

ELECTRONIC SUPPLEMENTARY INFORMATION

Novel Paramagnetic Clays obtained through intercalation of Gd³⁺-Complexes

Stefano Marchesi, Fabio Carniato,* Chiara Bisio,* Lorenzo Tei, Leonardo Marchese and Mauro Botta

Dipartimento di Scienze e Innovazione Tecnologica, Università del Piemonte Orientale, Viale Teresa Michel 11, 15121, Alessandria (Italy).

E-mail: fabio.carniato@uniupo.it; chiara.bisio@uniupo.it

Synthesis of SAP and Na-SAP clays

Aa gel with the molar composition of [SiO₂:MgO:Al₂O₃:Na₂O:H₂O] 1:0.835:0.056:0.056:110 was prepared. For that, 3.97 g of amorphous silica (SiO₂ fumed, 99.8%) were gradually dispersed in a solution prepared by dissolving 0.31 g of NaOH in 109 mL of ultrapure water (equal to 5/6 of the total water content). The obtained gel was then mixed accurately with a Teflon rod and a mechanical stirrer. After 1 h, 11.93 g of magnesium acetate tetrahydrate (Mg(CH₃COO)₂·4H₂O, 99%) and 1.75 g of aluminium isopropoxide (Al[OCH(CH₃)₂]₃, ≥ 98 %) were added to the reaction mixture, along with the remaining ultrapure water (22 mL). After 2 h, the gel, with a pH between 8-9, was introduced in a Teflon cup (125 mL capacity) of an autoclave (Anton PAAR 4748) and heated in an oven for 72 h at 240 °C. The water amount used to prepare saponite gel was chosen in relation to the quantity of silicon within the gel: the H₂O/Si molar ratio of 110 was adopted. After hydrothermal treatment, the product was filtered, washed with hot ultrapure water up to neutral pH and dried in an oven for 24 h at 100 °C. The so-produced material called SAP (6.592 g of white powder) was submitted to cation-exchange procedure in 250 mL of saturated NaCl solution for 36 h at RT to replace all possible cations present (i.e. aluminium and magnesium ions) with Na⁺ in the interlayer space. Then, the solid (hereafter named Na-SAP) was filtered and washed with hot ultrapure water until the complete elimination of chlorides (tested by AgNO₃ solution).

Characterization Methods

- The Elemental analyses were carried out with a Spectro Genesis Inductively-Coupled Plasma Atomic Emission Spectrometer equipped with a cross-flow nebulizer (ICP-AES). Prior to the analysis, the samples were mineralized by treatment with a mixture of HNO₃ (5 mL) and HF (5 mL) at 100 °C for 8 h.
- The cationic exchange capacity (CEC) of saponite was determined by the UV-Vis method reported in literature (C. Bisio, G. Gatti, E. Boccaleri, G. Superti, H. Pastore and M. Thommes, *Microporous Mesoporous Mater*, **2008**, 107, 90-101). In details, 0.200 g of Na-SAP were exchanged with 10 mL of a 0.02 M solution of [Co(NH₃)₆]³⁺ at RT for 60 h. After separation by centrifugation (5000 rpm for 5 min, two times), the solution was analysed by UV-Vis spectroscopy. UV-Vis spectra were recorded at RT in the range 300-600 nm with a resolution of 1 nm, using a double-beam Perkin Elmer Lambda 900 Spectrophotometer. The decrease of absorbance at 475 nm (¹A_{1g} → ¹T_{1g}), (J. C. Dabrowiak, *Metals in Medicine*, **2009**, Wiley, ISBN: 978-0-470-68196-144), relative to a *d-d* spin-allowed laporte-forbidden transition of Co³⁺, has been quantitatively related to the difference in concentration by means of a calibration with standard solutions.
- X-Ray diffractograms (XRPD) were collected on unoriented ground powders with a ThermoARL X'TRA-048 Powder Diffractometer with a Cu-K_{α1} (λ = 1.54062 Å) monochromatic radiation. Diffractograms were recorded at room temperature between 2°-65° 2θ with a step size of 0.02 and a rate of 1.2°/min. The X-ray profiles at low angles (2-15° 2θ) were collected with narrower slits and rate of 0.25°/min.
- High-resolution transmission electron microscope micrographs (HRTEM) images were collected on a Zeiss libra200 FE3010 High Resolution Transmission Electron Microscope operating at 200 kV. Specimens were prepared by depositing the samples on carbon-coated grids.
- Infrared spectra (FTIR) were collected on a Bruker Equinox 55 Spectrometer in the range 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. Self-supporting pellets were placed into an IR cell with KBr windows permanently connected to vacuum line (residual pressure lower than 10⁻⁴ mbar). Before measurements, the Na-SAP sample was outgassed at 350 °C with a heating ramp of 10 °C/min for 3 h, using a special oil-free apparatus and grease-free vacuum line in order to remove adsorbed water from the surface, while the GdL1/SAP and GdL2/SAP were outgassed at 100 °C with a heating ramp of 10 °C/min for 1 h.

