# Supporting Information

## Alkyl phosphonic acid-based ligands as tools for converting hydrophobic iron nanoparticles into water soluble iron-iron oxide core-shell nanoparticles.

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## SI1: TEM and size histogram of FeNP:

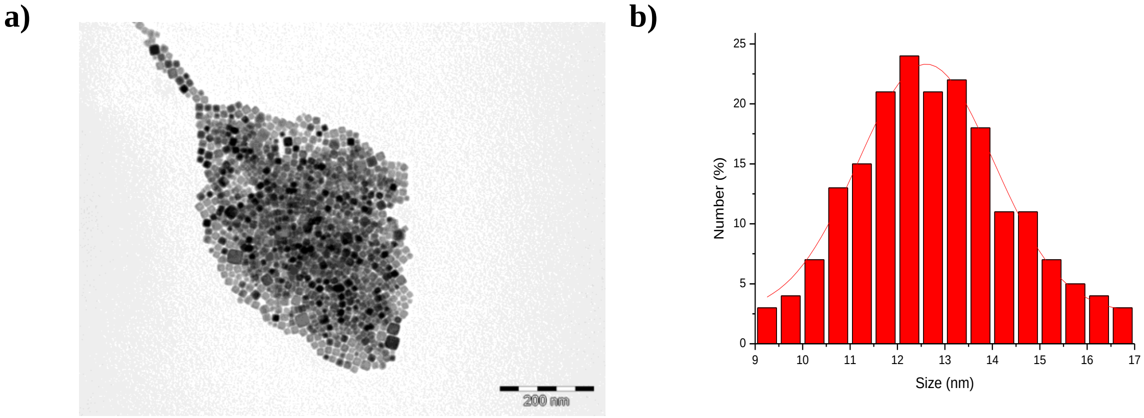


Figure SI1: Transmission electron micrograph of **FeNP** deposited onto a Cu grid from a solution of nanoparticles in THF (a) and size distribution from TEM images of nanoparticles (b)

## SI2: FTIR-ATR of FeNP:

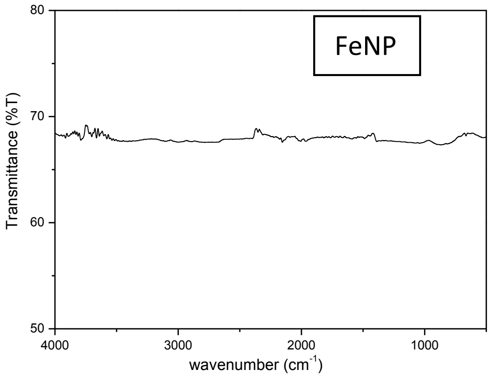


Figure SI2 : FTIR –ATR spectrum of **FeNP.**

## SI3: TEM of FeNP dispersed in water and water-ethanol

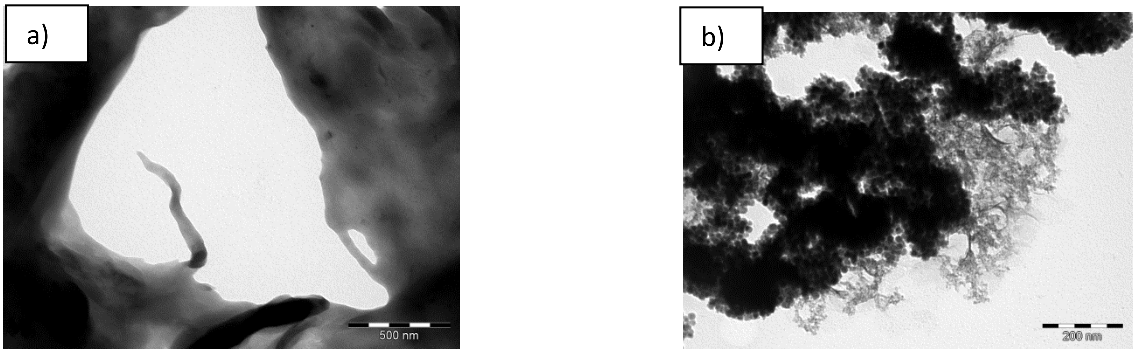


Figure SI3: TEM of **FeNP** deposited onto a Cu carbon covered grid from a suspension of **FeNP** in water (a) and water-ethanol mixture (b) respectively, without phosphonic acid protection.

