

## Up-converting $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$ nanoparticles coated by superparamagnetic $\gamma$ - $\text{Fe}_2\text{O}_3$ nanosatellites: Elaboration, characterization and *in vitro* cytotoxicity

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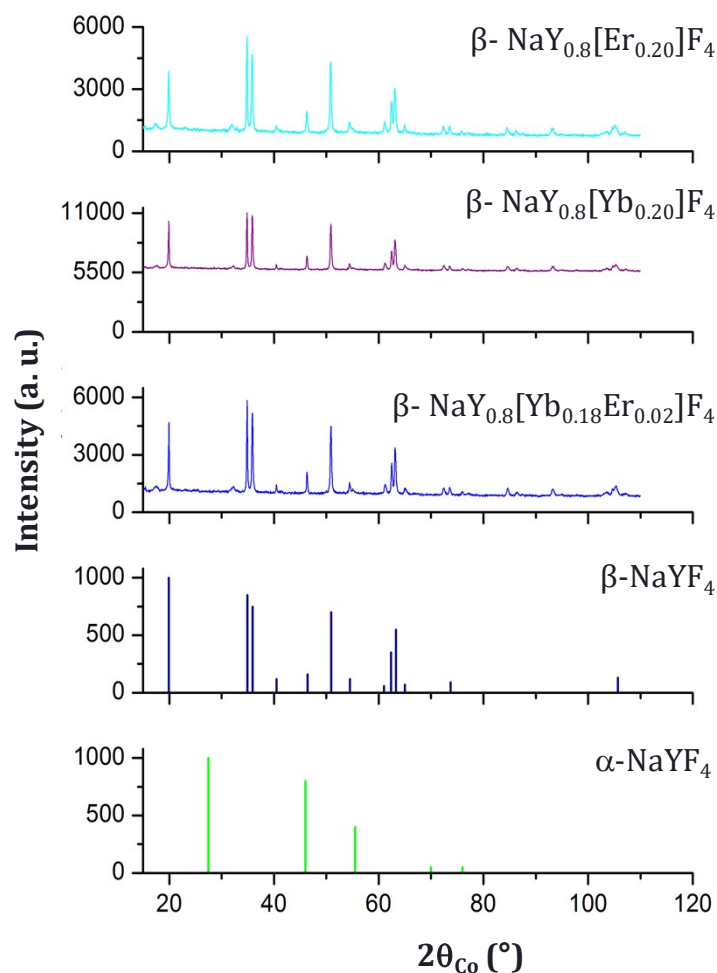
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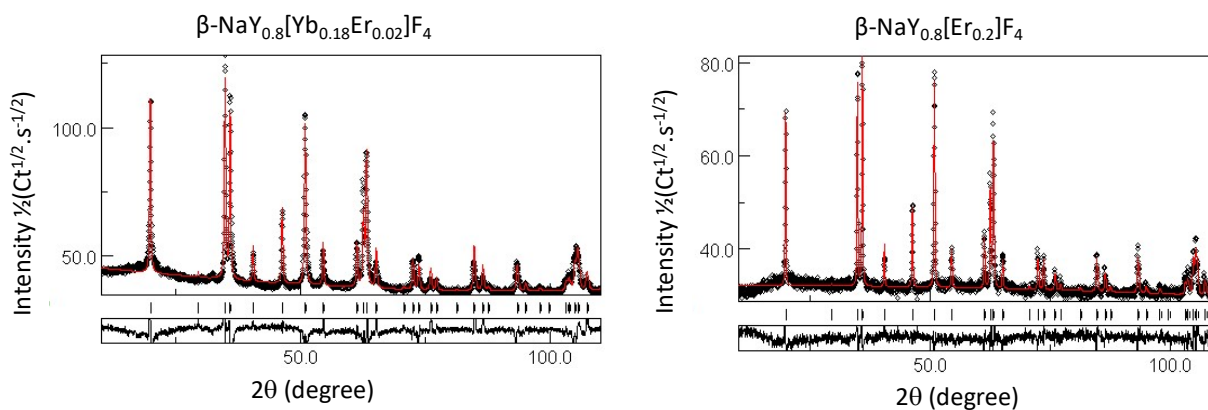
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### Supporting information



**Figure S1.** XRD patterns of the as-produced  $\beta$ - $\text{NaY}_{0.8}[\text{Er}_{0.2}]\text{F}_4$ ,  $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.2}]\text{F}_4$  and  $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  powders, recorded at room temperature and compared to those of tabulated cubic  $\alpha$ - $\text{NaYF}_4$  (ICDD n°98-006-0257) and hexagonal  $\beta$ - $\text{NaYF}_4$  (ICDD n°98-005-1916) references.



