Electronic Supporting Information for

Dendronized iron oxide nanoparticles as contrast agent for MRI

Brice Basly, ^a Delphine Felder-Flesch, ^{*a} Pascal Perriat, ^b Claire Billotey, ^c Jacqueline Taleb, ^c Geneviève Pourroy, ^a and Sylvie Begin-Colin^{*a}

^a IPCMS, 23 rue du loess BP 43, 67034 Strasbourg, France. Fax: + 33 388 10 72 47; Tel:+ 33 388 10 71 92; E-mail: <u>Sylvie.Begin@ipcms.u-strasbg.fr</u>, <u>Delphine.Felder@ipcms.u-strasbg.fr</u>

^b Groupe d'Etudes de Métallurgie Physique et de Physique des Matériaux, UMR 5510 CNRS-INSA de Lyon, F-69621 Villeurbanne Cedex, France. Fax: + 33 472 43 85 28 ; Tel:+ 33 472 43 82 53; E-mail: Pascal.Perriat@insa-lyon.fr

^c Service de Médecine Nucléaire, Pavillon B - Hôpital Edouard Herriot, 5 place d'Arsonval, 69437 Lyon cedex 03, France. Fax: + 33 472 11 69 57; Tel:+ 33 472 68 46 17; E-mail: claire.billotey@univ-lyon1.fr

Synthesis of 12 nm iron oxide nanoparticles

Distilled water degassed with argon for half an hour was used for the preparation of 1M FeCl₃.6H₂O and 2M FeCl₂.4H₂O by dissolving iron salts in 2M HCl solutions. 10 mL of a 1M FeCl₃ solution were mixed with 2.5 mL of a 2M FeCl₂ solution. The so-obtained mixture was stirred and heated up to 70°C while kept under argon before slow addition of 21 mL of a 25% aqueous solution of N(CH₃)₄OH. Vigorous stirring was maintained for 20 min. The solution colour changed from orange to black, leading to a black precipitate and the suspension was slowly cooled to room temperature. The so-obtained powder was washed by magnetic decantation in water.

Characterization of iron oxide nanoparticles

X-ray diffraction (XRD) pattern of the grafted NPs (Fig1.) was recorded at room temperature using a Bruker D8 equipped with a monochromatic copper radiation, (K α = 0.154056 nm). All peaks were found to correspond to an iron oxide spinel structure. The calculated parameter *a* = 0.8383Å is intermediate to the one of magnetite (0.8396Å) and maghemite (0.8346Å) according to JCPDS cards numbers 19-629 and 39-1346, respectively. This observation is significant of nanoparticles which mainly consist in magnetite partially oxidized at their surface.

Transmission electron microscopy (TEM), a TOPCON 002B, operating at 200 kV, (point resolution 0.18 nm) and equipped with a GATAN GIF 200 electron imaging filter, was used to study the morphology and crystalline structure of the nanoparticles.



X-ray diffraction pattern of nanoparticles coated with the dendritic molecule.

IR analyses

Infrared spectra of the NPs, grafted NPs and the dendron were recorded with a Fourier Transform Infrared (FTIR) spectrometer (Digilab FTS 3000). Samples were gently ground and diluted in nonabsorbent KBr matrices. The comparison between the IR spectra of the nude nanoparticles, the dendron and the grafted nanoparticles confirmed the presence of the dendritic core shell at the surface of the nanoparticles showing the disappearence of typical phosphonate bands (P=O band at 1200 cm⁻¹ and P-O-H bands at 850 and 1000 cm⁻¹) thus confirming grafting through the phosphonate group.



Infrared spectra of the NPs, grafted NPs and the dendritic molecule (Mol).

Thermogravimetric analyses

Thermogravimetric analyses (TGA) were performed under air using a TA INSTRUMENT apparatus with a heating rate of 5°C /min. On TGA curve of NPs, only a small weight decrease was observed resulting from the competition between the oxidation of Fe^{2+} and the loss of adsorbed water. Grafted NPs display a larger weight loss than non-grafted NPs proving the presence of organic molecules. The molecule decomposes in air in three steps with a strong weight loss between 180 and 320°C and the resulting amount observed at 700°C is approximately 8%wt. However, the grafting rate cannot be determined easily by these analyses due to a competitive effect between weight gain due to oxidation of the NPs and weight loss due to decomposition of the dendritic shell and dehydration.



Fig3. Thermogravimetric curves of the NPs and grafted NPs.

Magnetization

Hysteresis cycles of the NPs and the grafted NPs were recorded at room temperature using a Foner EG&G model 155 vibrating sample magnetometer. The magnetization curves are characteristic of superparamagnetic nanoparticles and demonstrate that the magnetic properties of the nanoparticles are preserved after the grafting step. Indeed, the saturation magnetization of the grafted nanoparticles after subtracting the organic part is about 70 emu/g, slightly higher than the starting NPs (65 emu/g).

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Magnetization curves of the NPs and grafted NPs (NPs@Mol).

In vitro relaxivity measurements at 7T, 37°C



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In vitro relaxivity measurements at 1.5T, 25°C

