Supporting Information

A new approach to nanoscopic rare earth metal fluorides: the fluorolytic sol-gel synthesis of ytterbium fluoride

Larisa Schmidt, Anton Dimitrov and Erhard Kemnitz

Humboldt-Universität zu Berlin, Department of Chemistry, Brook-Taylor-Straße 2, 12489 Berlin, Germany, *erhard.kemnitz@chemie.hu-berlin.de*

Experimental Part

1. *Synthesis of the sol and xerogel*

Ytterbium oxide (Chempur, 99.9%) was dissolved in HOAc (Carl Roth, 100% p.a.) and H_2O, respectively, under reflux resulting in the formation of ytterbium acetate tetrahydrate. The formed ytterbium acetate tetrahydrate was dried *in vacuo* at 90 °C for 6 h to give the anhydrous precursor compound. In a typical procedure for the preparation of a 0.1 M sol, 50 mL methanol (Aldrich, >99.6%) solution containing 1.75 g anhydrous ytterbium acetate (5 mmol) was stirred at reflux by heating for 30 min. Afterwards 0.96 mL (12.5 mmol) trifluoroacetic acid (Acros Organics, 99% extra pure) were added to the solution and stirred at reflux by heating for 1 h giving a transparent solution. 0.42 ml (10 mmol) of anhydrous HF solution (in methanol, c= 23.87 M) were added to obtain a transparent sol after 1 day of stirring at room temperature. The xerogel was obtained by removing the solvent and the resulting powder was finally dried under vacuum at temperatures up to 60 °C.

2. *Crystallization of* $[(H_2O)Yb(CF_3COO)_2(CH_3COO)]_n \cdot n[CH_3COOH]$

Single crystals have been obtained by the reaction of 0.7 g ytterbium acetate with 0.38 mL trifluoroacetic acid in an aqueous solution at about 90 °C for 3 hours, followed by evaporation and crystallization at room temperature. Anal. Calcd for $C_8H_9O_9F_6Yb$: C, 17.97; H, 1.68, Found: C, 17.19; H 1.57.

3. *Characterization*

The X-Ray powder patterns were recorded at room temperature on a XRD 3003 TT from Seiffarth using a CuKα radiation (Wavelength $CuK\alpha 1$ = 1.54056 Å).

The viscosity was measured with the Anton Paar Falling ball viscometer. For determining the dynamic viscosity, glass capillary with an inner diameter of 1.6 mm was used. The viscosity was detected at a temperature of 25 °C.

The measurements of the hydrodynamic particle diameter using DLS were carried out with a Zetasizer Nano from Malvern. Samples were analysed in the Malvern supplied "size" operating procedure, the light being detected at an angle of 173 ° and at a temperature of 25 °C.

The high-resolution transmission electron microscopy (HRTEM) measurements were performed on a JEOL TEM/STEM 2200 FS, with an acceleration voltage of 200 kV and a field emission source. Carbon coated 300 mesh copper grids were used as sample carrier.

IR spectra were recorded on a Digilab FTIR 3000 Excalibur series in ATR mode configuration.

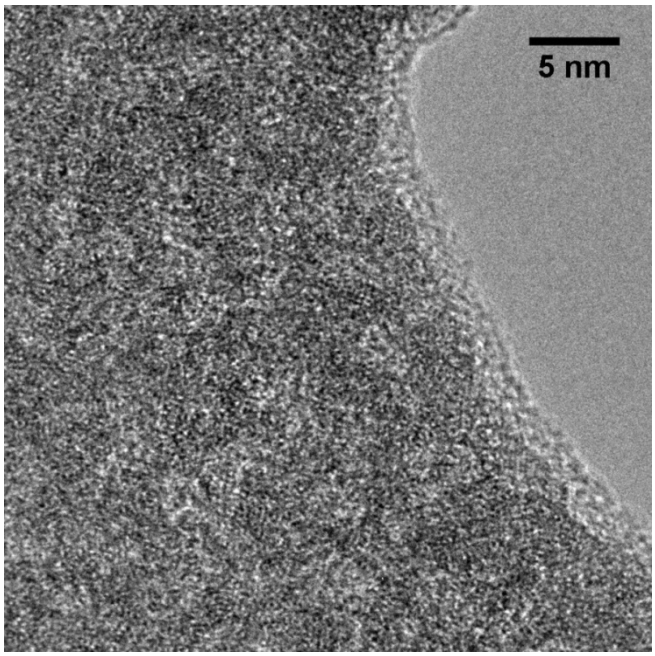

Fig S1: High-resolution TEM image of $YbF_{3-x}(O_2C_2F_3)_x$ nanoparticles obtained *via* sol-gel synthesis. The TEM grid was dip-coated into a 0.1 M sol and dried at 50 °C for 2 h.

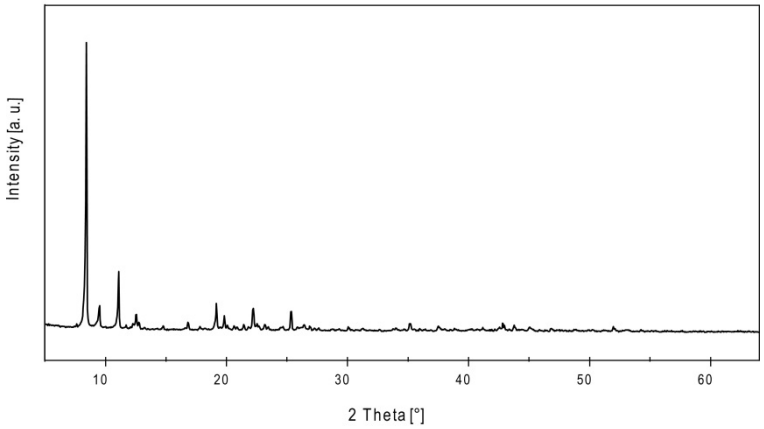

Fig S2: X-ray powder diffraction pattern of compound **1**.