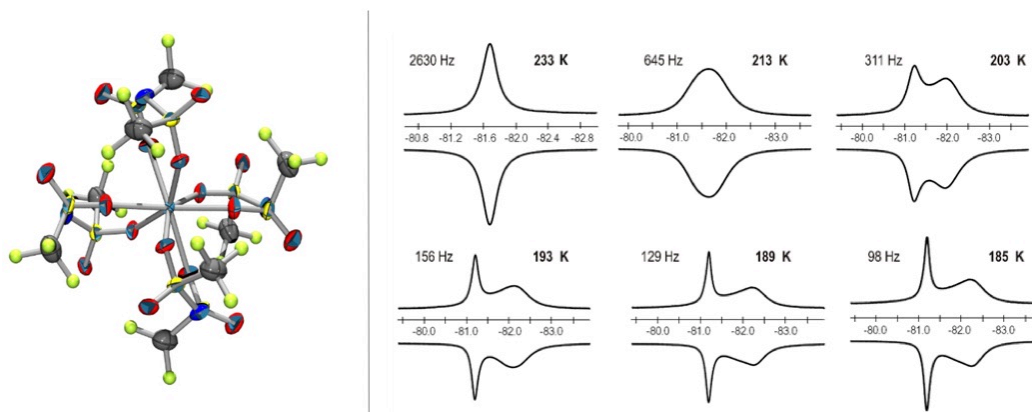


## Gadolinium Complexes Exhibiting Ultra-fast Ligand Self-exchange in Ionic Liquids for Application in NMR Field Probes

A. Looser<sup>1</sup>, S. Gross<sup>2</sup>, J. Nussbaum<sup>2</sup>, C. Barmet<sup>2,3</sup>, K. Prüssmann<sup>2\*</sup>, R. Alberto<sup>1\*</sup>

<sup>1</sup>Departement of Chemistry, University of Zürich, <sup>2</sup>Institute for Biomedical Engineering, University of Zürich, ETH Zürich, <sup>3</sup>Skope Magnetic Resonance Technologies LLC

The technology used in Magnetic Resonance Imaging (MRI) relies on the observation of nuclear magnetic resonance (NMR) during complex choreographies of time-varying magnetic fields. Hardware imperfections as well as other external perturbances influence these field evolutions, limiting image quality and the feasibility of high-performance methods. Continuous concurrent magnetic field monitoring<sup>1</sup> is a method for probing the spatiotemporal magnetic field evolution in an MR system by the usage of a set of NMR field sensors. For these sensors, highly homo-perfluorinated liquid compounds with short fluorine NMR relaxation times ( $T_1$  and  $T_2 < 1$  ms) are required. Effective relaxation enhancement requires a close contact between the  $^{19}\text{F}$  atoms and a paramagnetic centre – ideally in the first coordination sphere. Herein we present that a homo-perfluorinated ionic liquid in which the anions also act as ligands for the paramagnetic metal complex, offers such a possibility. The model Gd(III) complex  $[\text{N}^n\text{Bu}_4][\text{Gd}(\text{Tf}_2\text{N})_4]$  ( $\text{Tf}_2\text{N}^- = \text{bis}(\text{trifluoromethylsulfonyl})\text{imide}$ ), obtained from the reaction of its precursor  $[\text{Gd}(\text{NTf}_2)_3]$  with  $[\text{N}^n\text{Bu}_4](\text{NTf}_2)$ , shows the extension of the coordination sphere from six to eightfold with transoid configuration of the  $\text{NTf}_2$  ligands. Hence, the solution of the  $[\text{Gd}(\text{NTf}_2)_3]$  in ionic liquids of the triflimide type  $[\text{cat}^+][\text{Tf}_2\text{N}^-]$  ( $\text{cat}^+ = \text{AMIm} = 1\text{-allyl-3-methylimidazolium}$ ,  $\text{EthylMIm}$  or  $\text{PR}_3\text{R}'^+$ ) is shown (by evaluation of exchange rates of the non-paramagnetic parent Yttrium compound) to yield a single  $^{19}\text{F}$  signal, reflecting rapid ligand self-exchange, and relaxation times in the sub-millisecond range as targeted.



**Figure 1.** ORTEP of  $[\text{N}^n\text{Bu}_4][\text{Gd}(\text{Tf}_2\text{N})_4]$ . Cation omitted and fluorides shown as spheres for clarity. The transoid configuration is clearly visible for the  $[\text{NTf}_2^-]$  ligands. Ellipsoids except for fluorides are drawn on the 30% probability level.

**Figure 2.** Comparison of observed (upper) with calculated (lower)  $^{19}\text{F}$  NMR (282.39 MHz) spectra of a mixture of  $[\text{Y}(\text{NTf}_2)_3]$  with  $[\text{EthylMIm}][\text{NTf}_2^-]$  (1:1.5) in  $\text{CD}_2\text{Cl}_2$  displaying line broadening, coalescence and splitting into two signals upon cooling.

[1] C. Barmet, N. De Zanche, B. J. Wilm and K. P. Pruessmann, *Magnetic Resonance in Medicine*, **2009**, 62, 269.