Supporting Information

Ultra-fast Ligand Self-Exchanging Gadolinium Complexes in Ionic Liquids as NMR Field Probes

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Table of Content

1. General Information

1.1 Materials

All air-and water sensitive materials were either prepared by general Schlenk technique under argon atmosphere or in a glovebox (nitrogen atmosphere). The glassware was dried by the use of a heat gun or in an oven at 160°C overnight. Pentane and toluene used were dried using a MBRAUN SPS solvent purification system. THF was distilled from potassium metal under nitrogen before use. Tetrachloroethane was bought from Sigma-Aldrich (≥ 98.0 %, 185434 Lot # BC3369V), distilled and stored over molecular sieve 4A and filtered through a PTFE syringe filter (0.22 μm, BGB Part Number: SF2504-1G) before use. Deuterated solvents were bought from ARMAR Chemicals and were distilled, dried and stored in the glovebox. All other chemicals were purchased and used without further purification.

1.2 Characterization

^{1}H and ^{19}F NMR spectra were recorded on a Varian V 300 (300 MHz) or a Bruker DRX 400 MHz or Bruker DRX 500 MHz NMR spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (δ 0.00) ppm using the residual proton solvent peaks as internal standards (1H NMR experiments). Coupling constants (J) are quoted in Hertz (Hz), multiplicity abbreviated as follows: s (singulet), d (doublet), t (triplet), q (quadruplet), qui (quintet), sex (sextet). T_1, T_2 and T_2* measurements were carried out on a Varian V 300 (300 MHz) spectrometer following a π, τ, $\pi/2$ pulse sequence for T_1 and a $\pi/2$,τ, π sequence for T_2 pulse sequence. ^{19}F NMR spectra were referenced to hexafluorobenzene (C_6F_6 at -165ppm).

Mass spectra were recorded by Electrospray-ionization ESI-MS using a direct injection method (DI) on a Bruker esquire TM/LC spectrometer. IR spectra were recorded on a Spectrum Two FT-IR Spectrometer (Perkin–Elmer) equipped with a Specac Golden Gate TM ATR accessory.

Viscosity measurements were performed on an Anton Paar MCR 102 rotational rheometer equipped with CP25-1 cone plate type measuring system.

1.3 X-Ray Crystallography

Single-crystal X-ray diffraction data were collected at 183 (1) K on a Rigaku OD Xcalibur/Ruby diffractometer using a single wavelength X-ray source (Mo K$_a$ radiation: l = 0.71073 Å or Cu K$_\alpha$ radiation: λ = 1.54184 Å)[1] from a micro-focus sealed X-ray tube and an Oxford liquid-nitrogen Cryostream cooler. The selected suitable single crystal was mounted using polybutene oil on a flexible loop fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption correction[2] were performed with the program suite *CrysAlisPro*.[3] Using *Olex2*,[4] the structure was solved with the SHELXS[5] small molecule structure solution program and refined with the *SHELXL2016/6* program package[6] by full-matrix least-squares minimization on F^2. *PLATON*[7] was used to check the result of the X-ray analysis. Supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (CCDC nr. 1531945 (**3**)/ 1557761 (**7**)/ 1587081 (compd. **4**). The main Gd species in compound **3** as well as Y in compound **7** are disordered at 85% and the counter-ion $C_{16}H_{36}N^+$ at 47%. The different positions of the disordered atoms could clearly be located but many SHELXL restraints (DFIX, SADI, DANG, SIMU) and constraints (EADP) had to be used to correct the geometry of the different components and the thermal parameters of the corresponding atoms during the final refinements. In the two compounds **3** and **7**, both molecules lie on two two-fold axes, only one quarter of each molecule had to be refined, the rest of the molecules were reproduced by symmetry operations. In structure X the H atoms bound to

the O atoms (H13a, H14 and H15) were located in the Fourier difference maps, introduced in the model and refined with a restraint on the O-H bond distance.

2. Synthetic procedures

2.1 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][NTf$_2$]
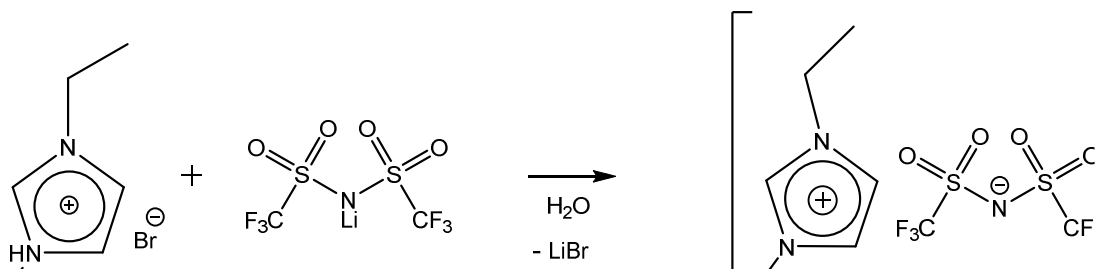
Scheme S1: *The Synthesis of [emim][NTf$_2$] was carried out in water by direct reaction of the respective bromo/lithium species of the imidazolium derivative cation and the NTf$_2$ anion.*

1-Ethyl-3-methylimidazolium bromide (Sigma-Aldrich ≥ 97.0 %, 15g, 76.9 mmol) was treated with LiNTf$_2$ (TCI > 98.0 %, 27 g, 92.3 mmol, 1.2 eq) in H$_2$O under stirring for 4 h. This produced a colorless solution which separated into two phases and was extracted with CH$_2$Cl$_2$ (200 ml). The organic phase was repeatedly extracted with water (~10·100ml) until no precipitation of AgBr with AgNO$_3$ could be detected anymore. The organic layer was thereafter dried over MgSO$_4$ and the solvent removed. This product was then dried under HV for 48h supported by heating to 100 °C several times. [emim][NTf$_2$] (27.8 g, 76.9 mmol) was produced in a yield of 92 % as a colorless liquid.

NMR: ^{1}H NMR (400 MHz, CD$_3$CN) δ ppm: 8.43 (s, 1H, N=C*H*-N); 7.38 (dt, J = 21.7/1.5, 2H, NC*HCH*N); 4.19 (q, J = 13.5, 2H, NC*H$_2$*CH$_3$); 3.84 (s, 3H, C*H$_3$*); 1.48 (t, J = 7.3, 3H, NCH$_2$C*H$_3$*).

^{19}F NMR (376.5 MHz, CD$_3$CN) δ ppm: -80.57 (s, 6F, CF$_3$).

ESI-MS: positive mode: 111.09 ([emim]$^+$), negative mode: 279.92 ([NTf$_2$]$^-$)

2.2 1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [amim][NTf$_2$]
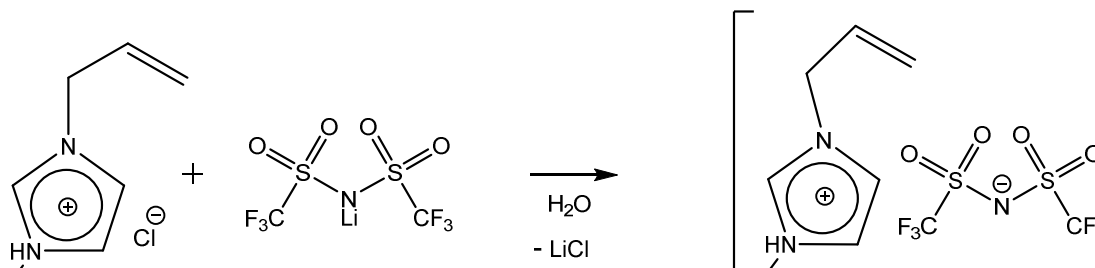
Scheme S2: *The Synthesis of [amim][NTf$_2$] was carried out in water by direct reaction of the respective chloro/lithium species of the imidazolium derivative cation and the NTf$_2$ anion.*

The compound was synthesized along the same method as described for [emim][NTf$_2$]. 1-Allyl-3-methylimidazolium chloride (abcr, 98%, 12 g, 74.1 mmol) reacted with LiNTf$_2$ (TCI > 98.0 %, 26 g, 88.8 mmol, 1.2 eq) resulted in [amim][NTf$_2$] as a colorless liquid in a 95.8% yield (28.6 g, 70.89 mol).

NMR: ^{1}H NMR (300 MHz, CD$_3$CN) δ ppm: 8.40 (s, 1H, N=CH-N); 7.34 (dt, J = 21.7/1.5, 2H, NCHCHN); 6.01 (m, 1H, CH$_2$=CH-CH$_2$); 5.41 (d, 1H, J = 9.6, CH_2(trans)=CH-CH$_2$); 5.35 (d, 1H, J = 16.5, CH_2(cis)=CH-CH$_2$); 4.74 (dt, 2H, J = 6/1.2, N-CH_2-CH=CH$_2$); 3.84 (s, 3H, CH_3).

^{19}F NMR (282.375 MHz, CD$_3$CN) δ ppm: -80.77 (s, 6F, CF$_3$).

