Supporting Information

Matrix-dependent cooperativity in spin crossover Fe(pyrazine)Pt(CN)$_4$ nanoparticles

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Experimental Section

I. Preparation of the nanoparticles

All samples are prepared in two steps. Step 1 is the preparation procedure for the nanoparticles in the microemulsion, which is the same for all samples. Step 2 corresponds to the recovering of the nanoparticles from the microemulsion and this step depends on the nature of each sample.

Step 1

Stable reverse microemulsions of precursor compounds with w=[H_2O/AOT]=10, *where AOT is sodium bis(2-ethylexyl sulfosuccinate*, are prepared as follows: (i) 6 mL of 0.1 M aqueous solution of $K_2Pt(CN)_4$ is mixed with 78 mL of 0.5 M of NaAOT in heptane, the mixture is stirred continuously until it becomes stable; (ii) 6 mL of 0.1 M aqueous solution of $Fe(BF_4)_2$ containing 10 equivalents of pyrazine is mixed with 78 mL of 0.5 M of NaAOT in heptane, the mixture is stirred continuously until it becomes stable. Microemulsions are cooled down to 2 °C and mixed under vigorous stirring.

Step 2

*Compound **1:*** 20 ml ethanolic solution containing 1/8 equivalents (with respect to Fe) of calix8 (calix8 = $C_{192}H_{264}N_8O_{16}S_8$) is added to the microemulsion after 15 minutes, leading to its flocculation. The solid is separated from the solution by centrifugation. Then it is thoroughly washed with acetone until all the AOT is removed (see IR spectra, Fig. S4). The sample is then dried and heated under vacuum to remove completely all the solvents.

Elemental analysis: unit formula for **1**: $FePt(CN)_4[C_4H_4N_2]_{0.4}\bullet[H_2O]_{0.5}\bullet C_{192} H_{264} N_8 O_{16} S_8]_{0.07}$

Experimental .% C 36.6, % H 3.81; % N 10.85, % S 3.34 % Fe 9.14.

Calculated % C 37.9, % H 3.52, % N 12.44, % S 3.00 % Fe 9.26.

EDS analysis for **1** show that the Fe/Pt ratio is close to 1.

*Compounds **2** and **3**:* Tetraethylorthosilicate (TEOS) is added into the reaction mixture after step 1 in the following ratio: 3 mL (compound **2**) and 5 mL (compound **3**) of TEOS is added on 14 mL of the microemulsion prepared at step 1. This microemulsion is left 1 hour under stirring without any flocculation. A microemulsion prepared from mixing 1mL of a 0.1 M HCl aqueous solution with 13 mL of heptane is then added to the microemulsion containing the particles. The resulting microemulsion is stirred for three days. Adding ethanol leads to the flocculation of the microemulsion and the solid is separated by centrifugation. The powders are washed with acetone to remove AOT, dried under vacuum and then heated to remove water and acetone.

EDS analysis for **2** and **3** leads to a Si:Fe:Pt ratio equal to 6:1:1 and 60:1:1 respectively.

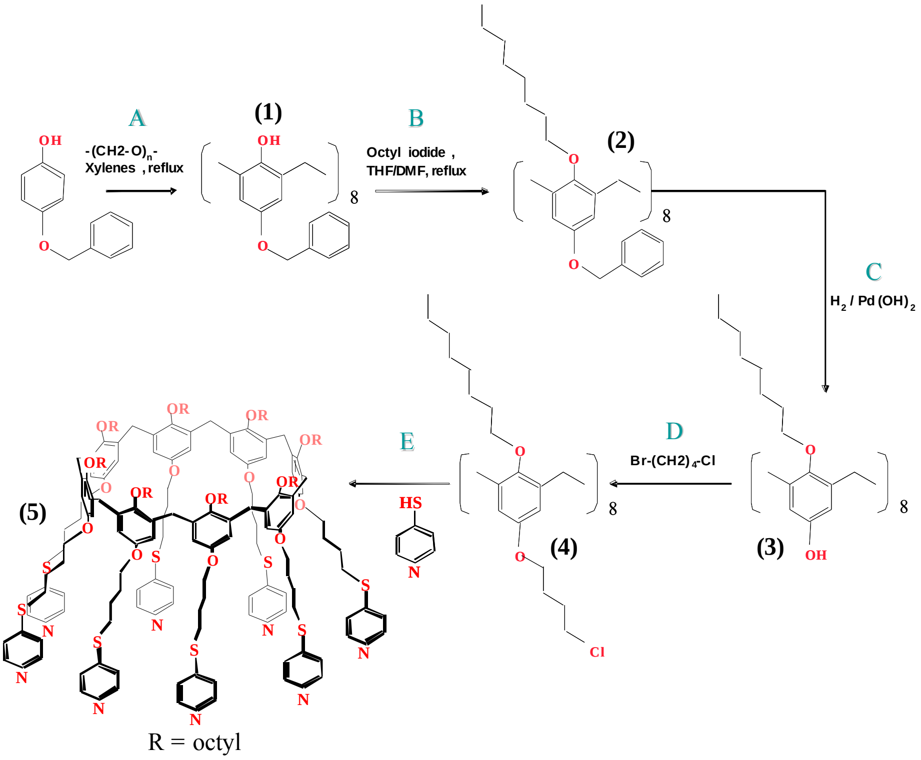
II. Synthesis of Calix8 **[octakis(octyloxy), octakis[4-(mercaptopyridyl)butyloxy]calix[8]arene**