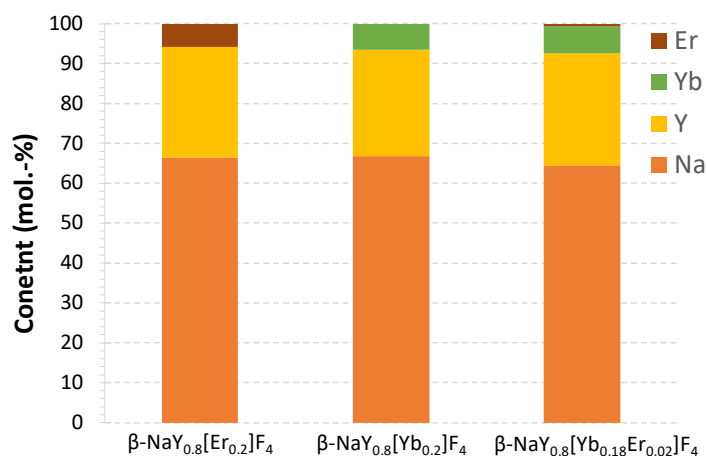
**Figure S2.**

Experimental (black scatter) and calculated (red line) XRD patterns of  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  (left) and  $\beta\text{-NaY}_{0.8}[\text{Er}_{0.2}]\text{F}_4$  (right). The residue, defined as the difference between the experimental and calculated diffractograms, is given separately, on the bottom of each graph. A pseudo-Voigt function was used for modelling the peak profile. A set of about 11 parameters was then refined, including the scale factor, the zero shift, the background polynomial coefficients, the peak profile parameters, and for the hexagonal fluoride phase, its cell parameters, average crystallographic coherence length (assuming isotropic crystals) and average lattice micro-deformation. The fitting was achieved with reliability Bragg factor  $R_B$  values close to 2.

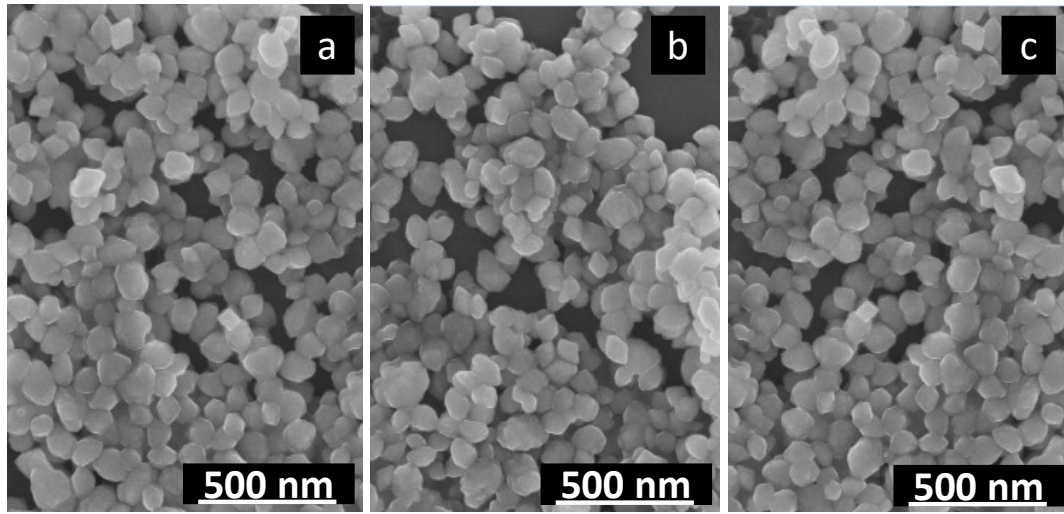
	$a / \text{\AA}^{(*)}$ $\pm 0.002$	$c / \text{\AA}^{(*)}$ $\pm 0.002$	$\langle L_{\text{XRD}} \rangle /$ nm $\pm 2$	$\langle \sqrt{\varepsilon^2} \rangle$ %
$\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$	5.970	3.511	98	<0.1
$\beta\text{-NaY}_{0.8}[\text{Yb}_{0.2}]\text{F}_4$	5.969	3.510	92	0.1
$\beta\text{-NaY}_{0.8}[\text{Er}_{0.2}]\text{F}_4$	5.975	3.513	95	<0.1