^{19}F NMR (282.375 MHz, pure AllylMIm triflimide with Hexafluorobenzene as internal reference) δ ppm: -80.36 (s, 6F, CF$_3$); -165 (s, 6F, Hexafluorobenzene).

ESI-MS: positive mode: 123.1([amim]$^+$), negative mode: 279.92 ([NTf$_2$]$^-$)

## 2.3 Gadolinium tris-trimethylsilazane [Gd(bta)$_3$] (1)
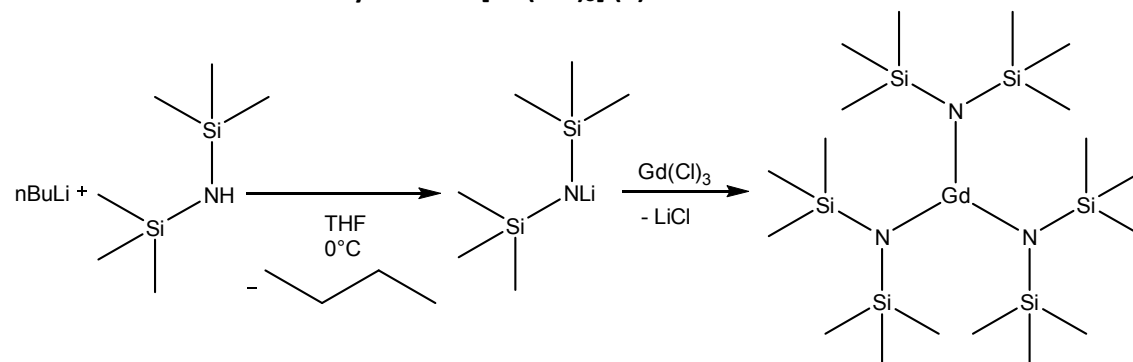
**Scheme S3**: *Preparation of Gd(bta)$_3$ **1** via preliminary lithiation of hexamethyldisilizane by nBuLi in THF at 0°C.*

HN(SiMe$_3$)$_2$ (Sigma-Aldrich, ≥ 99%, 9.24 ml, 7.02 g, 43.5 mmol) was dissolved in dry THF (5 ml) and a solution of 1.6 M nBuLi in THF (Sigma-Aldrich, ≥ 99%, 27.2 ml, 43.5 mmol) was added dropwise at 0°C. This solution was then slowly transferred to GdCl$_3$ (Acros anhydrous, 99.9 %, 3.60 g, 13.7 mmol) in THF (5 ml) at 0° and stirred for 24 h. The solvent was removed under reduced pressure and the residual solid extracted with pentane (25 ml). Filtration (PTFE syringe filter) and removal of the organic layer gave [Gd(bta)$_3$] (6.92 g, 10.84 mmol) in 79.7 % yield.

IR (neat): 2949w ν(CH); 1239s ν(SiC); 1045m; 961s ν$_a$(NSi); 822s σ(Si(CH$_3$)$_3$.
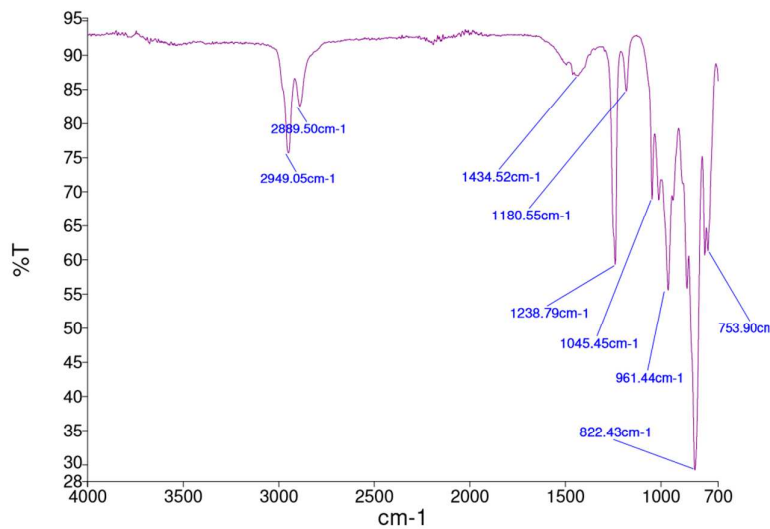
**Figure S1**: *IR spectrum of [Gd(bta)$_3$] (**1**)*

2.4 Gadolinium tris-(bis-(trifluoromethylsulfonyl)imide) [Gd(NTf$_2$)$_3$] (2)
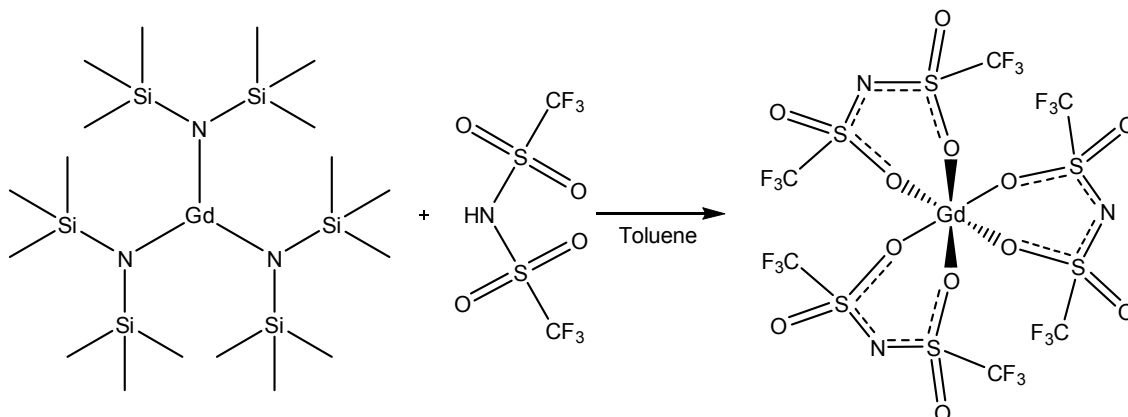
**Scheme S4**: *Synthetic pathway to Gd(NTf$_2$)$_3$* **2** *starting from the Gd(bta)$_3$* **1**.

[Gd(NTf$_2$)$_3$] **2** was prepared from the previously prepare Gd(bta)$_3$. Compound **1** (6.5 g, 10.2 mmol) was dissolved in dry toluene and Tf$_2$NH (Apollo Scientific, 10 g, 35.7 mmol), separately dissolved in toluene, was added into a Schlenk flask. Stirring was continued for 2h at r. t. During the addition of the acid, the formation of a white precipitate immediately started. The precipitate settled and the solvent layer was decanted. The precipitate was washed three times with 100 ml toluene. The Schlenk flask then dried under reduced pressure whilst stirring and heating to 100 °C for 24h resulting in a white powder of [Gd(NTf$_2$)$_3$] (7.26 g, 7.277 mmol, 71%).

IR (neat): 1331s ν_s(CF); 1195s ν_a(CF); 1110s ν_s(SO$_2$); 1048s ν_a(SNS).
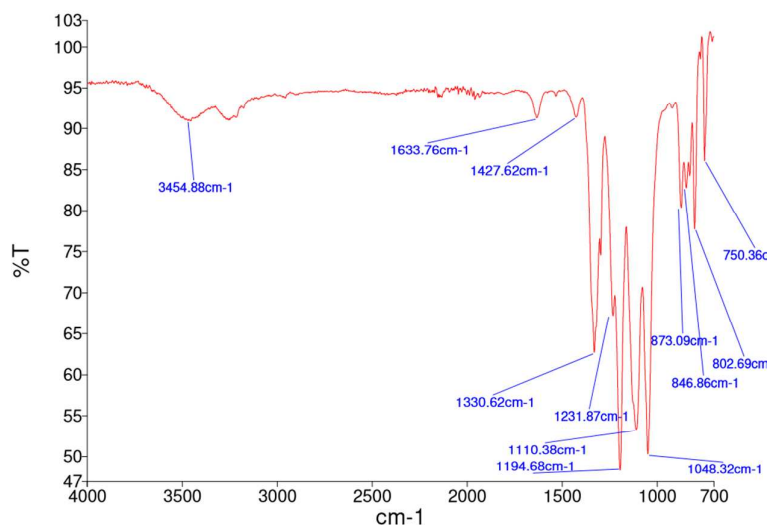
Figure S2: *IR spectrum of Gadolinium tris-(bis-(trifluoromethylsulfonyl)imide) [Gd(NTf$_2$)$_3$]* **2**

