Synthesis, Characterization, and Utility of Trifluoroacetic Acid Lanthanide Precursors for
Production of Varied Phase Fluorinated Lanthanide Nanomaterials

**Timothy J. Boyle^{*}, Daniel T. Yonemoto, Jeremiah M. Sears, LaRico J. Treadwell,
Nelson S. Bell, Roger E. Cramer, Michael L. Neville, Gregory A. K. Stillman,
Samuel P. Bingham**

*Sandia National Laboratories, Advanced Materials Laboratory, 1001 University
Boulevard, SE, Albuquerque, NM 87106*

*Author to whom correspondences should be sent. E-mail tjboyle@Sandia.gov, Ph:
(505)272-7625; Fx: (505)272-7336

Abstract. The synthesis of a series of lanthanide trifluoroacetic acid (H-TFA) derivatives which contain only the TFA and its conjugate acid has been developed. From the reaction of $\text{Ln}(\text{N}(\text{SiMe}_3)_2)_3$ with an excess amount of H-TFA, the products were identified as: $[\text{Ln}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n$ ($\text{Ln} = \text{Y, Ce, Sm, Eu, Gd, Tb, Dy}$), $[\text{Ln}(\mu\text{-TFA})_3(\mu\text{-H-TFA})]_n \cdot \text{solv}$ ($\text{Ln} \cdot \text{solv} = \text{Pr} \cdot 2\text{H-TFA}, \text{H}_3\text{O}^+, \text{Ho} \cdot 2\text{py}, \text{Er} \cdot \text{py}, \text{Yb} \cdot \text{py}, \text{H-TFA}$), $3[\text{H}][(\text{TFA})\text{La}(\mu\text{-TFA})_3\text{La}(\text{TFA})(\mu\text{-TFA})_2(\mu\text{-TFA})_2]_n \cdot \frac{1}{2}(\text{H}_2\text{O}) \cdot \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$ ($\text{La} \cdot \frac{1}{2}(\text{H}_2\text{O}) \cdot \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$), $[(k^2\text{-TFA})\text{Nd}(\mu\text{-TFA})_3]_n \cdot \text{H-py}^+$ ($\text{Nd} \cdot \text{H-py}^+$), $[(\text{py})_2\text{Tm}(\mu\text{-TFA})_3]_n$ (Tm), or $[\text{Lu}(\mu\text{-TFA})_4\text{Lu}(\mu\text{-TFA})_3 \cdot \text{H}_3\text{O}^+]_n$ ($\text{Lu} \cdot \text{H}_3\text{O}^+$). The majority of samples formed long chain polymers with 3 or 4 $\mu\text{-TFA}$ ligands. **Tm** was isolated with py coordinated to the metal, whereas **Ho**, **Er**, and **Yb** were isolated with py located within the lattice. Select samples from this set of compounds were used to generate nanomaterials under solvothermal (SOLVO) conditions using pyridine (py) or octylamine at 185 °C for 24 h. The SOLVO products were isolated as: (i) from py: **La** - fluocerite (LaF_3 , PDF 98-000-0214, $R = 9.64\%$, 35(0) nm), **Tb** - terbium fluoride (TbF_3 , PDF 00-037-1487, $R = 4.76\%$, 21(2) nm), **Lu** lutetium oxy fluoride (LuOF , PDF 00-052-0779, $R = 8.24\%$, 8(2) nm); (ii) from octylamine: **La** – fluocerite/lanthanum oxide carbonate (LaF_3 , PDF 98-000-0214, $R = 7.47\%$, 5(0) nm; $\text{La}_2\text{O}_2(\text{CO}_3)$, PDF 01-070-5539, $R = 12.32\%$, 12(0) nm), **Tb** - terbium oxy fluoride (TbOF , PDF 00-008-0230, $R = 7.01\%$, 5(0) nm); **Lu** - lutetium oxide (Lu_2O_3 , PDF 00-012-0728, $R = 6.52\%$, 6(1) nm).

Keywords: metal carboxylates, trifluoroacetic acid, TFA, scintillators, crystal structure

Introduction

Lanthanide fluoride (LnF_3) materials have found widespread use in diverse applications, such as scintillators ($\beta\text{-NaYF}_4\text{:Ln}$), [1-8] fluorescent tracers, [4, 5, 7-11] fiber optics, [4, 6, 9] optical lenses, [4, 9] nuclear reprocessing, [12-14] and electrode applications ($\text{LaF}_3\text{:Ln}$) [4, 15-18]. The structure of the LnF_3 is reported to be the tysonite phase for the light lanthanides, wherein the 11-coordinated Ln cation adopts a fully-capped trigonal prismatic coordination geometry. [19, 20] For the heavier LnF_3 (Sm to Lu) the central cation adopts a tri-capped trigonal prismatic arrangement of the F atoms around the 9-coordinated metal center. [16, 19, 21] Applicable characteristics of these low water-soluble LnF_3 materials include high density (5.94 g/cm^3), hardness (4.5 Mohs), specific heat (506 J/kgK), thermal conductivity (5.1 W/mK@300K), high melting point (1493°C), dielectric constant 14(3), and high fluoride mobility leading to good ionic conductivity. [20] For this study, we are interested in exploiting the various properties of the LnF_3 material, especially the low water solubility and high ionic conductivity, for use as F^- detecting ion electrodes [4, 15-18] in tracking of geothermal underground water flow applications.

It is not surprising that a number of methods have been reported to generate LnF_3 nanomaterials, including: solution precipitation (SPPT), solvothermal (SOLVO), solution gelation, ionic liquid based synthesis, combustion decomposition, and flame decomposition. [3, 6] Solution routes are of interest due to the necessary large scale synthesis that can be achieved by these simple experimental setups and would be necessary for industrial (i.e., geothermal or oil) applications. For a typical solution route, metalorganic precursors are decomposed in a solvent system that often contains a polar

surfactant to cap the growth of the particles. Of the precursors studied, trifluoroacetic acid (H-TFA) has been shown to be an effective and reliable precursor for the production of high quality LnF_3 and $\text{NaLnF}_4\cdot\text{Ln}'$. [3, 9, 22-28] The TFA adducts used in these experiments involved water-based [22, 23, 25-28] derivatives. It has been reasoned that removal of the water may lead to improved properties [29] and numerous efforts have focused on exploiting organic modifiers (i.e., Lewis bases, crown ethers, etc.) in place of water. [29, 30]

While this has proven to be an acceptable approach, the inclusion of additional organic matter only seems to complicate the decomposition pathway. Therefore, we elected to study the non-modified H-TFA derivatives, following eq 1, in hopes of generating a series of ' $\text{Ln}(\text{TFA})_3$ ' complexes that either were solventless or had bound H-TFA (termed Ln-TFA/H-TFA). The products from eq 1 were identified as: $[\text{Ln}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n$ ($\text{Ln} = \text{Y, Ce, Sm, Eu, Gd, Tb, Dy}$), $[\text{Ln}(\mu\text{-TFA})_3(\mu\text{-H-TFA})]_n \cdot \text{solv}$ ($\text{Ln} \cdot \text{solv} = \text{Pr} \cdot 2\text{H-TFA}, \text{H}_3\text{O}^+, \text{Ho} \cdot 2\text{py}, \text{Er} \cdot \text{py}, \text{Yb} \cdot \text{py}, \text{H-TFA}$), $3[\text{H}][(\text{TFA})\text{La}(\mu\text{-TFA})_3\text{La}(\text{TFA})(\mu\text{-TFA})_2(\mu\text{-TFA})_2]_n \cdot \frac{1}{2}(\text{H}_2\text{O}) \cdot \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$ ($\text{La} \cdot \frac{1}{2}(\text{H}_2\text{O}) \cdot \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$), $[(k^2\text{-TFA})\text{Nd}(\mu\text{-TFA})_3]_n \cdot \text{H-py}^+$ ($\text{Nd} \cdot \text{H-py}^+$), $[(\text{py})_2\text{Tm}(\mu\text{-TFA})_3]_n$ (Tm), or $[\text{Lu}(\mu\text{-TFA})_4\text{Lu}(\mu\text{-TFA})_3 \cdot \text{H}_3\text{O}^+]_n$ ($\text{Lu} \cdot \text{H}_3\text{O}^+$). The majority of samples formed long chain polymers with multiple bridging TFA ligands. The **Pr** and **Lu** were isolated as hydronium derivatives (H_3O^+). While **Tm** was isolated with py bound to the metal, **Ho**, **Er**, and **Yb** had py located within the lattice and no interaction with the central cation. The structural properties of these unusual compounds and attempts to convert them to LnF_3 by SOLVO methods were explored.