(\*) Bulk  $\beta\text{-NaYF}_4$  cell parameters  $a = 5.986 \text{ \AA}$  and  $c = 3.524 \text{ \AA}$  (ICDD n°98-005-1916)

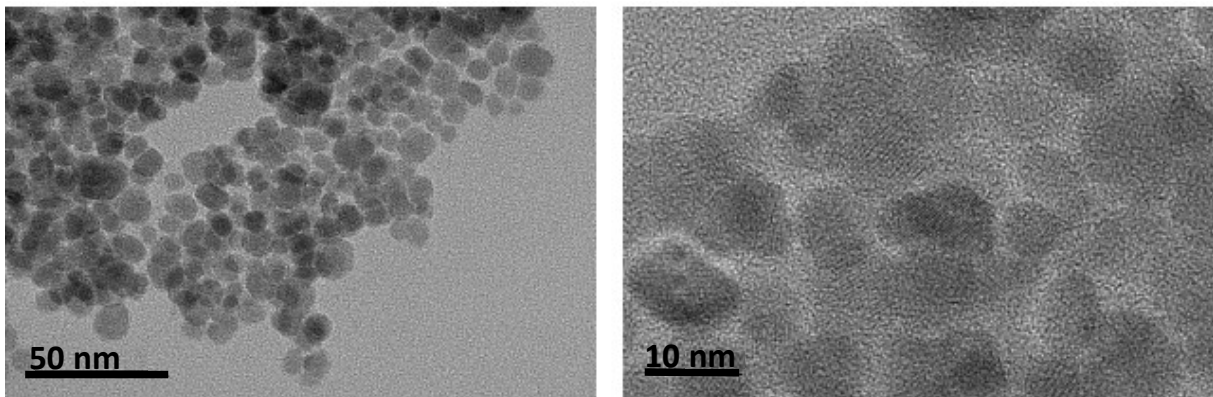
**Table S1.** Unit cell parameters, mean crystallite size  $\langle L_{\text{XRD}} \rangle$  and average lattice micro-deformation  $\langle \sqrt{\varepsilon^2} \rangle$  determined by Rietveld analysis of the XRD pattern of the as-produced  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$ ,  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.2}]\text{F}_4$  and  $\beta\text{-NaY}_{0.8}[\text{Er}_{0.2}]\text{F}_4$ .