A) General :

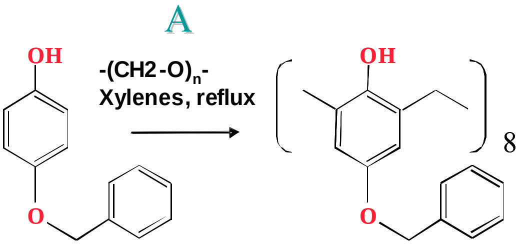
All the reagents were purchased from Sigma-Aldrich (highest available purity) and used as received. THF was dried by refluxing over sodium/benzophenone; DMF was used as received without any further purification.

1H NMR spectra were recorded at ambient temperature on a BRUKER DPX 300 spectrometer.

B) synthetic scheme :



Step A :

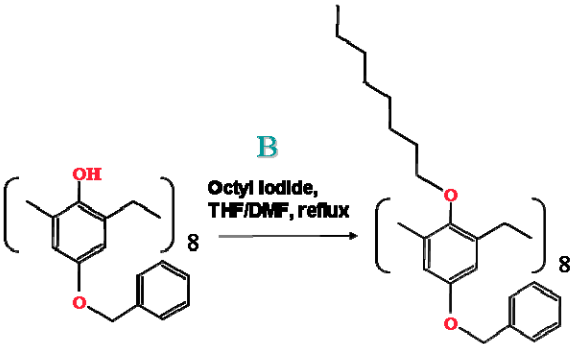


The synthesis of the p-(benzyloxy)calixarene (compound **(1)**) from p-(benzyloxy)phenol has already been described [1].

Briefly, a slurry of 50g of p-(benzyloxy)phenol, 12g of paraformaldehyde, 600 mL of xylene and a catalytic amount of base (KOH, 0,03 equivalents of the phenol) is refluxed for 6 hours under mechanical stirring.

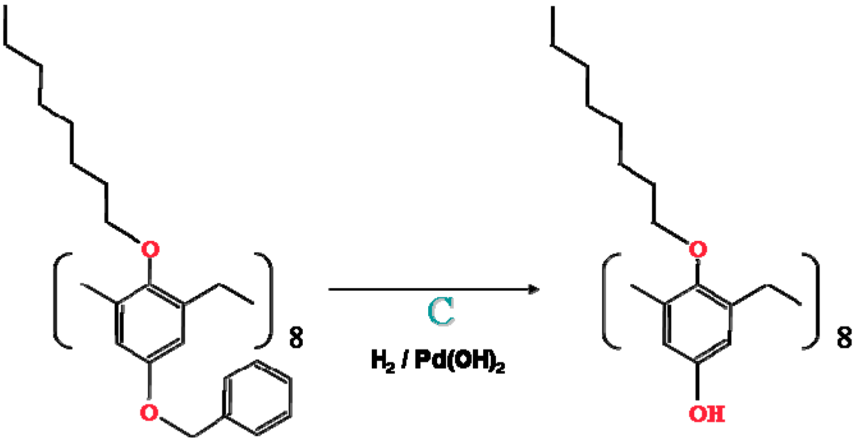
The resulting white precipitate is filtered, washed with xylene, acetone, pentane and dried up to constant weight. Yield : 70%.

Step B :



To a 250 mL three-necked round bottomed flask, fitted with a reflux condenser and an argon intake are added 10 g of compound **(1)** (5,89.10^{-3} mol) , 160 ml of THF and 30 mL of DMF. The resulting slurry is flushed with argon and 1,3 g of NaH (32,5 mmol) are added at ambient temperature. Once a clear, light yellow solution is obtained, 5,6 ml of n-(octyl)iodide (34,7 mmol) are added and the solution is then refluxed for half an hour and cooled down to ambient temperature.
This NaH/ n-(octyl)iodide addition sequence is repeated four more times.
The product is precipitated with methanol and filtered. The resulting light yellow solid is then washed with pentane, filtered and dried up to constant weight.
Compound **(2)** is obtained as a cream-colored solid in nearly quantitative yield (15g, 97%).
^{1}H NMR (293K, $CDCl_3$) δ (ppm) : 0,86 (br. t.), CH_3; 1,24 (br. s.), 1,39 (br. m.), 1,62 (br. m.) CH_2; 3,6 (br. t.) Ar-O-CH_2-); 3,97 (s., Ar-CH_2-Ar); 4,58 (s., Ph-O-CH_2-); 6,48 (s., Ar-H); 7,07 (br. s.), Ar-H.
MALDI mass spectrometry : 2616,72 (M+Na)$^+$.

