Electronic Supplementary Information

Infrared-to-Visible Upconversion Luminescence in Er:Yb:SrFBr Nanocrystals

K. Tauni Dissanayake[a] and Federico A. Rabuffetti[a,†]

[a]Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

[†] Corresponding Author: far@chem.wayne.edu

Experimental

Synthesis. *General procedures.* All manipulations were conducted under nitrogen atmosphere using standard Schlenk techniques.

Reagents. $SrCO_3$ (99.9%), Yb_2O_3 (99.9%), Er_2O_3 (99.99%), CBr_3COOH (99%), oleic acid (90%), and octadecene (90%) were used as reagents. All chemicals were purchased from Sigma Aldrich and used as received. CBr_3COOH was stored in a glove box (oxygen and water levels below 1 ppm).

Synthesis of Metal Trifluoroacetate Precursors. Metal trifluoroacetate precursors were synthesized using a solvent evaporation method. Briefly, $SrCO_3$ (0.80 mmol, 0.1182 g), Yb_2O_3 (0.09 mmol, 0.0355 g), and Er_2O_3 (0.01 mmol, 0.0038 g) were added to a 50-mL three-neck reaction flask equipped with a condenser. 5 mL of double-deionized water and 1 mL of CF_3COOH were added to this mixture. The system was heated at 65 °C for 12 h under static nitrogen atmosphere to dissolve the rare-earth oxides; vigorous magnetic stirring was employed throughout. After 12 h, a clear solution was obtained. Crystallization of the metal trifluoroacetates was accomplished by solvent evaporation, which was induced by flowing dry nitrogen gas over the precursor solution. A glass adapter was placed in one of the necks of the flask to allow venting of the nitrogen gas. Then, it was immersed on a sand bath at 65 °C and nitrogen gas flow was started. A needle-valve rotameter was employed to regulate the nitrogen flow rate. A constant flow rate of 200 mL min^{-1} was employed. The system was left undisturbed for 48 h at 65 °C under flowing nitrogen. After 48 h, a mixture of trifluoroacetate powders was

obtained at the bottom of the reaction flask. Owing to its deliquescent nature, the mixture was kept under static nitrogen atmosphere until starting the synthesis of the Er:Yb:SrFBr nanocrystals.

Synthesis of Er:Yb:SrFBr Nanocrystals. Er:Yb:SrFBr nanocrystals were synthesized using a modified two-step route first reported by Chen et al.[1]

In the first step, Er:Yb:SrF$_2$ nanocrystals were synthesized as follows. An equimolar mixture of oleic acid (35 mmol) and octadecene (35 mmol) was added to the flask containing the mixture of metal trifluoroacetates. The total volume was ~25 mL. The flask was closed, immersed in a sand bath with a thermocouple sitting in the sand, and heated to 115 °C under low vacumm (~2 mTorr) to evacuate oxygen and water. The temperature was kept constant for 1 h. A clear solution was obtained. After 1 h, the atmosphere was switched back to nitrogen and a needle thermocouple was placed inside the flask in direct contact with the solution. The temperature was then raised to 250 °C and kept constant for 1 h. Magnetic stirring was employed throughout. After 1 h, the flask was removed from the sand bath and quenched to room temperature. A slightly turbid solution was obtained. Three drops of the solution were removed from the flask for transmission microscopy imaging.

In the second step, Er:Yb:SrFBr nanocrystals were prepared. This was done by adding CBr$_3$COOH (1 mmol, 0.2997 g) to the solution containing the Er:Yb:SrF$_2$ nanocrystals. CBr$_3$COOH was weighed inside a glove box and transferred to the reaction flask. Then, the flask was closed, immersed in a sand bath with a thermocouple sitting in the sand, and heated to 115 °C under low vacumm (~2 mTorr) to evacuate oxygen and water. The temperature was kept constant for 0.5 h. Then, the atmosphere was switched back to nitrogen and a needle thermocouple was placed inside the flask in direct contact with the solution. The temperature was raised to 225 °C and kept constant for 0.5 h. Magnetic stirring was employed throughout. After 0.5 h the flask was removed from the sand bath and quenched to room temperature using a stream of air. A turbid solution was obtained. Er:Yb:SrFBr nanocrystals were worked up by adding 50 mL of EtOH to the native solution, followed by centrifugation at 8500 rpm for 10 mins. The supernatant was discarded and the precipitate was resuspended in 5 mL of toluene. Then 7 mL of EtOH and 3 mL MeOH were added. The suspension was centrifuged at 8500 rpm for 10 mins, the supernatant discarded, and the precipitate dried at room temperature in a vacuum

oven. The resulting powder was employed for X-ray diffraction and total scattering analyses, transmission electron microscopy imaging, and spectrofluorometric characterization.

Characterization. *Powder X-ray Diffraction (XRD).* Conventional X-ray diffraction patterns of Er:Yb:SrF$_2$ and Er:Yb:SrFBr nanocrystals were collected in the 10–60° 2θ range using a Bruker D2 Phaser diffractometer operated at 30 kV and 10 mA. Cu Kα radiation (λ = 1.5418 Å) was employed. A nickel filter was utilized to remove Cu Kβ. Diffractograms were collected in 10−60° 2θ range using a step size of 0.025° and a step time of 1 s. Diffraction patterns were recorded at room temperature.