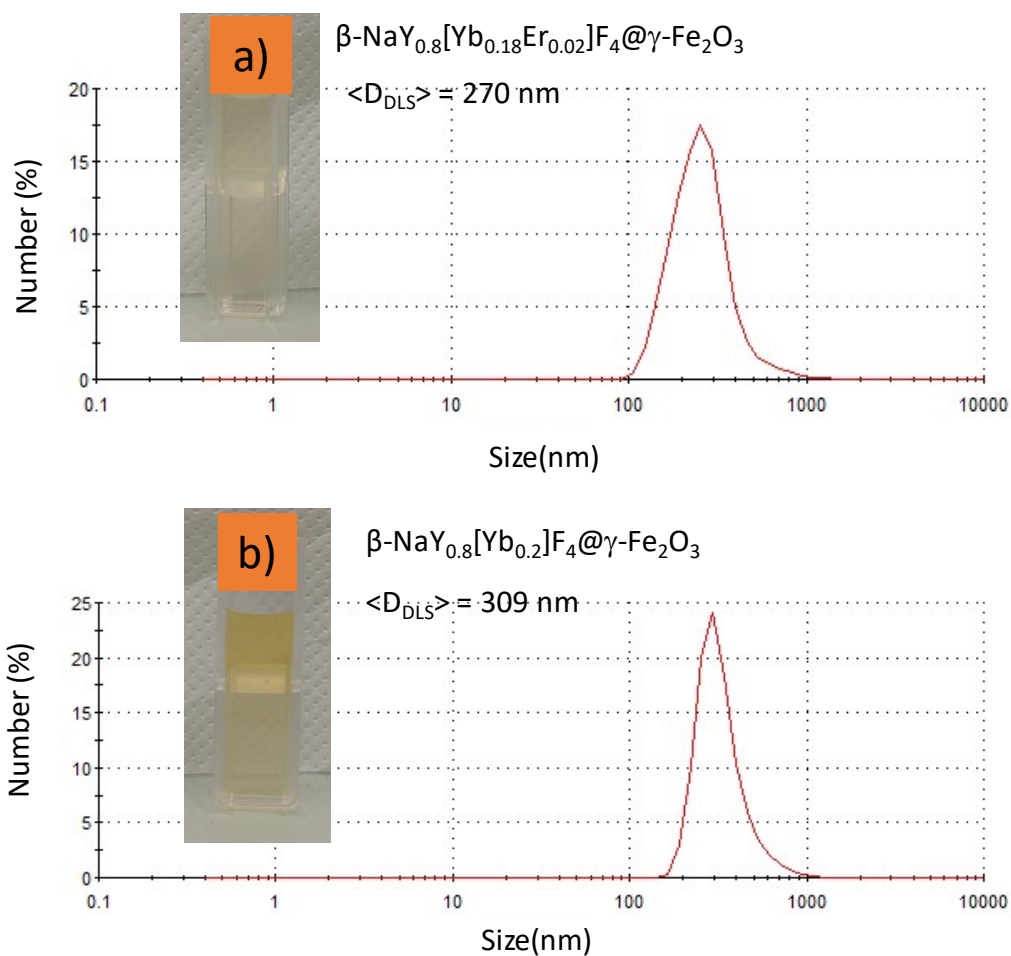
**Figure S3.** XRF chemical analysis of the as-produced  $\beta\text{-NaY}_{0.8}[\text{Er}_{0.2}]\text{F}_4$ ,  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.2}]\text{F}_4$  and  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  powders.



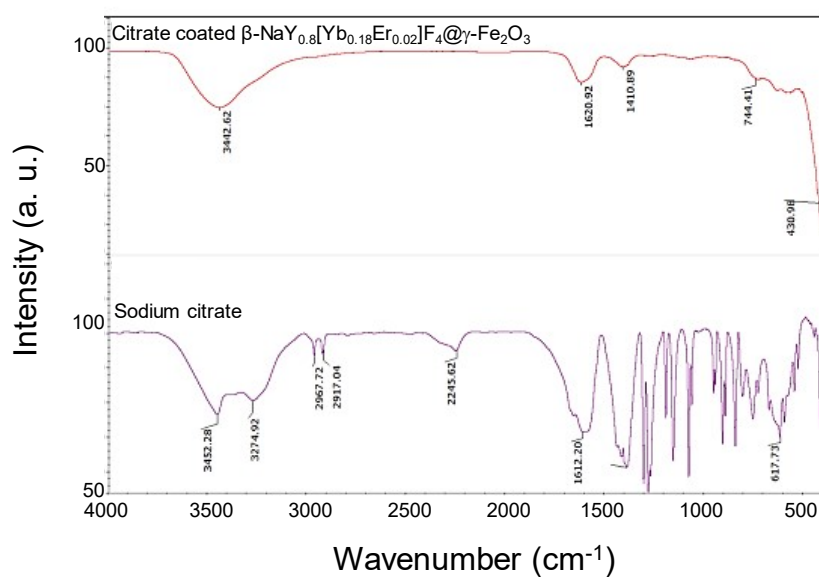
**Figure S4.** SEM Images recorded on the as-produced (a)  $\beta$ - $\text{NaY}_{0.8}[\text{Er}_{0.2}\text{F}_4]$ , (b)  $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.2}\text{F}_4]$  and (c)  $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}\text{F}_4]$  powders.