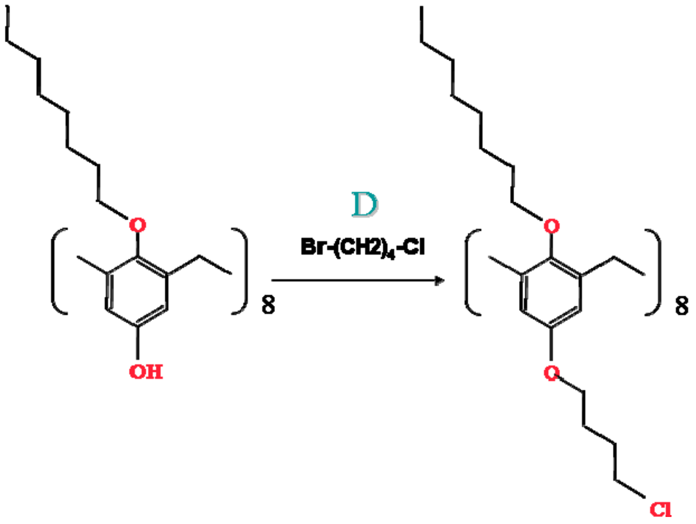
Step C :



To a solution of 15 g of **(2)** (5,73 mmol) in 100 mL THF and 10 mL EtOH is added 1 g of Pearlsman's catalyst (Pd(OH)$_2$/C).
The resulting black suspension is loaded into a pressure cell and left for 48 hours under hydrogen (40 atmospheres).
After releasing the pressure, the black suspension is filtered over Celite, and washed with acetone. The filtrate is evaporated to dryness, leaving compound **(3)** as a light yellow resinous solid in quantitative yield.

^{1}H NMR (293K, $CDCl_3$/CD3OD 90/10 v/v) d {ppm} : 0,88 (br. t.), CH_3; 1,32 (br. s.), 1,52 (q.), 1,76 (q.) CH_2; 3,72 (t.) Ar-O-CH_2-); 3,96 (s., Ar-CH_2-Ar); 4,58 (s., Ph-O-CH_2-); 6,38 (s., Ar-H); 7,8 (s.), OH.
MALDI mass spectrometry : 1896,29 (M+Na)$^+$.

Step D :



3 g of **(3)** (1,6 mmol) are dissolved into a mixture of 40 mL of 1-bromo-4-chlorobutane and 4 mL of DMF under an argon atmosphere.

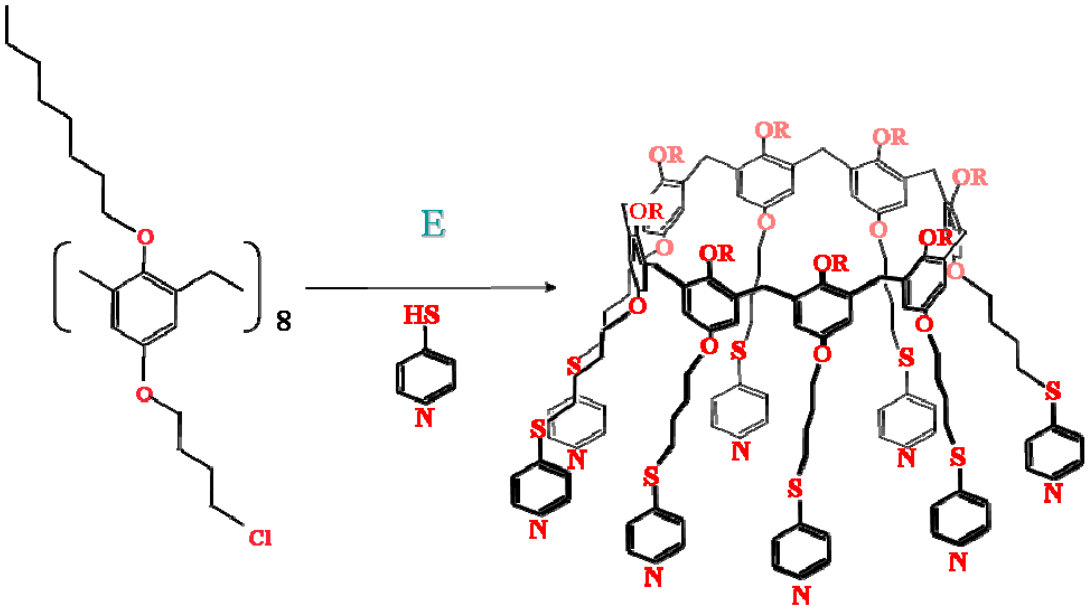
0,513 g of NaH (60% in mineral oil) are then added in 2 portions (0,213 and 0,3 g), at a 15 min interval. The resulting suspension is left at 60°C overnight. 0,110 g of NaH 60% are then added, and the suspension left for 3 more hours.

The product is precipitated with methanol, washed with pentane and dried in vacuum.

Compound **(4)** is recovered as a light orange solid in quantitative yield.

^{1}H NMR (293K, $CDCl_3$) d {ppm} : 0,89 (br. t.), CH_3; 1,28 (br. s., CH_2), 1,49→1,81 (br. m.), CH_2; 3,32 (t, Cl-CH_2-); 3,60 (t, ArO-CH_2-), 3,77 (t, ArO-CH_2-); 3,95 (s, Ar-CH_2-Ar); 6,43 (s, Ar-H).
MALDI mass spectrometry : 2616,52 $(M+Na)^+$.

