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

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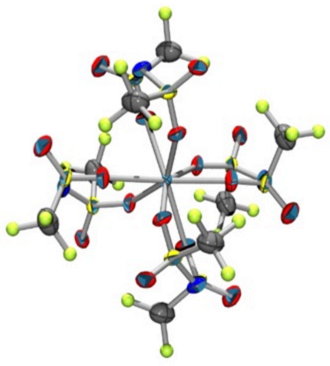
The technology used in Magnetic Resonance Imaging (MRI) relies on the observation of nuclear magnetic resonance (NMR) during complex choreographies of time-varying magnetic fields. Hardware imperfections as well as other external perturbances influence these field evolutions, limiting image quality and the feasibility of high-performance methods. Continuous concurrent magnetic field monitoring[1] 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}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 $[N^nBu_4][Gd(Tf_2N)_4]$ (Tf_2N^-= bis(trifluoromethylsulfonyl)imide), obtained from the reaction of its precursor $[Gd(NTf_2)_3]$ with $[N^nBu_4](NTf_2)$, shows the extension of the coordination sphere from six to eightfold with transoid configuration of the NTf_2 ligands. Hence, the solution of the $[Gd(NTf_2)_3]$ in ionic liquids of the triflimide type $[cat^+][Tf_2N^-]$ (cat^+=AMIm=1-allyl-3-methylimidazolium, EthylMIm or $PR_3R'^+$) is shown (by evaluation of exchange rates of the non-paramagnetic parent Yttrium compound) to yield a single ^{19}F signal, reflecting rapid ligand self-exchange, and relaxation times in the sub-millisecond range as targeted.



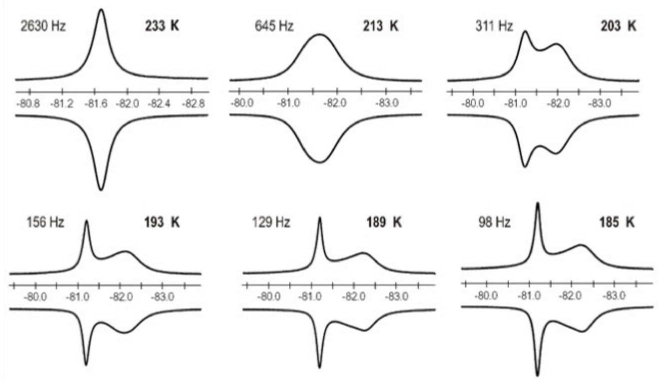


Figure 1. ORTEP of $[N^nBu_4][Gd(Tf_2N)_4]$. Cation omitted and fluorides shown as spheres for clarity. The transoid configuration is clearly visible for the $[NTf_2^-]$ ligands. Ellipsoids except for fluorides are drawn on the 30% probability level.

Figure 2. Comparison of observed (upper) with calculated (lower) ^{19}F NMR (282.39 MHz) spectra of a mixture of $[Y(NTf_2)_3]$ with $[EthylMIm][NTf_2]$ (*1:1.5*) in CD_2Cl_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.