2.5 Tetrabutylammonium Gadolinium tetrakis-(bis-(trifluoromethylsulfonyl)imide) [N^{n}Bu$_4$][Gd(NTf$_2$)$_4$] (3)
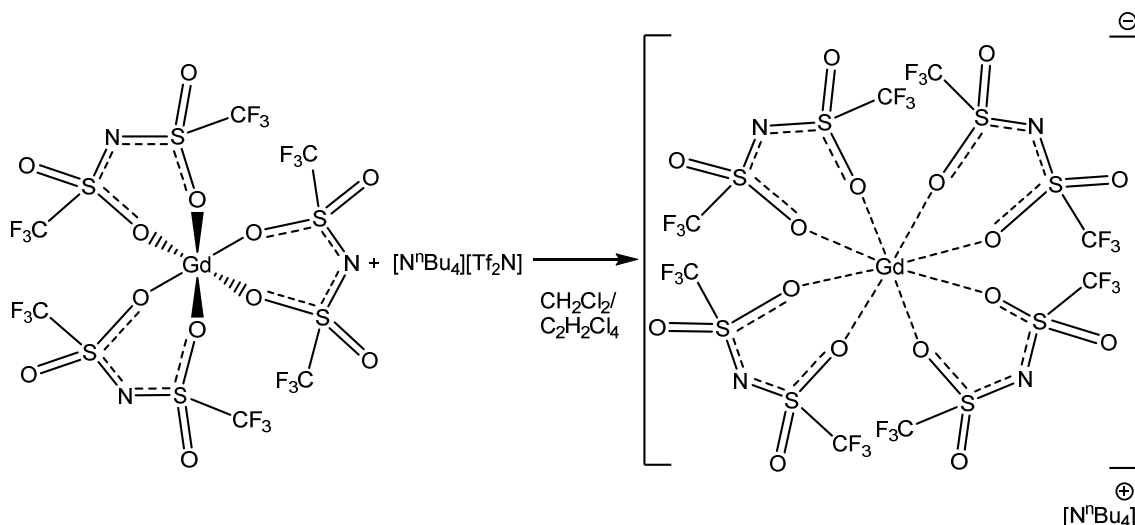
Scheme S5: *Synthetic procedure to [N^{n}Bu$_4$][Gd(NTf$_2$)$_4$]* **3**

[Gd(NTf$_2$)$_3$] **2** (100.2 mg (0.1 mmol) was reacted over night with [N^{n}Bu$_4$][NTf$_2$] (52.3 mg, 0.1 mmol) in dry CH$_2$Cl$_2$ or tetrachloroethane. The solution was filtered through a PTFE syringe filter strongly under N$_2$.The solvent was slowly evaporated which resulted in colorless crystals (plates). NMR spectroscopy was performed with the CH$_2$Cl$_2$ mother liquor or in d^6-acetone with hexafluorobenzene as internal standard.

NMR: ^{1}H NMR (300 MHz, d^6-acetone) δ ppm: 3.4 − 3.32 (br m, 8H, NC*H$_2$*CH$_2$); 1.8 − 1.7 (br m, 8H, C*H$_2$*CH$_2$CH$_3$); 1.41 (dt, 8H, J = 7.5, CH$_2$C*H$_2$*CH$_3$); 0.965 (t, 12H, J = 7.5, CH$_2$C*H$_3$*).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ ppm: 3.71 − 3.49 (br m, 8H, NC*H$_2$*CH$_2$); 2.93 − 2.70 (br m, 8H, C*H$_2$*CH$_2$CH$_3$); 1.94 − 1.69 (br m, 8H, CH$_2$C*H$_2$*CH$_3$); 0.92 (t, 12H, J = 7.5, CH$_2$C*H$_3$*).).

^{19}F NMR (282.375 MHz, d^6-acetone with hexafluorobenzene) δ ppm: -80.88 (s, 24F, CF$_3$); -165 (s, hexafluorobenzene).

^{19}F NMR (376.5 MHz, CH$_2$Cl$_2$) δ ppm: − 92.2 (m, 24F, CF$_3$).
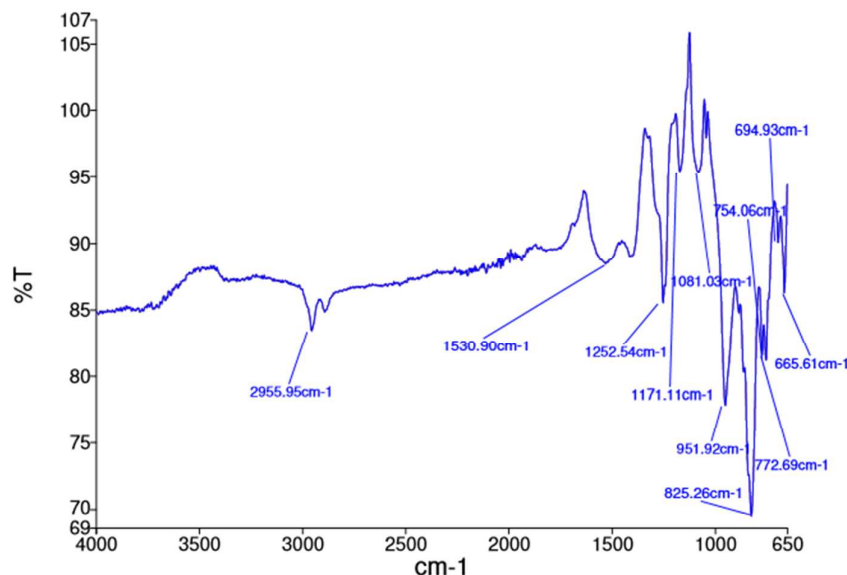
2.6 Yttrium tris-trimethylsilazane [Y(bta)$_3$] (5)
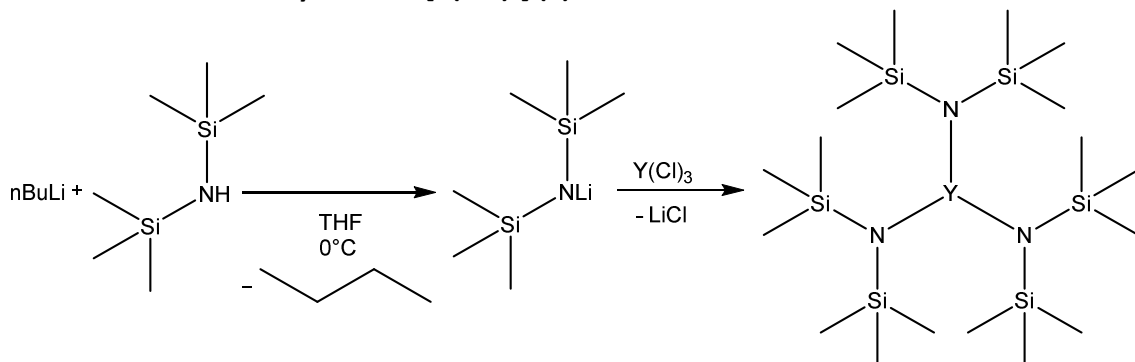
Scheme S6: *Preparation of Y(bta)$_3$* **5** *via preliminary lithiation of hexamethyldisilizane by nBuLi in THF at 0°C.*

HN(SiMe$_3$)$_2$ (1.9 ml, 1.43 g, 8.88 mmol) was dissolved in dry THF (3 ml) and a solution of 1.6 M ^{n}BuLi in THF (Sigma-Aldrich, ≥ 99%, 5.55 ml, 8.88 mmol) was added dropwise at 0°C under argon. This solution was then slowly added to YCl$_3$ (Sigma 0.5 g, 2.56 mmol) in THF (2 ml) at 0°C under argon and stirred for 24 h. The solvent was removed under reduced pressure and the solid residual extracted with pentane (10 ml). Filtration (PTFE syringe filter) and removal of the organic solvent gave [Y(bta)$_3$] (1.43 g, 2.51 mmol) in 98 % yield.

IR (neat): 2955w ν(CH); 1252s ν(SiC); 1081m; 952s ν$_a$(NSi); 825s σ(Si(CH$_3$)$_3$.

Figure S3: *IR spectrum of Yttrium tris-trimethylsilazane [Y(bta)$_3$]* **5**

2.7 Yttrium tris-(bis-(trifluoromethylsulfonyl)imide) [Y(NTf$_2$)$_3$] (6)
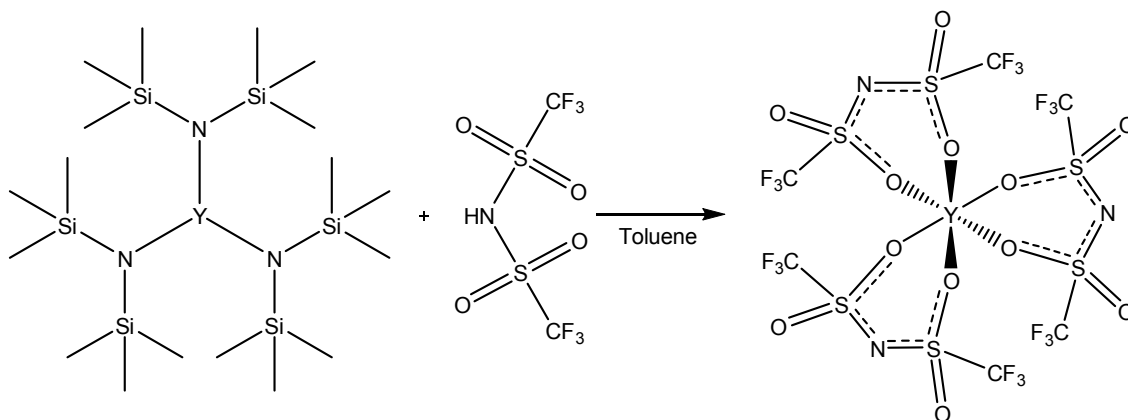
**Scheme S7**: *Synthetic pathway of Y(NTf$_2$)$_3$* **6** *starting from the Y(bta)$_3$* **5** *species.*

[Y(NTf$_2$)$_3$] **6** was prepared from Y(bta)$_3$ **5** (1.2 g, 2.11mmol) in analogy to **2** with 2.08 g, 7.38 mmol Tf$_2$NH. The reaction gave [Y(NTf$_2$)$_3$] **6** as a white powder (1.98 g, 1.985 mmol, 94%).

