Electronic Supplementary Information: Synthesis, characterization, and evaluation of PEGylated first-row transition metal ferrite nanoparticles as T_2 contrast agents for high-field MRI

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Sample	MX_2	Amount (mmoles)
$CoFe_2O_4$	$Co(acac)_2$	0.67
Fe_3O_4	$Fe(acac)_3$	2.0[a]
$MnFe_2O_4$	$Mn(acac)_2$	0.67
$NiFe_2O_4$	$Ni(acac)_2$	0.67
$ZnFe_2O_4$	$Zn(acac)_2$	0.67
$CuFe_2O_4$	$CuCl_2.2H_2O$	0.67[b]

[a] $Fe(acac)_3$ serves as a source of both Fe(II) and Fe(III).

[b] See discussion in the main paper and references therein.

Table S1 Source of the divalent cation in the synthesis of PEGylated MFe_2O_4 NPs

Sample	M_s, 1.9 K (emu g^{-1})	M_s, 300 K (emu g^{-1})	T_B (K)	r_1 (mM^{-1} s^{-1})	r_2 (mM^{-1} s^{-1})	r_2/r_1
$CoFe_2O_4$	52.8	33.7	280	0.45±0.04	99±14	219
Fe_3O_4	42.8	33.4	150	0.80±0.07	75±12	94
$MnFe_2O_4$	59.9	35.9	47	0.69±0.02	118±20	171
$NiFe_2O_4$	38.1	32.3	150	0.78±0.01	36±4	46
$ZnFe_2O_4$	35.4	19.1	32	0.60±0.02	49±5	82
$CuFe_2O_4$	30.7	23.2	400	1.21±0.16	34±2	28

Table S2 Summary of magnetometric and relaxometric measurements on PEGylated MFe_2O_4 NPs

