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Supporting information

Potential Theranostic and Multimodal Iron Oxide Nanoparticles Decorated with Rhenium-Bipyridine and -Phenanthroline Complex

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XRD

All nanoparticles were further characterized by X-ray powder diffraction (XRD) (Figure 1).

The nanoparticles showed strong resemblance to the crystalline pattern of magnetite cubic iron oxide nanoparticles (JPDS 19-629).

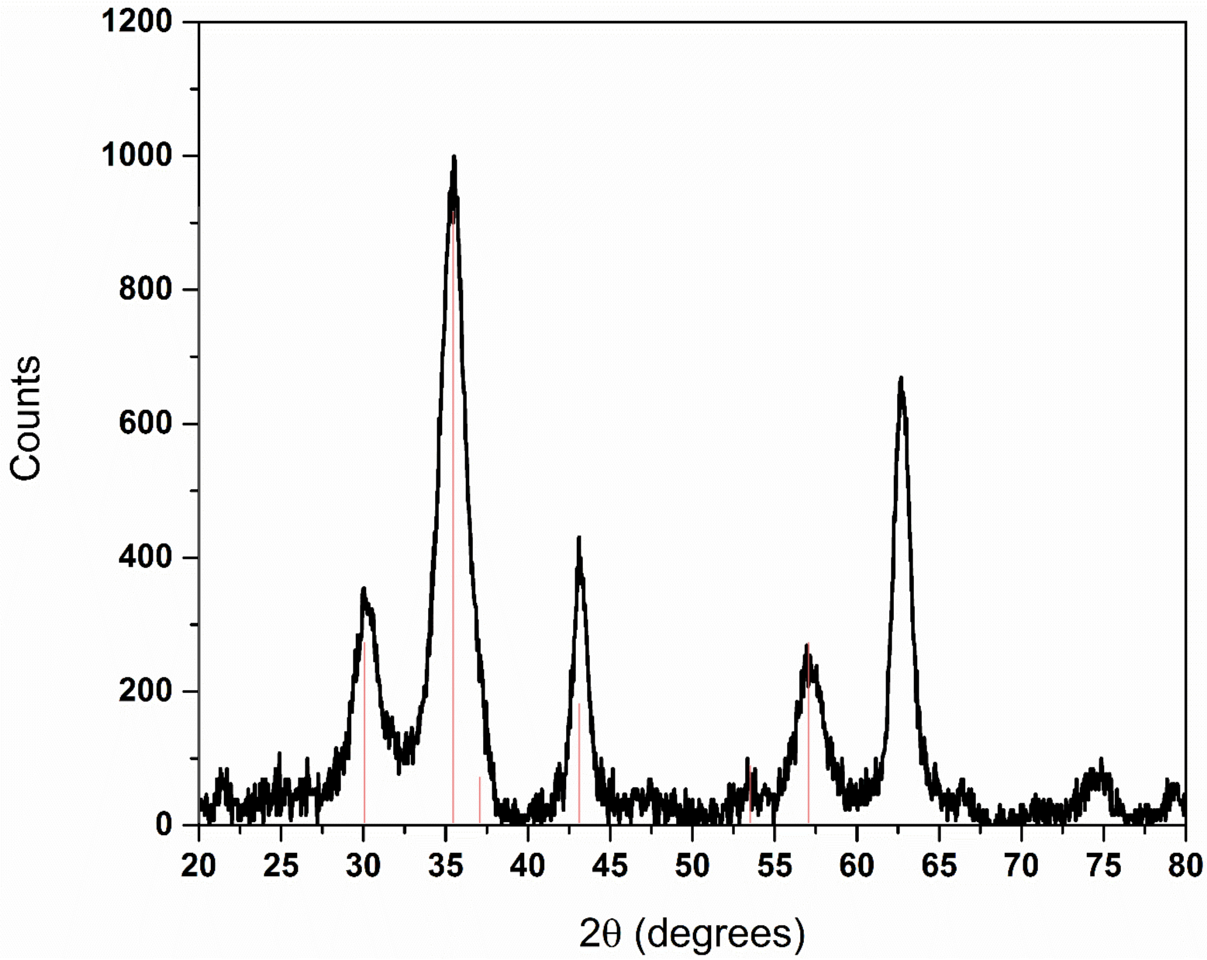
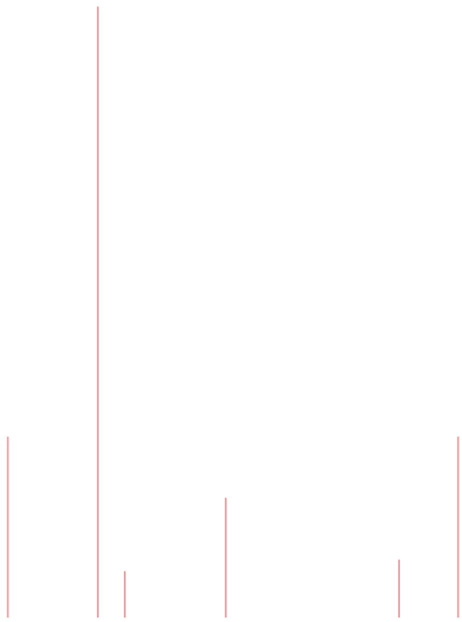