## SI4: Snapshots of the transfer of FeNP into water

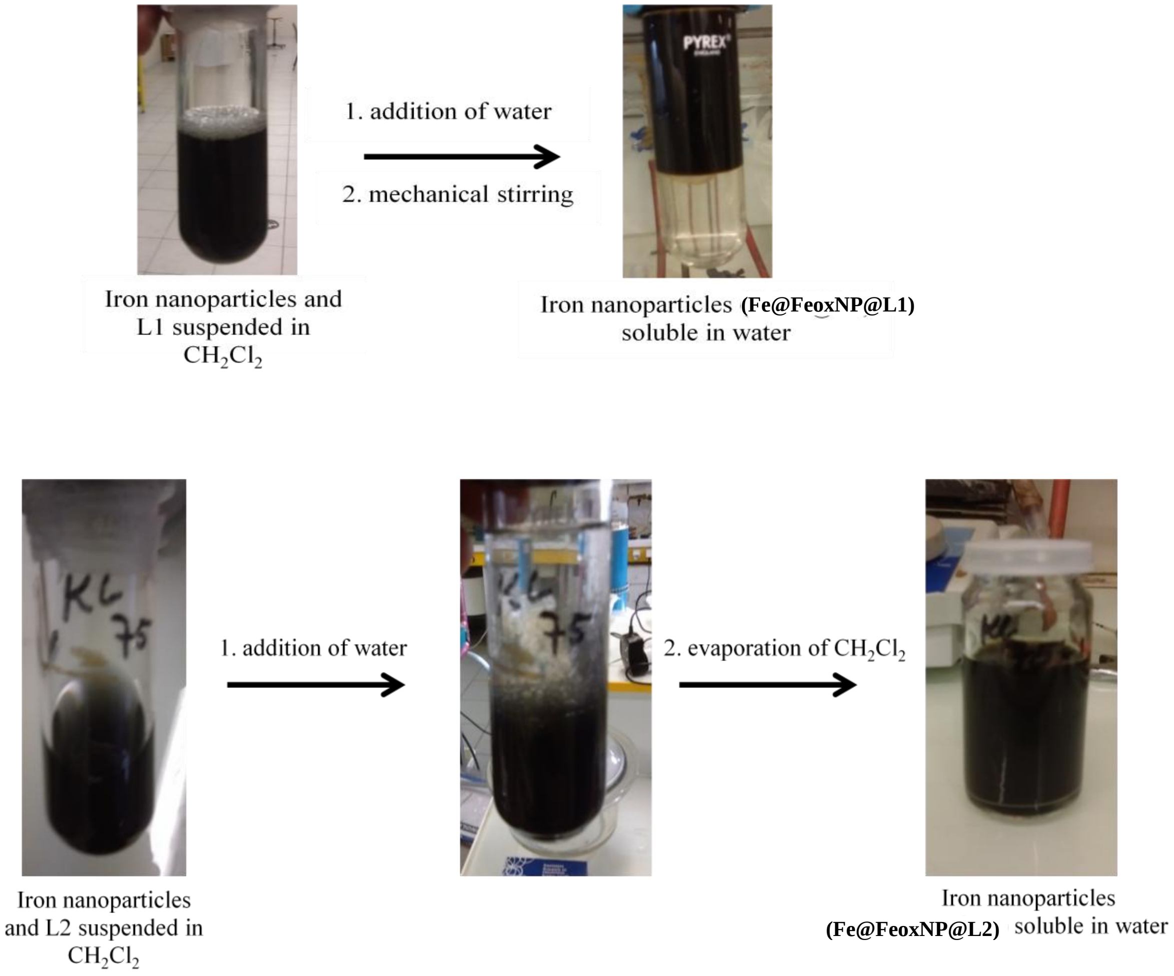


Figure SI4: Transfer into water of **FeNP** nanoparticles

## SI5: HRTEM of Fe@FeoxNP@L1 and Fe@FeoxNP@L2 and size distribution from TEM images of core and shell of Fe@FeoxNP@L1 and Fe@FeoxNP@L2