IR (neat): 1325s ν$_s$(CF); 1200s ν$_a$(CF); 1133s ν$_s$(SO$_2$); 1047s ν$_a$(SNS).
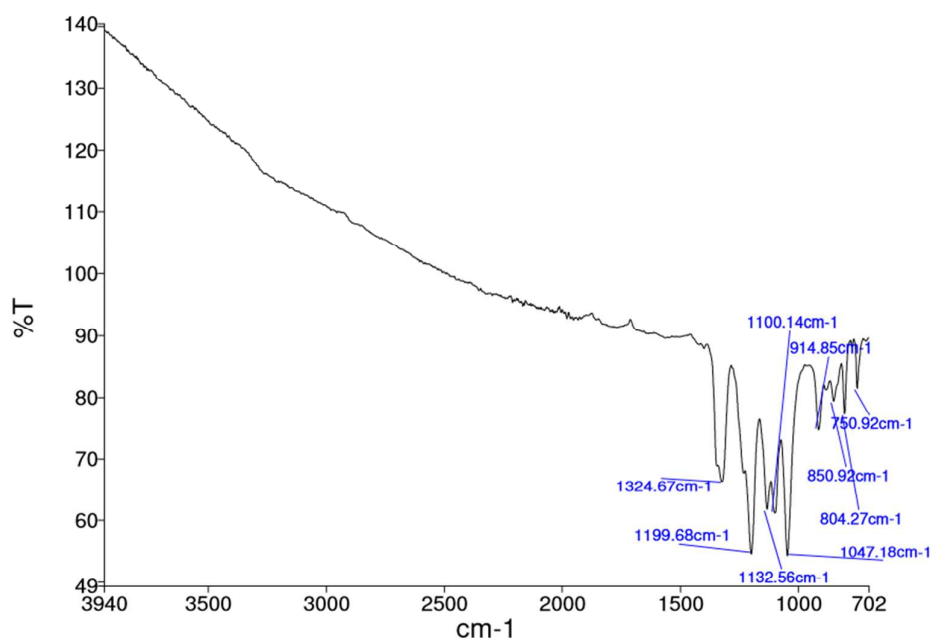
Figure S4: IR spectrum of Yttrium tri(bis(trifluoromethylsulfonyl)imide) [Y(NTf₂)₃] 6

2.8 Tetrabutylammonium Yttrium tetrakis-(bis-(trifluoromethylsulfonyl)imide) [N^{n}Bu$_4$][Y(NTf$_2$)$_4$] (7)
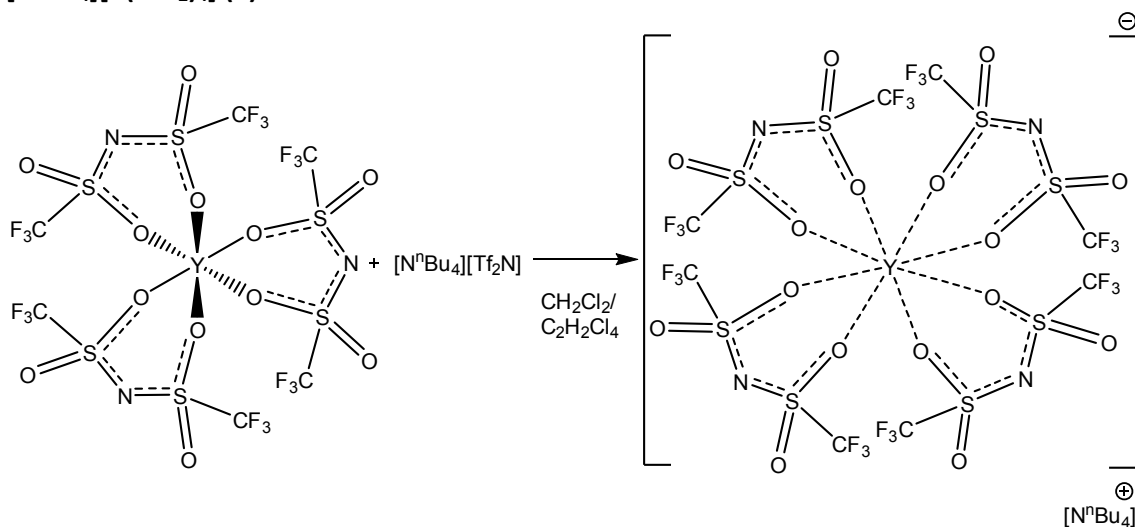
Scheme S8: Synthetic procedure to [N^{n}Bu$_4$][Y(NTf$_2$)$_4$] 7

[Y(NTf$_2$)$_3$] **6** (49.7 mg (0.0535 mmol) was reacted over night with [N^{n}Bu$_4$][NTf$_2$] (28 mg, 0.054 mmol) in dry tetrachloroethane. The solution was filtered through a PTFE syringe filter. Slow evaporation of solvent resulted in colorless crystals. NMR was performed with a 0.1 ml tetrachloroethane solution in d^6-acetone and hexafluorobenzene as internal reference.

NMR: ^{1}H NMR (300 MHz, d^6-acetone) δ ppm: 3.8 – 3.39 (br m, 8H, NCH_2CH$_2$); 1.9 – 1.75 (br m, 8H, CH_2CH$_2$CH$_3$); 1.436 (dt, 8H, J = 7.2, CH$_2$CH_2CH$_3$); 0.983 (t, 12H, J = 7.2, CH$_2$CH_3).

^{19}F NMR (282.375 MHz, d^6-acetone with hexafluorobenzene) δ ppm: -80.388 (s, 24F, CF$_3$); -165 (s, hexafluorobenzene).

3. Analytical Section

3.1 Preparation of Gd(NTf$_2$)$_3$ 2 and Y(NTf$_2$)$_3$ 6 solutions

The solutions of ionic liquids and compounds **3** and **6** respectively for any experiment where always prepared in the following manner, strictly under N$_2$ or Ar:

The compound was weighed into a vial, containing a magnetic stir bar. Then, the required amount of ionic liquid was added and the total weight taken. The mixtures were stirred for at least 24h until dissolution was complete. Subsequently, the solutions were always filtered through a PTFE syringe filter before further use.

3.1.1 Density measurements and concentration calculation Gd(NTf$_2$)$_3$ 2 solutions

The Gd^{3+} and F concentrations of the solutions were calculated taking the volume and density changes into account. The densities of the pure ionic liquids and of each of the solutions was experimentally determined by carefully weighing at least 10 different samples, 0.5ml volume each. Average and standard deviations were then calculated.

Example for the highest concentration Gd(NTf$_2$)$_3$:

Experimentally determined **density ρ_{exp}=1.625 g/cm^3** after dissolving 0.6003 g Gd(NTf$_2$)$_3$ (0.6017 mmol Gd, mw=997.7 g/mol and 10.83 mmol F) in 1ml pure [emim] [NTf$_2$] (ρ_{av}=1.526 g/ml, 1.526g, mw=391g/mol, 23.4mmol F).

ρ_{exp} and total mass (2.126g) give the final volume of the solution = 1.308ml.

This volume comprises 23.4+10.83mmol F which results in an overall fluoride concentration of 26M.

The Gd^{3+} and F concentrations determined according to this method after experimental density measurements but with different amounts of Gd(NTf$_2$)$_3$ correlate linearly as shown in figure 5 for emim.

Intercept = 17.62737, Slope = 0.24988
X Intercept = -70.5435
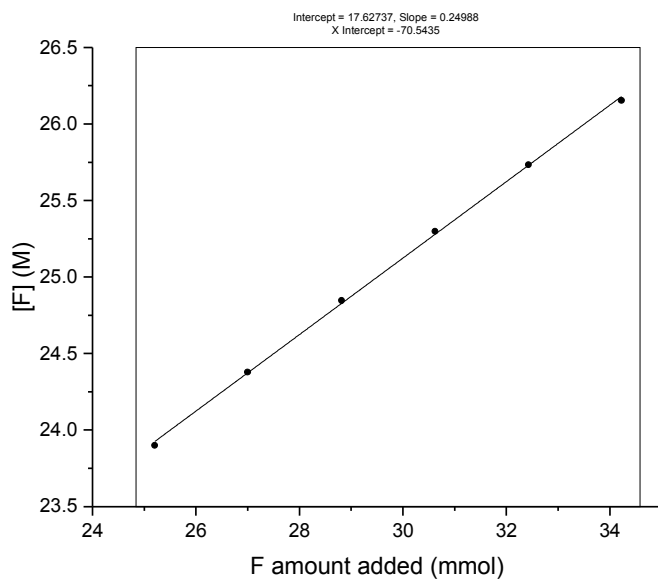
*Figure S5*: Linear relation between added amount of compound *2* and resulting [F]

### 3.1.2 ^{19}F Relaxation time measurements

The relaxation times were measured following a $\pi, \tau, \pi/2$ pulse sequence (inversion-recovery) for T_1 and a $\pi/2, \tau, \pi$ sequence (spin echo experiment) for T_2. T_2^* was calculated from line-width at half height according to $T_2^* = 1/(\pi * \nu_{1/2})$. In general, the T_2 results revealed, that the spin echo experiment on the instrument is at the limit (the only exception was the dilution experiment). Therefore, the T_2^* values are more reliable. The measurements were done at 298 K and 313 K.

