

Supporting Information

Structure and dynamics of the hydration shells of citrate-coated GdF₃ nanoparticles

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1. Materials

Synthesis of GdF₃ NPs:

0.13 g of NaF (3 mmol) were added to a solution of citric acid (0.41 g, 2.13 mmol) in 25 mL of water, neutralized with NH₄OH (aq) and the final solution was heated at 348 K. A solution of GdCl₃·6H₂O (0.49 g, 1.33 mmol) in 2 mL of water was added dropwise to the previous solution and stirred at 348 K for 3h. Few mL of ethanol were added to the solution in order to promote the precipitation of GdF₃-citrate nanoparticles (named Gd-NPs). The particles were then isolated by centrifugation, washed and suspended in water. GdF₃ NPs prepared with low citrate loading (0.041 g, 0.213 mmol, named Gd-NPs-LL) was also prepared following the same synthetic conditions.

2. Characterization

- X-ray diffraction (XRD) patterns were obtained on a ARL XTRA48 diffractometer using Cu K α radiation ($\lambda = 1.54062 \text{ \AA}$).
- HRTEM images were collected on a JEOL 3010 High Resolution Transmission Electron Microscope operating at 300 kV. Specimens were prepared by dispersing the sample by sonication in water and by depositing few drops of the suspension on carbon-coated grids.
- Energy dispersive X-ray spectroscopy (EDS) coupled to LEO 1450 VP scanning electron microscope was used to provide rapid semiquantitative elemental analyses on the samples surface.
- Infrared spectra were collected under vacuum conditions at 298 K in the range 4000 - 400 cm⁻¹ and with a resolution of 4 cm⁻¹ resolution by using a Bruker Equinox 55 spectrometer. Prior to the analysis, the sample was dispersed in KBr matrix (10 wt%).
- Thermogravimetric analyses (TGA/DTG) of materials were performed under oxygen flow (20 ml/min) with a SETSYS Evolution TGA-DTA/DSC thermobalance, heating from 50°C to 800°C at 10°C/min.
- Dynamic Light Scattering experiments were carried out on the particles suspension in water medium by using a Zetasizer NanoZS, Malvern, UK, operating in a particle size range from 0.6 nm to 6 μm and equipped by a laser He-Ne with $\lambda = 633 \text{ nm}$.
- The water proton longitudinal relaxation rates of diluted aqueous suspensions of GdF₃ NPs were measured by using a Stelar Spinmaster spectrometer operating 20 and 70 MHz at 310 K. The standard inversion-recovery method was employed (16 experiments, 2 scans) with a typical 90° pulse width of 3.5 ms, and the reproducibility of the T_1 data was $\pm 0.5\%$. The temperature was controlled with a Stelar VTC-91 airflow heater equipped with a copper-

constantan thermocouple (uncertainty of ± 0.1 °C). The proton $1/T_1$ NMRD profiles were measured on a fast field-cycling Stellar SmarTracer relaxometer over a continuum of magnetic field strengths from 0.00024 to 0.25 T (corresponding to 0.01-10 MHz proton Larmor frequencies). The relaxometer operates under computer control with an absolute uncertainty in $1/T_1$ of $\pm 1\%$. Additional data points in the range 15-70 MHz and at 400 and 500 MHz were obtained using a conventional spectrometer using WP 80 magnet interfaced with a STELAR console and Bruker NMR spectrometers, respectively.

Variable-temperature ^{17}O NMR measurements were recorded on a Bruker Avance III spectrometer (11.74 T, 67.8 MHz for ^{17}O) equipped with a 5 mm probe and standard temperature control units. Aqueous solutions of the particles containing 1.0% of the ^{17}O isotope (Cambridge Isotope) were used. The observed transverse relaxation rates were calculated from the signal width at half-height.