Experimental

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glovebox techniques unless otherwise discussed. Analytical data were collected on dried crystalline samples. All solvents and chemicals were used as received from Aldrich and Alfa Aesar unless otherwise stated, without further purification, including: toluene (tol), pyridine (py), octylamine and H-TFA. The lanthanide bis(trimethylsilyl)amide ($\text{Ln}(\text{NR}_2)_3$) precursors were synthesized from the reaction of LnX_3 and potassium bis(trimethylsilyl)amide (KNR_2) in THF.[31] Crystalline materials were used for all analytical analyses. FTIR data were collected on a Nicolet 6700 FTIR spectrometer using a KBr pellet press under a flowing atmosphere of nitrogen. Complexometric titration analyses were conducted according to literature reports using ethylenediaminetetraacetic acid (EDTA), hexamethylenetetramine (HMTA), and xylenol orange indicator.[32]

General reaction. In an inert atmosphere glovebox, toluene was added via pipette to a pre-weighed sample of $[\text{Ln}(\text{NR}_2)_3]$. To this solution, H-TFA was added until the evolution of gas ceased and the solution formed a solvent bilayer. The reaction was then heated until the two layers mixed and was then set aside to slowly cool. *Note:* the reaction

was *not* stirred. Once cool, the reaction was set aside with the cap loose until crystals grew. If a precipitate formed (versus crystals as originally noted for **Ho**, **Er**, or **Yb**), the mother liquor was decanted, the remaining precipitate was washed with cold toluene (3 times), and then py was added to redissolve the off-white powder. For the samples that followed this process, the reaction mixture in py was set aside to slowly evaporate until crystals formed.

3[H][(TFA)La(μ -TFA)₃La(TFA)(μ -TFA)₂(μ_c -TFA)₂]_n•($\frac{1}{2}$ H₂O, $\frac{1}{2}$ (H₂O,H-TFA)

((La• $\frac{1}{2}$ (H₂O) $\frac{1}{2}$ (H₂O,H-TFA)). Used [La(NR₂)₃] (0.500 g, 0.806 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 77.9% (0.518 g). FTIR (KBr pellet, cm⁻¹): 3067(w, Br), 1645(s), 1458(m), 1195(s), 1152(s), 862(m), 800(s), 730(s), 722(s), 711(m), 606(m), 250(m), 448(m, sh), 433(m). Complx. Titr. calc'd for C₆F₉LaO₆: 29.1%. Found: 29.2%.

[Ce(μ -TFA)₃(H-TFA)₂]_n (Ce). Used [Ce(NR₂)₃] (0.500 g, 0.804 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 72.8% (0.413 g). FTIR (KBr pellet, cm⁻¹): 3089(w, br), 1736(m, sh), 1657(s), 1461(m), 1201(s), 1148(s), 860(m), 802(s), 723(s), 711(m), 606(m), 521(w), 464(w), 434(w). Complx. Titr. calc'd for C₆CeF₉O₆: 29.2% Found: 29.4%.

[Pr(μ -TFA)₃(μ -H-TFA)]_n •2H-TFA,H₃O⁺ (Pr•2H-TFA, H₃O⁺). Used [Pr(NR₂)₃] (0.500 g, 0.954 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 82.4% (0.659 g). FTIR (KBr pellet, cm⁻¹): 3071(w, br), 1738(m), 1644(s), 1460(m), 1198(s), 1152(s), 861(m), 841(w), 818(w, sh), 801(s), 730(s), 723(s, sh), 712(m), 605(w), 520(w), 447(w, sh), 436(m). Complx. Titr. calc'd for C₉H₇F₉O₆Pr: 29.4% Found: 29.7%.

$[(k^2\text{-TFA})\text{Nd}(\mu\text{-TFA})_3]_n \cdot \text{H-py}^+ (\text{Nd} \cdot \text{H-py}^+)$. Used $[\text{Nd}(\text{NR}_2)_3]$ (0.500 g, 0.799 mmol), H-TFA in excess ~5 mL, and ~3 mL py. Yield 65.9% (0.402 g). FTIR (KBr pellet, cm^{-1}): 3111(w br), 1664(s), 1545(w), 1451(w), 1200(s), 1141(s), 858(m), 839(s), 801(s), 754(m), 723(s), 682(s), 606(m), 521(w), 433(w). Complx. Titr. calc'd for $\text{C}_6\text{F}_9\text{NdO}_6$: 29.8% Found: 30.2%.

$[\text{Sm}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n (\text{Sm})$. Used $[\text{Sm}(\text{NR}_2)_3]$ (0.500 g, 0.792 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 78.2% (0.442 g). FTIR (KBr pellet, cm^{-1}): 3087(w, br), 1794(m, sh), 1744(s), 1662(s), 1476(m), 1427(m), 1157(s), 871(s), 749(s), 800(s), 738(s), 724(s), 693(w), 609(m), 521(s), 451(m), 436(m), 410(w). Complx. Titr. calc'd for $\text{C}_6\text{F}_9\text{O}_6\text{Sm}$: 30.7% Found: 31.0%.

$[\text{Eu}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n (\text{Eu})$. Used $[\text{Eu}(\text{NR}_2)_3]$ (0.500 g, 0.790 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 67.9% (0.384 g). FTIR (KBr pellet, cm^{-1}): 2963(w, br), 1740(s), 1648(s), 1482(m), 1453(m), 1163(s, br), 852(m), 797(s), 725(s), 699(m), 612(m), 521(m), 459(w). Complx. Titr. calc'd for $\text{C}_6\text{EuF}_9\text{O}_6$: 31.0% Found: 31.1%.

$[\text{Gd}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n (\text{Gd})$. Used $[\text{Gd}(\text{NR}_2)_3]$ (0.500 g, 0.783 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 78.5% (0.443 g). FTIR (KBr pellet, cm^{-1}): 3240(w, br), 1794(m), 1702(w), 1671(m), 1467(m), 1221(s), 1135(s), 874(w), 760(s), 739(w), 711(s), 663(w), 609(w), 520(m), 438(m). Complx. Titr. calc'd for $\text{C}_6\text{F}_9\text{GdO}_6$: 31.7% Found: 32.1%.

$[\text{Tb}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n (\text{Tb})$. Used $[\text{Tb}(\text{NR}_2)_3]$ (0.500 g, 0.781 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 74.2% (0.419 g). FTIR (KBr pellet, cm^{-1}): 2926(w, br), 1743(s), 1647(s), 1484(s), 1454(m), 1162(s), 854(m), 797(s), 725(s), 699(s), 613(m),

521(m), 461(m), 441(m), 410(w). Complx. Titr. calc'd for $C_6F_9O_6Tb$: 31.9% Found: 32.2%.

[Dy(μ -TFA) $_3$ (H-TFA) $_2$] $_n$ (Dy). Used [Dy(NR $_2$) $_3$] (0.500 g, 0.777 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 83.1% (0.469 g). FTIR (KBr pellet, cm $^{-1}$): 3667(w), 3636(w), 6432(w, br), 3190(w, br), 1127(s), 1671(s), 1624(s), 1475(m), 1459(m), 1206(s), 1155(s), 860(w), 847(w), 799(s), 730(s), 723(s), 702(w), 607(m), 523(m), 455(m). Complx. Titr. calc'd for $C_6DyF_9O_6$: 32.4% Found: 32.5%.

[Ho(μ -TFA) $_3$ (μ -H-TFA)] $_n$ •2py (Ho•2py). Used [Ho(NR $_2$) $_3$] (0.500 g, 0.774 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 64.3% (0.384 g). FTIR (KBr pellet, cm $^{-1}$): 3102(w, br), 1773(w), 1665(s), 1546(w), 1491(w), 1466(w), 1439(w), 1400(w), 1202(s), 1142(s), 859(m), 842(m), 801(s), 752(m), 723(s), 682(m), 607(w), 522(w), 454(w), 437(w). Complx. Titr. calc'd for $C_6F_9HoO_6$: 32.7% Found: 33.1%.

[Er(μ -TFA) $_3$ (μ -H-TFA)] $_n$ •py (Er•py). Used [Er(NR $_2$) $_3$] (0.500 g, 0.771 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 76.7% (0.412 g). FTIR (KBr pellet, cm $^{-1}$): 3125(w, br), 1735(m, sh), 1666(s, br), 1482(m), 1205(s), 1163(s), 847(m), 852(m), 798(s), 724(s), 705(w), 683(w), 612(m), 522(m), 462(m), 441(m). Complx. Titr. calc'd for $C_6ErF_9O_6$: 33.0% Found: 33.4%.