**^{19}F T_1 and T_2^* values for [amim][NTf$_2$] with increasing concentration in [Gd(NTf$_2$)$_3$] (2)**
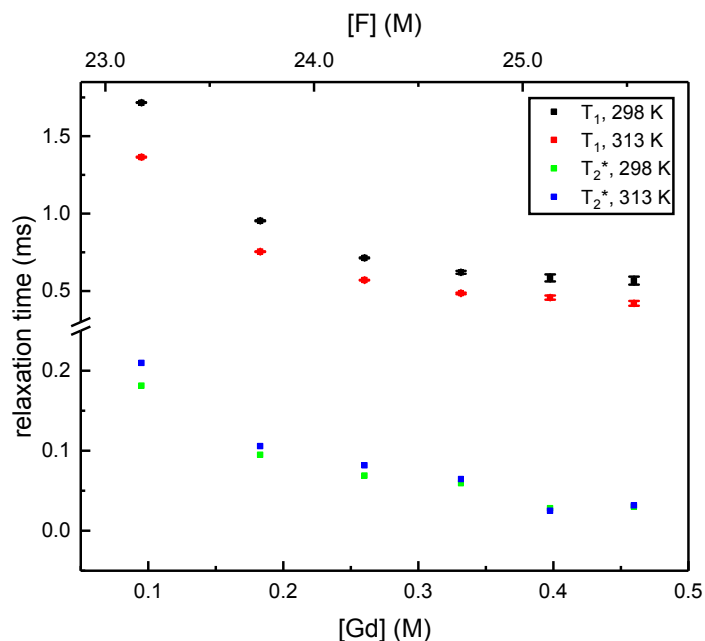
Figure S6: *Decrease of ^{19}F relaxation times T_1 and T_2^* with increasing [Gd]/[F] content from [Gd(NTf$_2$)$_3$] **2** at 298 K and 313 K*

^{19}F T_1 and T_2* values for [emim][NTf$_2$] with increasing concentration in [Gd(NTf$_2$)$_3$] (2)
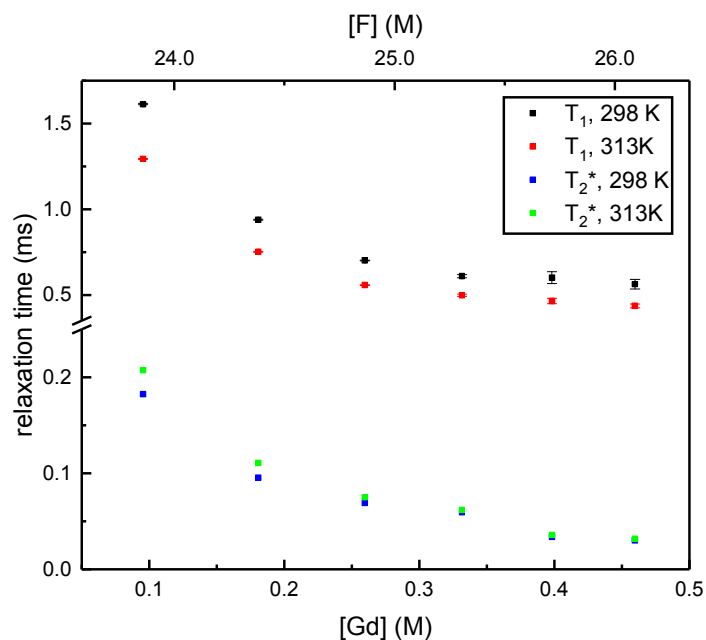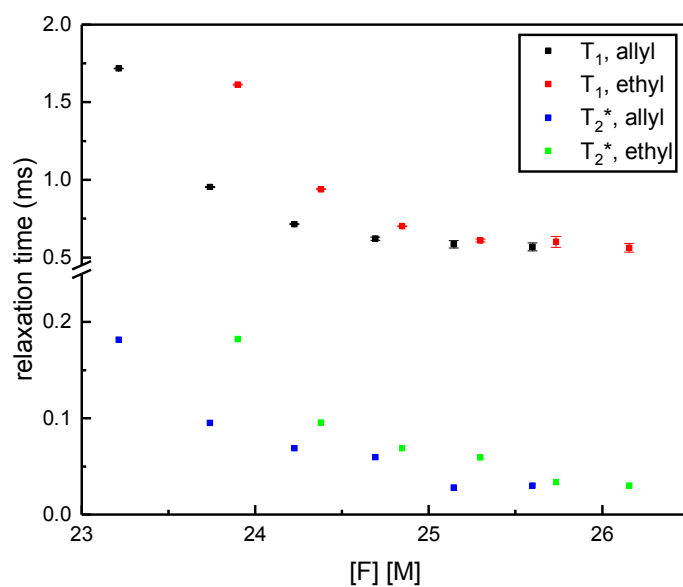

Figure S7: Decrease of ^{19}F relaxation times T_1 and T_2* with increasing [Gd]/[F] content from [Gd(NTf$_2$)$_3$] **2** at 298 K and 313 K

Comparison of ^{19}F T_1 and T_2* values for [emim][NTf$_2$] and [amim][NTf$_2$] at 298 K
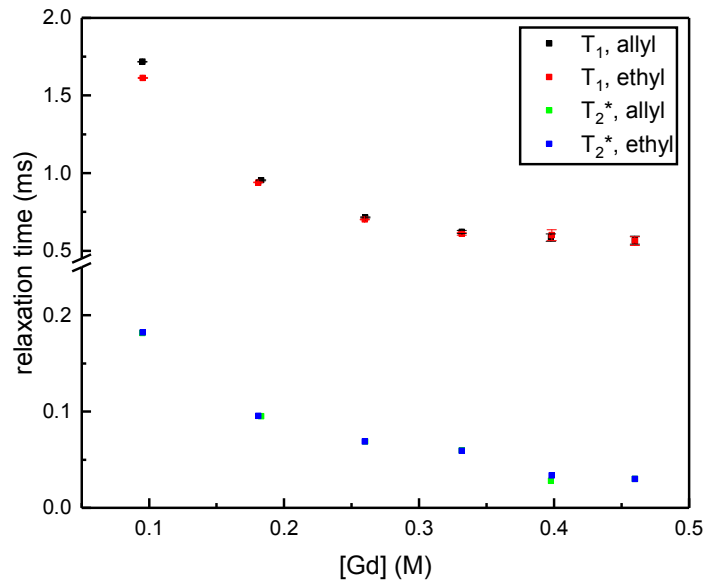
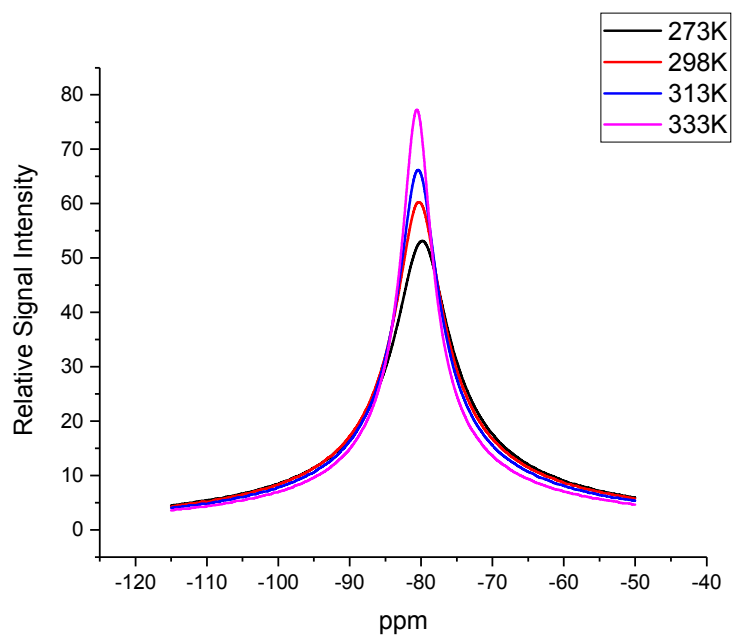*Figure S8*: Decrease of ^{19}F relaxation times T_1 and T_2* with increasing [Gd] content from [Gd(NTf$_2$)$_3$] **2** at 298 K

