ELECTRONIC SUPPLEMENTARY INFORMATION

Combination of solid-state NMR and ^{1}H NMR relaxometry for the study of intercalated saponite clay with macrocycle derivatives of Gd(III) and Y(III)

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1) Experimental Approach

1.1 Macrocycle derivatives of Gd(III) and Y(III)

The synthesis of the novel TETA monoamide ligand bearing a 2-aminoethylacetamide pendant arm (TETAMA-En, named **L,** Scheme S1), used for the preparation of the relative Gd^{3+} and Y^{3+} chelates (Gd**L** and Y**L**, respectively; Schemes S1 and S2), was carried out starting from 1,4,8,11-tetraazacyclotetradecane (Cyclam, Scheme S1).[1,2]

- **Bromoacetamide pendant arm (1)**

In the first step, the bromoacetamide pendant arm (1) was synthesized following the optimized procedure reported in the literature.[3] In detail, N-Boc-ethylendiamine (0.40 g, 2.50 mmol), dissolved in 4 mL of dichloromethane (CH_2Cl_2/DCM), was added to a 1 M NaOH solution (8.0 mL, 7.49 mmol) and slowly stirred at 0 °C for 15 min. Afterwards, a solution of 2-bromoacetyl bromide (620 μL, 3.74 mmol) in 15 mL of DCM was added dropwise to the reaction mixture, under nitrogen flow and at 0 °C. The mixture was then slowly stirred at RT for 20 h. After that, several purification treatments were performed in order to obtain the pure bromoacetamide pendant arm (1). In detail, 15 mL of water were added to the mixture, followed by concentration *in vacuo*; the residue/organic phase was extracted in DCM (3 x 15 mL), dried with sodium sulphate (Na_2SO_4), filtered and evaporated *in vacuo* until a whitish powder was obtained. The desired product was isolated through purification in chromatographic column (DCM:MeOH 90:10) and the fraction in DCM was finally concentrated *in vacuo* (bromoacetamide pendant arm (1), 0.30 g, 1.07 mmol, 38% yield).

HPLC-MS ESI^+ (*m/Z*) = 281.2 [$(M + H)^+$]; calculated $C_9H_{17}BrN_2O_3$ = 281.15.

^{1}H-NMR ($CDCl_3$) 500 MHz, δ [ppm] = 3.95 (s, 2H, BrC*H*$_2$), 3.48 (t, 2H, NHC*H*$_2$), 3.40 (t, 2H, C*H*$_2$NH), 1.54 (s, 9H, C*H*$_3$).

^{13}C-NMR ($CDCl_3$) 100 MHz, δ [ppm] = 171.6 (*C*=ONH), 166.3 (NH*C*=OO), 77.3 (*C*$(CH_3)_3$), 41.5 (*C*H_2NH), 39.8 (NH*C*H_2), 29.4 (*C*H_3), 28.7 (Br*C*H_2).

TE3A(*t*-BuO)$_3$ (2)

The sample was prepared by reacting cyclam with *tert*-butyl 2-bromoacetate. In detail, cyclam (0.50 g, 2.50 mmol) was dissolved in 25 mL of anhydrous acetonitrile (ACN), under nitrogen flow and at RT, and slowly stirred at 273 K for 10 min. Sodium hydrogen carbonate ($NaHCO_3$, 0.31 g, 3.75 mmol) was added and the mixture was slowly stirred at 273 K for 30 min. Next, *tert*-butyl 2-bromoacetate (1.10 mL, 7.51 mmol) was added dropwise at 273 K and the reaction

mixture was slowly stirred at RT for 48 h. After that, the solution was concentrated *in vacuo* until a yellowish oil-*like* compound was recovered. The desired product was isolated through purification in chromatographic column (DCM:MeOH 95:5) and the fraction in DCM was finally concentrated *in vacuo* until a whitish powder was obtained (TE3A(*t*-BuO)$_3$ (2), 0.73 g, 1.35 mmol, 55% yield).

HPLC-MS ESI$^+$ (*m/Z*) = 543.7 [(M + H)$^+$]; calculated $C_{28}H_{54}N_4O_6$ = 542.76.

^{1}H-NMR (ACN-*d*) 500 MHz, δ [ppm] = 3.29 (s, 6H, C*H*$_2$C=O), 2.80-2.65 (t, 16H, other C*H*$_2$), 1.68 (m, 4H, apical C*H*$_2$), 1.50 (s, 27H, C*H*$_3$).

^{13}C-NMR (ACD-*d*) 100 MHz, δ [ppm] = 170.8 (*C*=O), 82.5 (quaternary *C*(CH$_3$)$_3$), 57.8 (C*H*$_2$C=O), 65.0-40.0 (other *C*H$_2$), 31.7 and 30.8 (apical *C*H$_2$), 28.8 (*C*H$_3$).

- **TE3A(*t*-BuO)3-monoacetamide-Boc (3)**

TE3A(*t*-BuO)$_3$ (2) (0.200 g, 0.368 mmol) was dissolved in 20 mL of ACN and potassium carbonate (K_2CO_3, 0.150 mg, 1.085 mmol) was added at RT; then, a solution of bromoacetamide pendant arm (1) (0.137 g, 0.487 mmol) in 10 mL of ACN was added dropwise at RT and the reaction mixture was slowly stirred at 333 K for 48 h. After that, the mixture was filtered and finally concentrated *in vacuo* until a yellowish powder was obtained (TE3A(*t*-BuO)$_3$-monoacetamie-Boc (3), 0.30 g, 0.40 mmol, 98% yield).

HPLC-MS ESI$^+$ (*m/Z*) = 744.0 [(M + H)$^+$]; calculated $C_{37}H_{70}N_6O_9$ = 743.00.

^{1}H-NMR ($CDCl_3$) 500 MHz, δ [ppm] = 3.39 (t, 2H, NHC*H*$_2$ pendant arm), 3.30 (t, 2H, C*H*$_2$NH pendant arm), 3.21 (s, 2H, NHC=OC*H*$_2$ pendant arm), 3.05 (s, 6H, C*H*$_2$C=O), 2.75 and 2.63 (t, 16H, other C*H*$_2$), 1.62 (m, 4H, apical C*H*$_2$), 1.51 (s, 36H, C*H*$_3$).

^{13}C-NMR ($CDCl_3$) 100 MHz, δ [ppm] = 173.5 (NH*C*=O pendant arm), 170.7 (*C*=O), 157.6 (O*C*=ONH pendant arm), 82.8 (quaternary *C*(CH$_3$)$_3$), 79.3 (quaternary *C*(CH$_3$)$_3$ pendant arm), 59.3 (NHC=OC*H*$_2$ pendant arm), 58.2 (C*H*$_2$C=OO), 55.0-50.0 (other *C*H$_2$), 41.2 (*C*H$_2$NH pendant arm), 38.1 (NH*C*H$_2$ pendant arm), 29.8 and 29.3 (apical *C*H$_2$), 28.1 (*C*H$_3$).