- Thermogravimetric analyses (TG) were carried out with a Setaram SETSYS Evolution Thermobalance. The data were collected in the range 50-1100 °C with scan rate of 10 °C/min under O₂ flow (100 mL/min).
- Dynamic light scattering experiments (DLS) were carried out at 25 °C by using a Malvern Zetasizer NanoZS operating in a particle size range from 0.6 nm to 6 mm and equipped with a He-Ne laser with $\lambda = 633$ nm. The samples were dispersed in ultrapure water in the presence of Xanthan Gum (0.1 wt%) to improve particle dispersion. Before the measurement, the suspensions were sonicated for 30 min. The particles dispersed in water tend to form large aggregates. In the solution stabilized with xanthan gum this effect is strongly limited and no precipitation is observed after hours.
- The chromatographic analyses, performed during the synthesis of GdL1 and GdL2, were carried out with a Waters System based on a High-Performance Liquid Chromatography-Mass Spectrometry equipped with an Electrospray Ion Source (HPLC-MS ESI^{+/-}), a Waters 1525 Binary HPLC Pump, a Water 2489 UV-Vis Detector and a Water SQD 3100 Mass Detector. The mass spectra, obtained through the MS-ESI^{+/-} technique, were recorded using the Waters SQD 3100 Mass Detector.
- The ¹H and ¹³C-NMR spectra were recorded at 27 °C with a Bruker Advance III spectrometer equipped with a wide bore 11.7 Tesla magnet. All chemical shifts are reported using δ [ppm] scale and are externally referenced to tetramethylsilane (TMS) at 0 ppm. The samples were dissolved in deuterated chloroform (CDCl₃) or deuterated water (D₂O) for analyses.
- The water proton longitudinal relaxation rates (T_1) were measured by using a Stelar Spinmaster Spectrometer (Mede, Italy) operating in the range of proton Larmor frequencies of 20-70 MHz (0.47-1.64 T). The measurements were performed using the standard inversion recovery sequence (20 experiments, 2 scans) with a typical 90° pulse width of 3.5 μ s and the reproducibility of the data was within $\pm 0.5\%$. The temperature was controlled with a Stelar VTC-91 heater airflow equipped with a copper-constantan thermocouple (uncertainty of ± 0.1 °C). The $1/T_1$ ¹H-NMRD profiles were measured on a Fast-Field Cycling (FFC) Stelar 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 20-70 MHz were obtained on the Stelar Spinmaster Spectrometer. The concentration of Gd³⁺ for each sample was estimated by ¹H-NMR (500

MHz) measurements using Evans's method (D. F. Evans, *J. Chem. Soc.*, **1959**, 2003-2005; D. F. Evans, G. V. Fazakerley and R. F. Phillips, *J. Chem. Soc. (A)*, **1971**, 1931-1934).