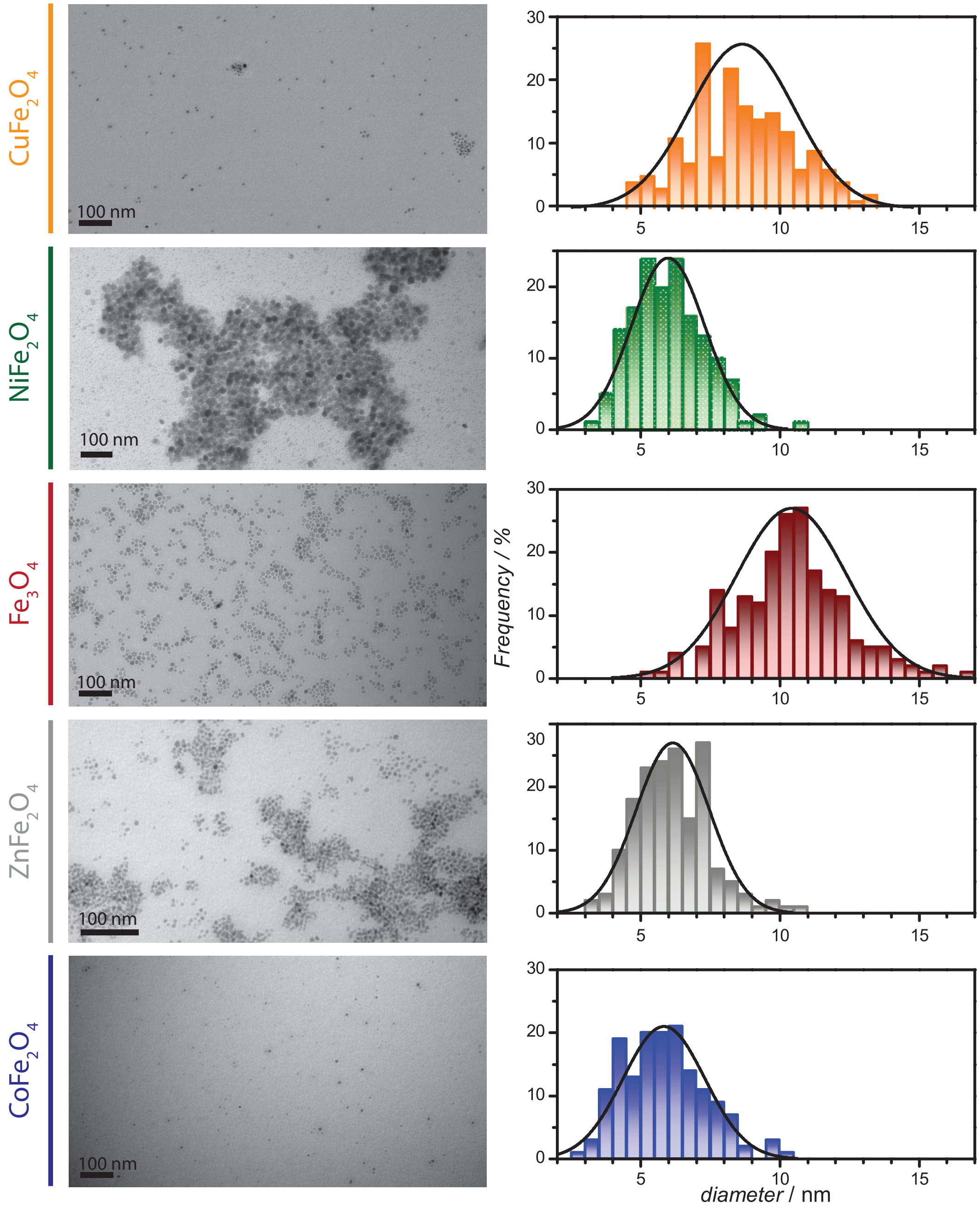

Fig. S1 Transmission electron micrographs of PEGylated MFe$_2$O$_4$ NPs and derived size distributions.

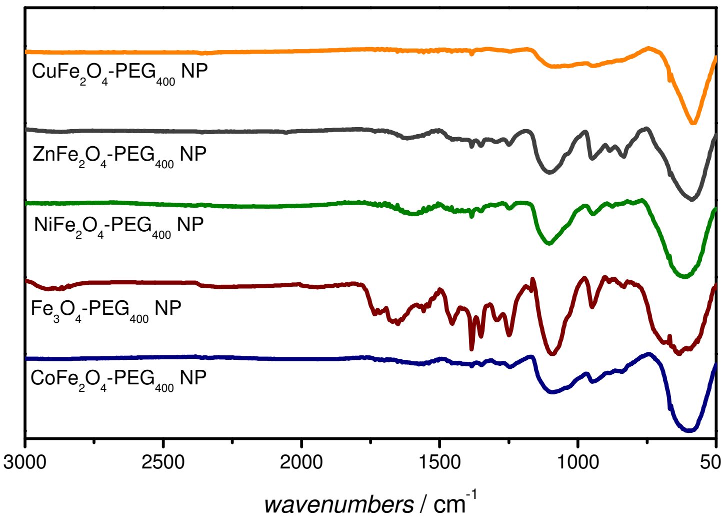

Fig. S2 Fourier Transform Infrared Spectra for MFe$_2$O$_4$-PEG$_{400}$ NPs (M= Co, Ni, Cu, Zn, Fe).

