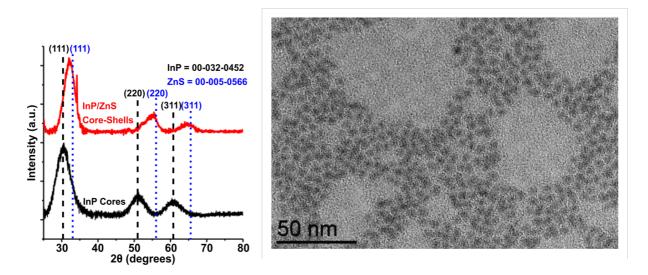


Figure SI- 2: XRD and TEM analysis of the InP@ZnS QD.

Solid-state NMR experiment was recorded on a Bruker Avance III HD 400 wide-bore spectrometer equipped with a HX 3.2 mm probe. Chemical shifts were externally referenced to liquid TMS. The sample was packed into 3.2 mm zirconia rotors inside a glove box. The rotor was spun at 10 kHz at room temperature and the ¹³C CP-MAS was recorded with a recycle delay of 3 s and contact times of 2 ms.

The ¹H-¹³C CP-MAS NMR (Figure SI- 3) shows one peak of high intensity at 30 ppm, and two lowintensity peaks at 47 and 129 ppm. All peaks can be attributed to various signals from oleylamine: the peak at 129 ppm corresponds to vinylic carbons, the peak at 30 ppm to the allylic carbons, and that at 47 ppm to the carbon alpha to the nitrogen.

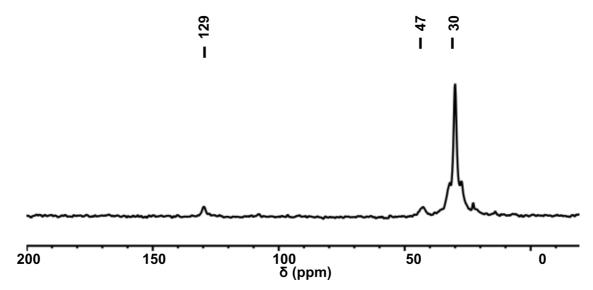


Figure SI- 3: ¹H-¹³C Cross-Polarization-MAS NMR Spectrum of InP@ZnS Core-Shell NCs.

SPION. The size of the SPIONs measured from TEM analysis (Figure SI- 4) is of 4.8 (0.9) nm (measurement of 70 particles). Fe_2O_3 NP's are stabilized by a mixture of oleic acid and octylamine that may partially react to form carbamates.

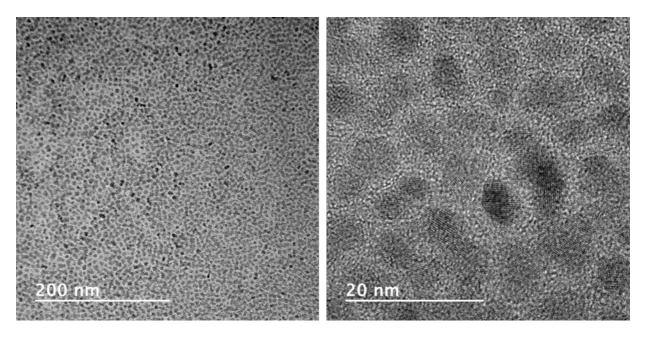


Figure SI- 4: HR-TEM analysis of the SPION.

B. NTA videos along a dilution line without NP

Videos of NTA recordings are displayed for three representative samples along $\Phi_{THF} = 0.2$:

Video SI-1 ($\Phi_{BHT} = 10^{-6}$): sample in the SFME domain

Video SI-2 ($\Phi_{BHT} = 10^{-5}$): monodisperse sample at maximum concentration of droplets

C. Effect of the nanoparticles along a dilution line

Five samples were prepared at water mass fraction 0.11; 0.32; 0.53; 0.67 and 0.77 and containing a constant concentration of QD from Cytodiagnostics Inc. (0.3 x10¹⁴ QD/mL from supplier information). These samples were prepared using commercial THF containing 320 mg.L⁻¹ of BHT.¹⁸ The first two samples (less diluted) correspond to compositions located out of the range of the diagram. The three other compositions are indicated by color spots. Pictures of the samples under natural light and UV illumination are shown Figure SI- 5. Only the most diluted sample ($\Phi_{water} = 0.77$) shows no sign of precipitation.