Step E :



3 g of **(4)** (1,144 mmol) are suspended in 15 mLof off-the-shelf DMSO. 5 g (0,045 mol) of 4-mercaptopyridine are then added, followed by 6,3 mL of Et3N. Upon addition of triethylamine, the initial yellowish suspension turns dark orange.
The mixture is left 48 hours under argon at 60°C.
The product is precipitated with methanol, and dried under vacuum. Compound **(5)** is obtained as a light orange resinous solid in nearly quantitative yield.

^{1}H NMR (293K, $CDCl_3$) d {ppm} : 0,84 (br. t.), CH_3; 1,23 (br. s., CH_2), 1,4 →1,8 (br. m.), CH_2; 2,6 (br. m., -S-CH_2-); 3,72 (br. s., ArO-CH_2-); 3,92 (s, Ar-CH_2-Ar); 6,38 (br. s., Ar-H); 6,97 (br.d., Py-H); 8,31 (br.d., Py-H).
MALDI mass spectrometry : 3216,95 $(M+Na)^+$.

References :
[1] a) Leverd, Pascal ; Huc, Vincent; Palacin, Serge; Nierlich, Martine; *J. of Incl. Phenom. Macrocycl. Chem.* 2000, **36**(3), 259.; **b)** V. Huc, K. Pelzer; *J. Colloids and Int. Science*, 2008, **318**/1, 1;

Tomography study

The experimental tomography series were acquired by means of a spherical aberration (Cs) probe corrected JEOL 2100F field emission gun transmission electron microscope operating at 200 kV. The acquisition software (Digital Micrograph)provides an automated acquisition of the tilt series by varying the tilt angle step by step and by controlling the defocusing and the specimen drift at each tilt angle. In addition, it allows the automatic adjustment of the focal point of the beam in order to ensure that the focus is maintained on the tilted specimen, along the entire acquisition. Using a high tilt sample holder from the GATAN Company allowed a maximum tilt angle range of ± 80°. BF-TEM tilt series were simultaneously acquired between 70° and -70°, with a tilt increment given by a 2° Saxton scheme. The tilt series of BF images were recorded using a high spreading for the electron beam. A 2048*2048 pixel cooled CCD detector with a 1s exposure time was employed for each record. The pixel size corresponding to the chosen magnification, 60kx was 0.33 nm.
Once the acquisition was completed, the images were first roughly aligned using a cross correlation algorithm. A refinement of this initial alignment was then obtained with the IMOD software 1 where the nanoparticles of interest have been used as fiducial markers. The BF-TEM reconstructions were computed using algebraic reconstruction techniques (ART)[2] implemented in the TomoJ software[3] for 15 iterations. Visualization and quantitative analysis of the final volumes were carried out using ImageJ software. The characterization of the nanoparticles shape was performed using a statistical approach. More specifically, about 150 particles have been analyzed using cross-sections within the reconstructed volume.

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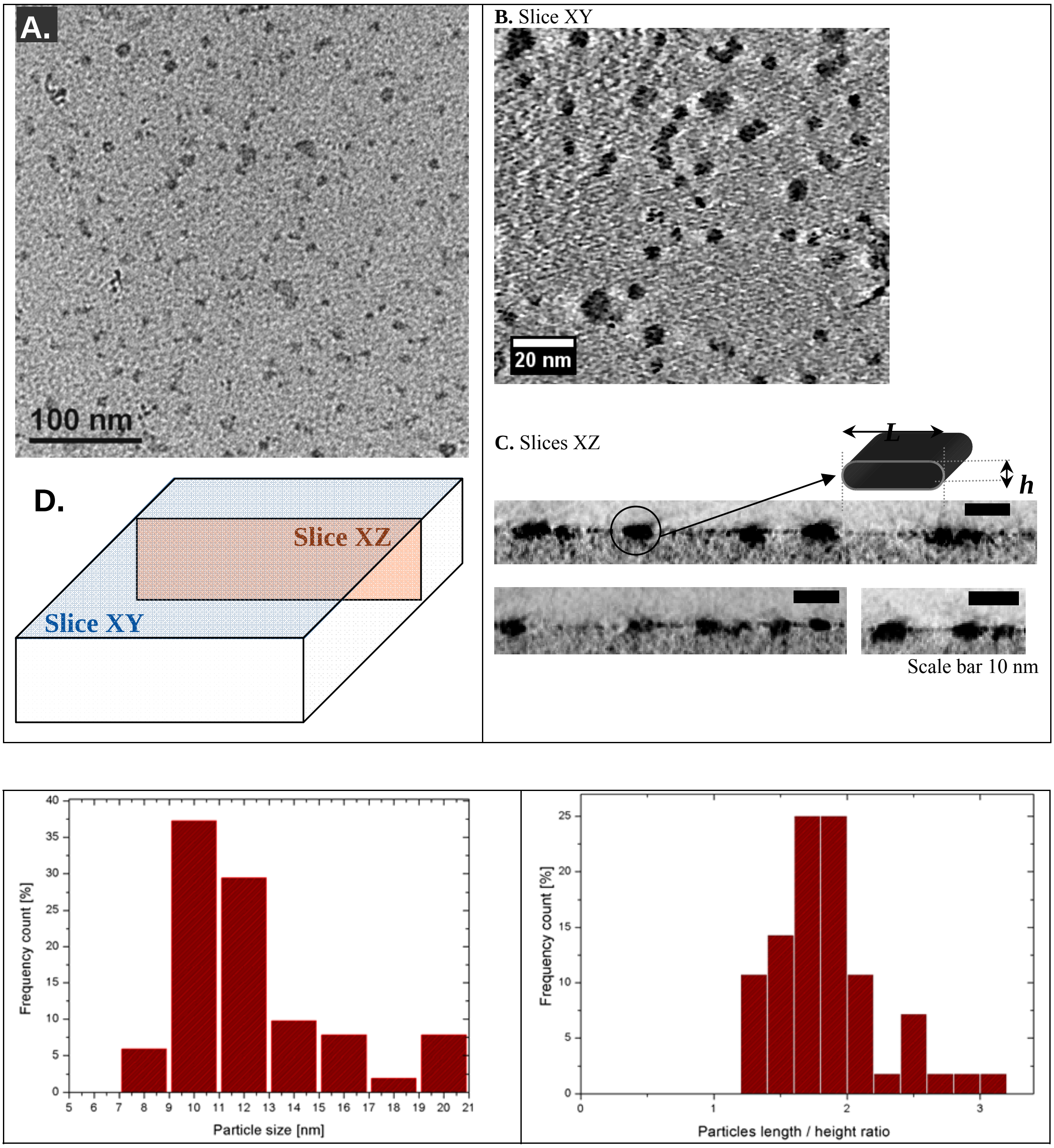