[(py) $_2$ Tm(μ -TFA) $_3$] $_n$ (Tm). Used [Tm(NR $_2$) $_3$] (0.500 g, 0.769 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 78.9% (0.402 g). FTIR (KBr pellet, cm $^{-1}$): 3123(w, br), 2905(w, br), 1775(m, sh), 1670(s, br), 1547(w), 1467(m), 1400(w), 1202(s), 1143(s), 1060(w), 1008(w), 859(m), 844(s), 824(m), 797(s), 750(s), 734(s, sh), 723(s), 681(s), 609(m), 522(m), 456(w). Complx. Titr. calc'd for $C_6F_9O_6Tm$: 33.3%. Found: 33.2%.

[Yb(μ -TFA)₃(μ -H-TFA)]_n •py, H-TFA (Yb•py, H-TFA). Used [Yb(NR₂)₃] (0.500 g, 0.764 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 77.2% (0.482 g). FTIR (KBr pellet, cm⁻¹): 3079(m, br), 2905(w, br), 1671(s), 1474(m), 1442(w), 1202(s), 1183(s), 1147(s), 1129(s), 842(m), 802(m), 726(m), 603(w), 463(w). Complx. Titr. calc'd for C₆F₉O₆Y: 33.7%. Found: 33.3%.

[Lu(μ -TFA)₄Lu(μ -TFA)₃•H₃O⁺]_n (Lu•H₃O⁺). Used [Lu(NR₂)₃] (0.500 g, 0.762 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 62.2% (0.273 g). FTIR (KBr pellet, cm⁻¹): 3370(w), 3185(w, br), 1734(s), 1647(s), 1478(m), 1459(m), 1198(s), 1154(s), 862(m), 840(w), 817(w), 801(s), 730(s), 723(s), 710(m), 605(m), 520(m), 446(w), 433(w). Complx. Titr. calc'd for C₆F₉LuO₆: 34.0%. Found: 33.8%.

[Y(μ -TFA)₃(H-TFA)₂]_n (Y). Used [Y(NR₂)₃] (0.500 g, 0.877 mmol), H-TFA in excess ~5 mL, and ~3 mL tol. Yield 65.9% (0.377 g). FTIR (KBr pellet, cm⁻¹): 3118(w, br), 1671(s), 1460(m), 1152(s), 878(m), 852(s), 802(s), 726(s), 700(m), 609(m), 521(m), 438(m). Complx. Titr. calc'd for C₆F₉O₆Y: 20.8%. Found: 20.6%.

General X-ray Crystal Structure Information. Single crystals were mounted onto a loop from a pool of Fluorolube™ and immediately placed in a cold N₂ vapor stream, on a Bruker AXS diffractometer employing an incident-beam graphite monochromator, MoK α radiation (λ = 0.71070 Å) and a SMART APEX CCD detector. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINTPLUS Version 6.01 software and corrected for absorption using the SADABS program within the SAINT software package. Structures were solved by direct methods or by using the PATTERSON

method that yielded the heavy atoms, along with a number of the lighter atoms. Subsequent Fourier syntheses yielded the remaining light-atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined using SHELX software. The final refinement of each compound included anisotropic thermal parameters for all non-hydrogen atoms. Colored structure depictions were obtained from OLEX2 [33]. All final CIF files were checked using the CheckCIF program (<http://www.iucr.org/>). Additional information concerning the data collection and final structural solutions can be found in the supplemental information or by accessing CIF files through the Cambridge Crystallographic Data Base. Table 1 lists the unit cell parameters for the structurally characterized compounds **La** - **Y**. Structural solutions that required additional manipulation are presented below.

The **La** crystal possessed a unit cell 4 times the nominal unit cell. There is a 1/2 occupied TFA ligand per each polymer unit. Due to the disorder in the CF₃ groups, they have been treated as rigid groups. Additional CF₃ disorder was not modeled. In one of the two polymers, the La positions are 95/5 disordered. For the **Ce** crystal, a minor second crystal was present which led to violations of the systematic absences and residual density near the Ce atom. Additionally, the TFA molecule with identical C-O bond lengths was identified as not having any H-bonding interactions. The **Nd** molecule had some disorder in two of the TFA ligands which was modeled using rigid groups. The pyridinium ion was found to be H bonded to one of the coordinated O atoms of a TFA ligand. **Sm** crystals had several residual Q peaks clustered around the metal, which were determined to from an unrefined twin. **Dy** crystals exhibited numerous structural refinement issues due to the presence of one or more satellite crystals, which were not

twins. Large disorder peaks were observed near the Dy atoms, which led to a high refinement value (R); however, the connectivity of the molecule is unequivocally established. The unit cell parameters are reported in Table 1 to assist the reader in identifying the compound. For **Lu-O**, pyridine molecules in the lattice were removed using Platon squeeze calculations for a total volume of 1088.4 Å³ (~4 py molecules).

Nanoparticle Synthesis. In an argon filled glovebox, “Ln(TFA)₃(H-TFA)” (1.0 g; Ln = **La**, **Tb**, **Lu**) was added to ~15 mL of py or octylamine, sealed in a 20 mL ParrTM digestion bomb, brought out of the glovebox, placed into an oven and heated (185 °C for 24 h). After this time, the sample was allowed to cool to room temperature and returned to the glovebox. Next, the insoluble material was isolated by centrifugation, washed three times with hexanes, and allowed to dry under ambient conditions. Samples of each were also used for TEM analyses and referred to as ‘green’. A portion of these samples were also thermally treated in a box furnace. The powders were placed in a ceramic boat, placed in a box furnace and heated to 450 °C. These powders were then slurried in methanol and then deposited on a TEM grid for analysis. These are referred to as ‘fired’.

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction (PXRD) was performed on a PANalytical X’Pert Pro diffractometer (10 – 100° two theta) employing CuKα radiation (1.5406 Å) and a RTMS X’Celerator detector at a scan rate of 3°/sec for the bulk powders or at a scan rate of 0.15°/sec using a zero background holder. The PXRD patterns were analyzed using: JADE 9 software (Materials Data, Inc., Livermore CA) and indexed

using The Powder Diffraction File PDF-4+ 2013. Crystallite sizes were determined using Jade v9.6.0. All samples were analyzed using a plastic dome holder (PED). [34]

TEM Analysis. Small amounts of samples from the ‘green’ or ‘fired’ materials were placed in vials and dispersed with methanol to form a cloudy solution. Aliquots of the sample solution were placed on holey-carbon copper coated TEM grids and was allowed to air dry. TEM images were obtained by utilizing a Phillips CM30 transmission microscopy instrument at 300 keV.

DLS Characterization. Measurement of particle size distributions for the fired nanomaterials (**La**, **Tb**, **Lu** from SOLVO: py or octylamine) was performed using dynamic light scattering (DLS) with a NANO-flex® 180° DLS System instrument from Particle Metrix (Particle Metrix, GmbH, Meerbusch, Germany. www.particle-metrix.de). Samples were prepared in methanol with polyvinylpyrrolidone (29,000 g/mol) as a dispersant (Sigma-Aldrich). Samples were prepared using ~50 mg of materials in ~10 mL of methanol, followed by a 5 min treatment of the suspension in an ultrasonic bath (Branson Ultrasonics). Measurements of particle size distributions were repeated six times and the average result taken as the particle size distribution.

Results and Discussion.

A search of a crystallographically characterized TFA moiety in the presence of a Ln (including Sc and Y) cation yields ~90 complexes, which is cut in half when the heteroleptic species are removed from this list.[30] Of these, only 14 compounds were

reported that possess TFA and a bound solvent (not water): $[\text{Ce}(\mu\text{-TFA})_2(k_2\text{-TFA})_2(\text{solv})_3]_2$, [29] ($\text{solv} = \text{DMSO}; (\text{DMSO})_2(\text{DMF})$), $[\text{Ce}(\mu\text{-TFA})_3(\text{solv})_2]_n$, [29] ($\text{solv} = \text{DMSO}; \text{DMF}$), $[\text{Ce}(\mu\text{-TFA})_2(k_2, \mu\text{-TFA})(\text{DMF})_2]$, [29] and $[\text{Gd}_2(\mu\text{TFA})(k_2\text{-TFA})_2(\mu\text{-pyridone})_2(\text{pyridone})]_2$ [35]. Only 24 compounds were found to possess only TFA and H_2O , forming polymeric (Ce , [36] Tm [37]), dinuclear $[(\text{H}_2\text{O})_3\text{Ln}(\mu\text{-TFA})_2(\text{TFA})]$ ($\text{Ln} = \text{Pr}$, [36, 38] Eu , [39, 40] Gd , [35, 41, 42] Tb , [43, 44] [45] [46] [47] Dy , [48] Tm , [37] Lu [36]) or monomeric $[\text{Ln}(\eta^2\text{-TFA})_3 \cdot \text{H}_2\text{O}]$ ($\text{Ln} = \text{Sm}$, Er , Yb) [39] arrangements. The rest of the $\text{Ln-TFA-H}_2\text{O}$ compounds range from mono- to di- to poly-nuclear with bound Lewis basic solvates, including dimethylsulfoxide, dimethylformamide, tetramethylenesulfoxide, 2,2'-bipyridine, THF, phenanthroline, iso-propoxyethanol, ethanol, diglyme, pyridone, azacyclononane, tetramethyldilane derivatives and other more complex organic species. [30]

Since the inclusion of H_2O or organic solvents add the potential for contamination in the final nanomaterials of interest, [49] it was reasoned that by synthesizing the TFA salts might allow for 'cleaner' formation of the desired LnF_3 nanomaterial. As can be discerned from the above compounds, there are no structurally characterized homoleptic TFA derivatives nor TFA/H-TFA available in the literature. [30] Therefore, we undertook the synthesis of Ln-TFA/H-TFA salts following eq 1, eventually using H-TFA as both the reactant and solvent.