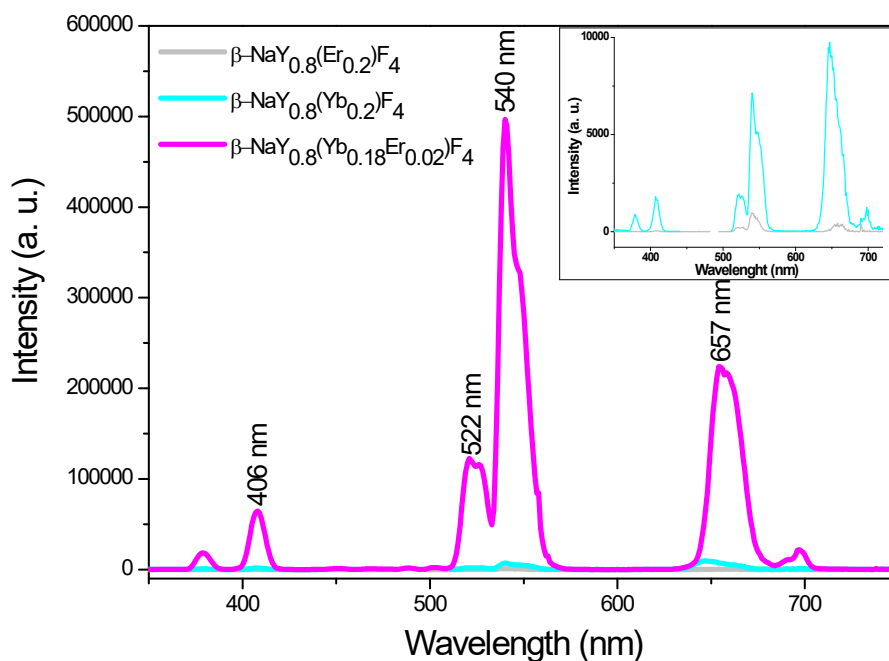
**Figure S5.** TEM Images, recorded at different magnifications, of an assembly of iron oxide nanoparticles prepared separately.



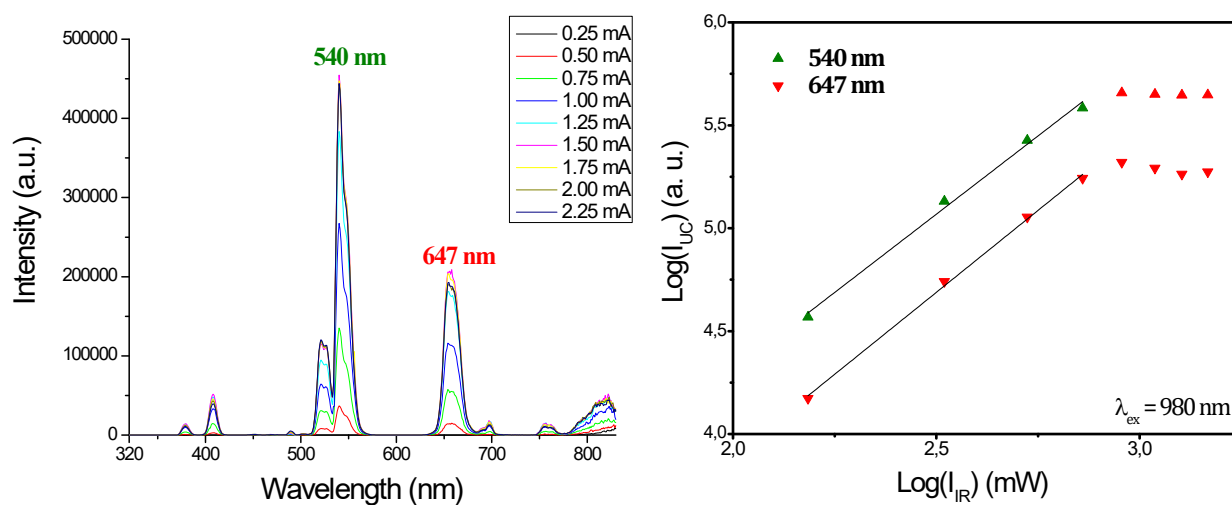
**Figure S6.** Hydrodynamic size distribution measured by DLS on the citrate treated (a)  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4@\gamma\text{-Fe}_2\text{O}_3$  and (b)  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.2}]\text{F}_4@\gamma\text{-Fe}_2\text{O}_3$  (lower graph) composite particles dispersed in milli-Q water. Numerical images of their aqueous colloids is given in the inset.



**Figure S7.** FTIR spectrum of citrate treated  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4@\gamma\text{-Fe}_2\text{O}_3$  composite particles compared to that of sodium citrate salt.