Gadolinium concentration was determined by a Spectro Genesis ICP-OES spectrometer (Spectro Analytical Instruments, Kleve, Germany) equipped with a crossflow nebulizer. Plasma was generated by argon and the power was of 1400 W. The flow conditions were: coolant flow = 12.00 L/min, auxiliary flow = 0.60 L/min and nebulizer flow = 1.00 L/min. Data were shown as mean of three measurement for every sample, introduced in the nebulizer by a peristaltic pump. Prior to the analysis, GdF_3 nanoparticles were mineralized in nitric acid solution (65%), at high temperatures (over 100°C) for 72 h. To check the occurrence of a complete digestion following this protocol, the Gd-NPs were also mineralized by treatment with a mixture of 5 mL of HNO_3 and 2 mL of HF. Finally, the exact Gadolinium concentration in Gd-NPs samples was also estimated by measurement of bulk magnetic susceptibility shifts of a *t*BuOH signal on a Bruker Avance III spectrometer (11.7 T). (D.M. Corsi, C. Platas-Iglesias, H. van Bekkum and J.A. Peters, *Magn. Reson. Chem.*, **2011**, *39*, 723; M. Norek et al. *J. Phys. Chem. C*, **2007**, *111*, 10240). In all the three procedures, quite similar results were obtained.

- The Gd amount both in the nanoparticles and exposed on the surface were calculated by adopting a method reported in the literature (N.J.J. Johnson, W. Oakden, G.J. Stanisiz, R.S. Prosser, and F.C.J.M. van Veggel, *Chem. Mater.*, 2011, *23*, 3714–3722).

3. Figures and Tables

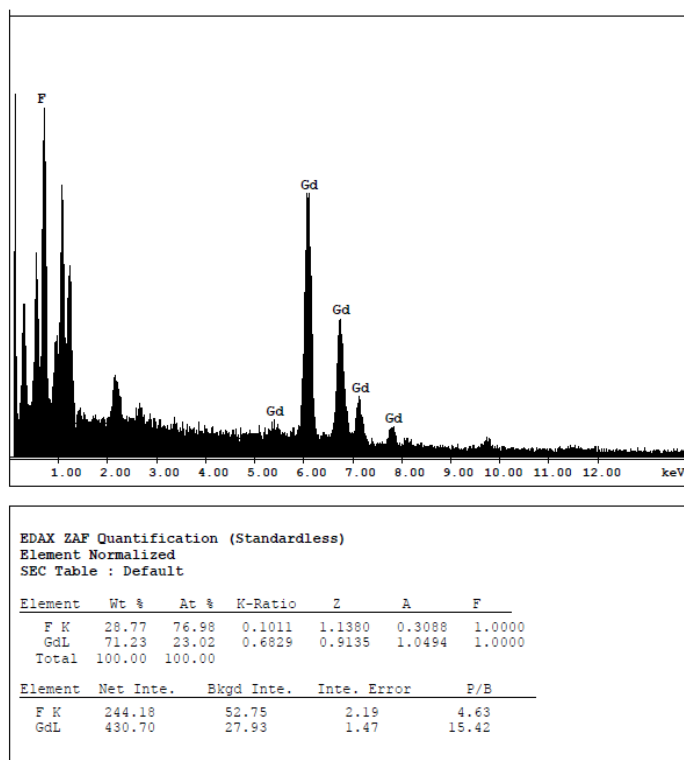


Figure S1. EDX analysis of Gd-NPs.

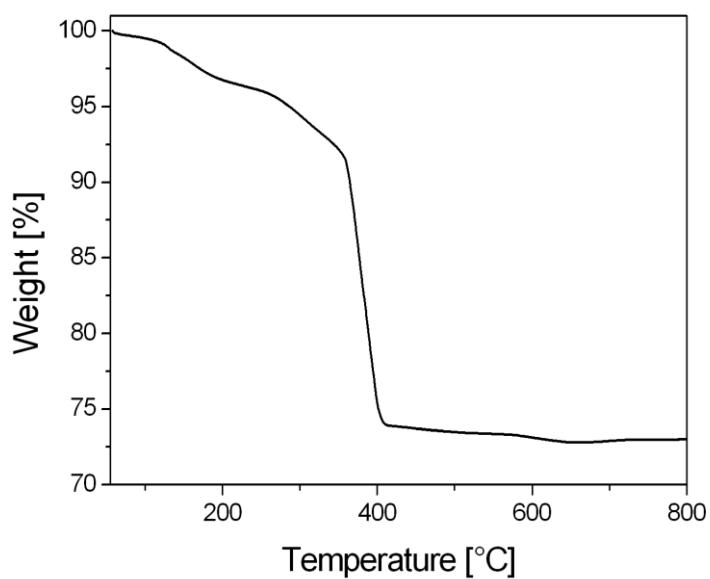


Figure S2. TGA profile collected under O₂ flow of Gd-NPs.