- **TETAMA-En (L)**

The simultaneous deprotection of *tert*-butyl esters and Boc group was accomplished by reacting the intermediate TE3A(*t*-BuO)$_3$-monoacetamide-Boc (3) (0.30 g, 0.40 mmol) with a 1:1 mixture solution of 13 mL of DCM and 13 mL of trifluoroacetic acid (TFA) at 273 K, then slowly stirred at RT for 48 h. After that, several purification treatments were performed in order to obtain the TETAMA-En ligand (**L**). In detail, 10 mL of diethyl ether were added to the mixture, followed by filtration and concentration *in vacuo*; 15 mL of ultrapure water were added

to the yellowish oil-*like* compound. The residue/aqueous phase was washed with DCM (3 x 15 mL) and finally evaporated *in vacuo* until a yellowish oil-*like* compound was obtained (TETAMA-En (**L**), 0.15 g, 0.31 mmol, 76% yield).

HPLC-MS ESI$^+$ (*m/Z*) = 475.6 [(M + H)$^+$]; calculated $C_{19}H_{39}N_6O_7$ = 474.56.

^{1}H-NMR (D_2O) 500 MHz, δ [ppm] = 3.38 (t, 4H, $^+H_3NCH_2CH_2NH$ pendant arm), 3.21 (s, 2H, NHC=OCH_2 pendant arm), 3.18 (s, 2H, CH_2C=O), 2.71 and 2.58 (t, 16H, other CH_2), 1.70 (m, 4H, apical CH_2).

^{13}C-NMR (D_2O) 100 MHz, δ [ppm] = 172.9 (*C*=O), 168.6 (NH*C*=O pendant arm), 60.0-50.0 (CH_2), 38.9 ($^+H_3NCH_2$ pendant arm), 37.2 (CH_2NH pendant arm), 22.5 (apical CH_2).

- **Gd(III)-TETAMA-En (GdL)**

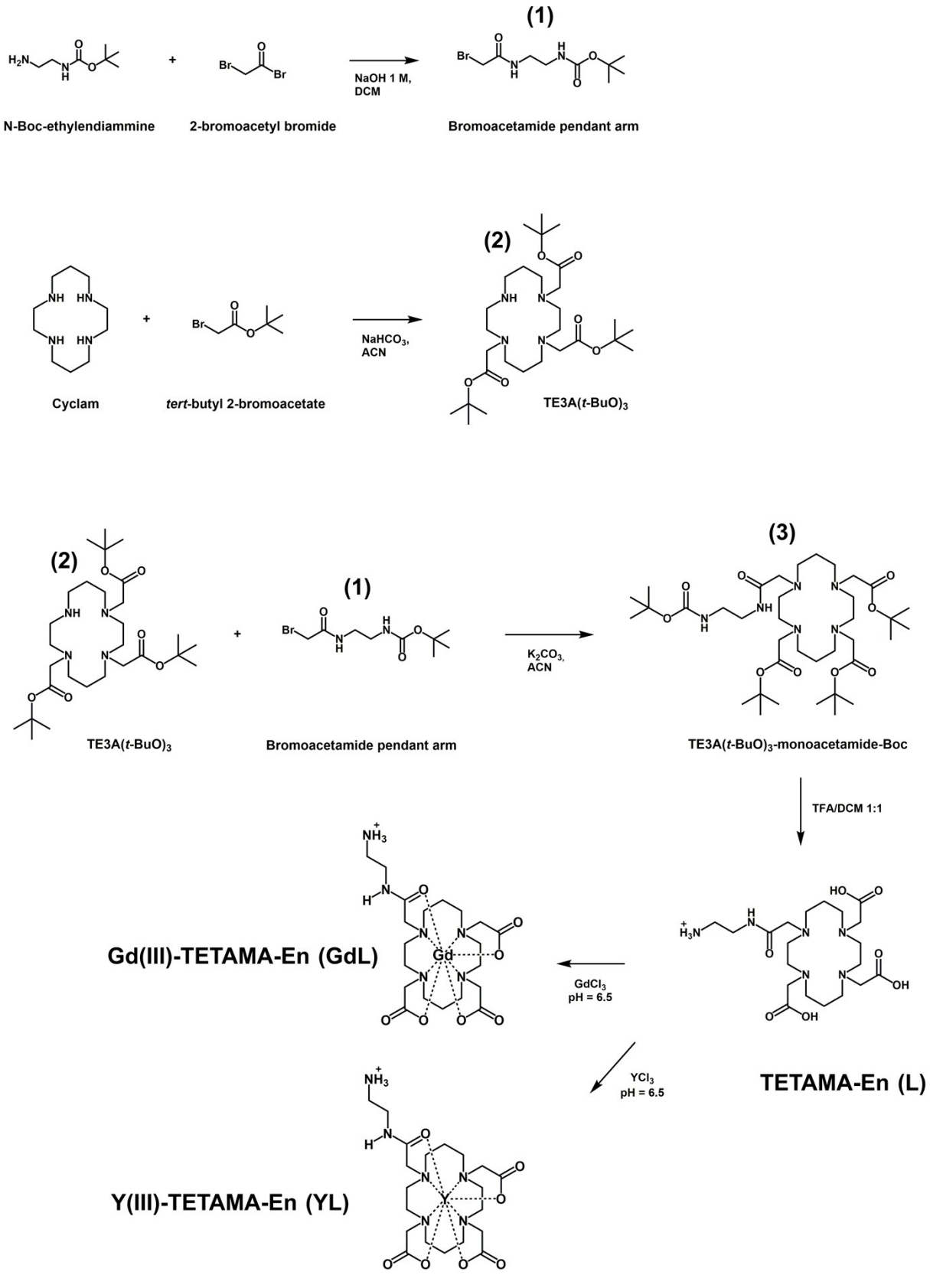
Finally, TETAMA-En (**L**), 0.15 g, 0.31 mmol) and gadolinium chloride hexahydrate ($GdCl_3 \cdot 6H_2O$; 0.13 g, 0.36 mmol) were dissolved at room temperature (RT) in 15 mL of ultrapure water and then the pH of the solution was brought to 6.5 with a NaOH solution. The reaction mixture was then stirred at RT overnight. After that, the pH was again corrected from 6.5 to 10, to precipitate free Gd^{3+} ions as hydroxide ($Gd(OH)_3$), which was eliminated by centrifugation (10000 rpm for 5 min) and filtration through 0.2 μm filters. The pH of the solution was finally adjusted to 7 with dilute hydrochloric acid and lyophilized overnight until a solid was obtained (Gd**L**, 0.23 g, 0.37 mmol, quantitative).