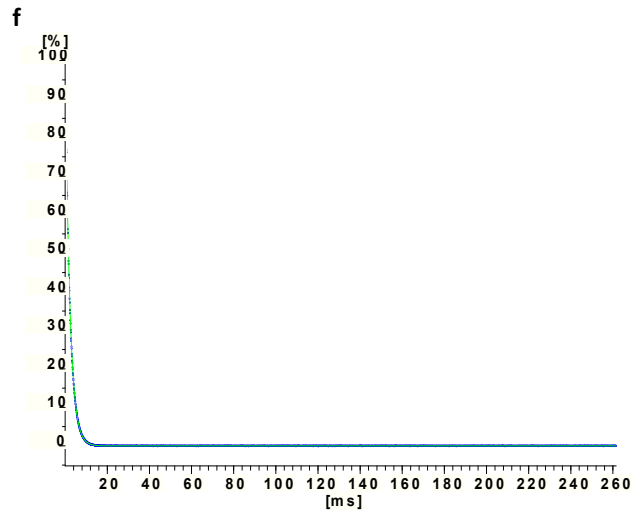
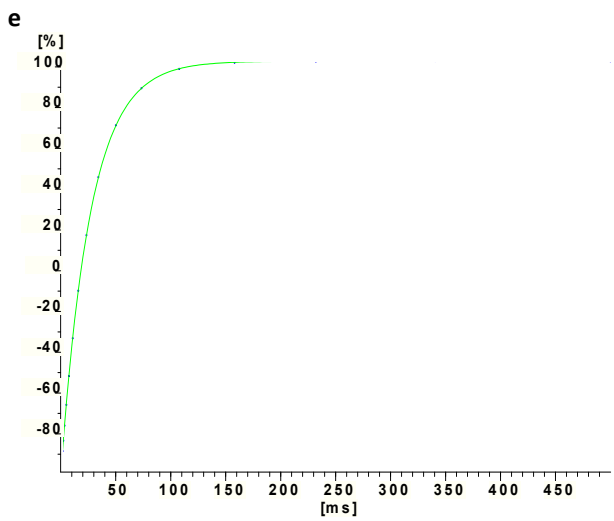
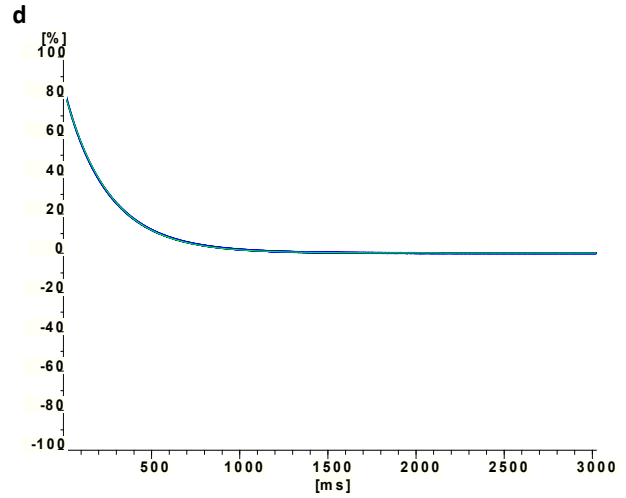
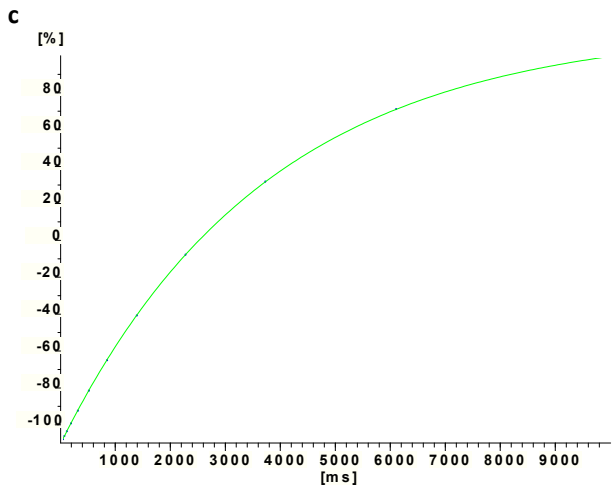
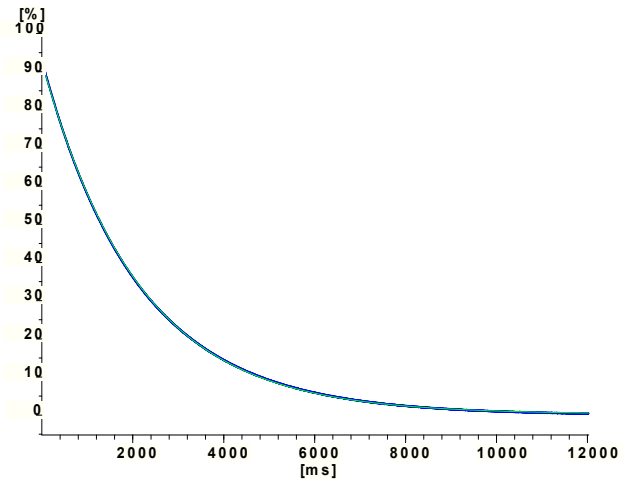
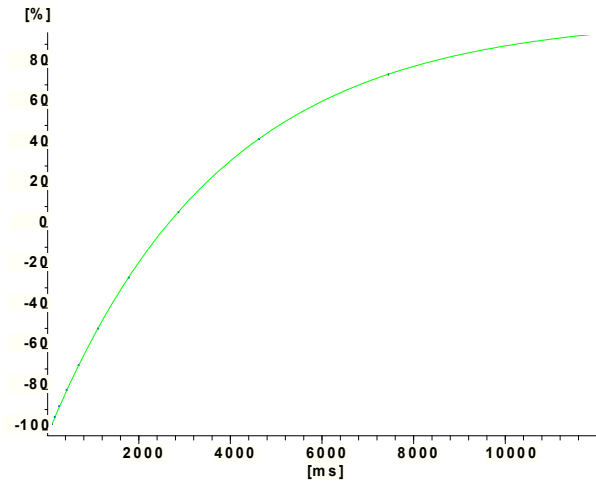
**Figure S8.** Emission spectra of  $\beta\text{-NaY}_{0.8}[\text{Er}_{0.2}]\text{F}_4$  (grey line),  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.2}]\text{F}_4$  (cyan line) and  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  (magenta line) aqueous colloidal dispersion in water milli-Q ( $1 \mu\text{g}\cdot\text{mL}^{-1}$ ) recorded at r.t. under a laser irradiation of 980 nm at the day of preparation. A zoom of the spectra with the lowest intensity is given in the inset to highlight their fine structure.