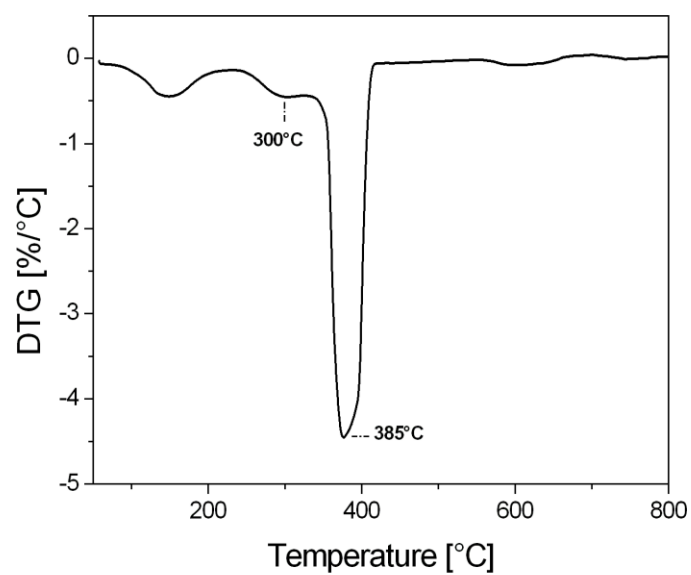


Figure S3. Derivative thermogravimetric profile collected under O₂ flow of Gd-NPs.

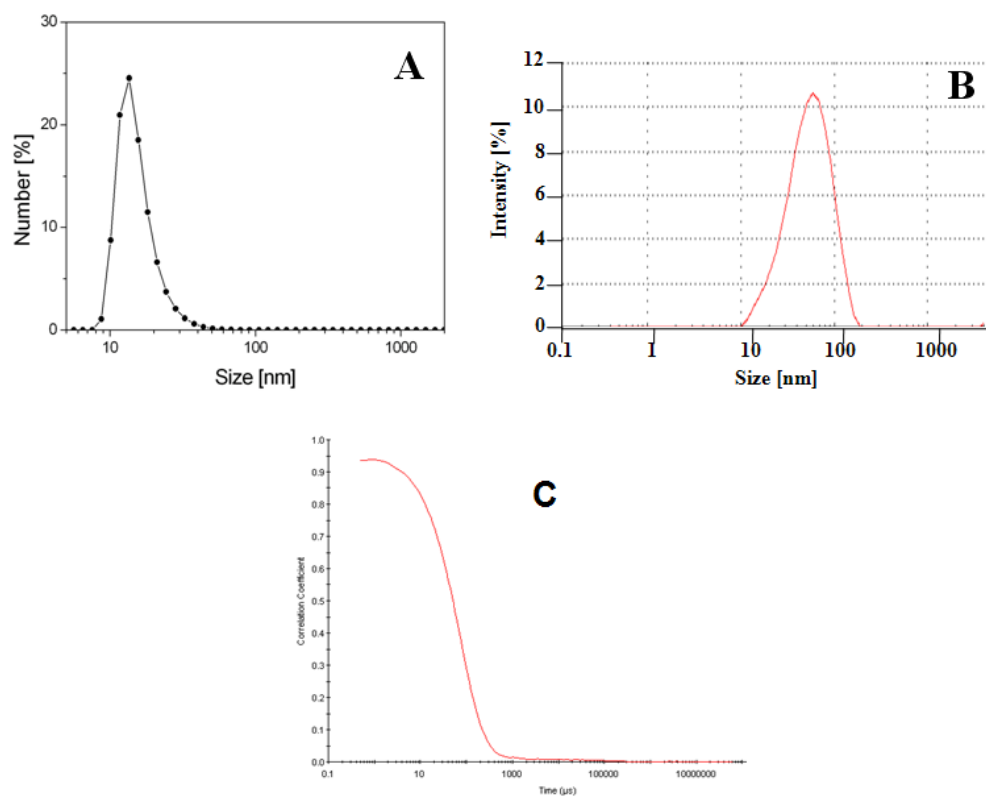


Figure S4. Number (A) and Intensity-weighted (B) DLS distributions for Gd-NPs in water. DLS correlogram is reported in C.