Figure 1: XRD-measurement of Fe3O4-oleate capped nanoparticles (black line) and the standard cubic phase with relative intensities according to JPDS 16-629 (red).



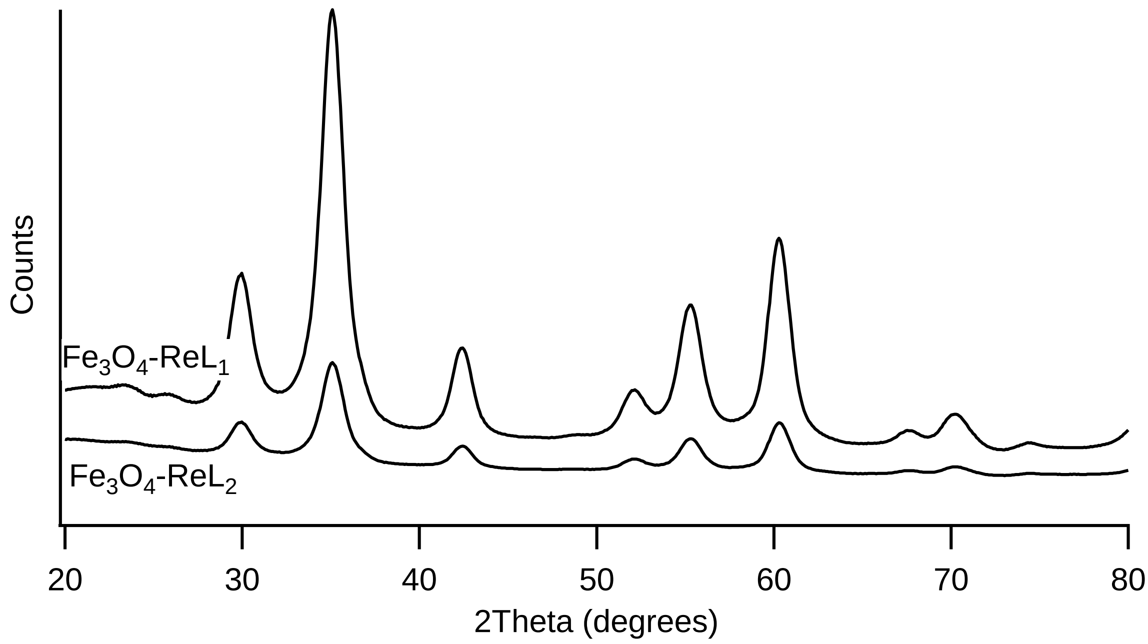


Figure 2: powder X-ray diffraction of Fe_3O_4-ReL_1 and Fe_3O_4-ReL_2. The pattern follows nicely the crystalline structure of magnetite nanoparticles (black line) and the standard cubic phase with relative intensities according to JPDS 16-629 (red).