Figure S1. (top) A. TEM micrograph of the region chosen for the tomography acquisition; B and C. Slices redrawn from the reconstructed volume in the XY and XZ directions, respectively; D. Schematic representation of the slicing planes within the volume and (bottom) Statistical distribution (counted on about 150 particles) of the particle size (*left*) and particles length to height ratio (*right*) as calculated from the sections within the reconstructed volume.

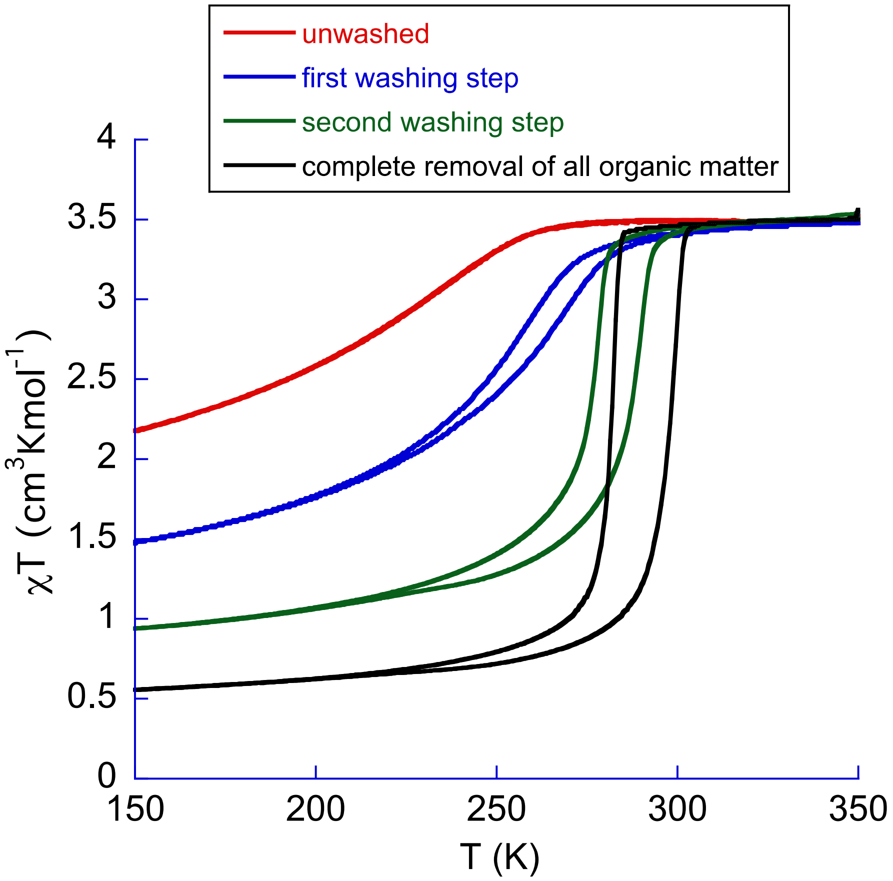

Figure S2. χT *vs*. T for the samples obtained from the microemulsion by recovering the particles by adding para-Nitrobenzyl pyridine (pNbp) after step 1: immediatetly after recovering the NPs (**T0**, red), after a first washing by acetone (**T1**, blue), after a second step of washing (**T2,** green) and after complete removal of AOT and pNbp (**Tf**, black).