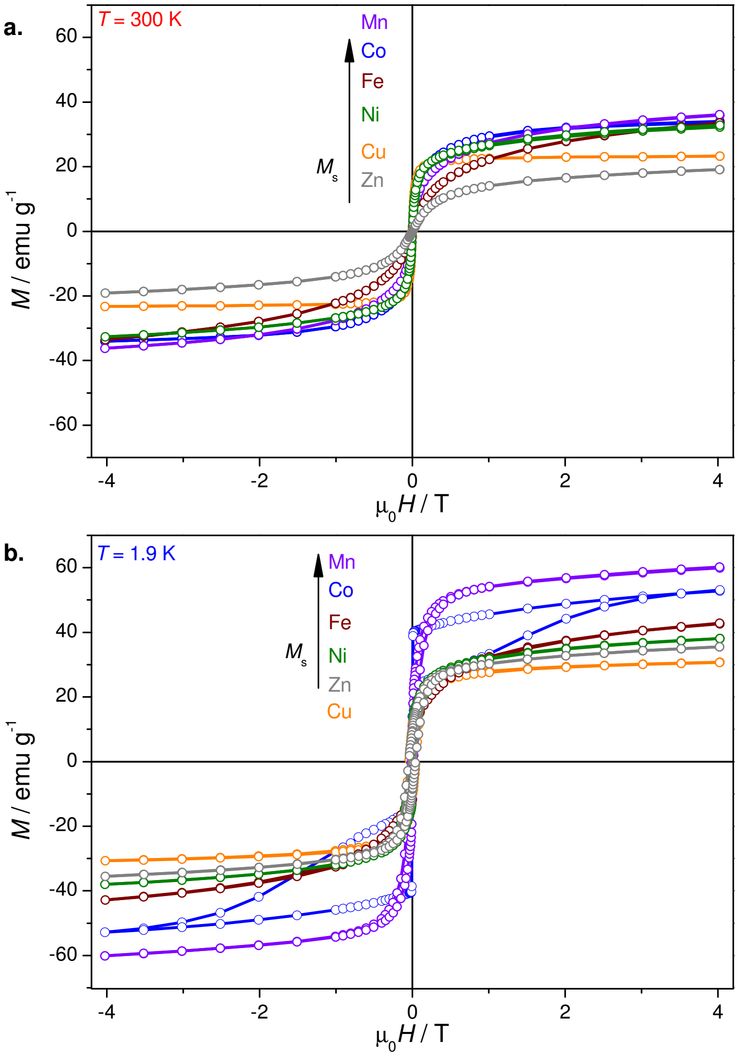

Fig. S3 Measured magnetization versus field strength curves for all powdered samples at (a) 300 K and (b) 1.9 K.

The T_B of our $NiFe_2O_4$ NPs was found to be $\sim$ 150 K. The M_s of 32.3 emu g^{-1} recorded for our $NiFe_2O_4$ NPs was smaller than the reported value of $\sim$ 55 emu g^{-1} for bulk $NiFe_2O_4$.[45] This M_s value also fell in the range (25.7 to 40 emu g^{-1}) reported by Menelaou *et al.* in their report on oleylamine-coated 9-11.7 nm $NiFe_2O_4$ NPs.[64]

The 6 nm $ZnFe_2O_4$ NPs showed M_s values of 35.4 emu g^{-1} and 19.1 emu g^{-1} at 1.9 and 300 K, respectively. The T_B for these NPs was found to be $\sim$ 33 K, which is very close to the value reported by Chen and co-workers for sub-10 nm $ZnFe_2O_4$ NPs.[68]

The magnetite NPs show a blocking temperature T_B of approx. 120 K, and a saturation magnetization M_s of 33.4 emu g^{-1} at 300 K, and 42.8 emu g^{-1} at 1.9 K, under a 4-T field. As noted in several reports on the magnetic properties of ferrite NPs, this low M_s value (*c.f.* the M_s of bulk Fe_3O_4 is $\sim$ 92 emu g^{-1}) is again consistent with the presence of a magnetically disordered (*i.e.* non-magnetic) iron oxide surface layer. We had noted in a previous communication[30] that lower synthesis temperatures lead to poor crystallinity and lowered magnetization of Fe_3O_4 NPs. More magnetic Fe_3O_4 NPs were indeed formed here at higher reaction temperatures.

The $CuFe_2O_4$-PEG_{400} NPs showed M_s values of 30.7 emu g^{-1} and 23.2 emu g^{-1} at 1.9 and 300 K; these are in accordance with values reported in the literature.[69]

