Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information.

Small Size Mesoporous Silica Nanoparticles Functionalized with Mannose for Retinoblastoma Cells Imaging.

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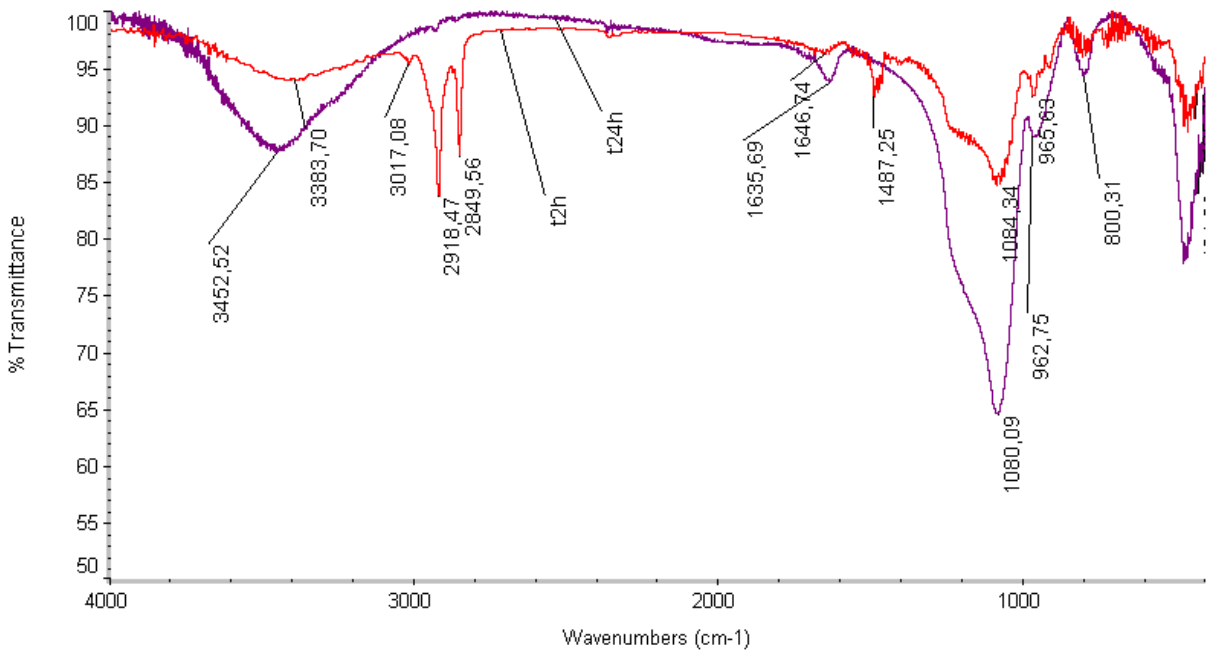

Figure S1. FTIR spectra of 25nm nanoparticles during (t2h, red line) and after (t24h, purple line) dialysis.

The removal of CTAB (C-H peaks at 3107 cm^{-1}; 2918 cm^{-1}; 2849 cm^{-1}) was followed by FTIR-KBr. The dialysis bath was renewed each 2h for the 8 first hours and the last one was maintained overnight. After a total dialysis time of 24h, no residual CTAB was monitored.