HPLC-MS ESI$^+$ (*m/Z*) = 629.9 {[(M + H)]$^+$}; calculated $C_{19}H_{36}GdN_6O_7$ = 628.79 (100.0 %) (isotopic distributions consistent with Gd^{3+}).

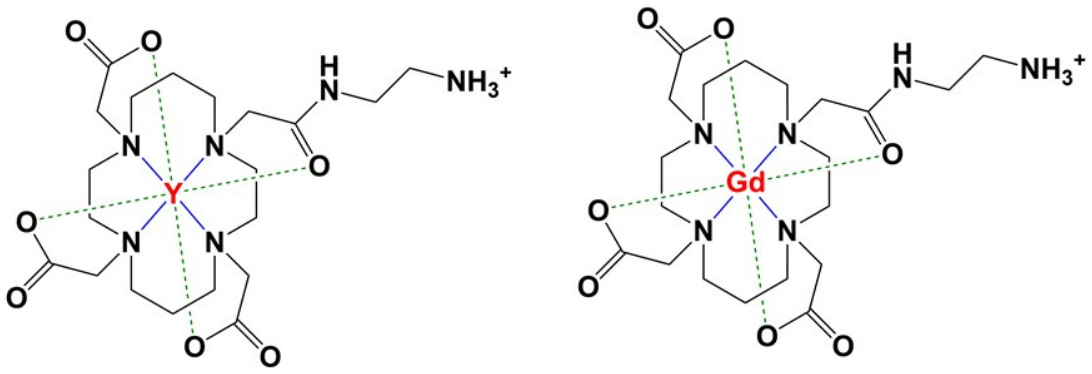
- **Y(III)-TETAMA-En (YL)**

For Y**L**, a slightly different complexation procedure than the one described above was used: **L** (0.19 mg, 0.40 mmol), yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$; 0.15 g, 0.48 mmol), 15 mL of ultrapure water, reaction mixture stirred for 5 days at 323 K.

HPLC-MS ESI$^+$ (*m/Z*) = 585.8 {[(M + Na)]$^+$}; calculated $C_{19}H_{36}YN_6O_7$ = 560.44.



Scheme S1. Synthetic procedure for the preparation of **L,** Gd**L** and Y**L**.



Scheme S2. Chemical structure of positive charged Y**L** and Gd**L** chelates.

1.2 Saponite clay

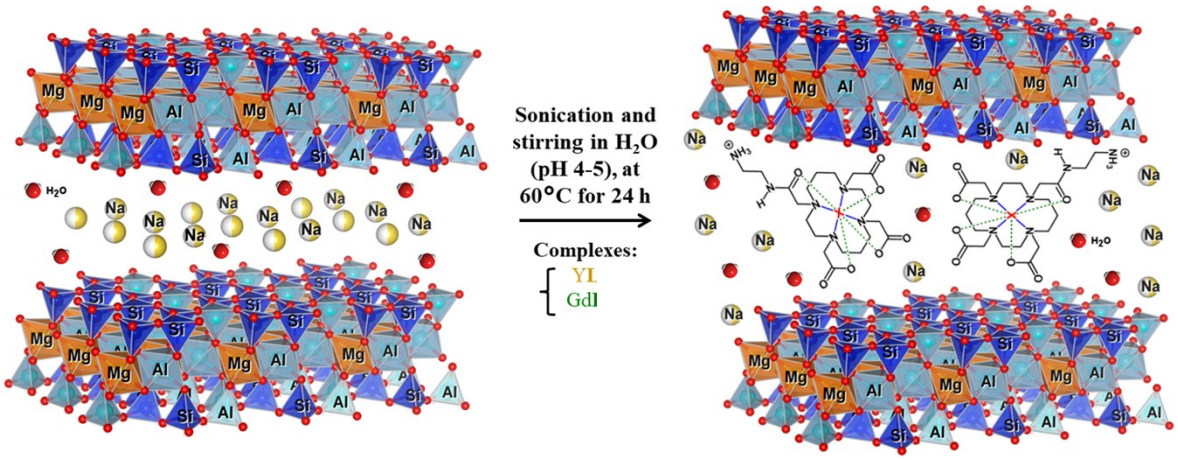
Nanosized synthetic saponite with a cationic exchange capacity (CEC) of 37.3 ± 1.8 meq/100 g was synthesized following the hydrothermal procedure reported in the literature by Costenaro *et al.*[4] A gel with the molar composition of [SiO_2:MgO:Al_2O_3:Na_2O:H_2O] 1:0.835:0.056:0.056:110 and H_2O/Si molar ratio of 110 was prepared. In detail, 3.97 g (0.06 mol) of amorphous silica (SiO_2 fumed, 99.8%) were gradually dispersed in a solution prepared by dissolving 0.31 g (0.007 mol) of sodium hydroxide (NaOH) in 109.00 g (6.05 mol) of ultrapure water. The obtained gel was then mixed accurately. After 1 h, 11.93 g (0.05 mol) of magnesium acetate tetrahydrate ($Mg(CH_3COO)_2{\cdot}4H_2O$, 99%) and 1.75 g (0.007 mol) of aluminium isopropoxide ($Al[OCH(CH_3)_2]_3$, ≥ 98 %) were added to the reaction mixture, along with the remaining ultrapure water (22.00 g, 1.22 mol). 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 513 K. After hydrothermal treatment, the product was filtered, washed with hot ultrapure water up to neutral pH and dried in an oven overnight at 373 K.

The so-produced material called SAP (6.59 g of white powder) was submitted to cation-exchange procedure (in order to ensure a chemical uniformity of the exchange sites): 2.50 g of SAP were dispersed in 250 mL of saturated sodium chloride (NaCl) solution for 36 h at room temperature to replace all possible cations present (*i.e.* Al^{3+}, Mg^{2+}, H^+) with Na^+ ions in the interlayer space. Then, the final solid (named Na-SAP) was filtered, washed with hot ultrapure water until the complete elimination of chlorides (confirmed by silver nitrate, $AgNO_3$, spot test) and dried in an oven overnight at 373 K.

1.3 Intercalated materials

- **Preparation of paramagnetic GdL/SAP clay:** The intercalation procedure of Gd**L** chelate in the interlayer of synthetic sodium-saponite Na-SAP was optimized following the procedures reported in the literature for similar systems (Scheme S3).[5,6] The Gd^{3+}-complex was added in a molar quantity equal to cation exchange capacity (CEC) of the saponite (37.3 ± 1.8 meq/100 g). In details, 0.300 g of Na-SAP were dispersed in 35 mL of ultrapure water in a round-bottom glass flask, which was placed in a crystallizer with water. The dispersion was then subjected to the following treatment: 1 h of sonication, 2 h of magnetic stirring with Teflon rod and a mechanical stirrer and the last hour of sonication. After 2 hours, 0.071 g (0.113 mmol) of Gd**L** were dissolved in 10 mL of ultrapure water and the pH was brought to 4-5 with a 0.1 M HCl solution. After 3 hours, the sonication was stopped, and subsequently the aqueous solution of the complex was transferred into the flask. The reaction was then stirred at 333 K for 20 h. After this time, the product was filtered, washed with hot ultrapure water up to neutral pH and dried in an oven overnight at 373 K.