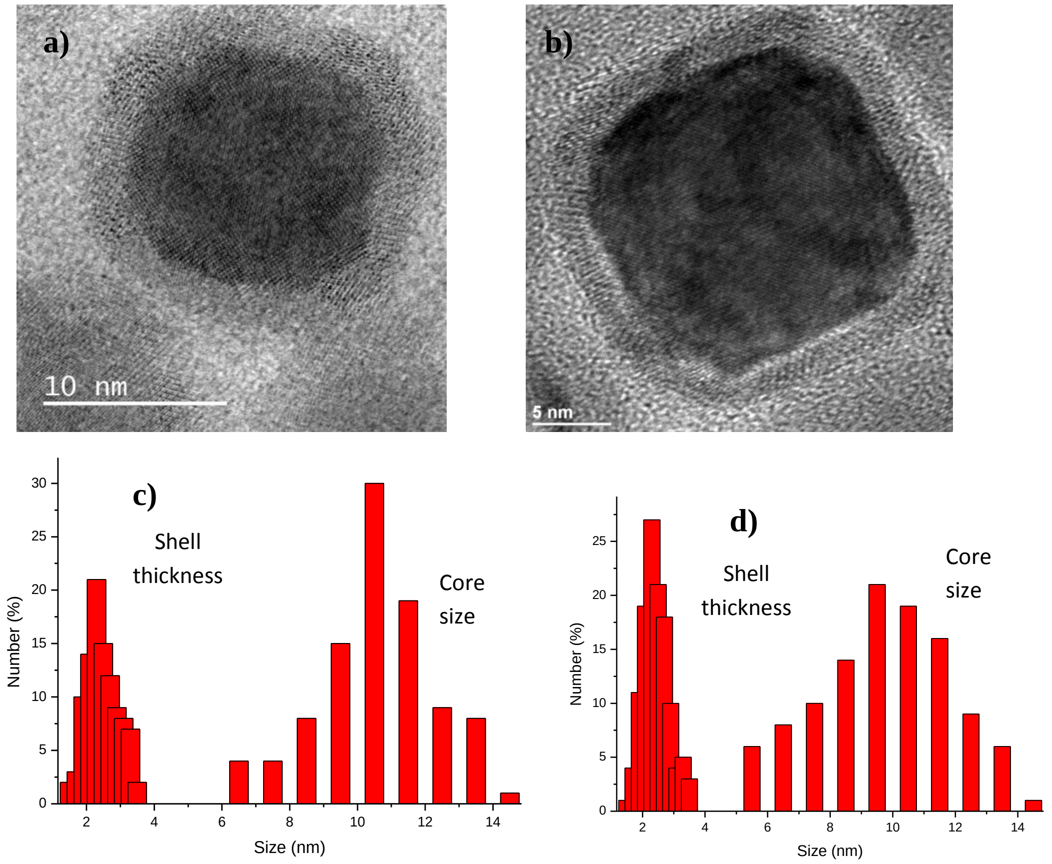
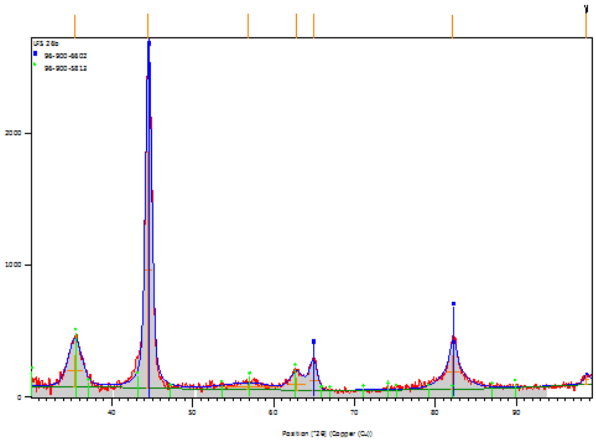
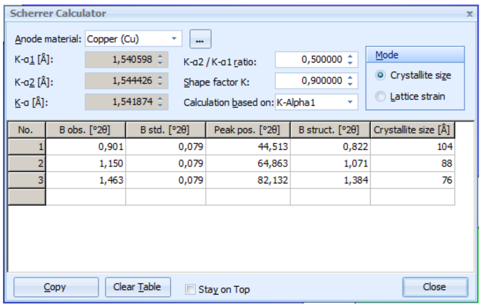


Figure SI5: HRTEM of **Fe@FeoxNP@L1** (a) and **Fe@FeoxNP@L2** (b), showing a core/shell structure and size distribution from TEM images of core and shell of **Fe@FeoxNP@L1** (c) and **Fe@FeoxNP@L2** (d) respectively

## SI6: XRD analysis and the calculation of coherent diffraction domains of the α-Fe component for Fe@FeoxNP@L1 and Fe@FeoxNP@L2





Anode material: Copper (Cu)

K-α1 [Å]: 1,540598

K-α2 [Å]: 1,544426

K-α [Å]: 1,541874

K-α2 / K-α1 ratio: 0,500000

Shape factor K: 0,900000

Calculation based on: K-Alpha1

● Crystallite size
○ Lattice strain

| No. | B obs. [°2θ] | B std. [°2θ] | Peak pos. [°2θ] | B struct. [°2θ] | Crystallite size [Å] |
|---|---|---|---|---|---|
| 1 | 0,901 | 0,079 | 44,513 | 0,822 | 104 |
| 2 | 1,150 | 0,079 | 64,863 | 1,071 | 88 |
| 3 | 1,463 | 0,079 | 82,132 | 1,384 | 76 |
| | | | | | |

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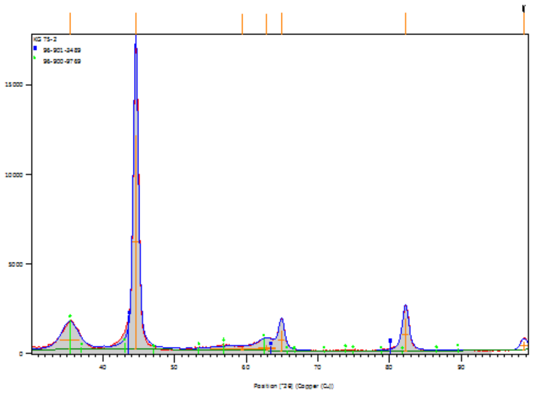

