

**Lanthanide-Based Polymerization Catalysts with Water Resistant Ligands**

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The research proposed was to create a family of fluorinated alkoxide complexes of lanthanide elements as potential polymerization catalysts. In particular, we proposed that the significantly reduced basicity of the fluorinated alkoxides (greater acidity of the companion alcohols) would make these compounds water tolerant, and therefore highly useful for industrial polymerizations. Two categories of polymers were envisioned: (i) olefins for the formation of hydrocarbon polymers and (ii) polar monomers including lactones and methyl methacrylate.

The synthetic aspects of the proposed work were generally successful. Four groups of rare earth complexes, comprising eleven new compounds, with fluorinated O-donor ligands ( $[\text{K}(\text{THF})_6]$   $[\text{Ln}(\text{OC}_4\text{F}_9)_4(\text{THF})_2]$ , **1-Ln** (Ln = Ce, Nd),  $[\text{K}][\text{Ln}(\text{OC}_4\text{F}_9)_4]$ , **2-Ln** (Ln = Eu, Gd, Dy),  $[\text{K}(\text{THF})_2][\text{Ln}(\text{pin}^{\text{F}})_2(\text{THF})_3]$ , **3-Ln** (Ln = Ce, Nd), and  $[\text{K}(\text{THF})_2][\text{Ln}(\text{pin}^{\text{F}})_2(\text{THF})_2]$ , **4-Ln** (Ln = Eu, Gd, Dy, Y) were synthesized and characterized.

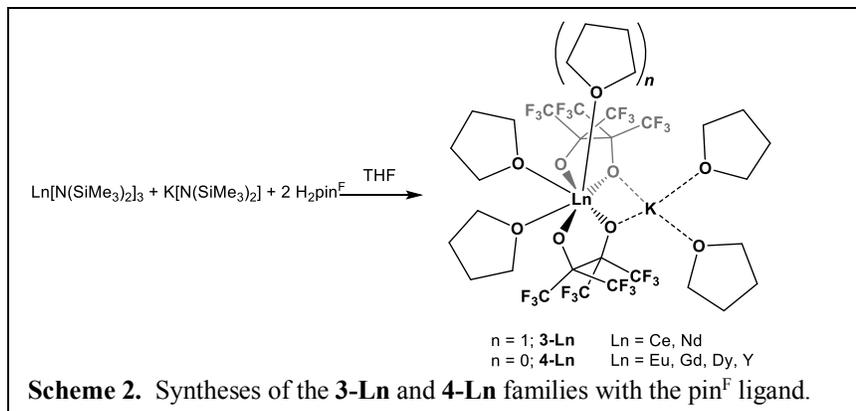
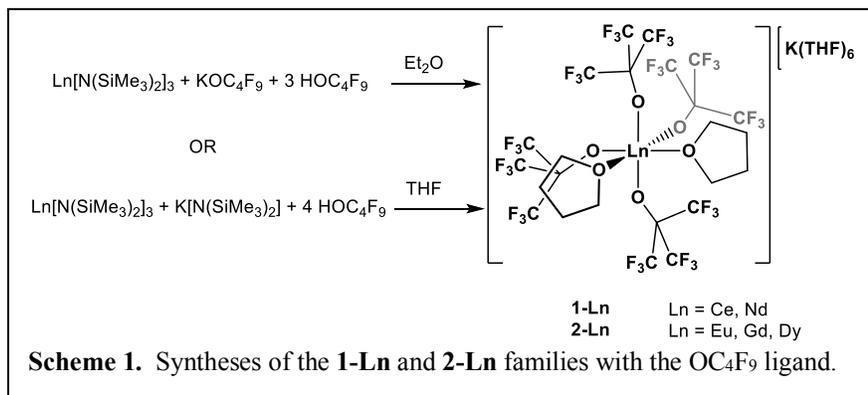
Single-crystal X-ray diffraction data were collected for all compounds except **3-Ln**. Species **1-Ln**, **2-Ln**, and **4-Ln** are uncommon examples of six- (Eu, Gd, Dy, Y) and seven- (Ce, Nd) coordinate  $\text{Ln}^{\text{III}}$  centers in all-oxygen-donor environments. The general procedures and resulting products are shown in Scheme 1 (six-coordinate species) and Scheme 2 (seven-coordinate species).