- **Preparation of diamagnetic YL/SAP clay:** The intercalation of Y**L** in the Na-SAP was carried out with the same procedure applied for Gd**L**/SAP.[6] The amount of the reactants was:
  - Y**L:** 0.27 g (0.48 mmol) dissolved in 10 mL of water
  - Na-SAP: 0.30 g dispersed in 40 mL of water.



Scheme S3. Schematic representation of the preparation of intercalated paramagnetic and diamagnetic saponite clays.

1.4 NMR characterization of Na-SAP sample

^{29}Si, ^{27}Al, ^{23}Na and ^{1}H Magic Angle Spinning (MAS) NMR spectroscopy has been used to characterize the structure of the synthetic saponite clay, or rather to gain atomic level information on the species composing the octahedral and tetrahedral sheets of the saponite layers (by accessing the population of octahedral and tetrahedral aluminium sites, and tetrahedral silicon sites) as well as on those residing in the interlayer space (sodium and water). A combination of one dimensional and two-dimensional NMR techniques, exploiting the direct detection of low-gamma nuclei at moderate magic angle spinning frequencies (12 kHz), has been employed for this purpose.

^{1}H-NMR spectroscopy has been exploited to access the structural water and hydroxyl molecules of the layers and those absorbed in the interlamellar region of the clay. The 1D ^{1}H MAS-NMR spectrum of Na-SAP shows two bands: one sharper, centred at 0.6 ppm and typical of structural hydroxyls groups, the other broader at 3.9 ppm, attributed to the water molecules within the sample (Figure S3). Previous ^{1}H MAS-NMR studies established that structural hydroxyl groups in trioctahedral saponite clays resonate around 0.5 ppm.[7] These are located in symmetrical environments, pointing toward the hexagonal cavities, and they are not involved hydrogen bonds with the oxygen atoms of the tetrahedral sheets. Indeed, these OH-groups are too far away from the adsorbed water, as confirmed by the absence of a correlation peak in two-dimensional ^{1}H-^{1}H spin diffusion experiment (Figure S3).

Thanks to its high sensitivity to the local environment, ^{29}Si has been exploited to gain insights into the coordination number, type of coordinating atoms, degree of polymerization (indicated as Q^n, where n is the number of oxygen atoms bridging neighboring silicon atoms), and substitution of next nearest neighbours.[8] In particular, the 1D ^{29}Si MAS-NMR spectrum acquired on the Na-SAP (reported as a projection of the 2D ^{1}H,^{29}Si HETCOR spectrum in Figure S4) shows two sets of signals resonating at ca. 97.65 and 92.20 ppm, assigned to [Q^3Si(0Al)] and [Q^3Si(1Al)] species, respectively. The relative population ratio of the two species, being ~90% and ~10%, provides an estimation of the incorporation degree of Al in the tetrahedral sheets and is in agreement with the chemical structure of the synthetic saponite. Two dimensional ^{1}H,^{29}Si HETCOR experiment makes use of the proton and silicon dipolar interactions to provide information about their spatial proximity.[9] The 2D spectrum shows two sets of cross peaks, one sharper resonating at proton frequency of 0.7 ppm and attributed to [Q^3Si(0Al)] and [Q^3Si(1Al)] ordered species that are close in space to the isolated Mg/Al-hydroxyls, one broader, to which both hydroxyls (2.5-3.5) and water protons (4 ppm) contribute, assigned to more disordered hydrogen bonded silanols and to the [Q^3Si(0Al)]

species in proximity to H_2O, respectively.

^{27}Al MAS-NMR investigations have been accomplished to access the chemical environment of aluminium in the tetrahedral and octahedral sheets of the saponite framework. 1D ^{27}Al MAS-NMR spectrum reported in Figure S5A shows two distinct peaks resonating at 67 and 8.5 ppm, attributed to tetrahedrally (Al^{IV}) and octahedrally (Al^{VI}) coordinated aluminium species, respectively. Quantitative analysis of the spectrum shows that aluminium ions in tetrahedral and octahedral sheets account for the 67% and 33% of the total metal content in the sample, which agrees with tetra-octa-tetra layers constituting the saponite clay. Additional information on the structural properties of saponite samples have been obtained by 2D ^{1}H,^{27}Al 2D HETCOR spectroscopy, where two distinct tetrahedral and octahedral coordinated aluminium species are detectable.[9] The major component of Al^{IV} resonating around 67 ppm can be ascribed to isolated alumina sites, while the minor component at 71 ppm can be attributed to Al^{IV} sites close to water molecules (Figure S5B). The correlation peaks of the octahedrally coordinated Al, can be ascribed to isolated sites of distorted Al-OH-Al Mg-OH-Al (resonating at a ^{1}H frequency of 1.5 ppm), to H-bonded alumina sites (resonating at a proton frequency of 2.5-3 ppm) and to well-ordered Al^{VI} Brønsted acid sites in large cavities (resonating at a ^{1}H frequency of 4.0 ppm).[10]

2) Analytical Methods

2.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The elemental analyses were performed on a Thermo Fisher Scientific X5 Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS; Waltham, MA, USA). Prior to the analysis, the solid samples were mineralized by treatment with a mixture of nitric acid (HNO_3; 5 mL) and hydrofluoric acid (HF; 5 mL) at 373 K for 8 h.

2.2 High-Performance Liquid Chromatography-Mass Spectrometry equipped with an Electrospray Ion Source (HPLC-MS $ESI^{+/-}$)

The chromatographic analyses, performed during the synthesis of Gd**L** and Y**L** chelates, 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.

2.3 X-ray Powder Diffraction Analyses (XRPD)

X-ray powder (XRPD) diffractograms were collected on unoriented ground powders with a ThermoARL X'TRA-048 Powder Diffractometer with a Cu-$K_{\alpha 1}$ (λ = 1.54062 Å) monochromatic radiation. Diffractograms were recorded at room temperature (RT) in the 2°-65° 2θ range with a step size of 0.02° and a rate of 1.0°/min. The X-ray profiles at low angles (2-15° 2θ) were collected with narrower slits and rate of 0.25°/min.

2.4. TEM microscopy

High-resolution transmission electron microscopy (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.