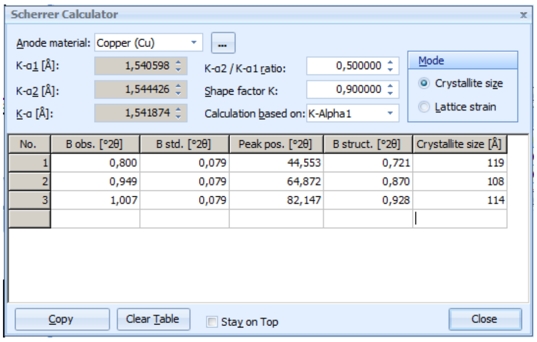
Scherrer Calculator

Anode material: Copper (Cu)

K-α1 [Å]: 1,540598

K-α2 [Å]: 1,544426

K-α [Å]: 1,541874

K-α2 / K-α1 ratio: 0,500000

Shape factor K: 0,900000

Calculation based on: K-Alpha1

Mode

● Crystallite size

○ Lattice strain

| No. | B obs. [°2θ] | B std. [°2θ] | Peak pos. [°2θ] | B struct. [°2θ] | Crystallite size [Å] |
|---|---|---|---|---|---|
| 1 | 0,800 | 0,079 | 44,553 | 0,721 | 119 |
| 2 | 0,949 | 0,079 | 64,872 | 0,870 | 108 |
| 3 | 1,007 | 0,079 | 82,147 | 0,928 | 114 |
|  |  |  |  |  |  |

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Figure SI6: XRD analysis and the calculation using Hifhscore Plus software of the size of coherent diffraction domains for the α-Fe component for **Fe@FeoxNP@L1** and **Fe@FeoxNP@L2** respectively.

## SI7: Stability investigations on Fe@FeoxNP@L2

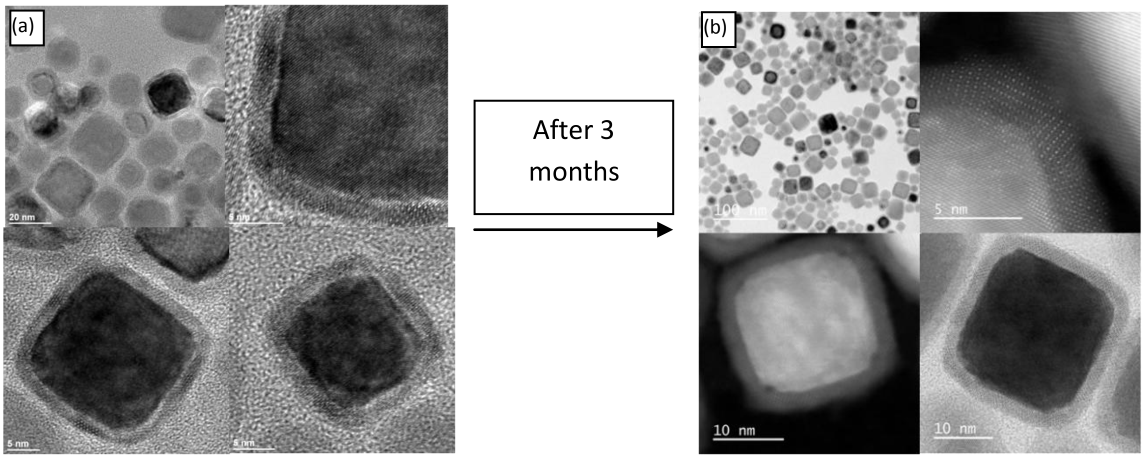


Figure SI7: HRTEM images of **Fe@FeoxNP@L2** (a) after the synthesis ; (b) 3 months later

**SI8: Control experiments**:

a) First control experiment: In the glove box, 30 mg of **FeNP** were dispersed in dry and $O_2$ free THF (15ml) together with 65 mg of **L2** ligand. 10 ml of degassed miliQ water were next transferred to the nanopaticle-THF solution using a cannula system in order to avoid air contamination. The obtained solution was of black color and free of any suspension which proves that the nanoparticles are highly soluble in this mixture. After two days of stirring, a TEM grid was realized from this solution (Figure SI8b) revealing the presence of nanoparticles which started to disintegrate. After magnetic precipitation of the nanoparticles and subsequent washing with degassed water the nanoparticles were no more soluble in water. TEM micrographs obtained from a suspension in water of the nanoparticles at the end of the washing process revealed seriously damaged nanoparticles. (Figure SI8c)