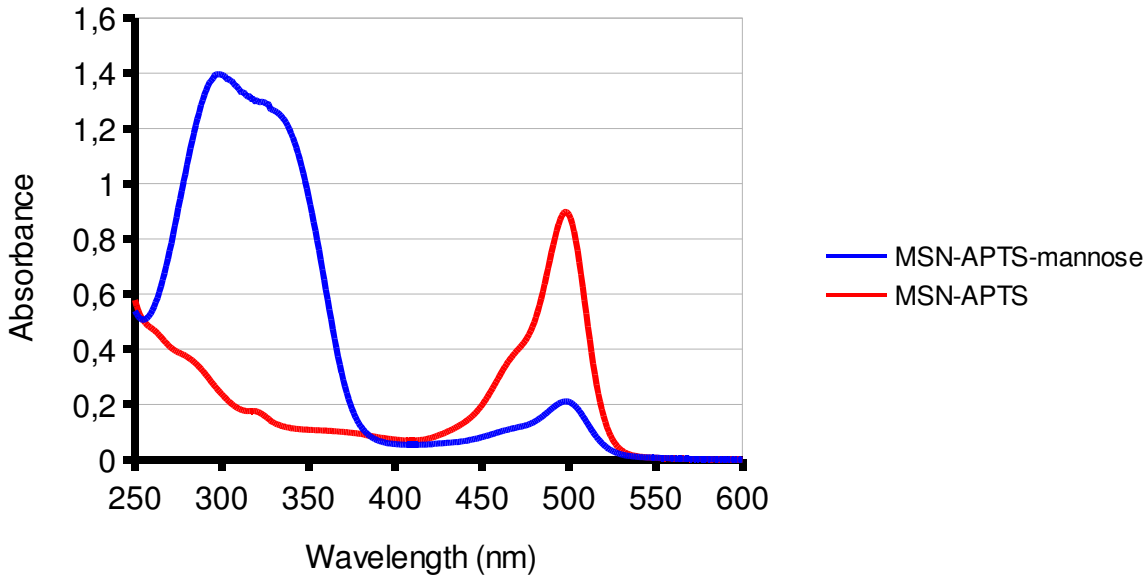

Figure S2. UV-visible spectra of MSN-APTS before (red line) and after functionnalization with mannose (blue line).

The 1/5 ratio between the absorbances at 500 nm is explained by the dilution of the nanoparticles before functionnalization with squarate mannose. The MSN-APTS were indeed diluted at 1/5 for the reaction with squarate mannose to limit their aggregation.

The amount of mannose grafted at the surface of the nanoparticles was determined by optical lecture of the absorbance at 330 nm (ε = 21000 $cm^{-1}.M^{-1}$) after correction of the absorbance spectrum to eliminate the diffusion of the light by the nanoparticles.

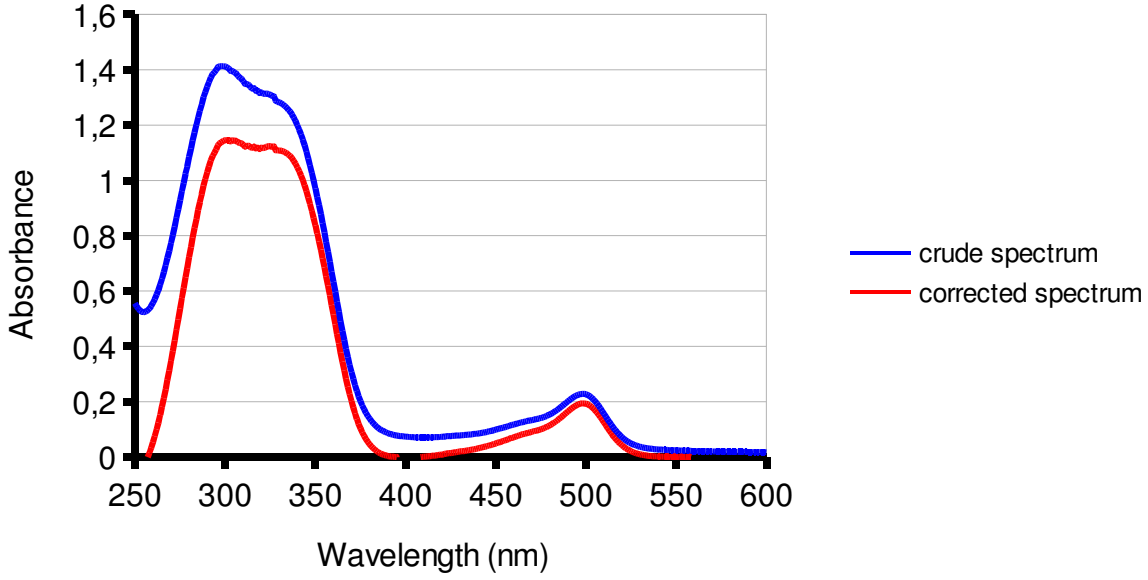

Figure S2bis. Absorbance of MSN-APTS-mannose, non-corrected (blue) and corrected (red).