2.5 Solution Nuclear Magnetic Resonance Spectroscopy (NMR)

The one-dimensional (1D) ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra of the reaction intermediates and of the ligand **L** in solution were recorded at 300 K with a Bruker Advance III Spectrometer equipped with a wide bore 11.7 Tesla magnet. The samples were dissolved in deuterated chloroform ($CDCl_3$) or isotopically enriched water (D_2O) for NMR analyses. The spectrometer is equipped with a 5 mm double resonance Z-gradient broadband probe, with the inner coil optimized for observation of nuclei between ^{31}P and ^{15}N and for ^{19}F (BBFO), and Bruker BVT-3000 unit for temperature control. A set of 1D and two-dimensional (2D) NMR experiments was acquired on Y**L**, dissolved in a solution of 1:1 molar ratio of H_2O:D_2O (130.85 mM), at 300 K: 1D ^{1}H and ^{13}C, plus 2D ^{1}H-^{1}H Correlation Spectroscopy (COSY),[11] ^{1}H-^{1}H Total Correlation Spectroscopy (TOCSY)[12] and ^{1}H-^{13}C Heteronuclear Single-Quantum Correlation Spectroscopy (HSQC)[13] spectra for resonance assignment. The 2D COSY spectrum was collected using a standard phase-insensitive COSY sequence with gradient coherence selection, with 2048 acquired data points in F2, 256 time increments in F1, 16 scans, a 2 s recycle delay and a spectral window (both F2 and F1) of 10 ppm. The 2D TOCSY using the mlev sequence for mixing,[12] with 2048 acquired data points in F2, 200 time increments in F1, 24 scans, a 2 s recycle delay and a spectral window (both F2 and F1) of 10 ppm. The ^{1}H-^{13}C HSQC spectrum was collected by standard gradient selected pulse sequence.[14-16] The spectrum was acquired with 2048 data points in F2 and 256 data points in F1, 64 scans, a 2 s recycle delay, an F2 (^{1}H) spectral width of 10 ppm (carrier frequency at

4.7 ppm), and an F1 (^{13}C) spectral width of 60 ppm (carrier frequency at 45 ppm). All chemical shifts are reported using δ [ppm] scale and are externally referenced to tetramethylsilane (TMS) at 0 ppm.

2.6 Solid-state Nuclear Magnetic Resonance Spectroscopy (ssNMR)

Solid-state NMR (ssNMR) spectra were acquired on a Bruker Avance III 500 Spectrometer equipped with a wide bore 11.7 Tesla and a 4 mm triple resonance probe. Solid samples (Y**L** and Y**L**/SAP) were packed on a zirconia rotor and spun at a Magic Angle Spinning (MAS) rate of 12 kHz, at RT. A set of 1D and 2D NMR experiments was recorded, including: 1D MAS-NMR (^{1}H, ^{29}Si, ^{23}Na and ^{27}Al), ^{13}C Cross Polarization (CP)-MAS-NMR, 2D ^{1}H-^{1}H Spin Diffusion,[17] ^{1}H-^{29}Si and ^{1}H-^{27}Al Heteronuclear Correlation (HETCOR) spectroscopy with Frequency Switched Lee Goldburg (FSLG) Heteronuclear decoupling.[9] The magnitudes of radio frequency (RF) pulses were 100, 42, 36, and 31 kHz for ^{1}H, ^{29}Si, ^{23}Na and ^{27}Al, respectively. The relaxation delay, D1, between accumulations was 2s for ^{1}H, ^{29}Si, ^{23}Na and ^{27}Al. ^{27}Al 1D MAS spectra have been acquired on large sweep width with small pulse angle ($\pi/12$) to ensure quantitative interpretation. The ^{1}H-^{29}Si CP was performed using a constant RF frequency applied to ^{29}Si of 37 kHz and a pulse linearly ramped from 50% to 100% of a maximum RF frequency of 22 kHz on ^{1}H. The ^{1}H-^{27}Al cross polarization (CP) was performed using a constant RF frequency applied to ^{27}Al of 3 kHz and a pulse linearly ramped from 50% to 100% of a maximum RF frequency of 31 kHz on ^{1}H with a contact time of 500 μs. High power Two Pulse Phase Modulation (TPPM)[18] decoupling of 100 kHz was applied for heteronuclear decoupling. The spectrum ^{1}H-^{27}Al FSLG HETCOR spectra were acquired with an acquisition time of 10 ms in F2 and 2 ms in F1, 64 scans and 2 s recycle delay. The spectrum ^{1}H-^{29}Si FSLG HETCOR spectra were acquired with an acquisition time of 10 ms in F2 and 2.4 ms in F1, 128 scans and 2 s recycle delay. 1D ^{27}Al High-Power Decoupling (HPDEC)/MAS ssNMR spectra were collected on Na-SAP and Y**L**/SAP samples (operational frequency of 130.33 MHz for Al, MAS rate of 5 kHz and d1 of 1 s). All chemical shifts are reported using δ [ppm] scale and are externally referenced to Adamantane.

2.7 Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared (FTIR) spectra 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 potassium bromide (KBr) windows permanently connected to vacuum line (residual pressure

lower than 10^{-4} mbar). Before measurements, the Na-SAP sample was outgassed at 623 K with a heating ramp of 10 K/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 intercalated Gd**L** sample was outgassed at 373 K with a heating ramp of 10 K/min for 1 h. The absorbance values are reported as arbitrary unit [a.u.].

2.8 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) experiments were carried out at 298 K 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 λ = 633 nm. The samples were dispersed in ultrapure water (5 mg in 3 mL) in the presence of xanthan gum (0.1 wt.%) to improve particle dispersion. Before measurements, the suspensions were sonicated for 10 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 pH of suspensions was 7.0.

2.9 ^{1}H-NMR Relaxometric Analyses

The $1/T_1$ ^{1}H Nuclear Magnetic Relaxation Dispersion (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 ± 1%. Additional data points in the range 20-120 MHz were obtained with a High Field Relaxometer (Stelar) equipped with the HTS-110 3T Metrology Cryogen-*free* Superconducting Magnet. The measurements were performed using the standard inversion recovery sequence (20 experiments, 2 scans) with a typical 90° pulse width of 3.5 μs and the reproducibility of the data was within ± 0.5%. The temperature was controlled with a Stelar VTC-91 heater airflow equipped with a copper-constantan thermocouple (uncertainty of ± 0.1 K).

Gd**L** chelate (1 mg) was dissolved in 1 mL of ultrapure water, while GdL/SAP (10 mg) was dispersed in 1.5 mL of ultrapure water in the presence of xanthan gum (0.1 wt.%) to improve particles dispersion. Before measurements, the suspension was sonicated for 10 min. The pH of solutions/suspension was 7.0. The concentration of Gd**L** was estimated by ^{1}H-NMR (500 MHz) measurements using Evans's method.[19]

For the stability test, the paramagnetic intercalated solid was dispensed in 1 mL of reconstituted human serum (Seronorm™).