Figure S9*: Decrease of ^{19}F relaxation times T_1 and T_2* with increasing [F] content from [Gd(NTf$_2$)$_3$] **2** at 298 K*

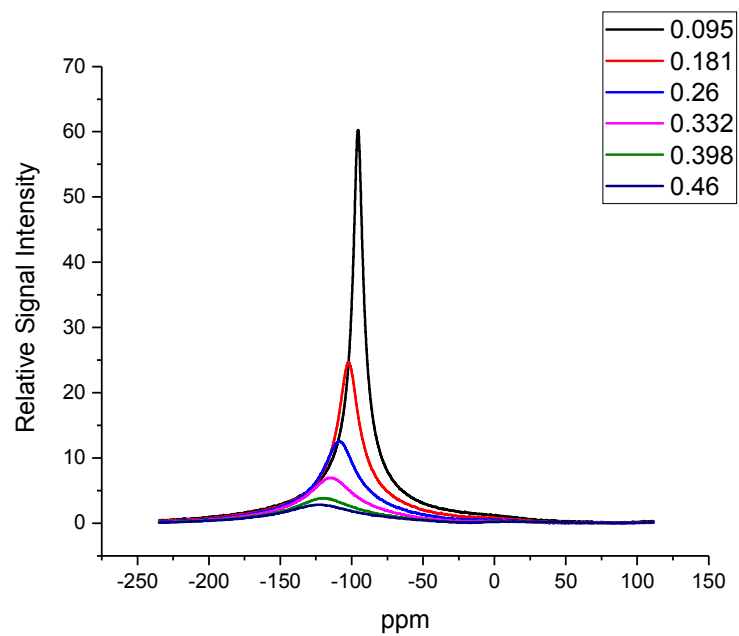**Temperature dependence of the ^{19}F-lineshape for [Gd(NTf$_2$)$_3$] (2) 0.095M and 0.46M in [emim][NTf$_2$]**

Figure S10: *Decrease of ^{19}F line width with temperature increase for 0.95 M [Gd(NTf$_2$)$_3$] **2** in [emim][NTf$_2$]*
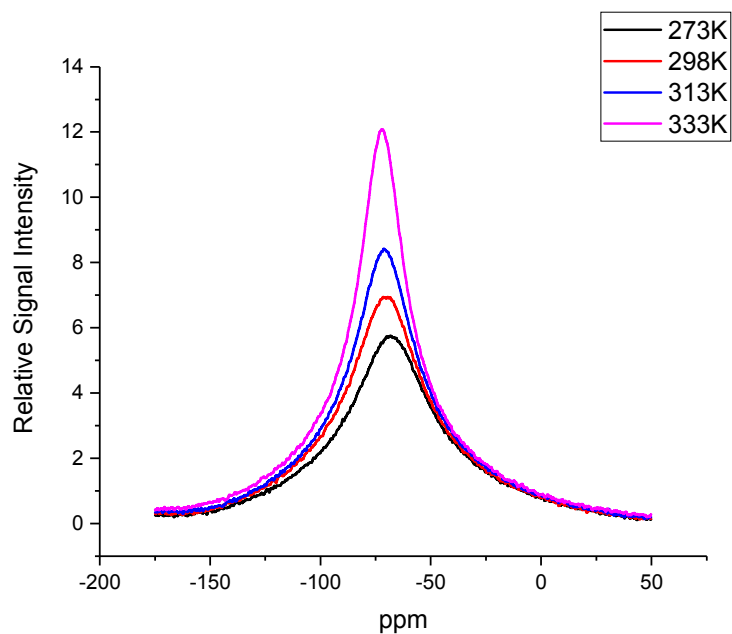
Figure S11: *Decrease of ^{19}F line width with temperature increase for 0.46 M [Gd(NTf$_2$)$_3$] **2** in [emim][NTf$_2$]*

***Figure S12***: *Increase of ^{19}F line width with increasing concentration of $[Gd(NTf_2)_3]$ **2** in $[emim][NTf_2]$ at 298 K*
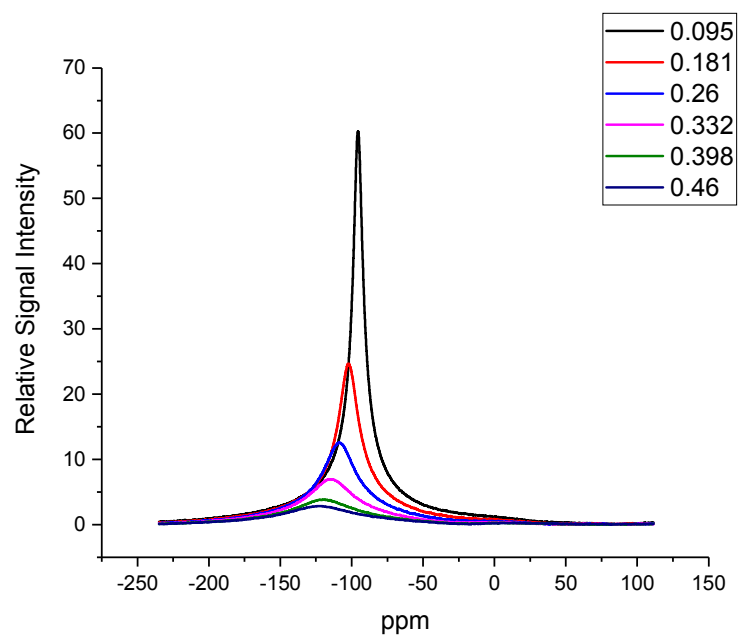
Figure S13: *Increase of ^{19}F line width with increasing concentration of $[Gd(NTf_2)_3]$ **2** in $[emim][NTf_2]$ at 313 K*

3.1.3 Relaxation times at constant [Gd^{3+}] and variable [F] concentration

The samples were prepared as follows: 0.1 mmol of the Gadolinium compound were weighed in the glovebox into vials equipped with magnetic stir bars and then dissolved in 1ml, 0.9ml, 0.8ml, 0.7ml, 0.6ml, 0.5ml, 0.4ml and 0.3ml of the ionic liquid. Overnight stirring ensured complete dissolution. The solvent volumes were then increased to 1ml by the addition of the appropriate amount of dichloromethane. Stirring was continued for 1h before filtration of the mixtures with syringe filters and transfer into NMR tubes. The relaxation time determinations were performed immediately thereafter.
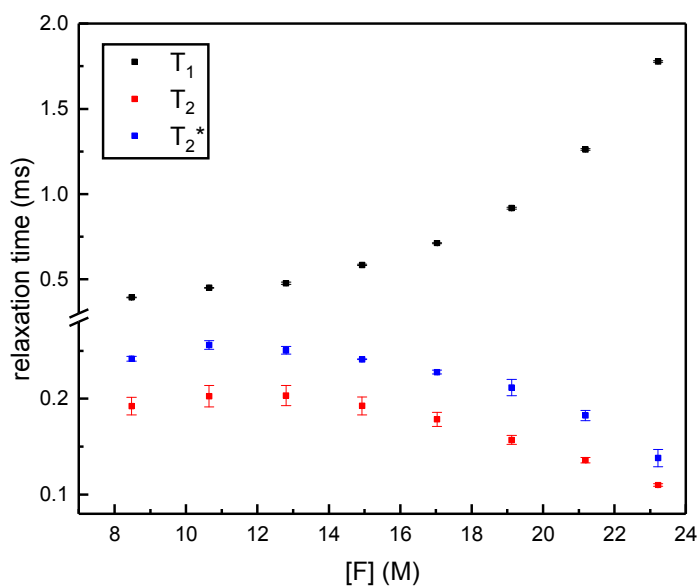

Figure S14: ^{19}F T1, T2 and T2* relaxation times at variable [F] (from [emim][NTf$_2$]) and constant [Gd^{3+}] ([Gd(NTf$_2$)$_3$] **2** 0.1M) concentrations.