The amount of grafted mannose was determined to be 2.96×10^{-1} $mmol/gram_{MSN}$.

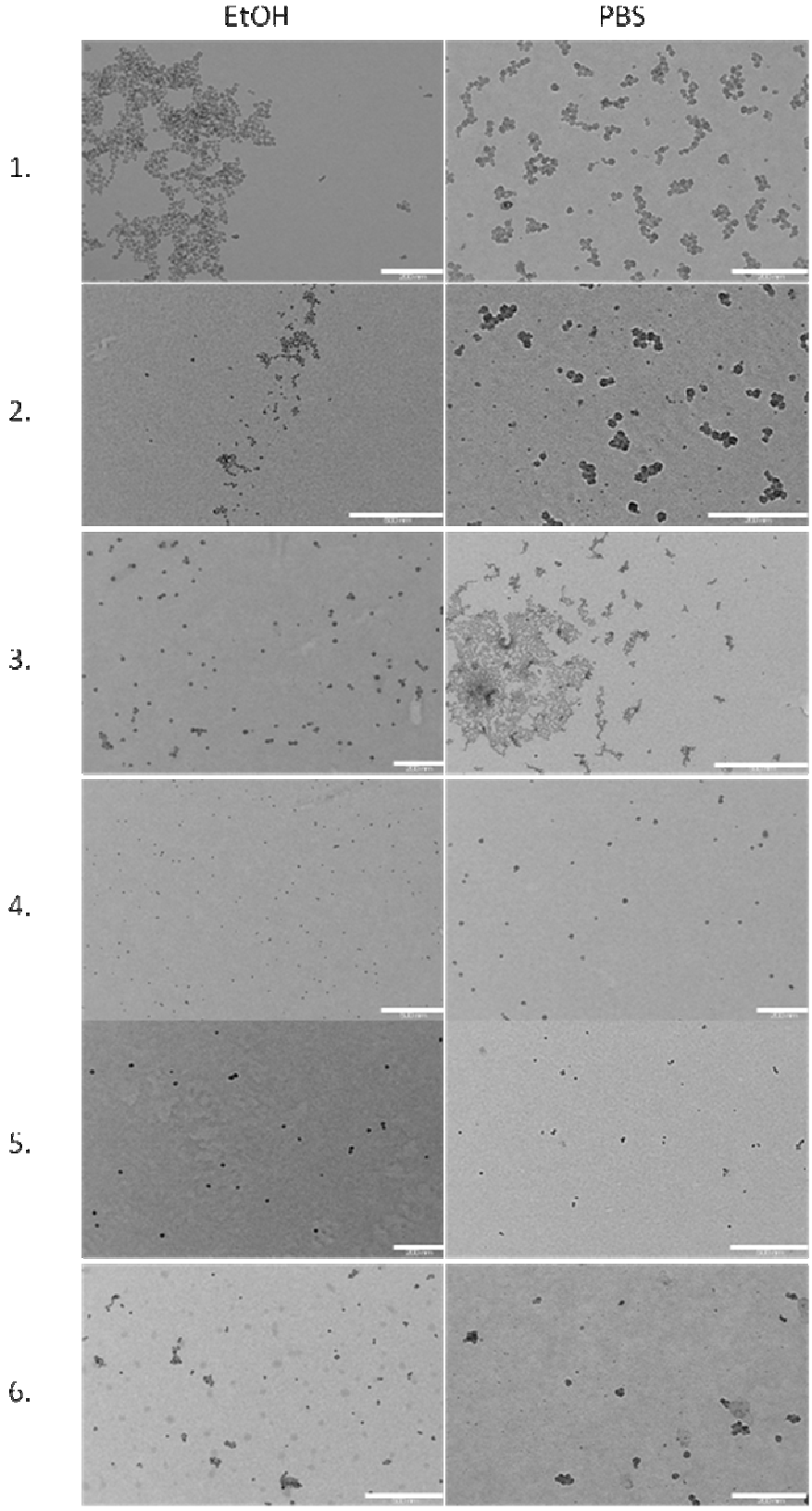

Figure S3. TEM images of MSN-PEG in EtOH or PBS.
The numbers 1, 2, 3, 4, 5 and 6 refer to the amount of PEG-Si investigated for the grafting of the MSN (0.05 eq., 0.1 eq., 0.25 eq.,0.5 eq., 1 eq. and 2.5 eq., respectively).