3) Figures

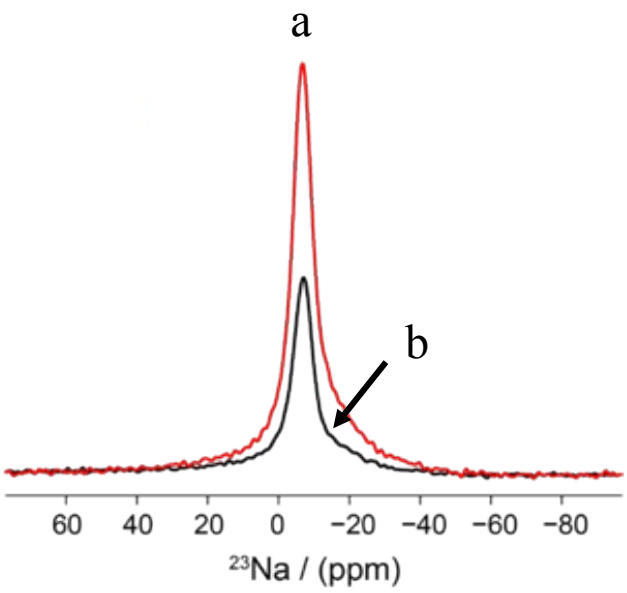


Figure S1. Comparison of 1D ^{23}Na spectra acquired on the Na-SAP (a) and Y**L**-SAP (b) at 11.7 T, at room temperature, spinning the samples at 12 kHz in a 4 mm rotor.

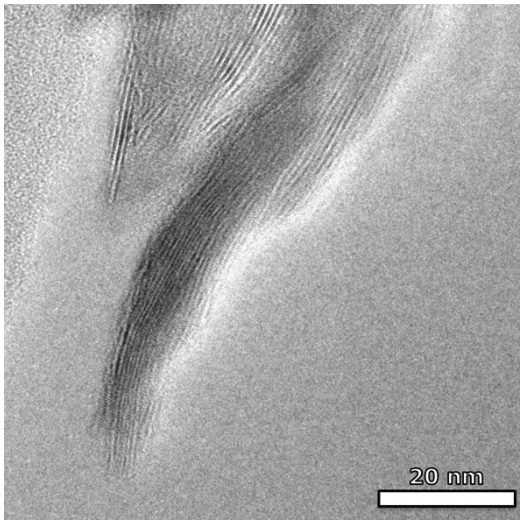


Figure S2. HRTEM image of Gd**L**/SAP sample.

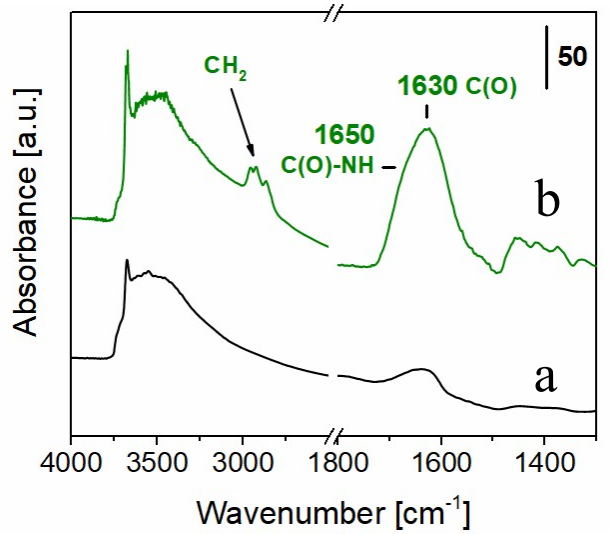


Figure S3. Normalized FTIR spectra in vacuum of Na-SAP (a) and Gd**L**/SAP (b), in the 2000-1300 cm^{-1} range. The spectra were collected in vacuum at room temperature.

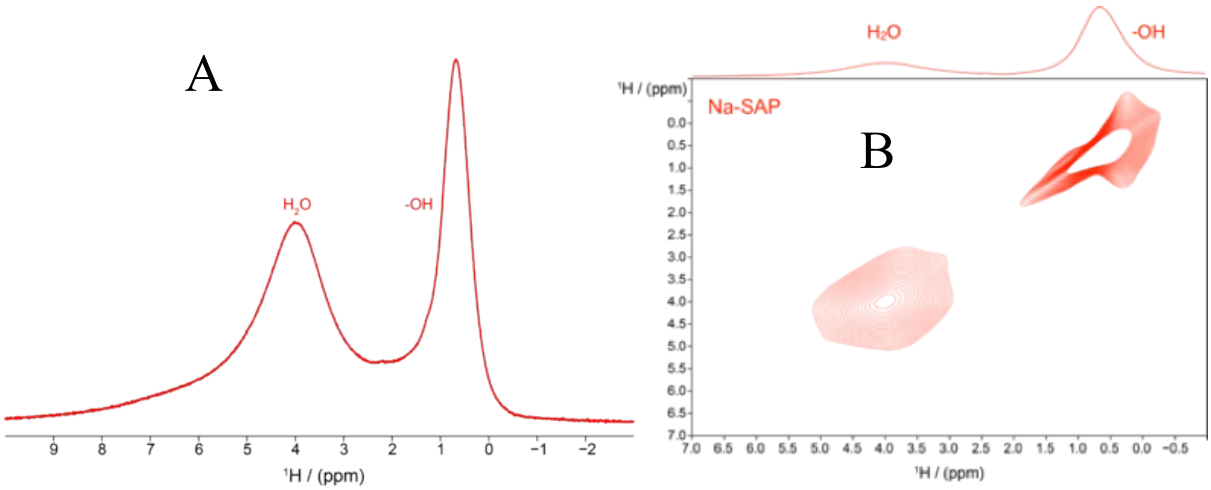


Figure S4: NMR characterization of the Na-SAP: assignment of the protons moieties. 1D ^{1}H (A) and 2D ^{1}H, ^{1}H spin diffusion spectrum (B) acquired on the Na/SAP at 11.7 T, at room temperature, spinning the sample at 12 kHz in a 4 mm rotor