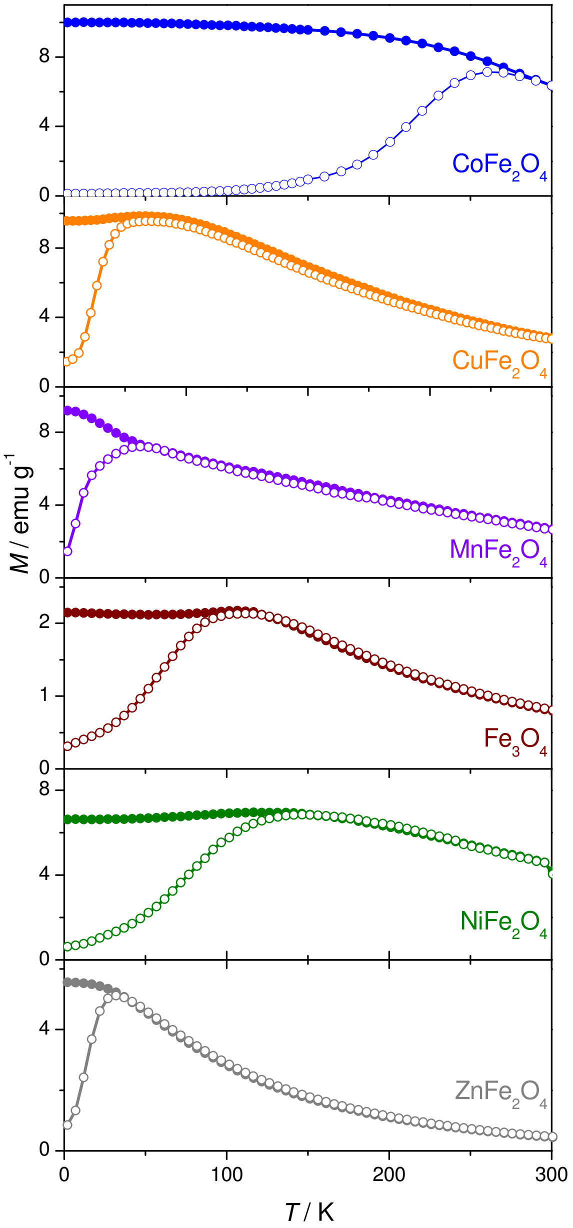

Fig. S4 FC-ZFC curves for MFe_2O_4-PEG_{400} NPs (M= Co, Ni, Cu, Zn, Fe).

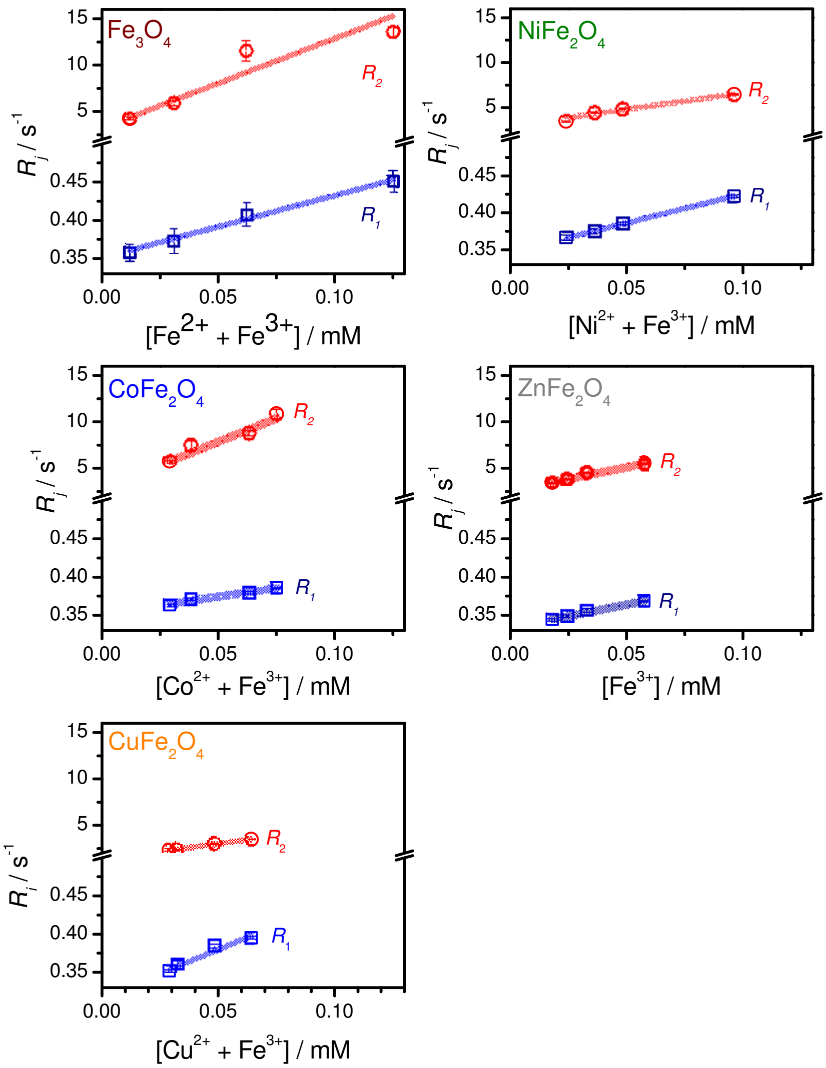

Fig. S5 Relaxometric plots for MFe_2O_4-PEG_{400} NPs (M= Co, Ni, Cu, Zn, Fe) at 9.4 T.