Precursor Synthesis. Several attempts to generate the desired Ln-TFA species were undertaken. Initially, the reaction shown in eq 1 was run in toluene, which produced a white precipitate. Addition of pyridine to this reaction mixture led to a nearly instant dissolution of the precipitate. While high quality crystals were easily grown by slow

evaporation of this reaction mixture, the structure of the isolated compounds proved to be py-H-TFA or $[\text{H}_3\text{O}][\text{TFA}(\mu\text{-H-TFA})]$. [50] The unit cell parameters for these compounds are listed for rapid identification. Therefore, the reaction was again undertaken in toluene to produce the expected white precipitate. This precipitate was washed several times with toluene to remove excess H-TFA. Crystallization from py, led to the isolation of both Ln-TFA adducts and TFA-py adducts, in some instances.

It has been reported that mixtures of organic solvents and fluorinated compounds will become miscible at elevated temperatures. [49] Therefore, an excess of H-TFA was added to a solution of the $\text{Ln}(\text{NR}_2)_3$ dissolved in toluene (the final H-TFA:tol ratio was ~6:4 v/v). After the initial effervescence was complete, the reaction mixture was then heated to dissolve the resultant precipitate. After cooling to room temperature, X-ray quality crystals of the desired ' $\text{Ln}(\text{TFA})_3(\text{H-TFA})_n$ ' were isolated. This became the preferred method for isolating these compounds.

Precursor Characterization. For each reaction of eq 1, a sample of the crystals was set aside for single crystal X-ray analysis, with the rest of the product dried under vacuum. The resulting white powders were analyzed by a variety of analytical methods; however, several standard tools could not be employed for these compounds due to the inherent properties of the Ln-TFA compounds. For instance, due to the paramagnetic nature for the majority of Ln cations NMR data was not useful for identifying the product. Also, the presence of the F atoms (>10% F) will cause unreliable results in the H and C data T Perkin-Elmer CHN/O Elemental Analyzer combustion system used for elemental analysis. [51, 52] Therefore, (a) FTIR spectroscopy, (b) single crystal, and (c)

complexometric titration analyses were used to identify the final products and are discussed below. Since the Group 3 cations do not suffer from the paramagnetic nature of the Ln cations, the solution behaviors of these compounds were investigated using multinuclear (^{13}C , ^{19}F) NMR experiments; unfortunately, the low solubility of these compounds prevented obtaining meaningful data.

(a) FTIR Spectroscopy. Often the loss of the OH stretches of the precursors can be used as an indication of completeness of reaction; however, the expected binding of the H-TFA precluded this interpretation. Therefore, the changes noted for the bends and stretches of the $\nu(\text{OH})$ (3610 , 3120 , 2940 cm^{-1})[53] and $\nu(\text{C=O})$ (1829 cm^{-1}) of the H-TFA moiety were closely inspected. Easily noted was the shift of the $\nu(\text{C=O})$ band to an average value of for the strong stretch around 1660 cm^{-1} , indicating some complexation of the TFA ligands. The exact nature of this is difficult to establish but suggests the TFA were bound to the Ln in either a bridging or chelating bridging mode.[54] The loss of the strong NR_2 stretches and bends noted in the $\text{Ln}(\text{NR}_2)_3$ precursor's spectrum, around $\nu(\text{Ln-N})$ 1247 and 593 cm^{-1} was another indication that the reaction had gone to completion. Finally, the $\nu(\text{O-C-O})$ [54] bends noted around 725 cm^{-1} for every sample, confirmed the formation of a 'Ln-TFA' complex. The $\nu(\text{Ln-O})$ stretch is not well established but has been reported for $\text{Ln-OCH}(\text{CH}_3)_2$ in the range of $520 - 370\text{ cm}^{-1}$ [55]. For the majority of samples, a strong stretch was present around 800 cm^{-1} and may represent the $\nu(\text{Ln-(O-C-O)})$.

(b) Crystal Structure. Due to the limited structural information that could be discerned from these data, additional studies were undertaken using single crystal X-ray diffraction.

The structures proved to be of high quality with a variety of polymeric structures being solved. In general, these structures are quite complex upon symmetry expansion; therefore, it is suggested that in order to visualize the structures properly, the reader is encouraged to use an imaging program. For the majority of these polymers there are three bridging TFA ligands, which are followed by either three or four μ -TFA moieties forming the polymeric chain. If the location of the H was not easily observed in the final structure, the H is assumed to be equally spread over the entire structure, represented by a proceeding [H].

The largest Ln metal center investigated, **La**• $\frac{1}{2}(\text{H}_2\text{O}) \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$ (Figure 1), formed a polymeric chain of alternating (i) three bridging TFA, along with (ii) two chelating-bridging and two chelating TFA ligands. For each La there is also a terminal TFA present, which results in an alternating 8- (CN-8) and 9- (CN-9) coordinated La metal center, with no interaction between the chains. In addition to the polymer chain, there is a half-occupied H-TFA molecule for each polymer unit. Due to the disorder in the CF_3 groups, these moieties were treated as rigid groups. In one of the two polymers, the La positions were found to be 95/5 disordered. The R value is below 10 % and unequivocally establishes the molecular connectivity. The structure of the **Nd**•H-py⁺ salt was comparable to the polymeric structure solved for **La**. The Nd salt possessed a k^2 -TFA ligand with an additional lattice pyridinium ion that was not present in the **La**• $\frac{1}{2}(\text{H}_2\text{O}) \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$ structure solution.

A similar polymeric chain was solved for **Ce** as well as for **Sm**, **Eu**, **Gd**, **Tb**, **Dy**, and **Y**. **Eu** is shown in Figure 2 as a representative species for the $[\text{Ln}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n$ derivatives. In contrast to the **La** and **Nd** polymers (*vide supra*), for this

structure, the Ln cations bridged to each other using only three μ -TFA ligands. In addition, each Ln has two terminal TFA ligands. Combined this means two H atoms are necessary to maintain charge balance but these were not readily observed for **Gd** or **Y**; however, for the **Eu** structure (shown in Figure 2), two H atoms, both bound to the terminal TFA with a H---O interaction between one of the bridging TFA, were observed. As such it is assumed that the same interaction is true for the **Gd** and **Y** molecules. The linear chains do not interact with each other.

An alternative polymeric arrangement, $[\text{Ln}(\mu\text{-TFA})_3(\mu\text{-H-TFA})]_n \cdot \text{solv}$, was noted for **Pr**, **Ho**, **Er** (see Figure 3), and **Yb**, while the structures solved contained different co-crystallized solvents. For this set of cations, again a polymeric chain was noted but there are four TFA bridging ligands present that force each Ln cation into a CN-8. This crystal motif is best described as a distorted square antiprismatic geometry. For **Pr**, 2 H-TFA solvent molecules were located in the lattice and not found to interact with the polymeric chains. In addition, an oxygen atom was observed in the lattice and is best represented as a hydronium ion due to the disordered H atoms that were successfully located around the atom. For the **Ho** structure a H-TFA was noted in the unit cell matrix.

For the smaller **Lu** cation, a chain structure similar to the **La** and **Nd** compounds was solved; fortunately, the 'missing' H^+ was identified as part of the lattice H_3O^+ moiety (Figure 4). In addition, the polymeric chains of the **Lu** structure were found to be interconnected by TFA ligands and adopt a CN-7 geometry.

Finally, the **Tm** derivative (shown in Figure 5) was also solved in a chain structure, with only bridging TFA ligands. No terminal TFA or protons were necessary to maintain the neutral charge. There are two py molecules bound to the Tm metal center

with an average Tm – N bond distance of 2.60 Å. These chains do not interact with other chains.

(d) Metrical data. While there are subtle variations in the structures noted for these compounds, the Ln-O distances show the expected systematic decrease as the Ln series is traversed. Table 1 shows the data collection parameters and Table 2 the select metrical data for **La** – **Y**. The Ln---Ln distances are not as constant and were found to vary between 5.13 Å (**Sm**) and 4.47 Å (**Pr**). A small O-C-O bite angle range was noted that did not match with the distance variances noted above: 129.4° for **Tm** versus 126.9° for **Gd**. One trend that can be noted is that the Ln-(H-TFA) derivatives have longer Ln---Ln distances than those which were co-crystallized with py.