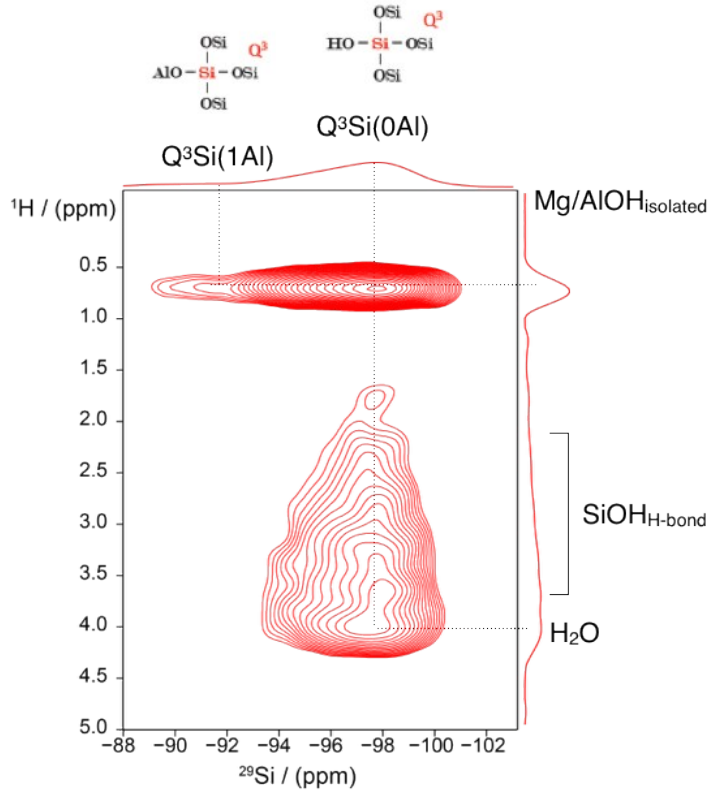


Figure S5: NMR characterization of the Na-SAP: assignment of the silicon moieties. 2D ^{1}H,^{29}Si HETCOR spectrum acquired on Na-SAP at 11.7 Tesla, at room temperature, spinning the sample at 12 kHz in a 4 mm rotor.

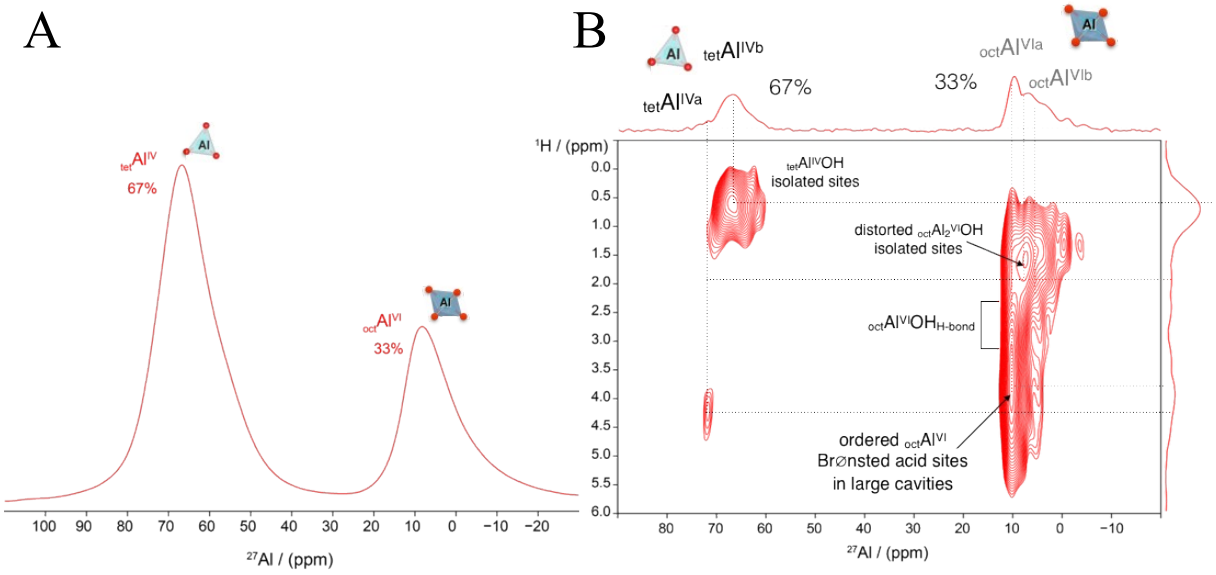


Figure S6: NMR characterization of the Na-SAP: assignment of the Aluminium moieties. 1D ^{27}Al (A) and 2D ^{1}H,^{27}Al HETCOR (B) spectrum acquired on Na-SAP at 11.7 Tesla, at room temperature, spinning the sample at 12 kHz in a 4 mm rotor.

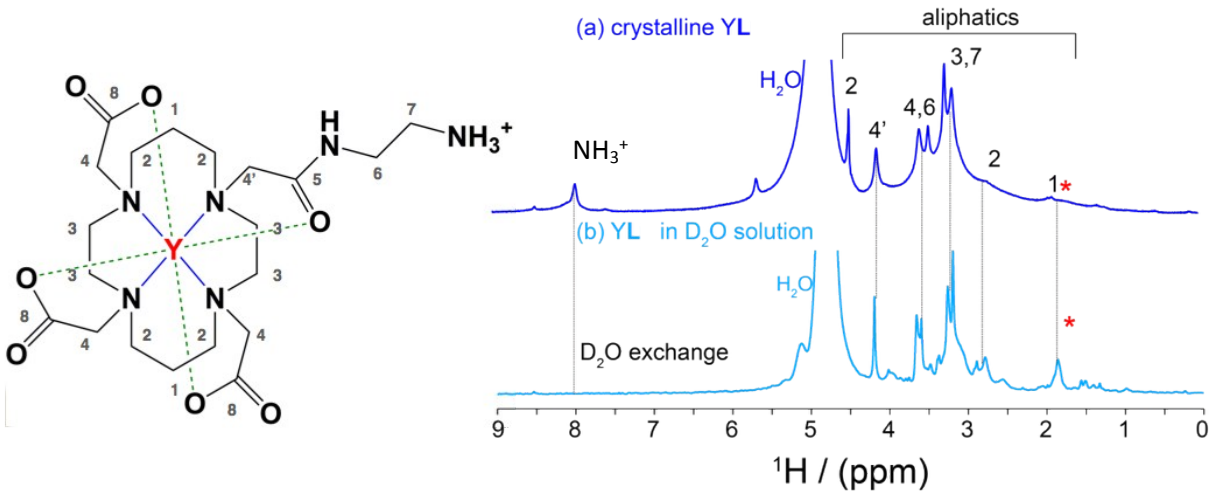


Figure S7. Comparison of 1D ^{1}H spectra acquired on the Y**L** complex in solid-state (a) and in D_2O solution (b). Both spectra were recorded at 11.7 Tesla, at room temperature. The solid-state NMR spectrum was acquired spinning the sample at 12 kHz in a 4 mm rotor.