Scale bars in EtOH: 1: 200 nm; 2: 500 nm; 3: 200 nm; 4: 500 nm; 5: 200 nm; 6: 500 nm.
Scale bars in PBS: 1: 200 nm; 2: 200 nm; 3: 500 nm; 4: 200 nm; 5: 500 nm; 6: 200 nm.

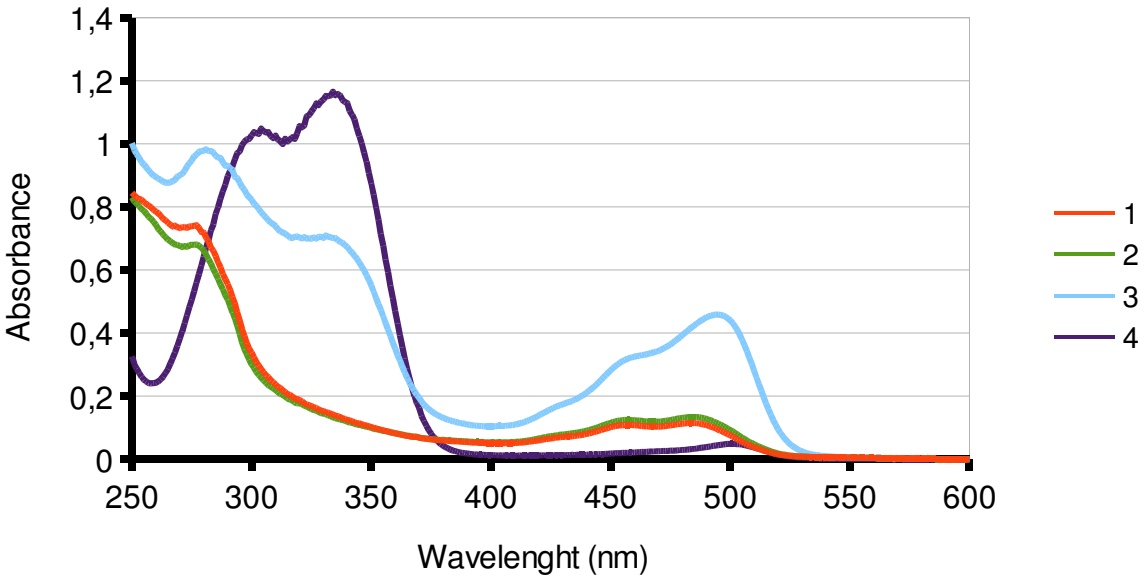

Figure S4. UV-visible spectra of MSN grafted with mannose (NH_2-Si route).

The numbers 1, 2, 3 and 4 refer to the amount of invested NH_2-Si for the grafting of the MSN (2.23×10^{-3}; 3.77×10^{-3}; 1.03×10^{-2} and 2.23×10^{-2} mmol, respectively).

The spectrum "4" was scaled 1/10 to fit with the 3 other spectra.

The quantity of grafted mannose was not determined for samples 1 and 2 because of too low absorbances at 330 nm.

Amount of grafted mannose: sample3: 1.99×10^{-3} mmol/g_{MSN}; sample4: 8.49×10^{-2} mmol/g_{MSN}.