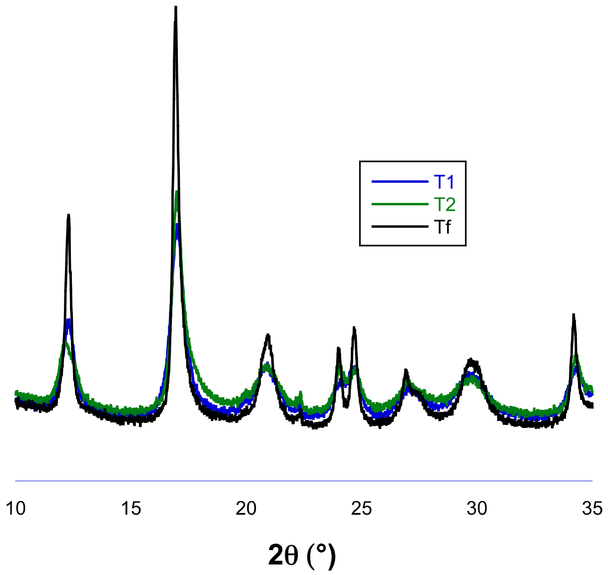

Figure S3. XRPD diffractograms of nanoparticles coated with AOT and pNBP, size T1 = 11 nm, size T2 = 13 nm, size Tf = 22 nm.

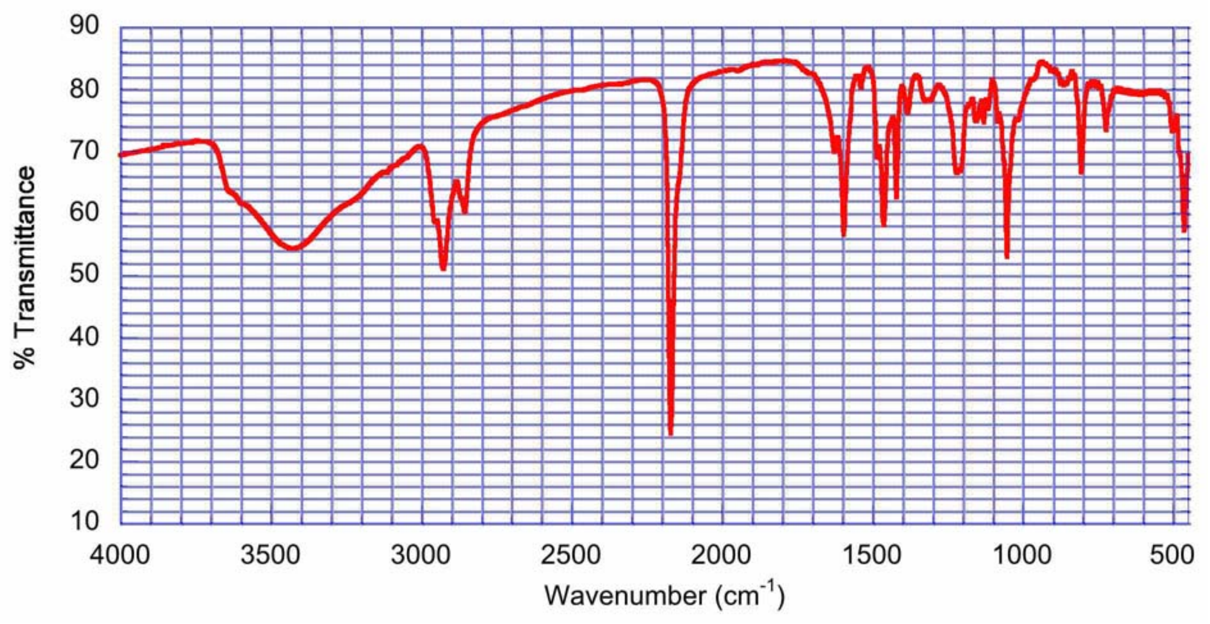

Figure S4. Infrared spectra of **1**. The band at 2170 cm^{-1} corresponds to the asymetric vibration of bridging cyanides.

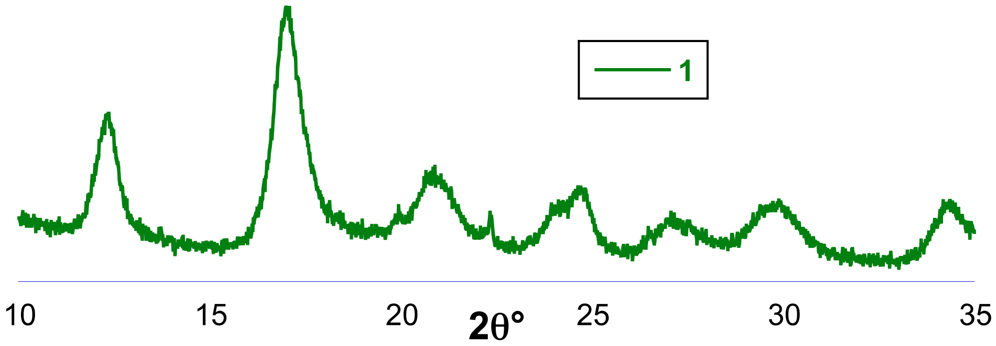

Figure S5. XRPD diagram of **1**, size (10 nm).