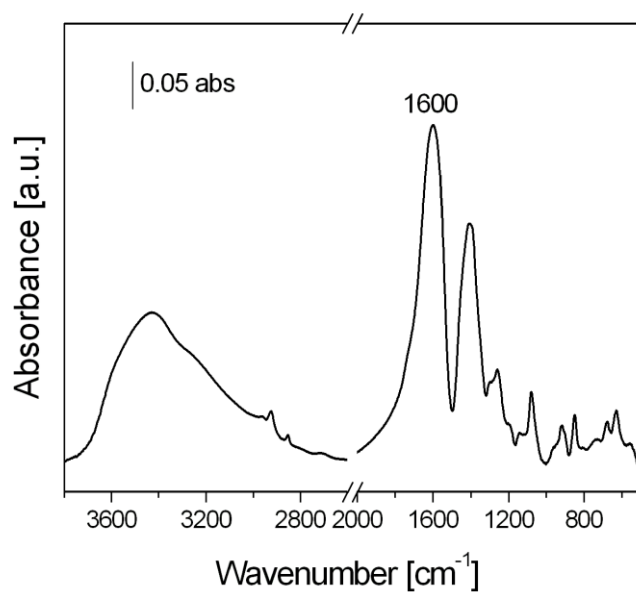


Figure S5. FT-IR spectrum of Gd-NPs sample diluted in KBr matrix.

Table S1. ζ -potential as a function of pH for Gd-NPs samples.