It was discovered in the process of developing this unusual family of compounds that an oxo species could be formed when the reaction mixture was dissolved in py and heated for a short time. Since the oxo core will make conversion to the desired LnF₃ more difficult, only a brief description of the structure is presented to assist the reader in identifying these products. While this general structure was noted for several cations (Dy, Lu, Ho, Yb), one of the best structures was isolated for Lu, identified as 8[H][(Lu(μ₃-O)₃(μ-TFA)₃(κ²-TFA))₂(Lu(TFA)₂)₃]•4py, 2H-py⁺, H₃O⁺ (**Lu-O**, Figure 6). The structure consists of a core of five Ln atoms bridged by μ₃-O forming a roughly trigonal bipyramidal geometry of the Ln atoms. The equatorial Ln atoms are Ln₂O₂ squares linked together. The three top and bottom oxygens bind to the axial Ln atoms. Further linking the axial and equatorial Ln atoms are six bridging TFA ligands. Finally, the axial Ln atoms each chelate a TFA molecule while the equatorial Ln bind two

terminal TFA moieties. It is also noted that there are a number of py and pyridinium solvent molecules interacting via hydrogen bonding throughout the lattice. Some H-bonding is depicted in the figure by a dashed line. The lone oxygen atom that appears in the lattice has an interaction with two py molecules as well as a terminal TFA molecule.

(d) Complexometric Titration. Elemental analyses of the bulk material using a Perkin-Elmer CHN/O Elemental Analyzer were attempted using standard combustion processes; however, due to instrument limitations and the high F content of the compounds (>10% F will cause unreliable results in the H and C data), [51, 52] the data generated was inconsistent. Complexometric titrations were undertaken as an alternative approach to characterize the bulk powder. The use of '[Ln(TFA)₃]' was used as the formulation and as can be noted in the Experimental Section the values agree with the proposed 'simple' formulations.

Nanoparticle Synthesis. With this new family of Ln-TFA/H-TFA salts in hand, their conversion to the LnF₃ nanomaterials was undertaken. Solution routes were of interest due the potential to convert these laboratory processes to larger scales. Prior to these studies TGA data was collected in order to verify that these compounds would transform under the conditions typically used (see Figure 7). As can be observed, small weight losses were noted up to ~350 °C, which are most likely due to the decomposition of the co-crystallized solvents, noted in some of the compounds.[54] The major weight loss occurs around 400 – 450 °C, which correlates with the high end decomposition of typical precursors used in SPPT routes; however, for SOLVO methods, the increased pressure

coupled with temperature was thought to facilitate the decomposition. Therefore, SOLVO (185 °C, 24 h) routes using py and octylamine were undertaken. The PXRD and TEM results for the powders isolated for **La**, **Tb**, and **Lu** in py and octylamine are shown in Figures 8 and 9, respectively and tabulated in Table 3. Under SOLVO conditions using py or octylamine, the ‘green’ samples’ powder patterns were typically too broad to definitively confirm the phase (i.e., amorphous). The crystallinity of these samples was increase by firing them in air, in a box furnace at 450 °C for 60 min. Based on the TGA data (Figure 7) this temperature should remove any residual organic species and facilitate crystallization. The TEM and PXRD results are tabulated in Table 3.

As can be discerned, the PXRD crystallite measurements indicate that the samples were significantly smaller in size than the TEM images. This can be explained by the fact that the values obtained by the PXRD patterns are based on peak broadening, which means they will represent the smallest crystallite sizes. Thus, the values via PXRD are generally indicative of primary crystal regions but do not reveal twinning or agglomeration behavior observed in the TEM images. In general, the **La** materials produce the largest crystallite sizes in both PXRD and TEM. The interfaces of the thermally treated particles in the TEM are rounded, as is typical for calcined powders, and indicates the formation of hard aggregates between the crystallites.

To further determine the size of the polycrystalline particles, DLS characterization was for each product and are tabulated in Figure 11 and Table 3. With the exception of the py/**Lu** samples, the trends in the resulting particle size distributions are remarkably similar ranging from ~200 to 300 nm with normal particle size distributions, which is typical for calcined powders. In contrast, the py/**Lu** material

behaved substantially differently yielding a bimodal distribution, dominated by agglomerated materials over 1 μm in effective size. This variation is not surprising since it is an oxide and the other compounds are either LnF_3 or LnFO . As noted from the TEM images, the products were an agglomeration with very small nanoparticles on the surface of larger materials (Figure 9c-ii). The DLS data of the dispersed sample indicates that there is a small content of material with diameter ranging from 10-20 nm (Figure 11c). Based on the DLS and TEM images, it is obvious that the **Lu/py** materials were not successfully processed to their agglomerate size; however, there is the possibility to obtain ultrafine or individual nanoparticle dispersions by more energetic comminution techniques. Powder processing to achieve individual nanocrystal dispersion needs to be explored.

Summary and Conclusion.

The first examples of TFA-Ln salts with its conjugated acid (H-TFA) acting as the solvent, have been reported (**La – Y**). These species do not contain an additional Lewis base, an organic co-ligand nor water present; however, in some instances, a hydronium ion is present (**Pr, Sm, Lu**). While py or H-py^+ was co-crystallized in the lattice for **Ho, Er, Yb, and Nd**, only **Tm** had the py bound to the metal. All the samples form polymeric structures with varying degrees of $\mu\text{-TFA}$ ligands with the majority of compounds adopting the $2[\text{H}][(\text{TFA})_2\text{Ln}(\mu\text{-TFA})_3]_n$ ($\text{Ln} = \text{Ce, Eu, Gd, Tb, Dy, Y}$) structure. Select members of this novel family (**La, Tb, Lu**) were studied to determine their utility in converting to LnF_3 nanomaterials by SOLVO (py or octylamine) thermal processes.

Most of these samples were successfully converted to F-containing Ln species; however, the full conversion to the desired LnF_3 material was noted only for **La** and **Tb** (from py). **La** from octylamine generated both LaF_3 as well as a carbonate phase; **Lu**/py and **Tb**/octylamine formed the oxyfluorides; **Lu**/octylamine yielded only the oxide. The variations in the phases of the samples for a specific solvent are preliminarily attributed to the size of the cation. It is not clear at this point why the lower boiling point py converts more cleanly to the LnF_3 than octylamine but the interaction of the more available electron pair of the later solvent with the F may play a role; previous reports on Ln-TFA compounds are focused more on the magnetic or fluorescent properties rather than their conversion to the nanomaterials and lend little insight into these phenomena. Therefore, while these compounds and their conversion in this work represent some of the first attempts to generate LnF_3 materials from the Ln-TFA system, additional work is necessary to determine the optimal conversion conditions. Furthermore, work on controlling the different phases is of interest, as these simple compounds can be used to generate a wide variety of materials based solely on their processing modes.

Acknowledgments. The authors would like to acknowledge the grateful use of the Bruker X-ray diffractometer purchased via the National Science Foundation CRIF:MU award to Prof Kemp of the University of New Mexico (CHE04-43580). For support of this research, the authors thank the Efficient Energy and Renewable Energy, Geothermal Technology Office of the Department of Energy program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

References.

- [1] G.Y. Chen, T.Y. Ohulchanskyy, R. Kumar, H. Agren, P.N. Prasad, *ACS Nano*, 4 (2010) 3163.
- [2] S. Jiang, Y. Zhang, *Langmuir*, 26 (2010) 6689.
- [3] C. Li, J. Lin, *J. Mater. Chem.*, 20 (2010) 6831-6847.
- [4] K. Binnemans, *Chem. Rev.*, 109 (2009) 4283-4374.
- [5] C.W.E. van Eijik, *Nucl. Inst. Meth. Phys. Res. A*, 460 (2001) 1-14.
- [6] F. Wang, X. Liu, *Chem. Soc. Rev.*, 38 (2009) 976-989.
- [7] C. Mi, Z. Tian, C. Cao, Z. Wang, C. Mao, S. Xu, *Langmuir*, 27 (2011) 14632-14637.
- [8] T.J. Boyle, L.M. Ottley, T.M. Alam, M.A. Rodriguez, P. Yang, S.K. McIntyre, *Polyhedron*, 29 (2010) 1784-1795.
- [9] X. Sun, Y.-W. Zhang, Y.-P. Du, Z.-G. Yan, R. Si, L.-P. You, C.-H. Yan, *Chem. Eur. J.*, 13 (2007) 2320-2332.
- [10] E.N.M. Cheung, R.D.A. Alvares, W. Oakden, R. Chaudhary, M.L. Hill, J. Pichaandi, G.C.H. Mo, C. Yip, P.M. Macdonald, G.J. Stniesz, F.C.J.M. van Veggel, R.S. Prosser, *Chem. Mater.*, 22 (2010) 4728-4739.
- [11] A. Ju, D. Tu, Y. Liu, R. Li, H. Zhu, J. Chen, Z. Chen, M. Huang, X. Chen, *J. Am. Chem. Soc.*, 134 (2012) 1323-1330.
- [12] P. Taxil, L. Massot, C. Nourry, M. Gibilaro, P. Chamelot, L. Cassayre, *J. Fluorine Chem.*, 130 (2009) 94-101.
- [13] P. Chamelot, L. Massot, C. Hamel, C. Nourry, P. Taxil, *J. Nucl. Mater.*, 360 (2007) 64-74.
- [14] O. Amano, A. Sasahira, Y. Kani, K. Hoshino, M. Aoi, F. Kawamura, *J. Nucl. Sci. Tech.*, 41 (2004) 55-60.
- [15] J. Komljenovic, S. Krka, N. Radic, *Anal. Chem.*, 58 (1983) 2893-2895.