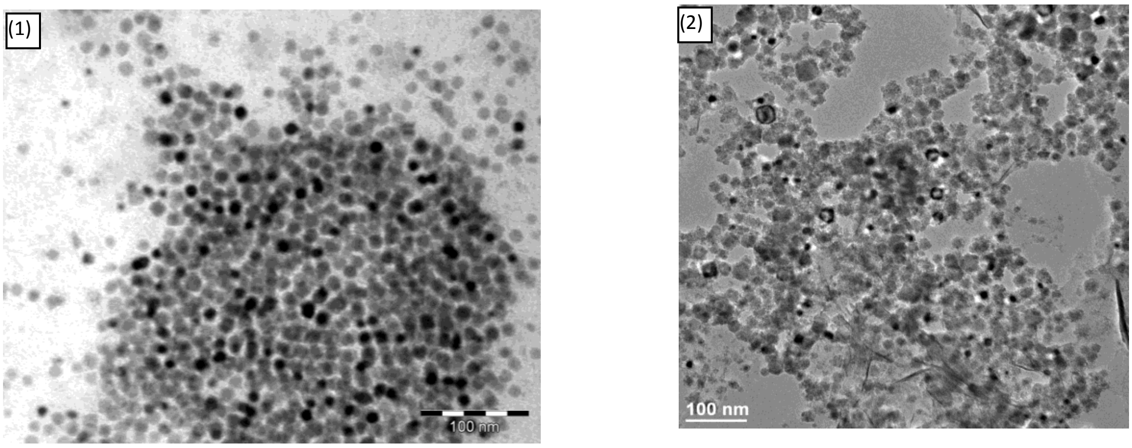


Figure SI8a: 1). TEM of **FeNP** from the THF-water degassed solution and 2) after magnetic precipitation and washing with degassed water.

b). Second control experiment: In the glove box, 30 mg of **FeNP** were dispersed in dry and $O_2$ free $CH_2Cl_2$ together with 60 mg of **L2**. The solution was then mechanically stirred during 12h after which the nanoparticles were magnetically isolated,

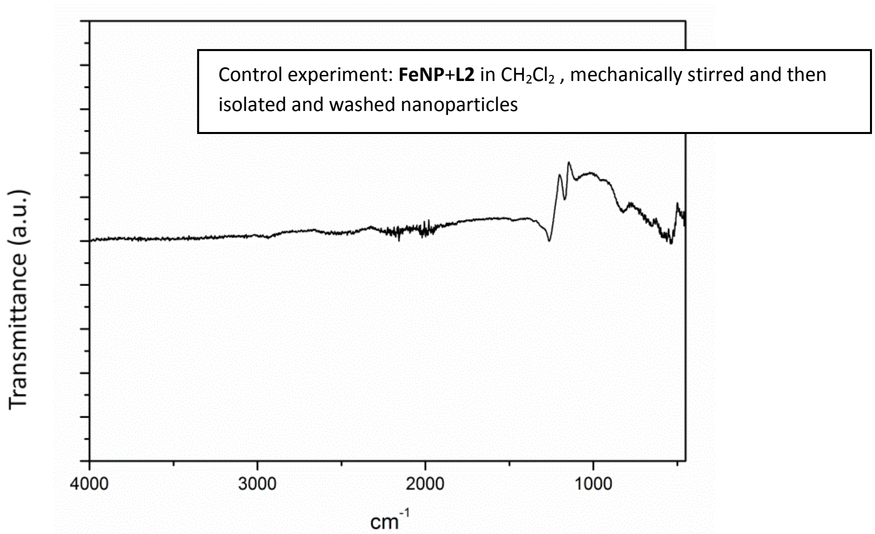


Figure SI8b: IR spectra of nanoparticles from the second control experiment washed several times with $CH_2Cl_2$ and dried under vacuum. The final powder was then analyzed by IR spectroscopy in order to evaluate the coordination of **L2** to the surface of the nanoparticles.

## SI9: Determination of the grafting density of the ligands

Mass concentration of Fe and P determined by ICP-AES after digestion of the sample in aqua regia (mixture of 3:1v/v HCl and $HNO_3$)

| **Sample** | **Iron concentration** | **Phosphorus concentration** (mg $L^{-1}$) |
|---|---|---|
| **Fe@FeoxNP@L1** | 177.8 ppm | 13.66 |
| **Fe@FeoxNP@L2** | 695.3 ppm | 3.283 |

**Calculation of P and Fe atoms number considering 1L of solution:**

Number (P)=$\frac{ICP(P)*N_A}{M(P)}$,

Number (Fe)= $\frac{ICP(Fe)*N_A}{M(Fe)}$

Where ICP (P) is the phosphorus concentration in the sample, $N_A$ the Avogadro number $6.022*10^{23}mol^{-1}$, M(P) the atomic weight of phosphorus 30.97 $g.mol^{-1}$, M(Fe) the atomic weight of iron 55.8 $g.mol^{-1}$.

| **Sample** | Fe atoms number (considering 1L) | P atoms number (considering 1L) |
|---|---|---|
| **Fe@FeoxNP@L1** | $19.18*10^{20}$ | $2.66*10^{20}$ |
| **Fe@FeoxNP@L2** | $75.03*10^{20}$ | $0.63*10^{20}$ |

**Calculation of Fe atoms number in one zerovalent iron cube of 12.8 nm:**

It was considered that the number of iron atoms in the cube (nanoparticle) remains the same after water transfer and oxidation of the surface.