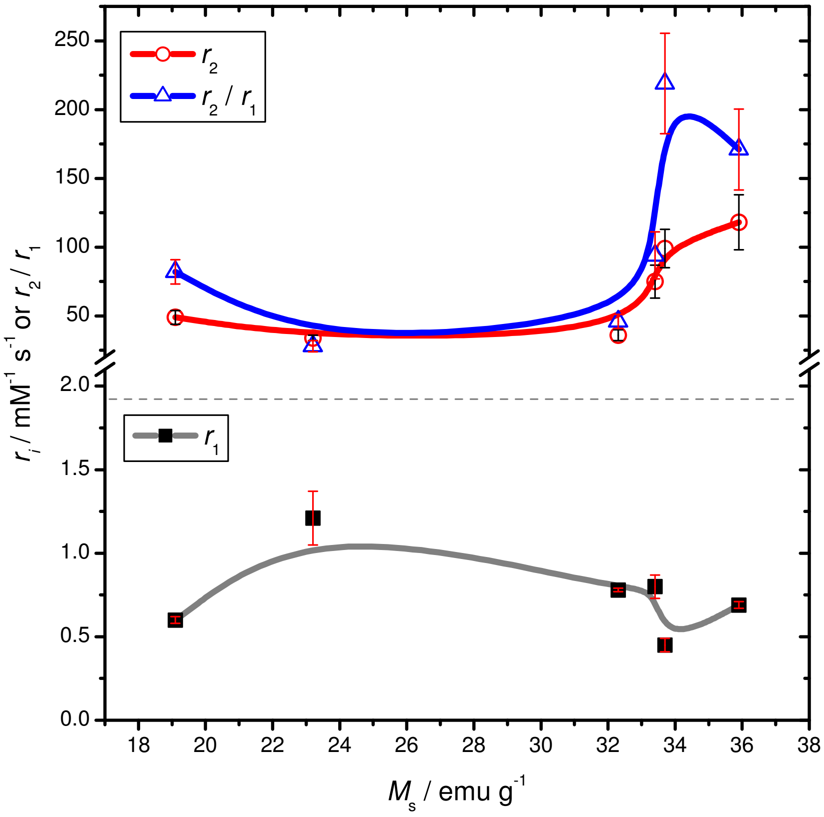

Fig. S6 Relaxivities and r_2 / r_1 as a function of saturation magnetisation. Lines are guides to the eyes.

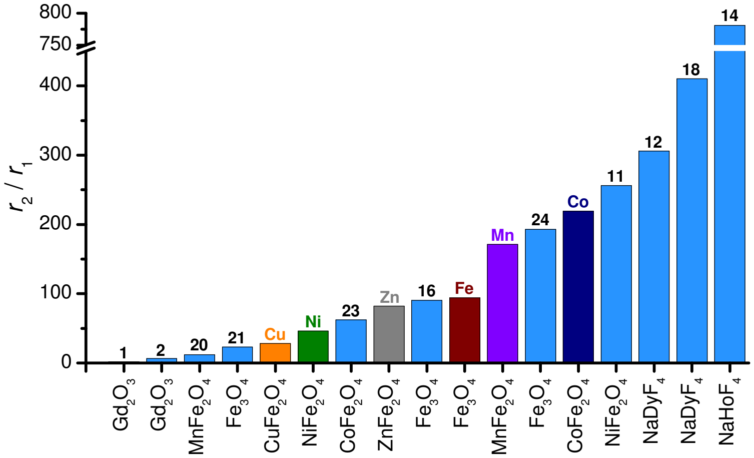

Fig. S7 Comparison of r_2 / r_1 values for various high-field NP contrast agents. Labels refer to Table 2.