Figures

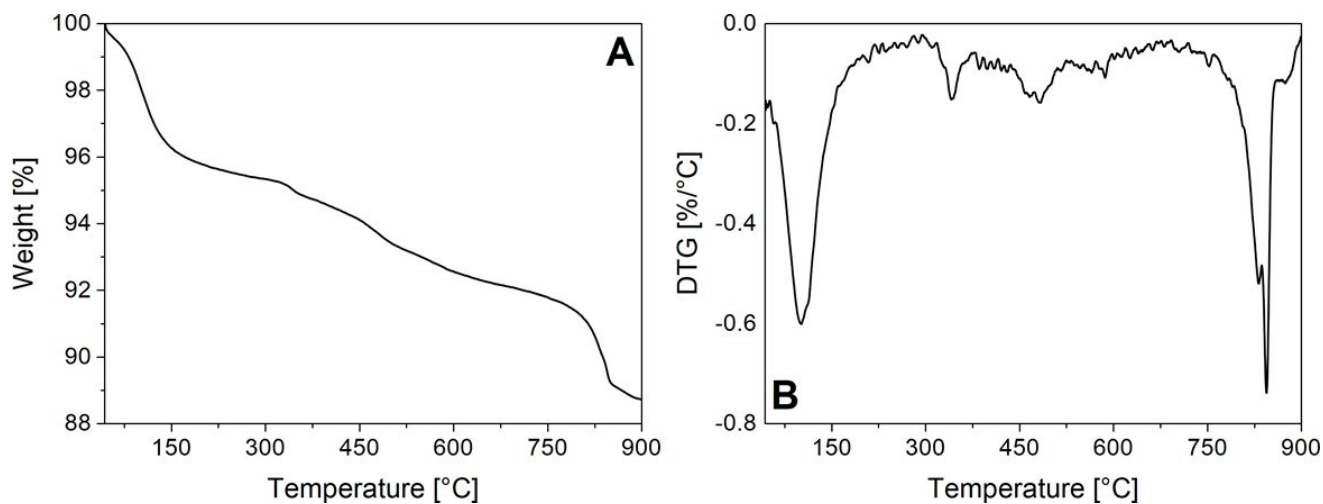


Fig. S1. TG (A) and DTG (B) profiles of Na-SAP. The analysis was carried out under oxygen flow.

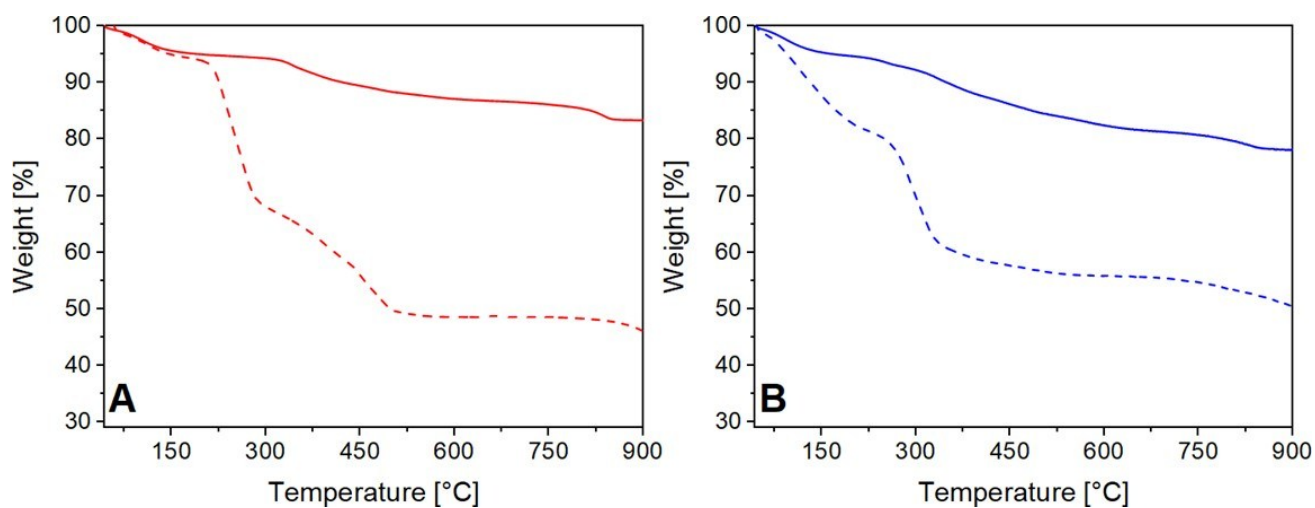


Fig. S2. **A)** TG profiles of GdL1 (dash line) and GdL1/SAP (solid line); **B)** TG profiles of GdL2 (dash line) and GdL2/SAP (solid line). The analyses were carried out under oxygen flow.