Number (Fe atoms in one cube)=$\frac{m(cube)*N_A}{M(Fe)}=\frac{d*V*N_A}{M(Fe)}=\frac{7.87*10^6*(12.8*10^{-9})^3*6.022*10^{23}}{55.8}$=178120 iron atoms in a cube

Where d is iron density ($7.87*10^6$ $g*m^{-3}$), V is the volume of the cube in $m^3$ ($N_A$ the Avogadro number $6.022*10^{23}mol^{-1}$ and M(Fe) the atomic weight of iron 55.8 $g.mol^{-1}$.

**Calculation of P atoms coverage on iron cubes:**

1. **Calculation of number of cubes in the sample:**

For **Fe@FeoxNP@L1** sample:

Number iron cubes=$\frac{Fe\ atoms\ in\ the\ sample}{Fe\ atoms\ in\ one\ cube}$=$\frac{19.18*10^{20}}{178120} = 10.7 * 10^{15}$ iron cubes

For **Fe@FeoxNP@L2** sample:

Number iron cubes=$\frac{Fe\ atoms\ in\ the\ sample}{Fe\ atoms\ in\ one\ cube}$=$\frac{75.03*10^{20}}{178120} = 42.12 * 10^{15}$ iron cubes

### 2. Calculation of number of P atoms per iron cube:

For **Fe@FeoxNP@L1** sample:

$$P/NP=\frac{number\ of\ P\ atoms}{number\ of\ iron\ cubes} = \frac{2.66*10^{20}}{10.7*10^{15}} = 24859\ P/NP$$

For the **Fe@FeoxNP@L2** sample:

$$P/NP=\frac{number\ of\ P\ atoms}{number\ of\ iron\ cubes} = \frac{0.63*10^{20}}{42.12*10^{15}} = 1495\ P/NP$$

### 3. Calculation of surface of the iron cube after transfer into water:

For **Fe@FeoxNP@L1** sample:

Surface cube (water)=6* $(edge)^2$=6 *$(13.8)^2$=1143 $nm^2$

For the **Fe@FeoxNP@L2** sample:

Surface cube (water)=6* $(edge)^2$=6 *$(13.5)^2$=1094 $nm^2$

### 4. Calculation of P coverage (P/nm$^2$):

For **Fe@FeoxNP@L1** sample:

P-coverage= $\frac{number\ of\ P\ atoms\ per\ cube}{surface\ of\ the\ cube} = \frac{24859}{1143} = 22\ P/nm^2$= 22 L1/$nm^2$

For **Fe@FeoxNP@L2** sample:

P-coverage= $\frac{number\ of\ P\ atoms\ per\ cube}{surface\ of\ the\ cube} = \frac{1495}{1094} = 1.4\ P/nm^2$=1.4 L2/$nm^2$

If we consider the footprint of phosphonate group to be 0.24 $nm^2$ as indicated by Daou et al.[1] the maximum grafting density for $L_1$ should be 1/0.24=4.2P/$nm^2$.

This means that in the case of L1 more than one monolayer of L1 is adsorbed on the nanoparticle surface. In the case of L2 the grafting of 1.4 P/$nm^2$ is six times more important than the one obtained when the same ligand was grafted on the iron oxide nanoparticles of the same size, but it correspond to the grafting density of dendritric molecules terminated with a phosphonate group anchored on iron oxide nanoparticles of about 11 nm.[2]

### 5. Calculation of the ratio P/Fe $_{\text{surface atoms}}$

**a) from the quantities of reactants:**

Calculation of Fe atoms number on the surface of one zerovalent iron cube of 12.8 nm:

Iron with a body centered cubic structure has a lattice contact a=0.28 nm.

Number of Fe on the surface of the cube=$6 * (\frac{edge}{a})^2$=$6*(\frac{12.8}{0.28})^2$=13696 Fe atoms

Where edge is the edge of the zerovalent iron cube determined by TEM (12.8 nm)

Quantity of Fe in the sample (mmol)=$\frac{mass\ of FeNP\ sample}{M(Fe)} * w\%$Fe=$\frac{30}{55.8} * 0.72 = 0.40\ mmol\ Fe$

% of iron atoms on the surface=$\frac{number\ of\ iron\ atoms\ at\ the\ surface\ of\ a\ cube}{number\ of\ iron\ atoms\ in\ the\ cube} * 100 = \frac{13696}{178120} * 100 \cong 8\%$

For **Fe@FeoxNP@L1** sample:

Quantity of P in the sample (mmol)=$\frac{mass\ of L1\ ligand}{M(L1)}$=$\frac{10}{139.09} = 0.07\ mmol\ P$

Ratio P/Fe surface atom =$\frac{mmol\ P}{mmol\ Fe*\%\ of\ iron\ on\ the\ surface} = \frac{0.07}{0.40*0.08} \cong 2$

For **Fe@FeoxNP@L2** sample:

Quantity of P in the sample (mmol)=$\frac{mass\ of L2\ ligand}{M(L2)}$=$\frac{10}{2120} = 0.005\ mmol\ P$

Ratio P/Fe surface atom =$\frac{mmol\ P}{mmol\ Fe*\%\ of\ iron\ on\ the\ surface} = \frac{0.005}{0.40*0.08} \cong 0.15 \cong \frac{1}{7}$

**b) after purification of the sample:**

For **Fe@FeoxNP@L1** sample:

Ration P/Fe surface atoms =

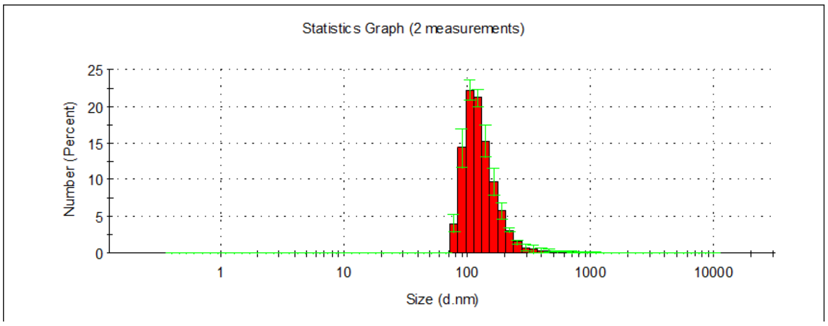
$$\frac{P\ atoms\ number\ in\ the\ sample}{\frac{Fe\ atoms\ number\ in\ the\ sample}{Fe\ atoms\ number\ in\ the\ cube} * Fe\ atoms\ \ number\ on\ the\ surface\ of\ a\ cube} = \frac{2.66*10^{20}}{\frac{19.18*10^{20}}{178120}*13696} = 1.8$$

For **Fe@FeoxNP@L2** sample:

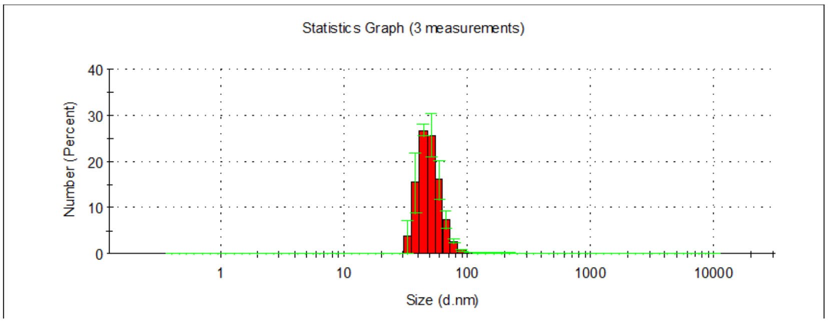
Ration P/Fe surface atoms =

$$\frac{P\ atoms\ number\ in\ the\ sample}{\frac{Fe\ atoms\ number\ in\ the\ sample}{Fe\ atoms\ number\ in\ the\ cube} * Fe\ atoms\ \ number\ on\ the\ surface\ of\ a\ cube} = \frac{0.63 * 10^{20}}{\frac{75.03 * 10^{20}}{178120} * 13696} = 0.1$$

## SI10: DLS measurements:



DLS particles size distribution for the **Fe@FeoxNP@L1**. The results are presented as number-based distribution.



DLS particles size distribution for the **Fe@FeoxNP@L2**. The results are presented as number-based distribution.

## SI11: Measurement of the T2 transverse relaxation time of the water protons as a function of iron concentration .

The measurements were performed with a Bruker Avance 500 MHz spectrometer (11.5T), equipped with a 5mm triple-resonance inverse Z-gradient probe. All chemical shifts were reported relative to tetramethylsilane (TMS). The temperature was set to 25°C.

The measurements were realized using as a solvent a mixture of 0.1% $H_2O$ in $D_2O$ in order to avoid the radiation damping effect.[3] In order to avoid the agglomeration of the nanoparticles in the magnetic field of the spectrometer the nanoparticles were fixed in a 4% agar gel. Transverse relaxation times were determined by fitting the $H_2O$ resonance linewidth as the magnetic field inhomogoneity contribution can be considered as negligible in the agar gel.