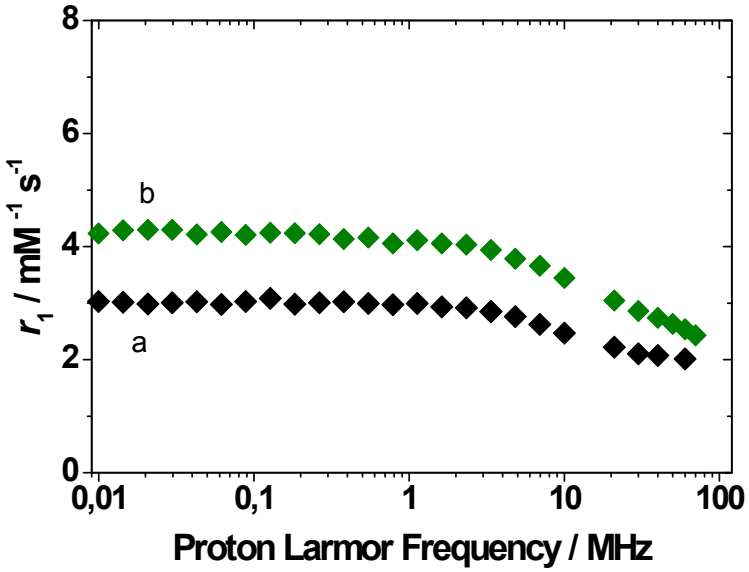


Figure S8. $1/T_1$ ^{1}H-NMRD profiles of GdTETA (a) and Gd**L** (b) at 298 K and neutral pH.

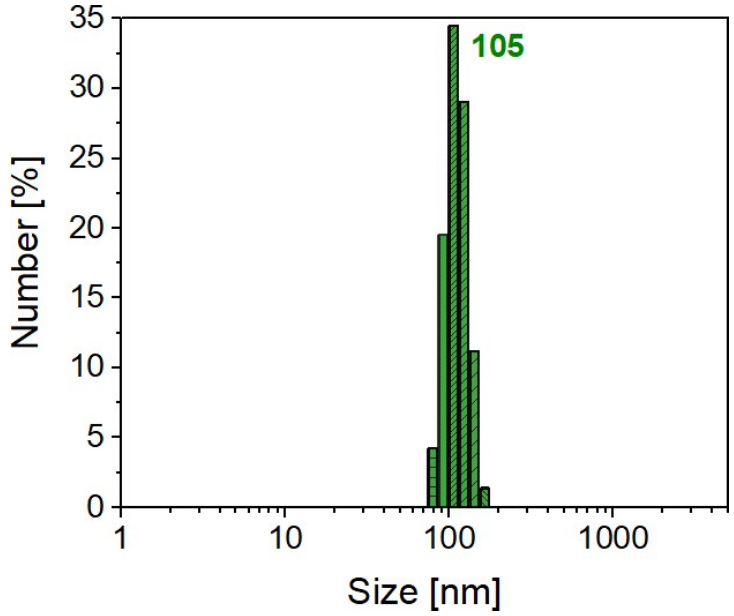


Figure S9. DLS analysis at 298 K of Gd**L**/SAP aqueous suspension containing 0.1 wt.% of xanthan gum.

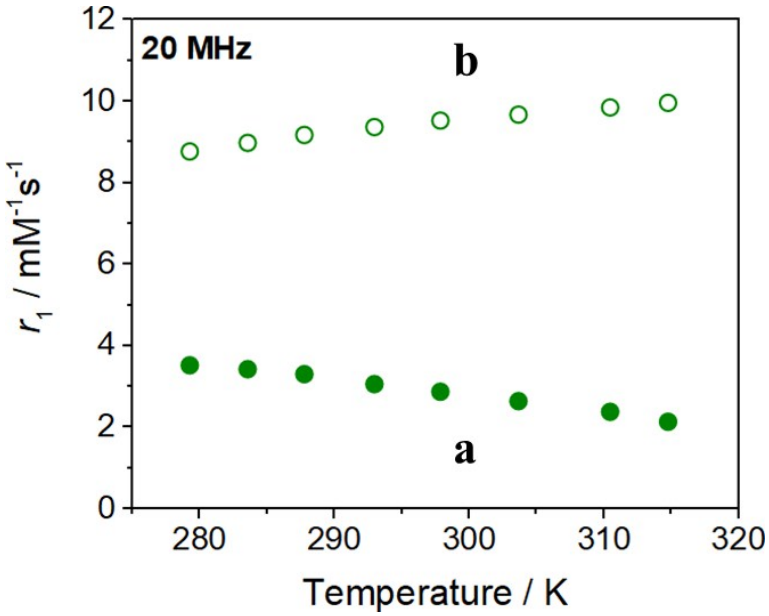


Figure S10. Variable-temperature dependence of r_1 for Gd**L** (a) and Gd**L**/SAP (b), at 20 MHz.

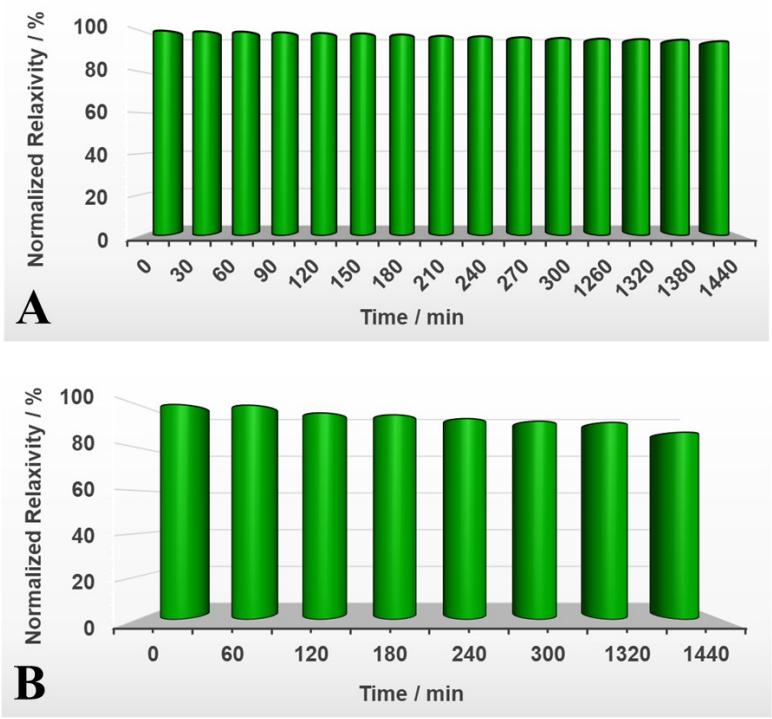


Figure S11. Plot of r_1 at 20 MHz and 310 K of Gd**L**/SAP in ultrapure water (A) and Human Serum matrix (Seronorm™) (B) over the time.

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