pH	ζ -potential (mV)
3.0	+25.0
5.0	+5.0
7.0	-30.0
8.0	-36.7
10.0	-35.0

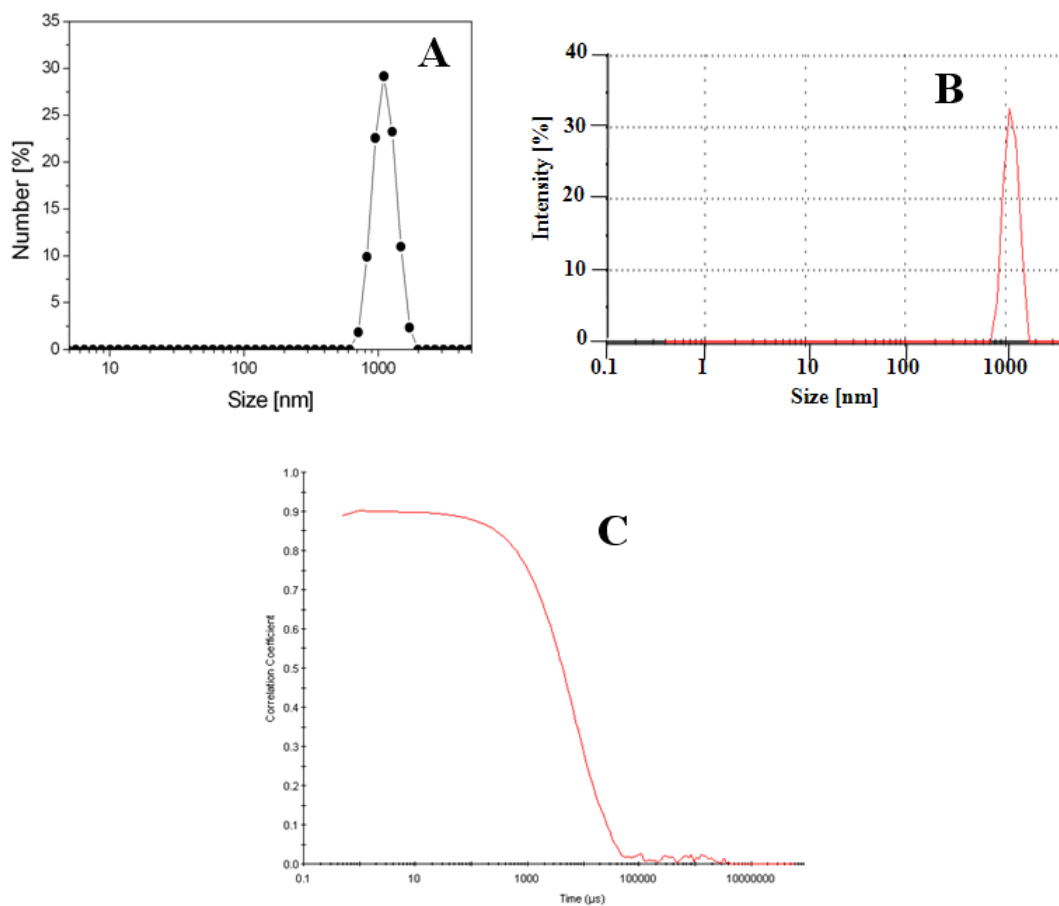


Figure S6. Number (A) and Intensity-weighted (B) DLS distributions for Gd-NPs-LL decorated with low citrate loading. DLS correlogram is reported in C.