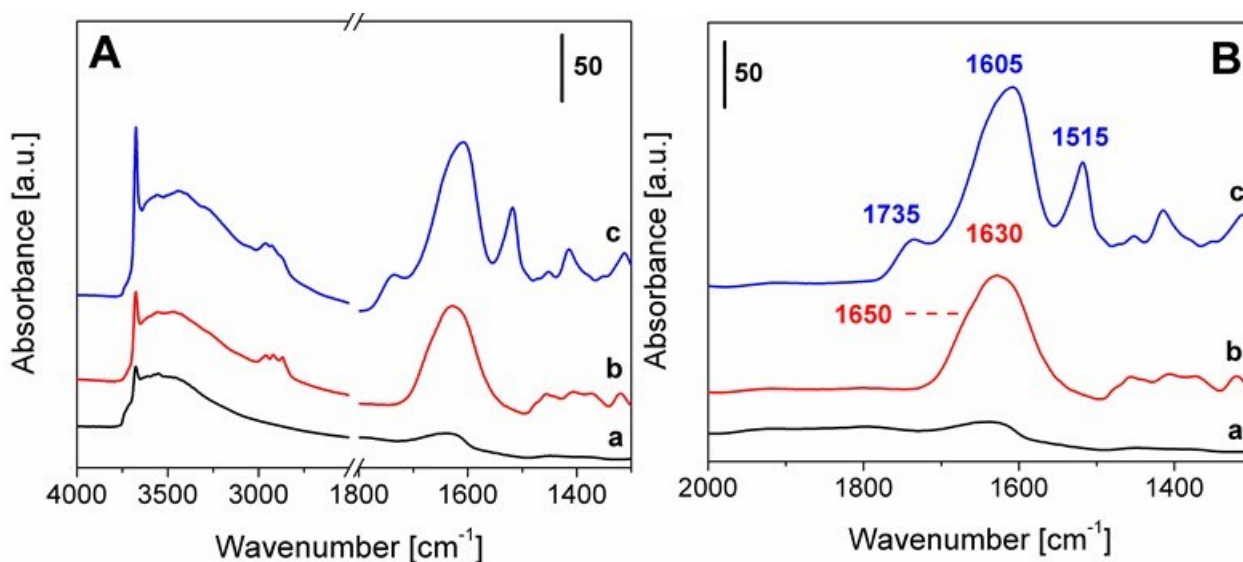


Fig. S3. A) Normalized FTIR spectra in vacuum of Na-SAP (a), GdL1/SAP (b) and GdL2/SAP (c); B) Magnification of the 2000-1300 cm⁻¹ range of spectra in frame A.

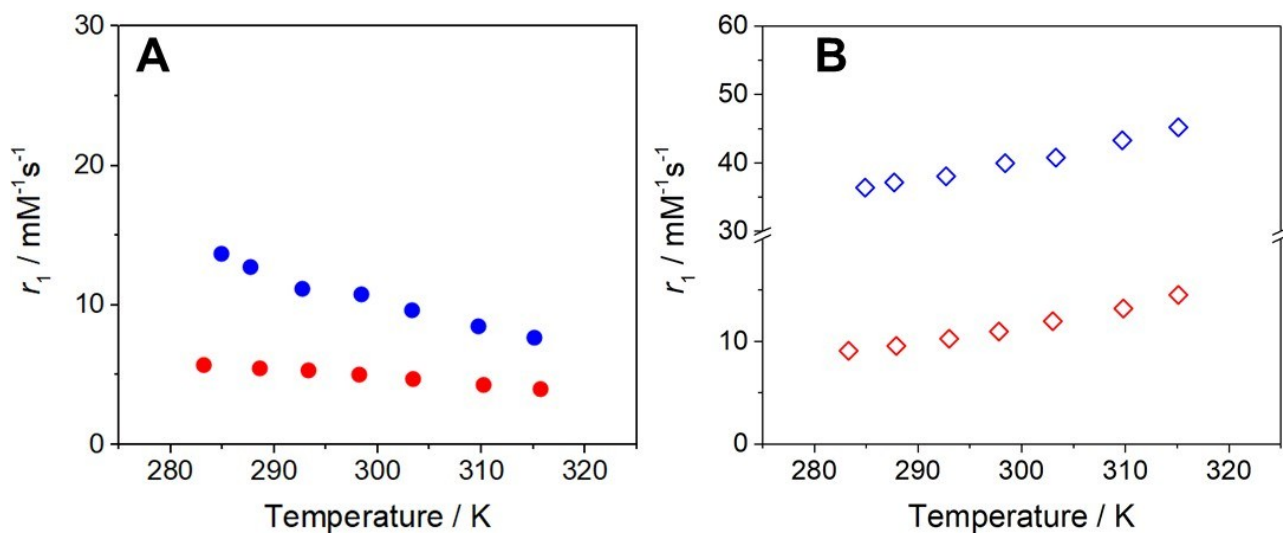


Fig. S4. A) Variable-temperature dependence of r_1 for GdL1 (red) and GdL2 (blue), at 20 MHz; B) Variable-temperature dependence of r_1 for GdL1/SAP (red) and GdL2/SAP (blue) at 20 MHz.

Tab. S1. Best-fit parameters obtained from the analysis of $1/T_1$ ¹H-NMRD profiles (37 °C) for GdL1, GdL2, GdL1/SAP and GdL2/SAP samples.