3.1.4 Ligand exchange rate determination

To obtain the ligand exchange rate constant, an Arrhenius plot of the obtained/calculated half line widths was performed. The linear relation according to $\ln(\mathrm{k}) = -\left(\frac{Ea}{R}\right) * \left(\frac{1}{T}\right) + const.$ results in a slope of -2948.5 ± 138.2 $JK^{-1}\cdot mol^{-1}$; this according to $Ea = m * (-R)$ gives an activation energy of 24.5 $kJ\cdot mol^{-1}$.
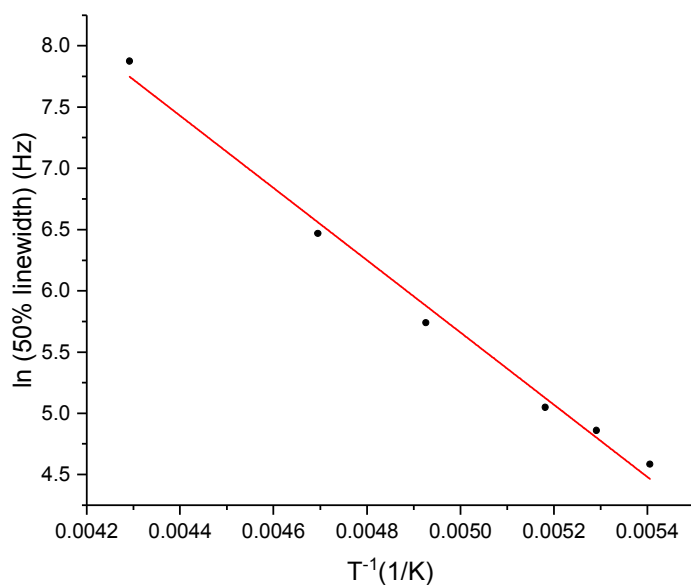
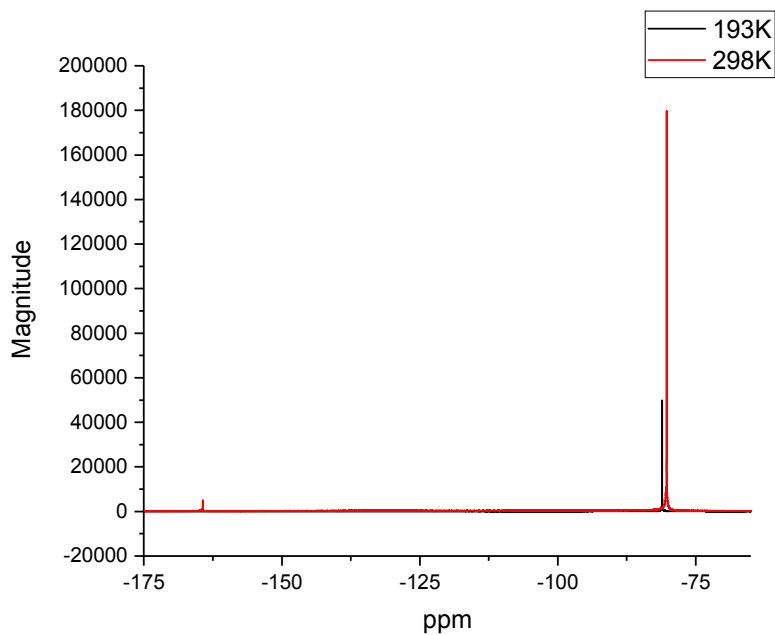***Figure S15****: Arrhenius plot showing the linear relationship between the half line widths of the ^{19}F signal (Hz) against T^{-1} (K^{-1}). Intercept: 20.4 ± 0.7 s^{-1} and slope: 2948.5 ± 138.2 K*mol*

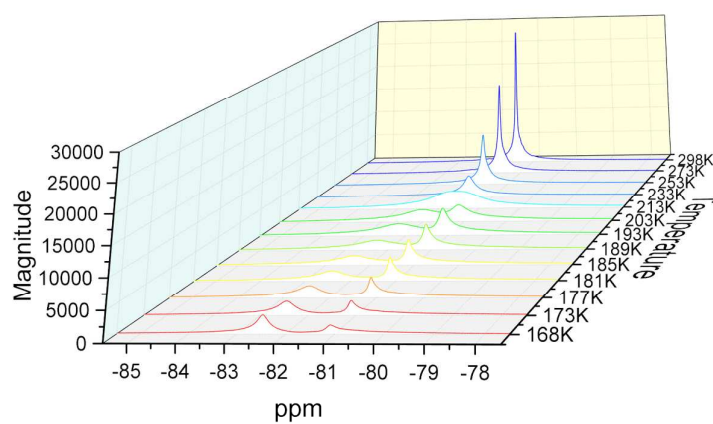**NMR spectra of pure [emim][NTf₂] and pure [Y(NTf₂)₃] 6 in CD₂Cl₂**
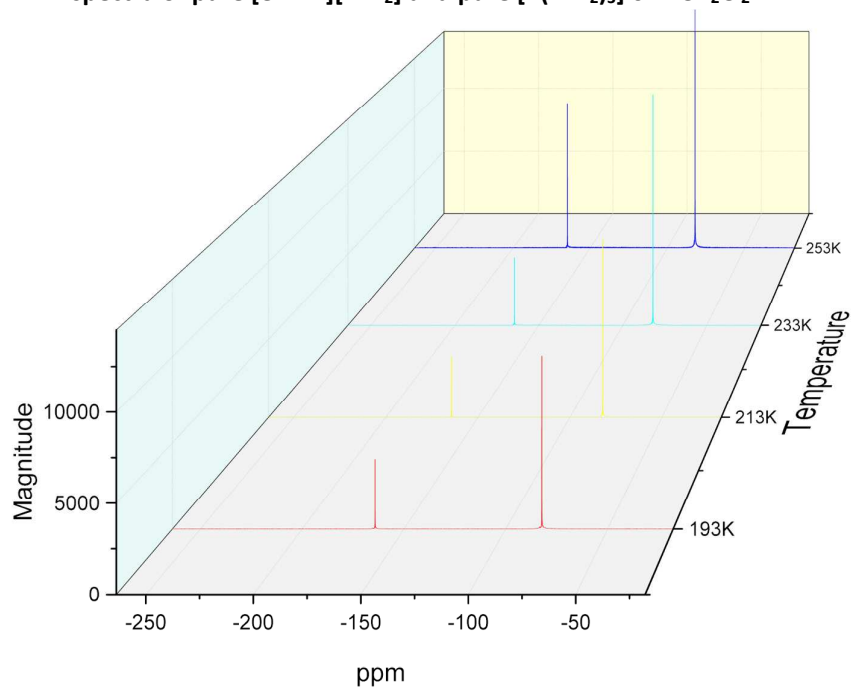
Figure S16*: ^{19}F NMR: 0.014M solution of [emim][NTf₂] in CD₂Cl₂ (referenced to hexafluorobenzene at -165 ppm)*

Figure S17*: ^{19}F NMR: 0.01M [Y(NTf₂)₃] in CD₂Cl₂ (referenced to hexafluorobenzene at -165 ppm)*

Solution of [emim][NTf₂] and [Y(NTf₂)₃] 6 in CD₂Cl₂ at bound/free ligand ratio of 19


Figure S18: Temperature dependence of ¹⁹F NMR spectra of 0.095mmol [Y(NTf₂)₃] and 0.015mmol [emim][NTf₂] dissolved in 1ml CD₂Cl₂

3.1.5 Viscosity determination

Viscosity determinations were carried out with the same samples as used for the relaxation time measurements. For every concentration and temperature, the measurements were repeated at least 3 times and the standard deviations for the obtained values were calculated. The samples were kept under argon. The measurements could not be performed under inert atmosphere but at exclusion of the atmosphere.