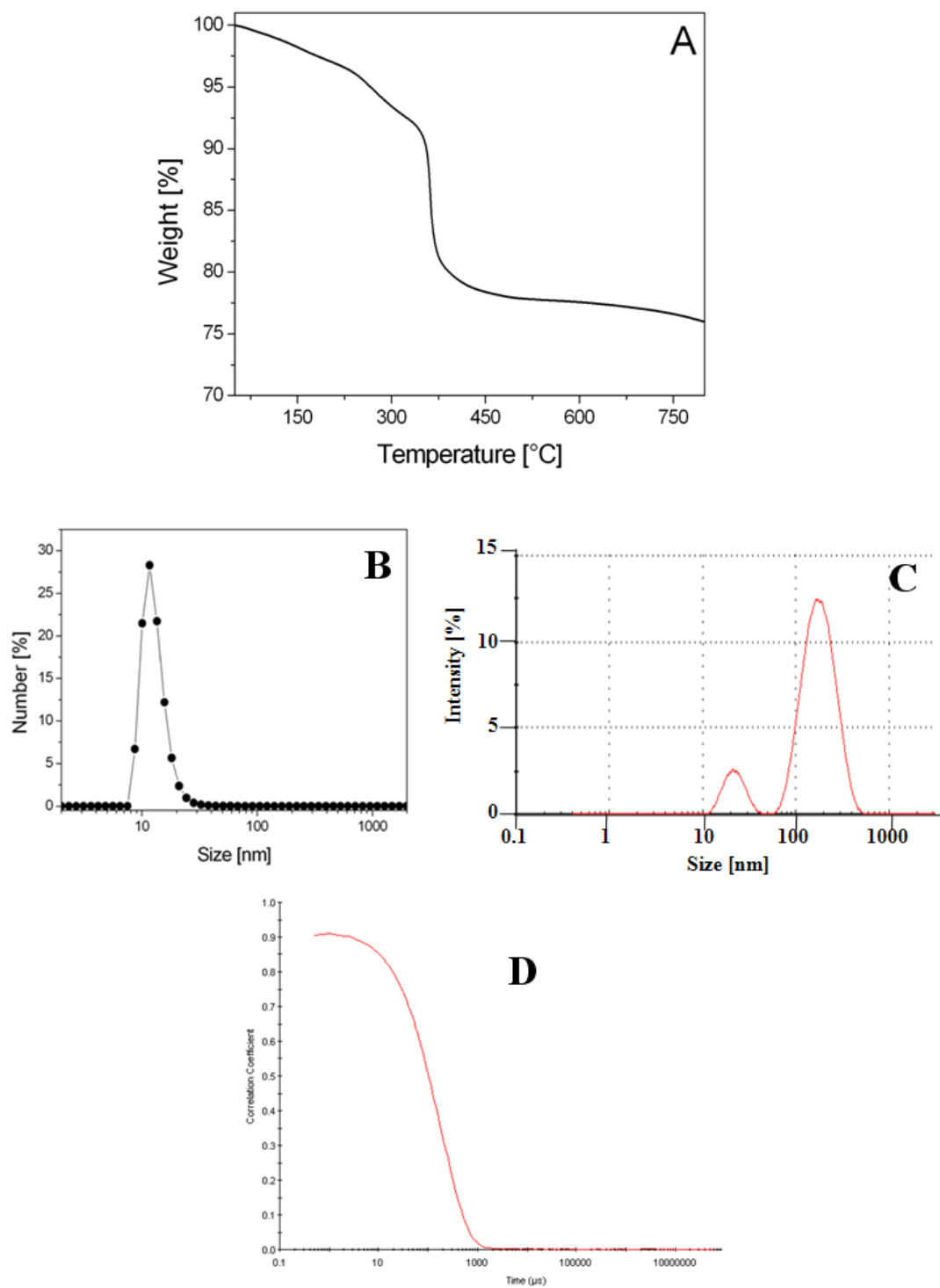


Figure S7. A) TGA profile collected under O₂ flow; Number (B) and Intensity-weighted (C) DLS distributions for Gd-NPs nanoparticles prepared with 0.43 mmol of citrate. DLS correlogram is reported in D.

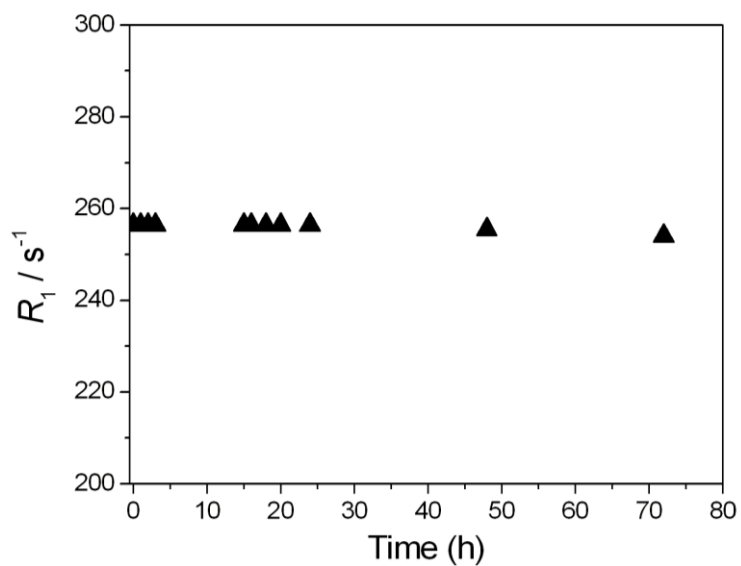


Figure S8. R_1 values of a Gd-NPs suspension in Seronorm™ at 20 MHz and 298 K as a function of time

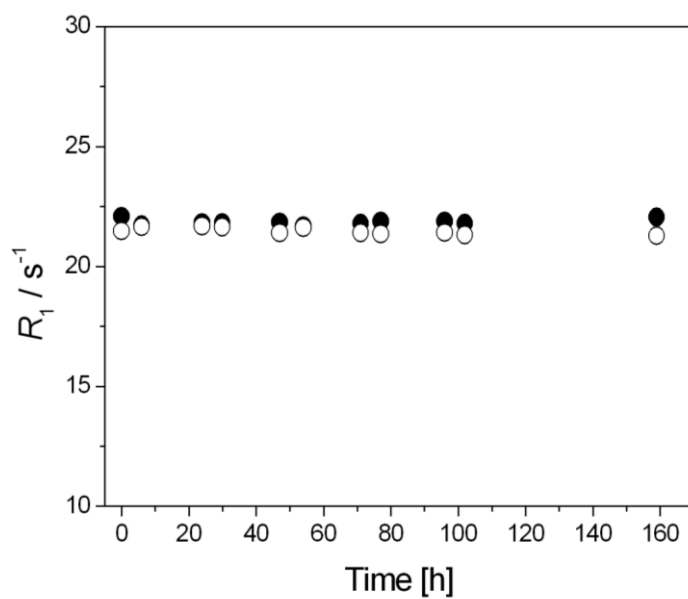


Figure S9. R_1 values for Gd-NPs suspension in the absence (●) and in the presence (○) of an excess of citrate (~ +30%) at 20 MHz and 298 K as a function of time.