	GdL1	GdL2	GdL1/SAP	GdL2/SAP

$^{20}r_1$ [mM ⁻¹ s ⁻¹]	4.3	8.5	12.4	43.1
Δ^2 [10 ¹⁹ s ⁻²]	3.70±0.22	2.82±0.77	1.82±0.11	1.36±0.07
τ_V [ps]	12.3±0.2	23.8±4.1	27.2±4.0	11.7±0.7
τ_{RL} [ns]	/	/	0.28±0.04	0.60±0.03
τ_{RG}	74±2 ps	92±3 ps	1 μs ^[a]	1 μs ^[a]
τ_M [μs]	0.7	0.07	1.08±0.10	0.30±0.06
S^2	/	/	0.26±0.07	0.24±0.02
r [Å] ^[a]	3.0	3.0	3.0	3.0
q ^[a]	1	2	1	2
a [Å] ^[a]	4.0	4.0	4.0	4.0
D^{310} [10 ⁻⁵ cm ² s ⁻¹] ^[a]	3.1	3.1	3.1	3.1

[a] Fixed during the best fit procedure

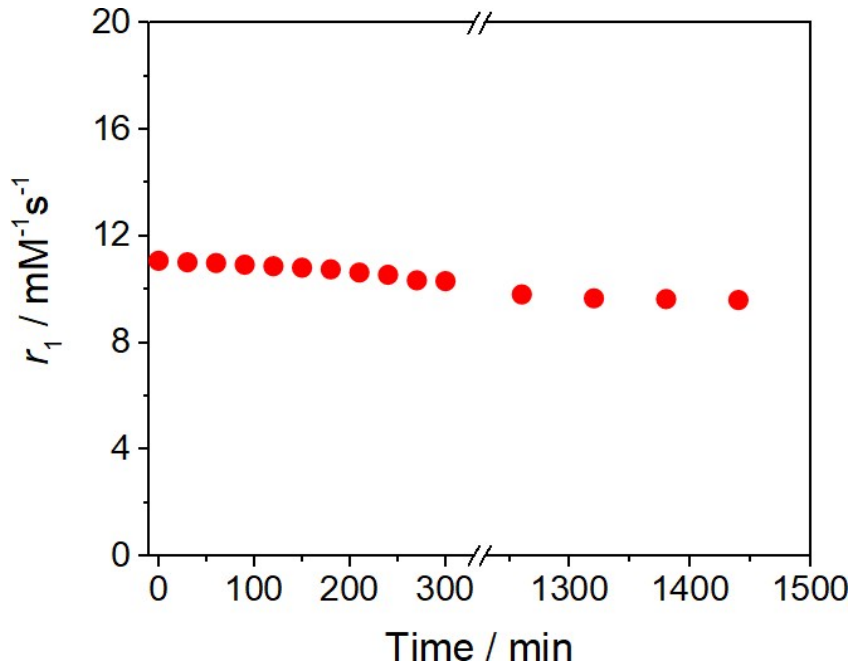


Fig. S5. Stability over time of r_1 of GdL1/SAP in ultrapure water at 20 MHz and 25 °C.

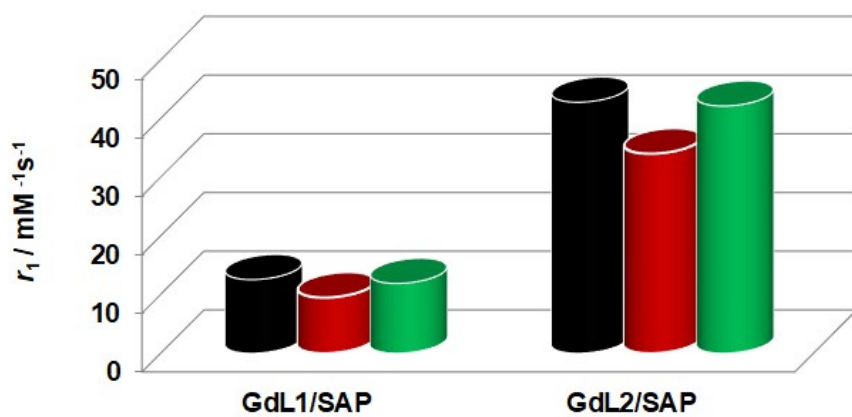


Fig. S6. Plot of r_1 at 20 MHz and 37 °C of GdL1/SAP and GdL2/SAP in ultrapure water (black), in Human Serum (Seronom™) (red) and PBS 0.01 M (green) matrices after 1h of suspension stabilization.