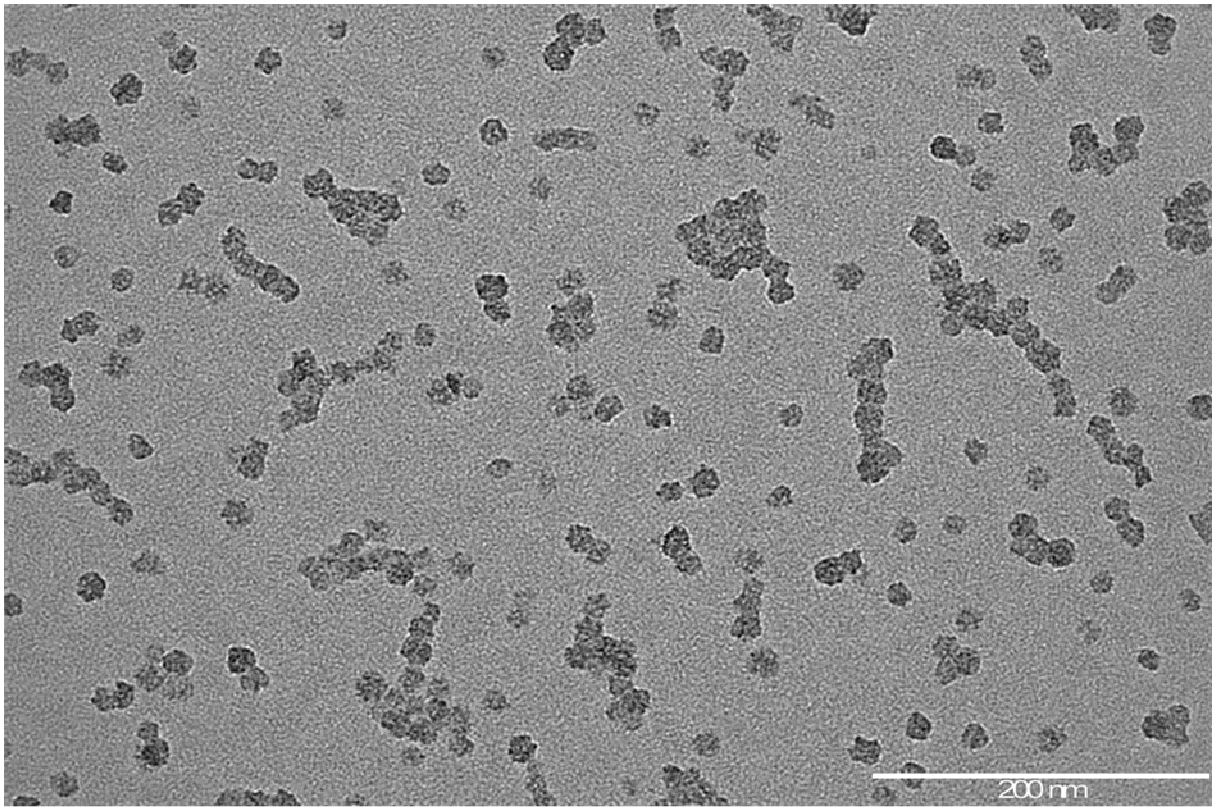

Figure S5. TEM image of MSN grafted with mannose (NH_2-Si route). Sample (3) in EtOH. Scale bar = 200 nm.

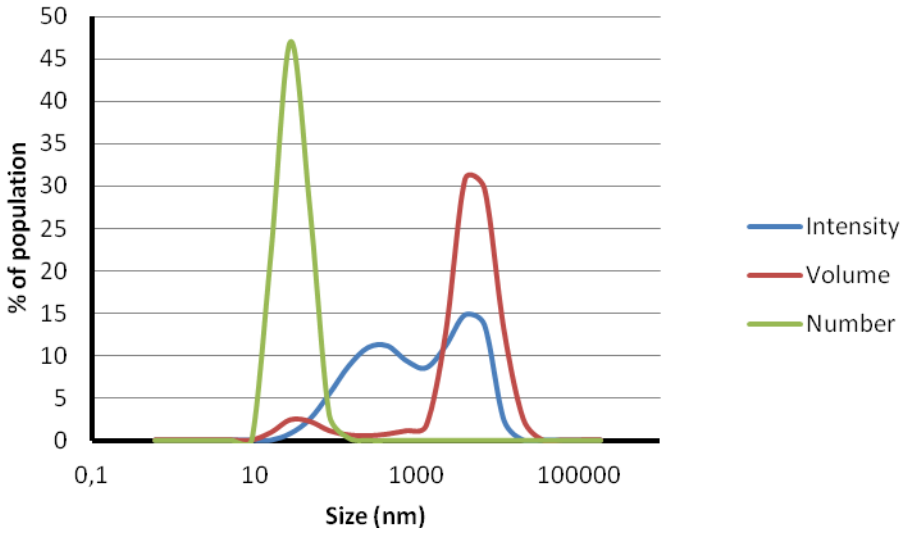

Figure S6. DLS measurements of MSN grafted with mannose (NH_2-Si route). (3) in PBS.
Two populations (480 nm and 4290 nm) are determined through the intensity spectrum (blue). 92.3% of the volume of the suspension is occupied by aggregates with size in the micrometer range. While a population of nanoparticles with a mean size of 33 nm is calculated (100% in number, green line), it doesn't reflect the macroscopic aspect of the suspension.