Disappointingly, the compounds proved much more sensitive to water than is practical for either family of monomers. Structural characterization revealed that although the steric bulk of the  $\text{OC}_4\text{F}_9$  and  $\text{pin}^{\text{F}}$  ligands did prevent alkoxide bridging between Ln centers, there was not sufficient bulk to prevent the THF from the reaction mixture from binding, as shown in Schemes 1 and 2. All efforts to effect the syntheses in non-donor solvents failed, and removal of

THF under vacuum did not lead to materials soluble in non-polar, non-donor solvents. The compounds were quite sensitive to hydrolysis in air, and formed products consistent with  $\text{Ln}_2\text{O}_3$  phases. Because transition metal complexes with such ligands are water soluble or water tolerant, we conclude that the strong oxophilicity of the  $\text{Ln}^{3+}$  centers attracts water which can readily protonate the alkoxide ligands. It may be that the reduced  $\pi$ -donor capability of these ligands contributes to this strong oxophilicity by making the Ln centers more electrophilic.

Interestingly, several of the prepared compounds proved to be fluorescent, and quite unusual fluorophores in comparison to other molecular Ln species in the literature. Species **1-Ln**, **2-Ln**, **3-Ln**, and **4-Ln** are all luminescent (except where Ln = Gd, Y) with the solid-state emission of **1-Ce** being exceptionally blue-shifted for a cerium complex. Excitation and emission spectra for the two Ce-containing complexes are shown in Figure 1. The emission spectra of the six Nd, Eu, and Dy complexes do not show large differences based on ligand and are generally consistent with the well-known free-ion spectra.

In order to gain some insight into the unusual energy of the Ce-based luminescence, computational studies were undertaken. Time-dependent DFT results show that **1-Ce** and **3-Ce** undergo allowed  $5f \rightarrow 4d$  excitations,



consistent with luminescence lifetime measurements in the nanosecond range. Both solution and solid-state absorption spectra were measured and shown to agree well with the computational results, as shown in Figure 2. Europium-containing **2-Eu** and **4-Eu**, however, were found to have luminescence lifetimes in the millisecond range, indicating phosphorescence rather than fluorescence. Computational studies with X methods of the absorption spectra of the Nd, Eu, and Dy species revealed sensitivity to different ligands only for the Nd pair, perhaps due to fewer *f*-electrons than in the Eu or Dy cases. In each case the SORCI<sup>emb</sup> calculations greatly outperform the NEVPT2 calculations.

After reading the literature on Ln-complexes with O-donor ligands, we observed that there is an extensive collection of a wide variety of compounds reported, but there was no comprehensive guide to this work. Therefore we wrote a review of those compounds which (i) created a comprehensive catalog of known compounds (ii) showed common structural features observed to date from non-fluorinated alkoxide ligands and (iii) showed how unusual the emission characteristics of our Ce compounds are.

Ultimately, two publications will result from this work, one on the Ln complexes themselves and the aforementioned review of molecular Ln species with O-donor ligand environments and their luminescent properties.

The work was achieved with sequential efforts from undergraduate and graduate students, as well as one postdoctoral associate, and led to the collaboration described above with the de Bettancourt-Dias group. This work was very effective training for them, such that the former undergraduate is now an NSF GRFP recipient pursuing his PhD at Yale University, one former graduate student has graduated, and the former postdoc is now an Assistant Professor at Wheaton College, MA.

The longer term effect on the Doerr group research has been to increase our understanding of what can and cannot be done with these fluorinated ligands. The water tolerance that they grant to certain complexes does not extend throughout the periodic table, but is more nuanced. This work has also given us a family of complexes with large coordination numbers whose metrical parameters will enable us to more accurately predict the steric effects of these ligands in future heteroleptic systems that we may target.