Theoretical calculation of amount ligands per nanoparticle

Starting from the crystallographic data of the JPDS card 19-629 the following parameters were obtained for the cubic structure of Fe_3O_4:

$$a = 0.8396\ nm$$

The volume of a the unit cell ($Vol_{unit\ cell}$) is calculated using the following equation:

$$\begin{aligned} Vol_{unit\ cell} &= a^3 \\ &= 0.592\ nm^3 \end{aligned}$$

However the unit cell exists of 24 iron atoms and 32 oxygen atoms and further calculations should take this into account.

The volume of one nanoparticle can easily be calculated from the average diameter size (8.6 nm), measured by TEM and treating a nanoparticle as a sphere.

$$Vol_{NP} = \frac{4}{3}\pi r^3$$

$$= 333\ nm^3$$

The total concentration of iron in the nanoparticle Fe_3O_4-ReL_1 (Fe_1) and Fe_3O_4-ReL_2 (Fe_2) acquired from TXRF measurements, and reported in the paper (**Error! Reference source not found.**).

$$c(Fe_1) = 1.85 \times 10^{-3} M$$
$$c(Fe_2) = 1.68 \times 10^{-3} M$$

In the next step the amount of iron ions in one nanoparticle is found by simply dividing the volume of one nanoparticle by the volume of the unit cell, taking into account that 24 iron ions are in one unit cell.

$$\#\frac{Ln}{NP} = \frac{333}{0.592} * 24$$

$$= 13506$$

From this result the amount of NPs per volume unit (L) is obtained, using the concentration of iron ions in the nanoparticles and Avogadro's number.

$$\#\frac{Fe_1}{L} = 1.85 \times 10^{-3} * N_A$$
$$\#\frac{Fe_2}{L} = 1.68 \times 10^{-3} * N_A$$

Dividing the last two equations by each other gives the amount of nanoparticles per liter (NP_1 resembles Fe_3O_4-ReL_1, whereas NP_2 Fe_3O_4-ReL_2).

$$\#\frac{NP_1}{L} = \frac{\#\frac{Fe_1}{L}}{\#\frac{Fe_1}{NP}} = 8.2425 \times 10^{16}$$

$$\#\frac{NP_2}{L} = \frac{\#\frac{Fe_2}{L}}{\#\frac{Fe_2}{NP}} = 7.4708 \times 10^{16}$$

In the final step of these theoretical calculations the amount of ligands at the surface of one nanoparticle is obtained as well as the concentration (moles) per nanoparticle.

$$\#\frac{ReL_1}{NP} = \frac{0.03 \times 10^{-3} * N_A}{8.2425 \times 10^{16}} = 201084$$

$$moles\frac{ReL_1}{NP} = \frac{0.03 \times 10^{-3}}{8.2425 \times 10^{16}} = 3.339 \times 10^{-19}$$