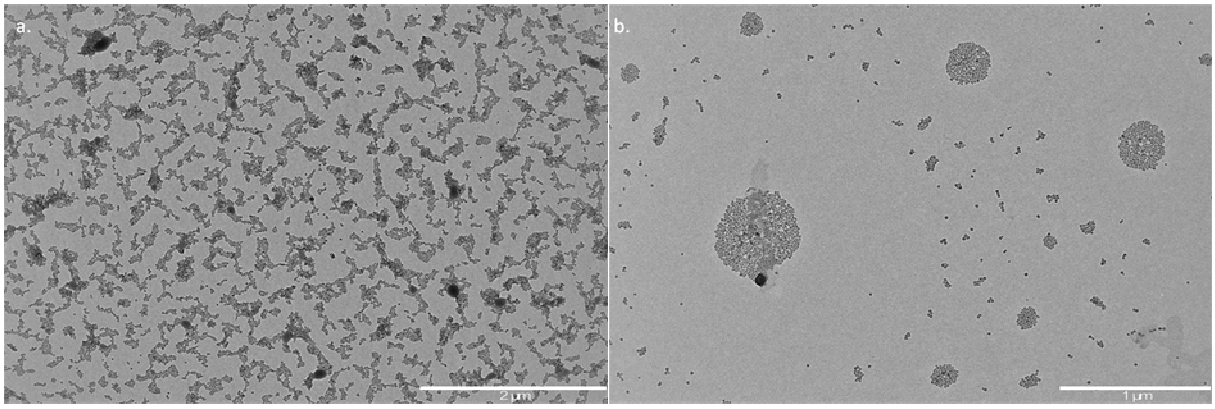

Figure S7. TEM images of MSN grafted with mannose-Si_1, sample (3) in PBS.

a. Preparation of the grid at 25°C. The nanoparticles appear to be randomly organized. Scalebar: 2 µm.

b. Preparation of the grid at 37°C. Some nanoparticles appear to be organized in round shaped patterns. Scalebar: 1 µm.

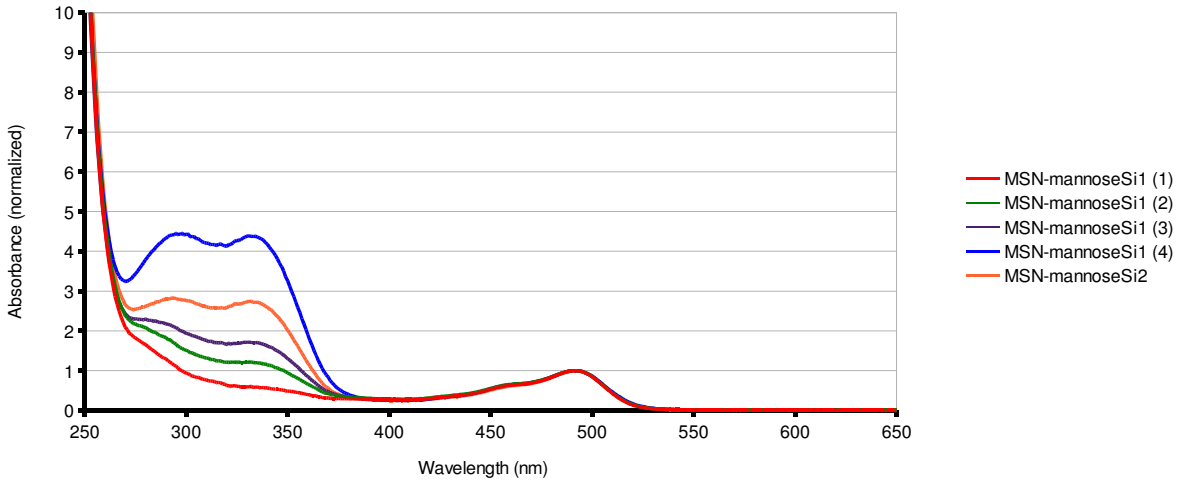

Figure S8. Overlay of the UV-visible spectra of MSN-mannose-Si_1 and MSN-mannose-Si_2 in PBS.
The spectra were normalized (fluorescein peak at 499 nm set as reference).