Viscosity of 2 in [amim][NTf$_2$] as a function of [Gd^{3+}] concentration
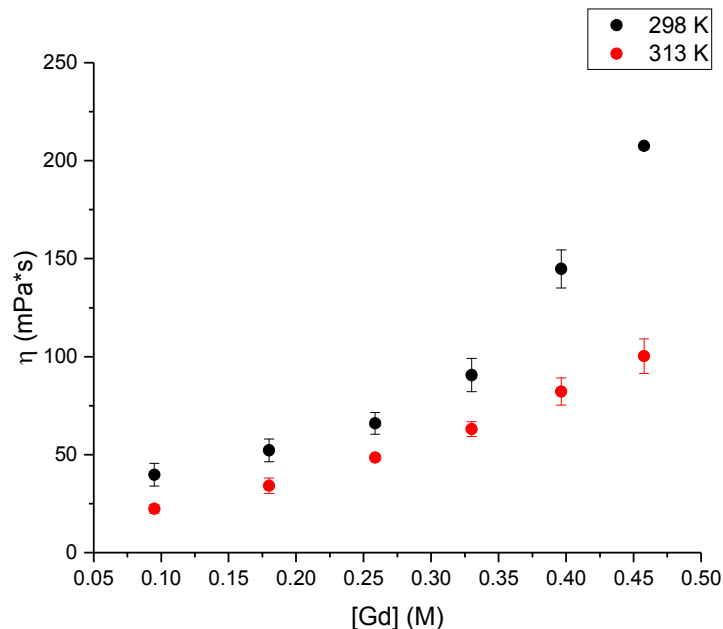
Figure S19: *Viscosity increase for [amim][NTf$_2$] IL as a function of increasing Gd(NTf$_2$)$_3$* **2** *concentrations.*
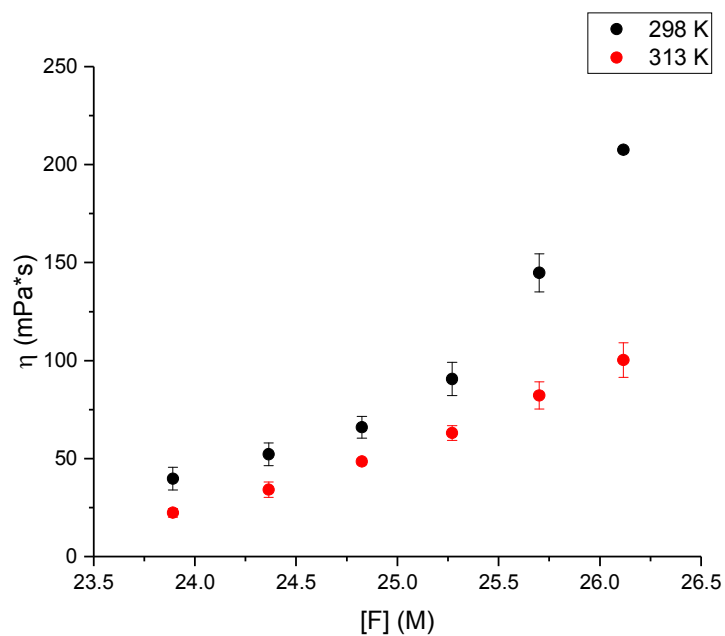
Figure S20: *Viscosity increase for [amim][NTf₂] IL as a function of increasing [F] concentrations (from Gd(NTf₂)₃ **2**).*
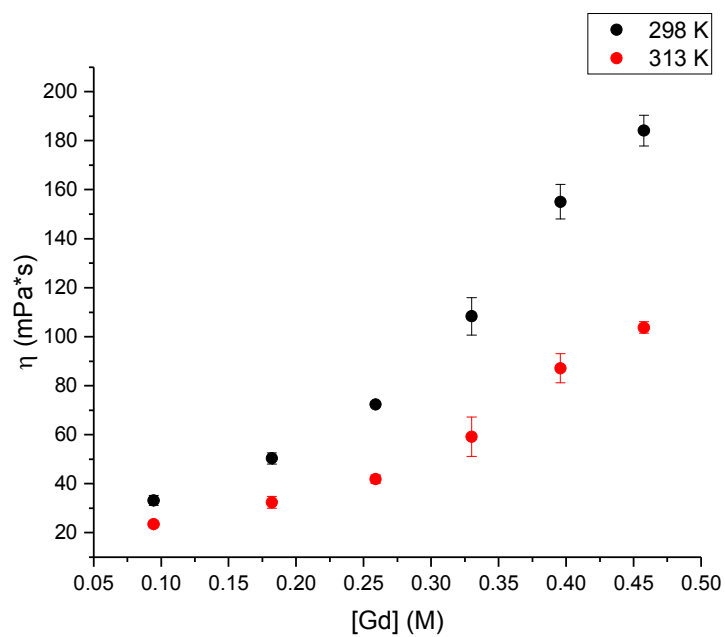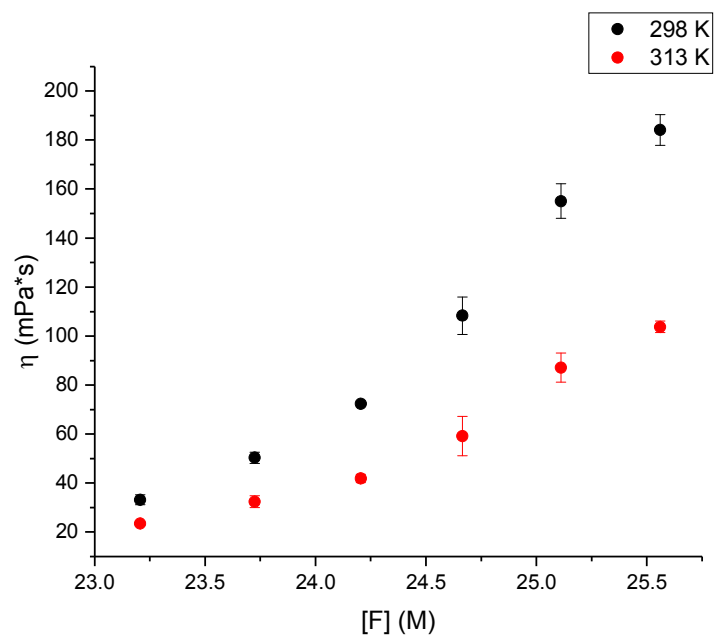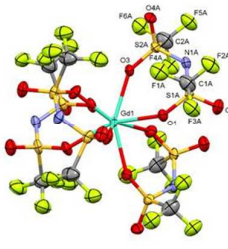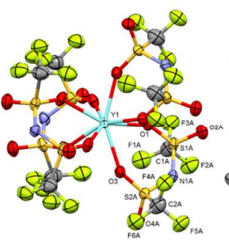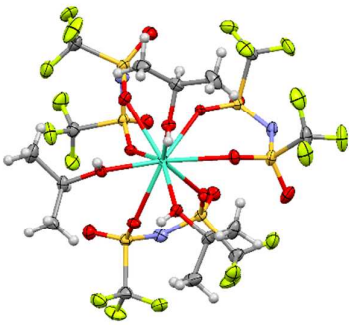
[emim][NTf₂]

Figure S21: *Viscosity increase for [emim][NTf₂] IL as a function of increasing Gd(NTf₂)₃ **2** concentrations.*

Figure S22*: Viscosity increase for [emim][NTf$_2$] IL as a function of increasing [F] concentrations (from Gd(NTf$_2$)$_3$ **2**).*

3.1.6 Crystal data of [N^{n}Bu$_4$][Gd(NTf$_2$)$_4$] (3), [N^{n}Bu$_4$][Y(NTf$_2$)$_4$] (7) and [Gd(NTf$_2$)$_3$ (HO-isoprop)$_3$] (4)

Empirical formula	C$_{24}$H$_{36}$F$_{24}$GdN$_5$O$_{16}$S$_8$	C$_{24}$H$_{36}$F$_{24}$N$_5$O$_{16}$S$_8$Y
Formula weight	1520.31	1451.97
Temperature/K	183(1)	183(1)
Crystal system	tetragonal	tetragonal
Space group	I4$_1$/acd	I4$_1$/acd
a/Å	18.6858(8)	18.66368(14)
b/Å	18.6858(8)	18.66368(14)
c/Å	31.7229(11)	31.6767(3)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	11076.3(10)	11034.0(2)
Z	8	8
ρ$_{calc}$g/cm^3	1.823	1.748
μ/mm^{-1}	1.640	5.650
F(000)	6008.0	5808.0
Crystal size/mm^3	0.50 × 0.11 × 0.06	0.23 × 0.09 × 0.07
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.04 to 50.68	8.722 to 136.48
Index ranges	-22 ≤ h ≤ 17, -19 ≤ k ≤ 22, -38 ≤ l ≤ 38	-22 ≤ h ≤ 22, -22 ≤ k ≤ 14, -38 ≤ l ≤ 35
Reflections collected	20726	16267
Independent reflections	2546 [R$_{int}$ = 0.0521, R$_{sigma}$ = 0.0255]	2536 [R$_{int}$ = 0.0303, R$_{sigma}$ = 0.0209]
Data/restraints/parameters	2546/425/298	2536/425/298
Goodness-of-fit on F^2	1.050	1.057
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0507, wR$_2$ = 0.1363	R$_1$ = 0.0689, wR$_2$ = 0.1940
Final R indexes [all data]	R$_1$ = 0.0672, wR$_2$ = 0.1488	R$_1$ = 0.0726, wR$_2$ = 0.1973
Largest diff. peak/hole / e Å^{-3}	0.81/-0.92	0.78/-0.58
CCDC Nr.	1531945	1557761

Empirical formula	$C_{15}H_{24}F_{18}GdN_3O_{15}S_6$
Formula weight	1177.98
Temperature/K	183(1)
Crystal system	monoclinic
Space group	P2$_1$/c
a/Å	12.4392(5)
b/Å	19.8475(7)
c/Å	16.7067(6)
α/°	90
β/°	110.015(4)
γ/°	90
Volume/Å^3	3875.5(3)
Z	4
ρ_{calc}g/cm^3	2.019
μ/mm^{-1}	15.505
F(000)	2308.0
Crystal size/mm^3	0.15 × 0.05 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.18 to 148.998
Index ranges	-12 ≤ h ≤ 15, -24 ≤ k ≤ 24, -20 ≤ l ≤ 20
Reflections collected	43866
Independent reflections	7848 [R_{int} = 0.0922, R_{sigma} = 0.0608]
Data/restraints/parameters	7848/3/538
Goodness-of-fit on F^2	0.994
Final R indexes [I>=2σ (I)]	R$_1$ = 0.0415, wR$_2$ = 0.1191
Final R indexes [all data]	R$_1$ = 0.0528, wR$_2$ = 0.1251
Largest diff. peak/hole / e Å^{-3}	1.58/-0.77
CCDC Nr.	1587081

(1)   *Rigaku Oxford Diffraction*, 2015.
(2)   Clark, R. C.; Reid, J. S. The Analytical Calculation of Absorption in Multifaceted Crystals. *Acta Cryst. A* **1995,** *51*, 887-897.
(3)   *CrysAlisPro (version 1.171.39.13a), Rigaku Oxford Diffraction*, 2016.
(4)   Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009,** *42*, 339-341.
(5)   Sheldrick, G. M. A short history of SHELX. *Acta Cryst.* **2008,** *A64*, (1), 112-122.
(6)   Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst. C* **2015,** *71*, 3-8.
(7)   Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Cryst.* **2003,** *36*, 7-13.