- [16] N.I. Sorokin, B.P. Sobolev, *Kristallografya*, 52 (2007) 870-892.
- [17] M. Bralic, N. Radic, S. Brinic, E. Generalic, *Talanta*, (2001) 581-586.
- [18] M.S. Frant, J.W. Ross, *Science*, 154 (1966) 1533.
- [19] H.C. Aspinall, *Chemistry of the f-block elements*, Gordon and Breach Science Publishers, Canada, 2001.
- [20] L. Crystran, Lanthanum Fluoride (LaF₃), - Materials Data Sheet, in, Crystran, <http://www.crystran.co.uk/>, 2011.
- [21] A. Kovacs, R.J.M. Konings, *J. Phys. Chem. Ref. Data*, 33 (2004) 377-.
- [22] Y.W. Zhang, X. Sun, R. Si, L.P. You, C.H. Yan, *J. Am. Chem. Soc.*, 127 (2005) 3260-3261.
- [23] H.X. Mai, Y.W. Zhang, R. Si, Z.G. Yan, L.S. Sun, L.P. You, C.-H. Yan, *J. Am. Chem. Soc.*, 128 (2006) 6426-6436.
- [24] G.S. Yi, G.M. Chow, *Adv. Funct. Mater.*, 16 (2006) 2324-2329.
- [25] J.C. Boyer, F. Vetrone, L.A. Cuccia, J.A. Capobianco, *J. Am. Chem. Soc.*, 128 (2006) 7444-7445.
- [26] G.S. Yi, G.M. Chow, *Chem. Mater.*, 19 (2007) 341-343.
- [27] J.C. Boyer, L.A. Cuccia, J.A. Capobianco, *Chem. Mater.*, 19 (2007) 3358-3360.
- [28] J.C. Boyer, L.A. Cuccia, J.A. Capobianco, *Nano Lett.*, 7 (2007) 847-852.
- [29] S. Mishra, E. Jeanneau, A.-L. Bulin, G. Ledoux, B. Jouguet, D. Amans, A. Belsky, S. Daniele, C. Dujardin, *Dalton Transactions*, 42 (2013) 126333-112643.
- [30] Conquest Version 1.16 (Build RC5) November 2013 update. Cambridge Crystallographic Data Centre:support@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/> in: Conquest Version 1.16 (Build RC5) November 2013 update. Cambridge Crystallographic Data Centre:support@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/>
- [31] H.-T. Sheng, J.-M. Li, Y. Zhang, Y.-M. Yao, Q. Shen, *Polyhedron*, 27 (2008) 1665-1672.
- [32] J.L. Atwood, W.E. Hunter, A.L. Wayda, W.J. Evans, *Inorg. Chem.*, 20 (1981) 4115.
- [33] L.J.B. O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, (2009) 339-341.
- [34] Bruker, PeD reference, in, <https://www.bruker.com/products/x-ray-diffraction-and-elemental-analysis/x-ray-diffraction/components/xrd-components/non-ambient-stages/material-download.html>, 2016.
- [35] D. John, A. Rohde, W. Urland, *Z. Naturforsch, B. Chem. Sci.*, 61 (2006) 699.
- [36] P.C. Junk, C.J. Kepert, L. Wei-Min, B.W. Skelton, A.H. White, *Aust. J. Chem.*, 52 (1999) 459.
- [37] S.I. Gutnikov, E.V. Karpova, M.A. Zakharov, A.I. Boltalin, *Zh. Neorg. Khim, (Russ.)(J. Inorg. Chem.)*, 51 (2006) 593.
- [38] S.P. Bone, D.B. Sowerby, R.D. Verma, *J. Chem. Soc., Dalton Trans.*, (1978) 1544-1548.
- [39] V.Y. Kavun, T.A. Kaidalova, V.I. Kostin, E.S. Panin, B.N. Chrnyshev, *Koord. Khim (Russ.)(Coord. Chem.)*, 10 (1984) 1502.
- [40] E.S. Panin, V.Y. Kavun, V.I. Sergienko, B.V. Butvetskii, *Koord. Khim (Russ.)(Coord. Chem.)*, 11 (1985) 1539.
- [41] Z. Jingjun, Z. Siyuan, M. Xiuqin, W. Gecheng, H. Ninghai, J. Zhongsheng, *Yingyong Huaxue (Chin.)(Chin. J. Appl. Chem.)*, 5 (1988) 30-36.

- [42] K.V. Katti, P.R. Singh, C.L. Barnes, *Synth. React. Inorg., Met.-Org., Nano-Met. Chem.*, 26 (1996) 349-355.
- [43] A.A. Rastorguev, A.A. Remova, G.V. Romanenko, N.P. Sokolova, V.I. Belyi, S.V. Larionov, *Zh. Strukt. Khim, (Russ.)(J. Struct. Chem.)*, 42 (2001) 907.
- [44] V.I. Belyi, A.A. Rastorguev, A.A. Remova, G.V. Romanenko, N.P. Sokolova, *Zh. Strukt. Khim, (Russ.)(J. Struct. Chem.)*, 43 (2002) 634.
- [45] B. Barja, R. Baggio, M.T. Garland, P.F. Aramendia, O. Pena, M. Perec, *Inorg. Chim. Acta.*, (2003) 187-196.
- [46] N.P. Sokolova, V.L. Varand, G.V. Romanenko, V.I. Lisoivan, V.P. Fadeeva, L.A. Sheludyakova, *Koord. Khim (Russ.)(Coord. Chem.)*, 29 (2003) 387.
- [47] V.I. Belyi, A.A. Rastorguev, A.A. Remova, G.V. Romanenko, N.P. Sokolova, 45, (2004) 135.
- [48] G.V. Romanenko, N.P. Sokolova, S.V. Larionov, *Zh. Strukt. Khim, (Russ.)(J. Struct. Chem.)*, 40 (1999) 387.
- [49] I.T. Horvath, J. Rabal, *Science*, 266 (1994) 72-75.
- [50] Unit cell paramters for: (i) [py-H][TFA] $a = 10.26$, $b = 14.56$, $c = 14.58$, $\alpha = 60.10$, $\beta = 89.97$, $\gamma = 89.65$, $V = 1888$; (ii) [H₃O][TFA(μ -H-TFA)] $a = 7.78$, $b = 7.86$, $c = 8.58$, $\alpha = 64.52$, $\beta = 64.64$, $\gamma = 86.31$, $V = 423$., in.
- [51] K.S. Fiorini, Running fluorinated Compounds using the Perkin Elmer 2400, in, Swanson Analytical Services, 2012.
- [52] <http://www.elementalanalysis.com/services/chno-combustion-services/> in, EAI: Elemental Analysis , Inc, 2016.
- [53] J.W.O. Tam, I.M. Klotz, *Spectrochim. Acta*, 29A (1972) 633-644.
- [54] L.B. Zinner, C.A. Alves de Carvalho, K. Zinner, *J. Alloys Cmpds.*, 180 (1992) 343-348.
- [55] D.C. Bradley, R.C. Mehrotra, D.P. Gaur, *Metal Alkoxides*, Academic Press, Lonson, 1978.

List of Tables.

Table 1. Data collection parameters for **La – Y**.

Table 2. Select metrical data for **La – Y**.

Table 3. Characterization of the nanoparticles generated from the **La** , **Tb**, and **Lu** precursors.

Table 1. Data collection parameters for **La – Y**.