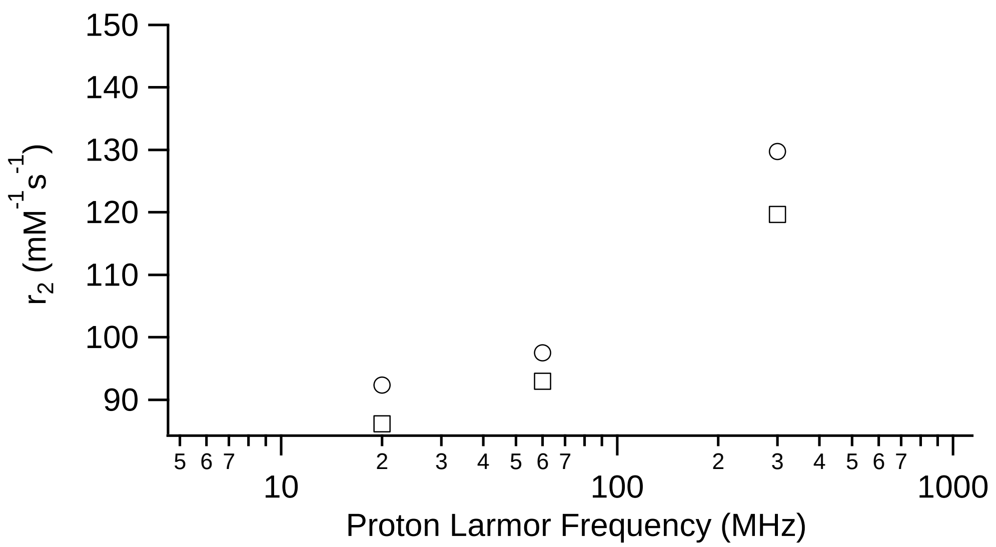
$$\#\frac{ReL_2}{NP} = \frac{0.03 \times 10^{-3} * N_A}{7.4708 \times 10^{16}} = 210554$$

$$moles\frac{ReL_2}{NP} = \frac{0.03 \times 10^{-3}}{7.4708 \times 10^{16}} = 3.496 \times 10^{-19}$$

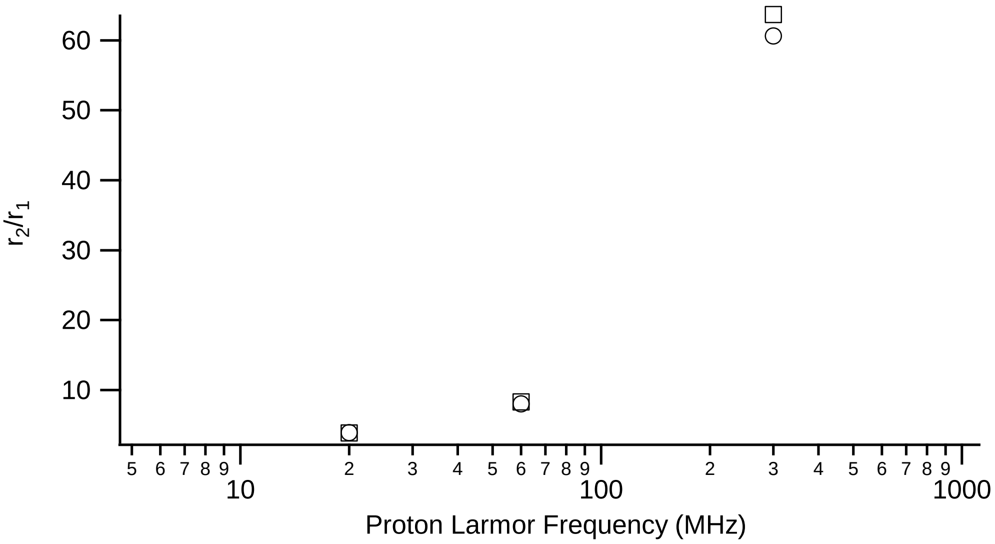
Relaxometric studies

Experimental values for the transverse relaxation and the ratio of transverse and longitudinal relaxation rate. Fe_3O_4-ReL_1 are visualized by squares whilst for Fe_3O_4-ReL_2 they are visualized by circles.

T_2-study



R_2/R_1



DLS

The samples IO-ReL$_1$ and IO-ReL$_2$ were dispersed in water at a concentration of 0.1 wt% and measured at room temperature at pH = 7.4.