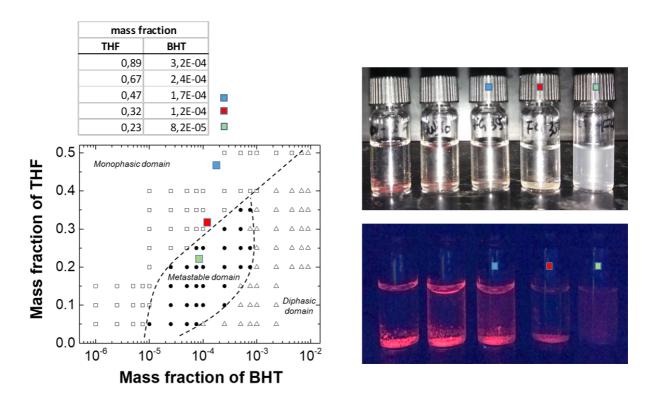
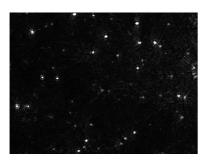


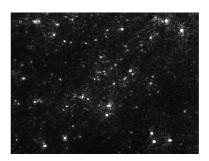
Figure SI- 5 : Effect of nanoparticles on the water/THF/BHT system along a dilution line (dilution with water). The two first compositions are out of the diagram. Photographs are under natural illumination (up) or UV (365 nm) illumination (down).

D. Effect of the nanoparticles: comparison of NTA acquisition

Video SI-a1: without nanoparticles



Video SI-b1: with nanoparticles



E. Dynamics of droplet growth

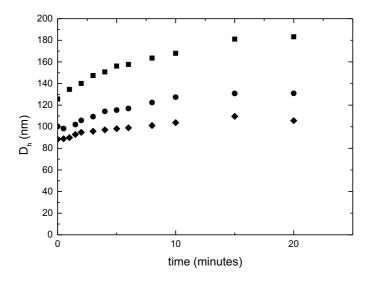


Figure SI- 6 : Growth dynamics of the droplets in the presence of increasing concentrations of QD: (\blacksquare) no QD; (\bullet) 2.8 µg/mL; (\bullet) 28 µg/mL.

F. ICP-AES titration of mixtures of QD- and -SPION-shells

Two samples of NP-shells were prepared: one sample with CdSe/ZnS NP (QD) and one sample with Fe_2O_3 NP. The halves of the two samples were taken and mixed together. The other half of the Fe_2O_3 samples was used as a reference for magnetic separation. After five hours, the NP-shells were crosslinked using PEG-PAA (0.22mg/mL). Then the THF was evaporated and the samples (mixed Fe_2O_3 /QD-shells and Fe_2O_3 -shells) submitted to magnetic separation. Then, Iron and Cadmium were titrated in the magnetic and non-magnetic fractions using ICP-AES (Figure SI-7).

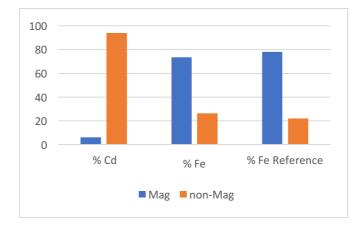


Figure SI- 7: Repartition of the QD (titration of Cd) and of the Fe₂O₃ NP (titration of Fe) between the magnetic and nonmagnetic fractions, after mixing QD-shells and Fe₂O₃-shells to assess NP-exchange. NP-shells prepared from the composition: $\Phi_{THF}=0.23$; $\Phi_{BHT}=7.3 \times 10^{-5}$ and $[QD]=27 \ \mu g/mL$ and $[Fe_2O_3]=2.5 \ \mu g/mL$. Mixing time: 5 hours.