Compound	La •½ H ₂ O, ½(H ₂ O, H-TFA)	Ce	Pr •2H-TFA, H ₃ O ⁺	Nd •H-py ⁺
chemical formula	C _{38.07} H _{7.07} F _{57.10} La ₄ O _{39.59}	C ₁₀ H ₂ CeF ₁₅ O ₁₀	C ₁₂ H ₅ F ₁₈ O ₁₃ Pr	C ₁₃ H ₆ F ₁₂ NNdO ₈
formula weight	2738.38	707.24	840.07	676.43
temp (K)	100.0(2)	100.0(2)	100.0(2)	100.0(2)
space group	Monoclinic P2 ₁ /n	Orthorhombic Pbca	Monoclinic P2 ₁ /n	TriclinicP -1
<i>a</i> (Å)	12.2632(14)	16.6046(14)	8.6796(9)	8.6770(5)
<i>b</i> (Å)	40.805(5)	9.3377(8)	14.3966(15)	10.3042(6)
<i>c</i> (Å)	16.3476(19)	25.475(2)	20.0594(18)	12.0523(7)
				83.894(3)
β (deg)	102.879(8)		101.120(7)	72.226(3)
				73.371(3)
<i>V</i> (Å ³)	7974.5(16)	3949.8(6)	2459.5(4)	983.03(10)
<i>Z</i>	4	8	4	2
D _{calcd} (Mg/m ³)	2.281	2.379	2.269	2.285
μ _s (Mo, Kα) (mm ⁻¹)	2.321	2.494	2.178	2.798
R1 ^a (%) (all data)	10.12(26.46)	8.07 (15.68)	4.44 (7.31)	7.36 (10.49)
wR2 ^b (%) (all data)	24.92(34.92)	16.25 (18.78)	10.69 (14.01)	17.58 (19.26)
Compound	Sm	Eu	Gd	Tb
chemical formula	C ₁₀ H ₂ F ₁₅ O ₁₀ Sm	C ₁₀ H ₂ EuF ₁₅ O ₁₀	C ₁₀ H ₂ F ₁₅ GdO ₁₀	C ₁₀ H ₂ F ₁₅ O ₁₀ Tb
formula weight	717.47	719.08	724.37	726.04
temp (K)	100.0(2)	173.0(2)	100.0(2)	100.0(2)
space group	Orthorhombic Pbca	Orthorhombic Pbca	Orthorhombic P2 ₁ 2 ₁ 2 ₁	orthorhombic P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	16.4969(8)	16.6167(5)	8.4667(13)	8.4594(3)
<i>b</i> (Å)	9.2511(5)	9.2720(3)	9.1769(15)	9.1812(4)
<i>c</i> (Å)	25.3396(14)	25.4792(8)	25.317(4)	25.3010(11)

V (Å ³)	3867.2(4)	3925.6(2)	1967.1(5)	1965.06(14)
Z	8	8	4	4
D _{calcd} (Mg/m ³)	2.465	2.433	2.446	2.454
μ _s (Mo, Kα) (mm ⁻¹)	3.230	3.386	3.561	3.789
R1 ^a (%) (all data)	10.94 (19.42)	2.58(4.32)	6.97(9.44)	2.94(3.46)
wR2 ^b (%) (all data)	26.37 (34.68)	7.02 (9.65)	14.28(15.12)	6.47(6.68)
Compound	Dy	Ho•2py	Er•py	Tm
chemical formula	C ₂₀ Dy ₂ F ₃₀ O ₂₀	C ₂₆ H ₁₀ F ₂₄ Ho ₂ N ₂ O ₁₆	C ₁₃ H ₆ ErF ₁₂ NO ₈	C ₁₆ H ₁₀ F ₉ N ₂ O ₆ Tm
formula weight	1455.20	1392.22	699.45	666.19
temp (K)	101.0(2)	100.0(2)	100.0(2)	188.0(2)
space group	Orthorhombic P2 ₁ 2 ₁ 2 ₁	Triclinic P(-1)	Monoclinic P 2 ₁ /n	Orthorhombic Pba2
a (Å)	9.2014(5)	11.4654(7)	8.7760(6)	19.452(3)
b (Å)	16.8070(10)	12.2083(8)	20.3324(14)	21.299(3)
c (Å)	25.2609(14)	15.3160(9)	12.1233(8)	5.1152(8)
α (deg)		106.573(2)		
β (deg)		100.492(2)	109.501(4)	
γ (deg)		102.867(2)		
V (Å ³)	3906.5(4)	1932.7(3)	2039.2(2)	2119.3(6)
Z	4	2	4	4
D _{calcd} (Mg/m ³)	2.474	2.392	2.278	2.088
μ _s (Mo, Kα) (mm ⁻¹)	4.016	4.252	4.267	4.301
R1 ^a (%) (all data)	11.91 (14.9)	4.32(5.89)	4.18(6.97)	3.76(5.08)
wR2 ^b (%) (all data)	27.05 (28.39)	10.65(11.74)	10.12(12.22)	8.19(8.90)
Compound	Yb•py, H-TFA	Lu•H₃O⁺	Lu-O	Y
chemical formula	C ₁₅ H ₇ F ₁₅ NO ₁₀ Yb	C ₁₄ H ₃ F ₂₁ Lu ₂ O ₁₅	C ₅₈ H ₄₀ F ₄₂ Lu ₅ N ₆ O ₃₅	C ₁₀ H ₂ F ₁₅ O ₁₀ Y
formula weight	819.26	1160.1	3053.81	656.03
temp (K)	100.0(2)	99.0(2)	100.0(2)	173.0(2)

space group	Triclinic P(-1)	triclinic P -1	Monoclinic P 2 ₁ /c	Orthorhombic P212121
<i>a</i> (Å)	8.7134(4)	8.5881(4)	26.0534(9)	8.5436(8)
<i>b</i> (Å)	11.7068(6)	11.2657(5)	14.9848(6)	9.1696(8)
<i>c</i> (Å)	13.3844(8)	15.0434(6)	27.3481(11)	25.377(3)
α (deg)	64.798(3)	76.123(2)		
β (deg)	88.793(4)	88.851(2)	112.1050(10)	
γ (deg)	80.153(3)	80.340(2)		
<i>V</i> (Å ³)	1215.08(11)	1392.64(11)	9892.0(7)	1988.1(3)
<i>Z</i>	2	2	4	4
<i>D</i> _{calcd} (Mg/m ³)	2.239	2.767	2.051	2.192
μ_s (Mo, K α) (mm ⁻¹)	4.015	7.257	5.099	3.121
R1 ^a (%) (all data)	4.33(5.50)	3.12 (5.49)	4.41(6.23)	6.43(9.27)
wR2 ^b (%) (all data)	11.78(13.58)	4.36 (4.84)	11.79(13.75)	16.96(19.18)

$$^a R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| \times 100$$

$$^b wR2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma (w |F_o|^2)^2]^{1/2} \times 100$$

Table 2. Metrical data for **La- Y**.

cmpd	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Distances (Å)								
Ln-O	2.37	2.48	2.49	2.46	2.41	2.40	2.40	2.40
Ln---Ln	4.56	5.15	4.47	4.76	5.13	5.10	5.10	5.103
Angles(deg)								
O-C-O	127.1	127.2	127.5	128.1	127.5	127.1	126.9	127.4
cmpd	Dy^a	Ho	Er	Tm	Yb	Lu	Lu-O	Y
Distances (Å)								
Ln-O	2.36	2.36	2.35	2.29	2.32	2.24	2.35	2.37
Ln---Ln	5.06	4.51	4.49	5.12	4.48	4.63 (Intrapolymer) 6.51 (Polymer bridge)	3.68	5.07
Angles(deg)								
O-C-O	125.6	129.6	129.3	129.4	128.8	128.1	128.8	127.4

^aThe metrical data reported for this structure is only for comparison as the final structure solution was problematic.

Table 3. Characterization of the nanoparticles generated from the **La**, **Tb**, and **Lu** precursors.