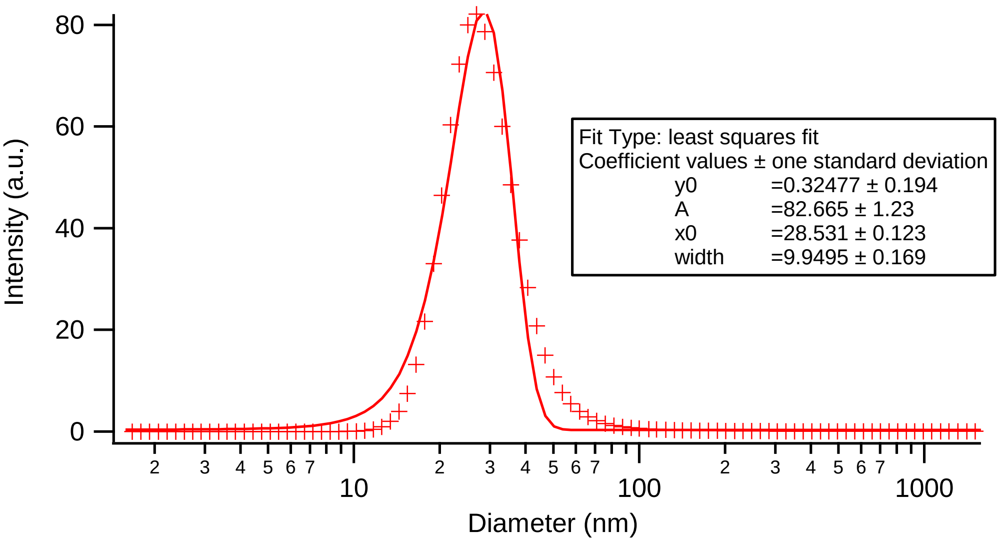


Figure 3: Hydrodynamic diameter of IO-ReL$_1$. The red crosses are the datapoints obtained by DLS measurement and the gaussfitting is visualized by a red line. The parameters acquired from the fitting are given in the textbox.

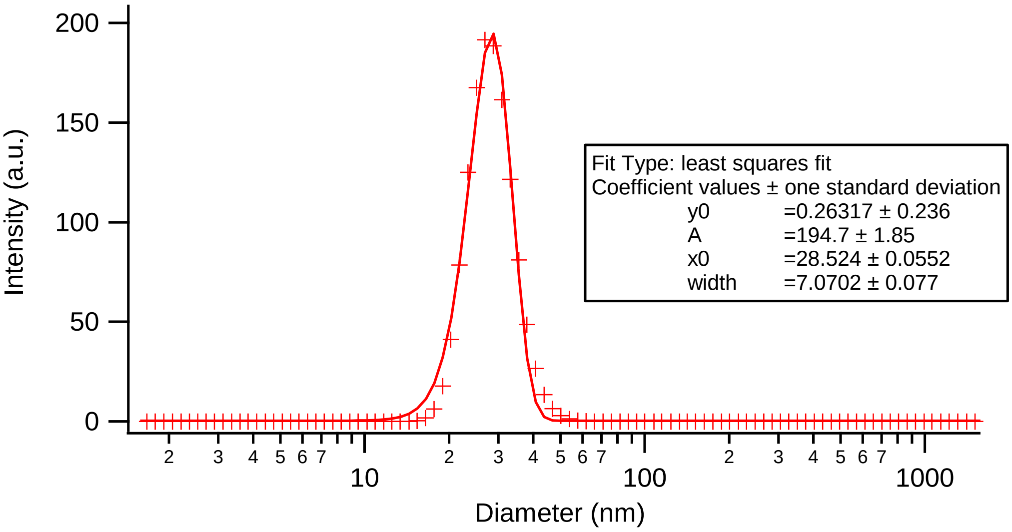


Figure 4: Hydrodynamic diameter of IO-ReL$_2$. The red crosses are the datapoints obtained by DLS measurement and the gaussfitting is visualized by a red line. The parameters acquired from the fitting are given in the textbox.