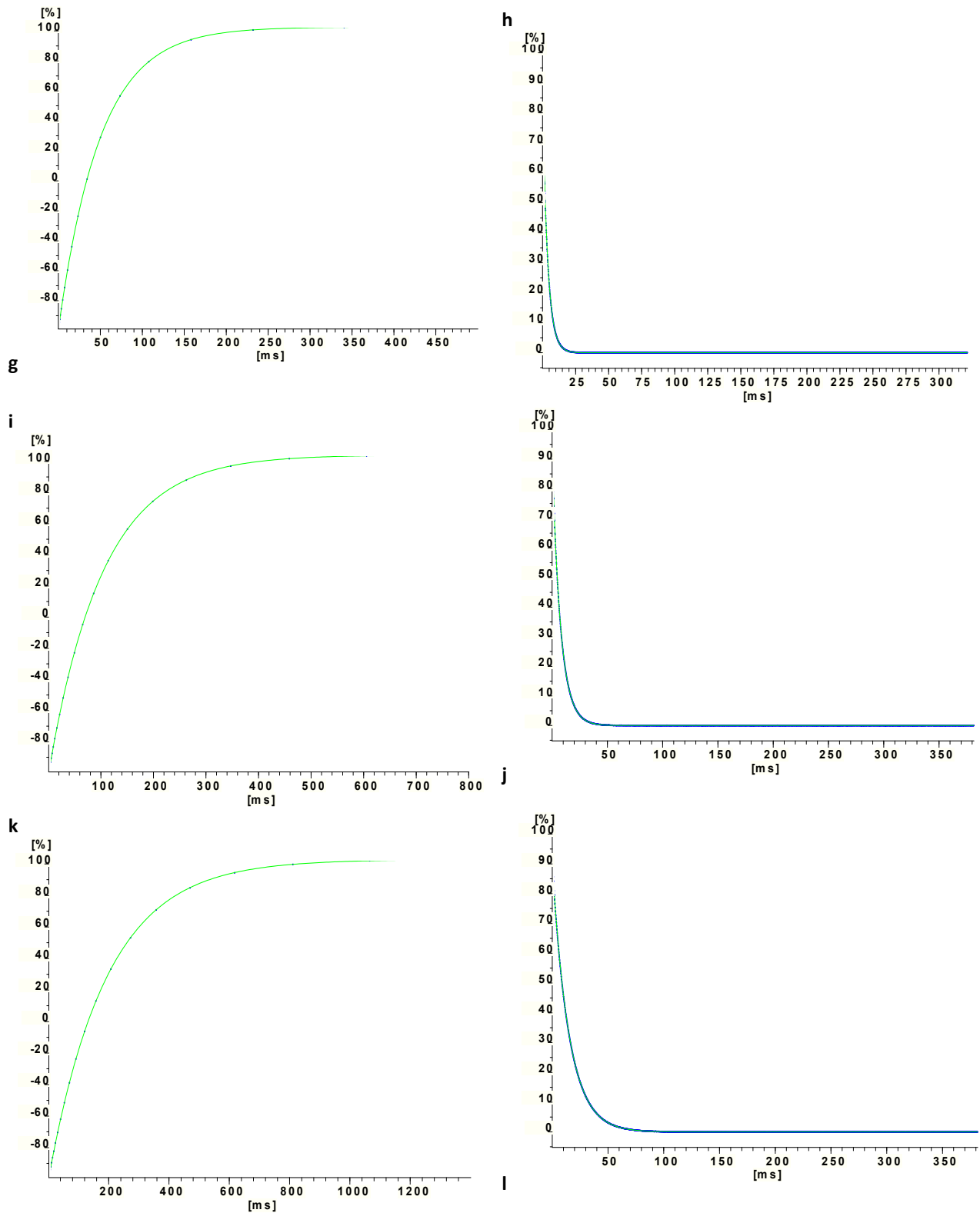


**Figure S9.** Emission spectra of  $\beta\text{-NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  aqueous colloidal dispersion in water milli-Q ( $1 \mu\text{g}\cdot\text{mL}^{-1}$ ) recorded at r.t. under a laser irradiation of 980 nm and various powers, the day of preparation. The emission intensity reached a maximum for a current laser alimentation of 1.00 mA. This value was chosen for the rest of the optical properties investigations.

a

b





**Figure S10.** Examples of proton relaxation curves of respectively longitudinal (a, c, e, g, i, k) and transverse (b, d, f, h, j, l) nuclear magnetization, measured respectively by an inversion-recovery (IR) or a Carr-Purcell-Meiboom-Gill (CPMG) sequence on a Minispec mq60 relaxometer at different total magnetic metal concentrations: a, b) pure water ( $T_1=3740\pm 10$  ms,  $T_2=2126.8\pm 0.6$  ms) ; c, d)  $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  at  $[\text{Er}]=25 \mu\text{M}$  ( $T_1=3549\pm 10$  ms,  $T_2=248\pm 0.1$  ms); e, f)  $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  at  $[\text{Er}]+[\text{Fe}]=2.36 \text{ mM}$  ( $T_1=27.22\pm 0.02$  ms,  $T_2=2.215\pm 0.001$  ms); g, h)  $\beta$ - $\text{NaY}_{0.8}[\text{Yb}_{0.18}\text{Er}_{0.02}]\text{F}_4$  at  $[\text{Er}]+[\text{Fe}]=1.18 \text{ mM}$  ( $T_1=49.68\pm 0.02$  ms,  $T_2=3.834\pm 0.002$  ms); i, j)  $\beta$ -

NaY<sub>0.8</sub>[Yb<sub>0.18</sub>Er<sub>0.02</sub>]F<sub>4</sub>@ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at [Er]+[Fe]= 0.59 mM (T<sub>1</sub>=103.07±0.03 ms, T<sub>2</sub>=7.855±0.002 ms); k, l)  $\beta$ -NaY<sub>0.8</sub>[Yb<sub>0.18</sub>Er<sub>0.02</sub>]F<sub>4</sub>@ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at [Er]+[Fe]= 0.295 mM (T<sub>1</sub>=193.1±0.2 ms, T<sub>2</sub>=14.867±0.003 ms).