The amount of grafted mannose were determined from the non modified spectra in PBS (ε = 21000 $cm^{-1}.M^{-1}$ at 330 nm):

MSN-mannoseSi_1(1): 9.72×10^{-3} mmol.g_{MSN}^{-1}; MSN-mannoseSi_1(2): 2.03×10^{-2} mmol.g_{MSN}^{-1}; MSN-mannoseSi_1(3): 3.04×10^{-2} mmol.g_{MSN}^{-1}; MSN-mannoseSi_1(4): 7.80×10^{-2} mmol.g_{MSN}^{-1}; MSN-mannoseSi_2: 4.02×10^{-2} mmol.g_{MSN}^{-1}.

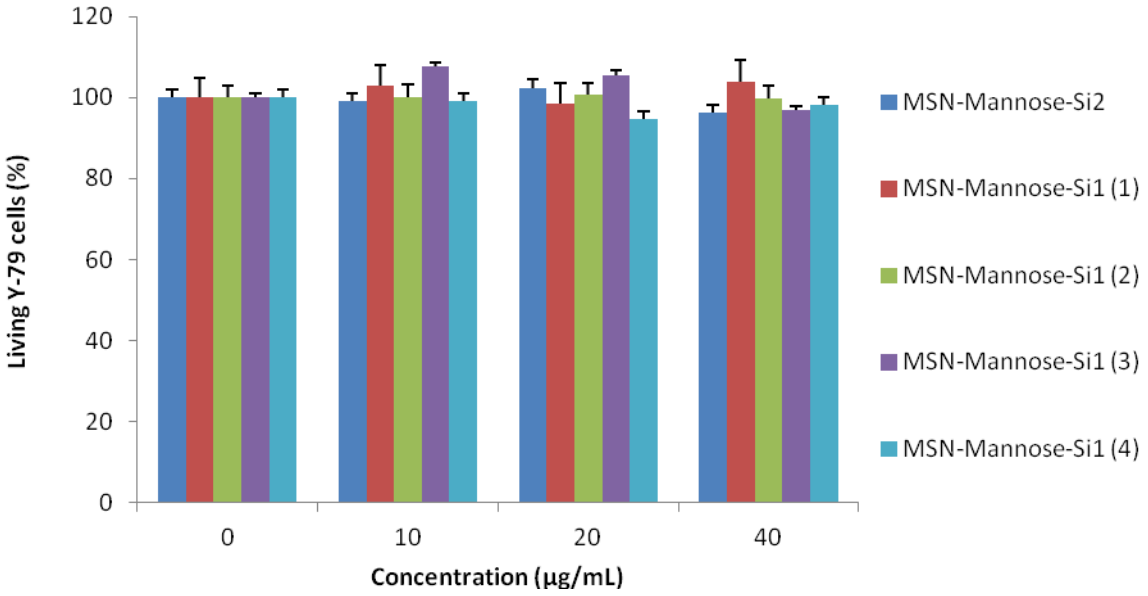

Figure S9. Toxicity of mannose-functionnalized nanoparticles MSN-mannose-Si_1 and MSN-mannose-Si_2.

Y-79 were incubated with mannose-functionalized nanoparticle (concentrations: 0, 10, 20 or 40 mg/mL in culture medium) for 72 hours. MTS assays were then performed and survival cells were determined (100% set for 0 mg/mL nanoparticles). The nanoparticles did not show significant cytotoxicity towards Y-79 cells. The numbers 1, 2, 3 and 4 refer to the amount of dry mannose-Si_1 investigaed for the grafting of the MSN (1 mg, 2 mg, 5 mg and 10 mg, respectively).