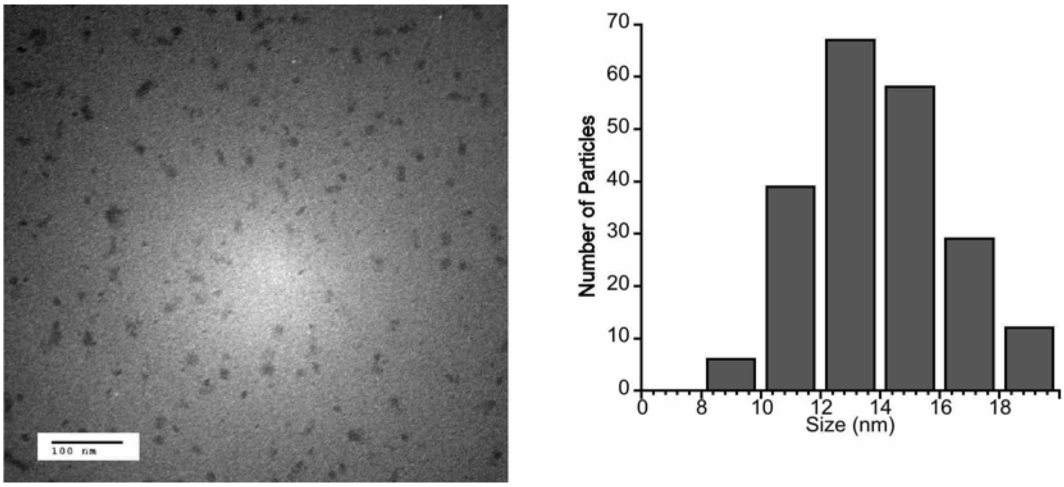

Fig S6. TEM image on microemulsion of compound **2** after 65h of TEOS condensation (right) and size distribution (left)

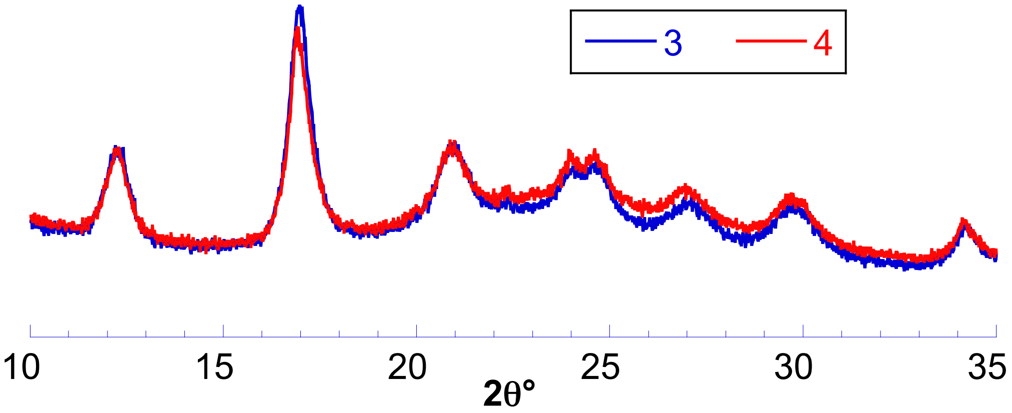

Figure S7. XRPD diagrams of **2** (size = 11 nm) and **3** (size = 10nm).

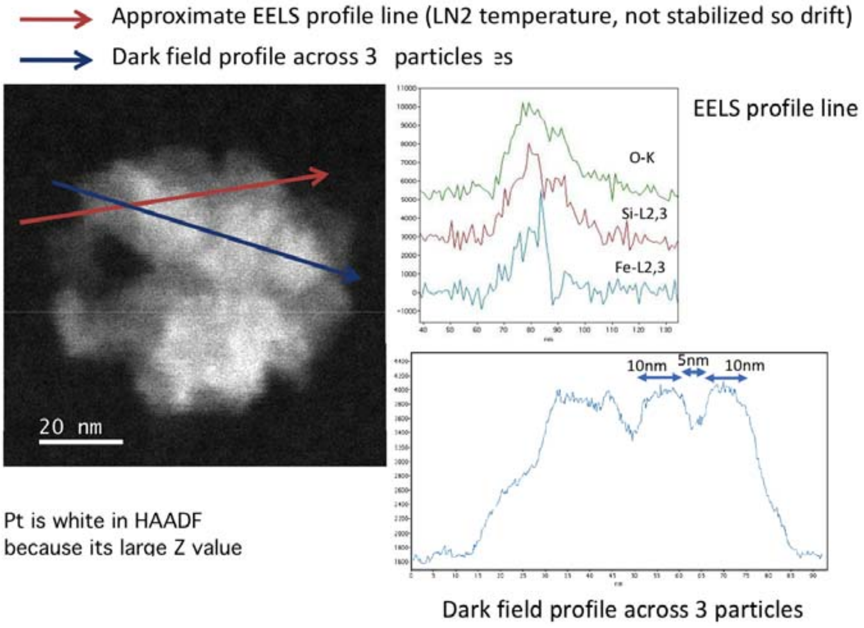

Figure S8. STEM imaging and EELS map of NPs of **2** showing the silica shell between the nanoparticles.