Several samples were prepared as described in the following table and the measurements were realized after three days of storage of the nanoparticles in these conditions.

| Sample | Quantity of Agar gel 4% (µL) | Solution of nanoparticles 0.1% $H_2O/D_2O$ (µL) | 0.1% $H_2O/D_2O$ (µL) |
|---|---|---|---|
| 1 | 750 | 0 | 750 |
| 2 | 750 | 50 | 700 |
| 3 | 750 | 100 | 650 |
| 4 | 750 | 150 | 600 |
| 5 | 750 | 200 | 550 |

Determination of transverse relaxivity (r2):

The $T_2$ times were determined from the inverse of half height linewidth of the water proton signal measured by spectral deconvolution (Figure S11a)

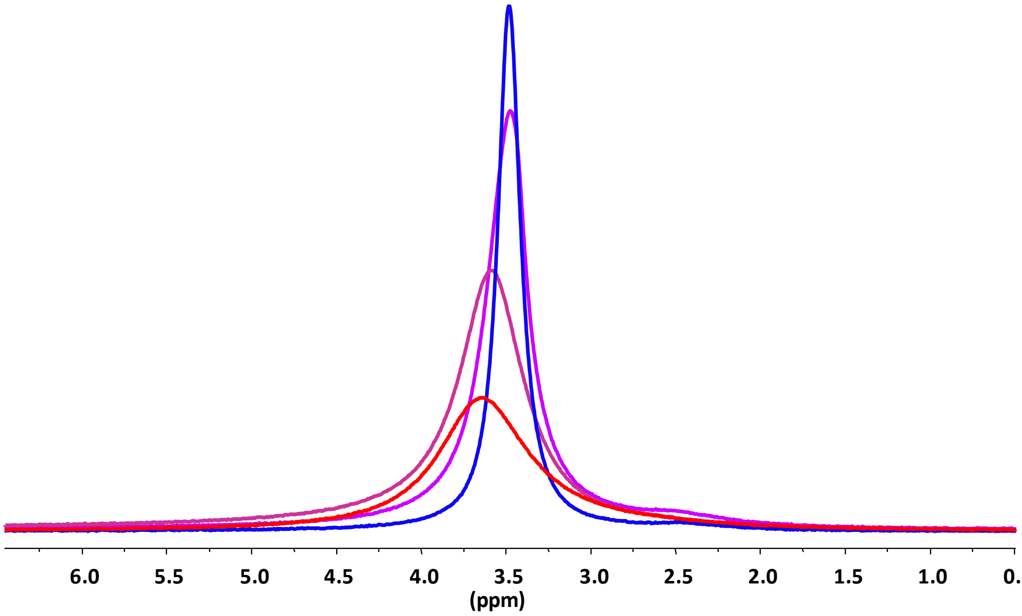


Figure SI11a: $^1$H-NMR signal of water protons. The peak widening is observed when the iron concentration increases.

The values obtained are listed in the following table as a function of iron concentration in each sample (determined after the measurement by ICP-AES)

| [Fe] mmol $L^{-1}$ | $1/T_2$ ($s^{-1}$) |
|---|---|
| 0 | 14 |
| 0.27 | 80 |
| 0.46 | 140 |
| 0.61 | 233 |
| 0.97 | 325 |

In order to determine transverse relaxivity (r2) the plot of $1/T_2$ (sample)-$1/T_2$(control) against iron concentration ([Fe] in mmol $L^{-1}$) (Figure SI14b) was fitted with a linear function: $1/T_2$ (sample)-$1/T_2$(control)=$r_2$x[Fe]; where the $r_2$ was determined as the slope of the fit. Control is the sample without nanoparticles.

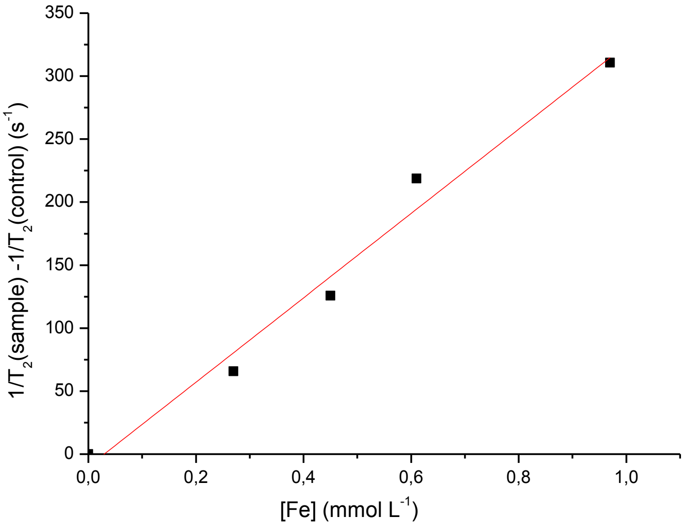


Figure SI11b: Sample plot using $T_2$ measurements of nanoparticles as varying iron concentrations to determine relaxivity.

1. T. J. Daou, S. Begin-Colin, J. M. Greneche, F. Thomas, A. Derory, P. Bernhardt, P. Legare and G. Pourroy, *Chemistry of Materials*, 2007, **19**, 4494-4505.
2. B. Basly, G. Popa, S. Fleutot, B. P. Pichon, A. Garofalo, C. Ghobril, C. Billotey, A. Berniard, P. Bonazza, H. Martinez, D. Felder-Flesch and S. Begin-Colin, *Dalton Transactions*, 2013, **42**, 2146-2157.
3. A. Vlassenbroek, J. Jeener and P. Broekaert, *The Journal of Chemical Physics*, 1995, **103**, 5886-5897.