SOLVO (py)	La	Tb	Lu
‘green’ PXRD	LaF ₃ PDF 98-000-0214	amorph.	amorph.
‘green’ TEM	1-2 nm wide rods (a/r < 20)	1-2 nm irregular	5-8 nm irregular
‘fired’ PXRD	Fluocerite (LaF ₃) PDF 98-000-0214 R = 9.64%, CS = 35(0) nm	terbium fluoride (TbF ₃) PDF 00-037-1487 R = 4.76%, CS = 21(2) nm	lutetium oxy fluoride (LuOF) PDF 00-052-0779 R = 8.24%, CS = 8(2) nm
‘fired’ TEM	< 40 nm rods	50 nm plate-like	~ 20 nm irregular
‘fired’ DLS	243 nm	289 nm	1635 nm
SOLVO (ON)	La	Tb	Lu
‘green’ PXRD	amorph.	amorph.	amorph.
‘green’ TEM	5-8 nm dots	~1-2 nm dots	~10 nm spheres 20 x > 40 nm rectangle plates
‘fired’ PXRD	Fluocerite (LaF ₃) PDF 98-000-0214 R = 7.47%, 5(0) nm; lanthanum oxide carbonate La ₂ O ₂ (CO ₃) PDF 01-070-5539 R = 12.32%, CS = 12(0) nm	terbium oxy fluoride (TbOF) PDF 00-008-0230 R = 7.01%, CS = 5(0) nm	lutetium oxide (Lu ₂ O ₃) PDF 00-012-0728 R = 6.52%, CS = 6(1) nm
‘fired’ TEM	40 nm irregular	10 - 15 nm irregular	5-10 nm irregular
‘fired’ DLS	204	204	243

‘green’ refers to sample isolated after SOLVO (180 °C, 24 h) treatment; ‘fired’ refers to ‘green’ samples that were subsequently processed at 450 °C for 60 min ambient atmosphere; ‘amorph’ = spectra width too large to adequately identify material (amorphous); a/r = aspect ratio; R = agreement with the PDF file; CS = crystallite size from Scheerer equation program.

List of Figures

Figure 1. Structural plot of $\text{La} \cdot \frac{1}{2}(\text{H}_2\text{O}) \cdot \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$. Thermal ellipsoids are drawn at 50 % level and disorder modeling removed for clarity. Two polymeric chains were solved in the unit cell.

Figure 2. Structural plot of $[\text{Ln}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n$ represented by **Eu**: (a) asymmetric unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level. Dashed lines show H-bonding interactions.

Figure 3. Structural plot of $[\text{Ln}(\mu\text{-TFA})_3(\mu\text{-H-TFA})]_n \cdot \text{solv}$ represented by **Er**·py: (a) symmetry generated unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level.

Figure 4. Structural plot of $\text{Lu} \cdot \text{H}_3\text{O}^+$: (a) asymmetric unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level.

Figure 5. Structural plot of $[(\text{py})_2\text{Tm}(\mu\text{-TFA})_3]_n$ (**Tm**) disorder modeling removed for clarity, represented by dashed bonds: (a) asymmetric unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level.

Figure 6. Structural plot of $8[\text{H}][(\text{Lu}(\mu_3\text{-O})_3(\mu\text{-TFA})_3(\kappa^2\text{-TFA}))_2(\text{Lu}(\text{TFA})_2)_3] \cdot 4\text{py}, 2\text{H-py}^+, \text{H}_3\text{O}^+$ (**Lu-O**). Thermal ellipsoids are drawn at 50 % level. Dashed lines show H-bonding interactions.

Figure 7. TGA/DSC data for representative compounds: (a) **La**, (b) **Nd**, (c) **Sm**, (d) **Tb**, and (e) **Y**.

Figure 8. TEM images of powders from the SOLVO routes using py for: (a) **La**, (b) **Tb** and (c) **Lu**; column (i) green and (ii) 450 °C processed. Scale bar is 20 nm.

Figure 9. TEM images of powders from the SOLVO routes using octylamine for: (a) **La**, (b) **Tb** and (c) **Lu**; column (i) green and (ii) 450 °C processed. Scale bar is 20 nm.

Figure 10. PXRD patterns of SOLVO routes for nanomaterials from (i) py and (ii) octylamine:

- (a) **La** [(i) fluocerite (LaF_3 , PDF 98-000-0214, $R = 9.64\%$, $35(0)$ nm); (ii) fluocerite/lanthanum oxide carbonate (LaF_3 , PDF 98-000-0214, $R = 7.47\%$, $5(0)$ nm; $\text{La}_2\text{O}_2(\text{CO}_3)$, PDF 01-070-5539, $R = 12.32\%$, $12(0)$ nm)],
 (b) **Tb** [(i) terbium fluoride (TbF_3 , PDF 00-037-1487, $R = 4.76\%$, $21(2)$ nm); (ii) terbium oxy fluoride (TbOF , PDF 00-008-0230, $R = 7.01\%$, $5(0)$ nm)], and
 (c) **Lu** (450°C) [(i) lutetium oxyfluoride (LuOF , PDF 00-052-0779, $R = 8.24\%$, $7(2)$ nm); (ii) lutetium oxide (Lu_2O_3 , PDF 00-012-0728, $R = 6.52\%$, $6(1)$ nm)].

Figure 11. DLS characterization of nanomaterials after 450°C processing, and methanol dispersion. py: (a) **La** – fluocerite, LaF_3 (b) **Tb** - terbium fluoride, TbF_3 (c) **Lu** lutetium oxy fluoride, LuOF octylamine: (d) **La** – fluocerite/lanthanum oxide carbonate, $\text{LaF}_3/\text{La}_2\text{O}_2(\text{CO}_3)$ (e) **Tb** - terbium oxy fluoride, TbOF , (f) **Lu** - lutetium oxide, Lu_2O_3 .

Figure 1. Structural plot of $\text{La} \cdot \frac{1}{2}(\text{H}_2\text{O}) \frac{1}{2}(\text{H}_2\text{O}, \text{H-TFA})$. Thermal ellipsoids are drawn at 50 % level and disorder modeling removed for clarity. Two polymeric chains were solved in the unit cell.

Figure 2. Structural plot of $[\text{Ln}(\mu\text{-TFA})_3(\text{H-TFA})_2]_n$ represented by **Eu**: (a) asymmetric unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level. Dashed lines show H-bonding interactions.

(a)

(b)

Figure 3. Structural plot of $[\text{Ln}(\mu\text{-TFA})_3(\mu\text{-H-TFA})]_n \cdot \text{solv}$ represented by **Er•py**: (a) symmetry generated unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level.

(a)

(b)

Figure 4. Structural plot of $\text{Lu}\cdot\text{H}_3\text{O}^+$: (a) asymmetric unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level.

(a)

(b)

Figure 5. Structural plot of **Tm** disorder modeling removed for clarity, represented by dashed bonds: (a) asymmetric unit cell and (b) expanded packing diagram. Thermal ellipsoids are drawn at 50 % level.

(a)

(b)

Figure 6. Structural plot of $8[\text{H}][\text{Lu}(\mu_3\text{-O})_3(\mu\text{-TFA})_3(\kappa^2\text{-TFA})_2(\text{Lu}(\text{TFA})_2)_3]\cdot 4\text{py}$, 2H-py^+ , H_3O^+ (**Lu-O**). Thermal ellipsoids are drawn at 50 % level. Dashed lines show H-bonding interactions.

Figure 7. TGA/DSC data for representative compounds:

(a) **La**, (b) **Nd**,
(c) **Sm**, d) **Tb**, and
(e) **Y**. X-axis scale 50 – 800 °C.

Figure 8. TEM images of powders from the SOLVO processing using py for: (a) **La**, (b) **Tb** and (c) **Lu** ; column (i) green and (ii) 450 °C processed. Scale bar is 20 nm.

Figure 9. TEM images of powders from the SOLVO routes using octylamine for: (a) **La**, (b) **Tb** and (c) **Lu**; column (i) green and (ii) 450 °C processed. Scale bar is 20 nm.

Figure 10. PXRD patterns of SOLVO routes for nanomaterials from (i) py and (ii) octylamine:

- (a) **La** [(i) fluorcerite (LaF_3 , PDF 98-000-0214, $R = 9.64\%$, $35(0)$ nm));
(ii) fluorcerite/lanthanum oxide carbonate (**red**: LaF_3 , PDF 98-000-0214, $R = 7.47\%$, $5(0)$ nm; **blue**: $\text{La}_2\text{O}_2(\text{CO}_3)$, PDF 01-070-5539, $R = 12.32\%$, $12(0)$ nm)],
(b) **Tb** [(i) terbium fluoride (TbF_3 , PDF 00-037-1487, $R = 4.76\%$, $21(2)$ nm);
(ii) terbium oxy fluoride (TbOF , PDF 00-008-0230, $R = 7.01\%$, $5(0)$ nm)], and
(c) **Lu** (450°C) [(i) lutetium oxyfluoride (LuOF , PDF 00-052-0779, $R = 8.24\%$, $7(2)$ nm);
(ii) lutetium oxide (Lu_2O_3 , PDF 00-012-0728, $R = 6.52\%$, $6(1)$ nm)].

Figure 11. DLS characterization of nanomaterials after 450 °C processing, and methanol dispersion. py: (a) **La** – fluocerite, LaF_3 (b) **Tb** - terbium fluoride, TbF_3 (c) **Lu** lutetium oxy fluoride, LuOF octylamine: (d) **La** – fluocerite/lanthanum oxide carbonate, $\text{LaF}_3/\text{La}_2\text{O}_2(\text{CO}_3)$ (e) **Tb** - terbium oxy fluoride, TbOF , (f) **Lu** - lutetium oxide, Lu_2O_3 .