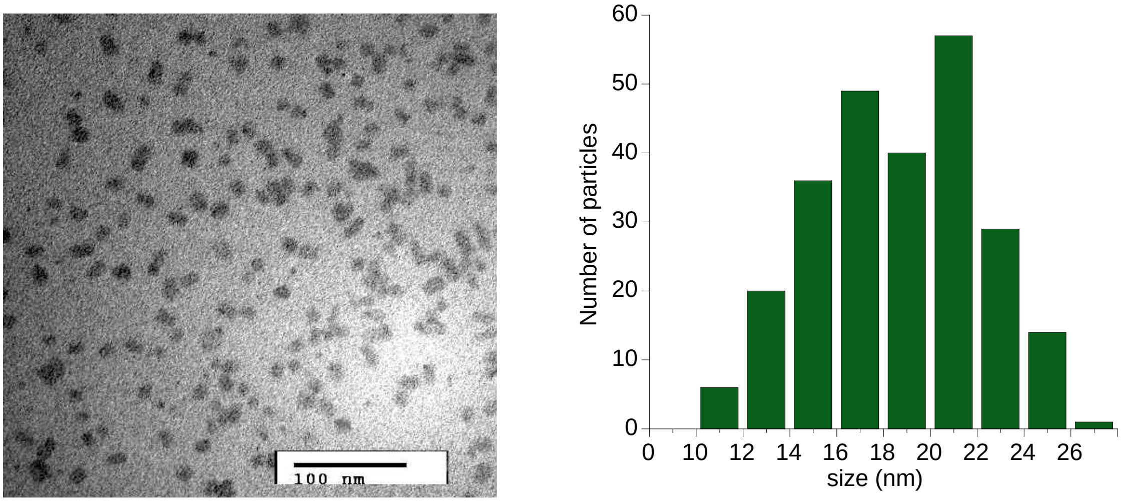

Figure S9. TEM on microemulsion **3** after 65 hours of TEOS condensation. TEM Image (top left), size distribution (top right) and TEM image after redispersion in CH_3OH (bottom).

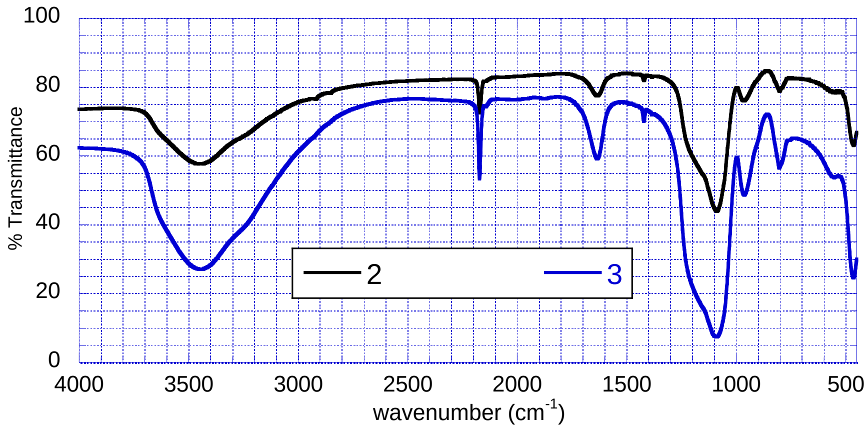

Figure S10. IR spectrum of **2** and **3**. The bands at 1100 cm^{-1} corresponds to SiO_2.

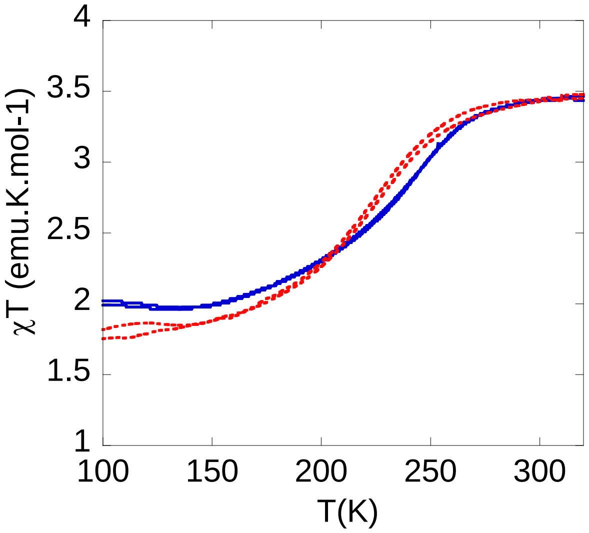

Figure S11. $\chi_M T = f(T)$ plots for **3** and the 10 nm NPs diluted in a polyvinypyrrolidone (PVP) organic matrix. Note that the magnetic behaviour of the two nanocomposites is mainly the same.

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