Transmission Electron Imaging (TEM). TEM images were obtained using a JEOL JEM2010F (JEOL Ltd.) electron microscope operated at 200 kV. Er:Yb:SrF$_2$ specimens were prepared by taking three drops of the native solution obtained after completing the first step of the synthesis, dispersing the nanocrystals in toluene, and drop-casting the resulting suspension on a 200 mesh Cu grid coated with a Lacey carbon film (Ted Pella Inc.). Er:Yb:SrFBr nanocrystals for TEM imaging were dispersed in ethanol and sonicated for 30 min. Then, a drop of the resulting suspension was deposited on a 200 mesh Cu grid coated with a Lacey carbon film.

Scanning Transmission Electron Microscopy – Energy Dispersive X-ray Spectroscopy (STEM−EDS). Elemental maps of F, Br, and Sr in Er:Yb:SrFBr nanocrystals were acquired using the ChemiSTEM mode of a Talos F200X S/TEM microscope (FEI Company) operated at 200 kV.

Inductively Coupled Plasma Mass Spectrometry (ICP−MS). Elemental analyses of Er, Yb, and Sr in SrF$_2$ and SrFBr nanocrystals were carried out using a 7700 Series ICP−MS (Agilent Technologies). 3−4 mg of each powder sample were digested in 20 mL of aqua regia for 24 h under ambient conditions. Erbium (989 ± 4 mg/L, Fluka), ytterbium (1000 μg/L, High Purity Standards), and strontium (1000 ± 2 mg/L, Fluka) in 2% HNO$_3$ were used as standards. For each composition, two samples of different batches were analyzed.

Synchrotron X-ray total scattering. X-ray total scattering data were collected at the 11−ID−B beamline of the Advanced Photon Source at Argonne National Laboratory. An incident photon energy of 58.649 keV (λ = 0.2114 Å) was employed. Er:Yb:SrFBr nanocrystals in powder form were loaded in a Kapton tube and scattering data were collected in transmission mode at room temperature.

Rietveld Analysis. Rietveld structural refinement was carried out using the GSAS software.[2–5] Experimental data and atomic X-ray scattering factors were corrected for sample absorption and anomalous scattering, respectively. The average crystal structure of Er:Yb:SrFBr nanocrystals was refined using the tetragonal *P4/nmm* space group. The occupancy of the metal site was fixed according to the ratios provided by ICP–MS: Er:Yb:Sr $\equiv$ 0.0015:0.0089:0.9896. The following parameters were refined: (1) scale factor, (2) background, which was modeled using a shifted Chebyschev polynomial function, (3) peak shape, which was modeled using a modified Thompson–Cox–Hasting pseudo-Voight function,[6] (4) lattice constants (*a* and *c*), (5) fractional atomic coordinates of the metal atom (zM) and of the bromine atom (zBr), and (6) an isotropic displacement parameter for each of the atoms of the structure (U_M, U_F, U_{Br}). The R_{wp} indicator was employed to assess the quality of the refined structural models.

Pair Distribution Function Analysis. The pair distribution function $G(r)$:

$$G(r) = 4\pi r[\rho(r) - \rho_0] = (2/\pi) \int_Q^{Q_{max}} Q[S(Q) - 1] \sin(Qr)\, \mathrm{d}Q$$

was employed for structural analysis. Here, r is the radial distance, $\rho(r)$ and ρ_0 are the local and average atomic number density, respectively. Q is scattering vector. The RAD software was employed to extract $G(r)$ from the raw scattering data.[7] These were first corrected for background, sample absorption, and Compton scattering. A normalized structure function $S(Q)$ was then obtained (Figure S4). Finally, $S(Q)$ was Fourier-transformed to yield $G(r)$. A Q_{max} of 22 Å^{-1} was employed in the Fourier transform. Structural refinements were carried out using the PDFgui software.[8] The local structure of Er:Yb:SrFBr nanocrystals was refined using the tetragonal *P4/nmm* space group. Fit of this structural model to the experimental PDF was performed in the 1.5–24 Å interatomic distance range. Similar to what was done in Rietveld analysis, the occupancy of the metal site was fixed according to the ratios provided by ICP–MS: Er:Yb:Sr $\equiv$ 0.0015:0.0089:0.9896. The following parameters were refined: (1) scale factor, (2) lattice constants (*a* and *c*), (3) fractional atomic coordinates of the metal atom (zM) and of the bromine atom (zBr), and (4) an isotropic displacement parameter for each of the atoms of the structure (U_M, U_F, U_{Br}). The R_w indicator was employed to assess the quality of the refined structural models.

Upconversion Spectrofluorometry. Spectrofluorometric analyses were conducted using a Fluorolog 3–222 fluorometer (Horiba Scientific). A PSU–III–LED (Opto Engine, LLC)

continuous-wave 980 nm laser was employed as the excitation source. Luminescence of Er:Yb:SrF$_2$ and Er:Yb:SrFBr nanocrystalline powders was probed using front-face geometry. Steady-state spectra were collected between 400 and 700 nm using a slit width of 1 nm. Time-dependent spectra were collected by operating the laser in pulsed-mode (pulse width ~275 µs and repetition rate of 180 Hz). All spectra were acquired at room temperature using an excitation power density of ~2.7 W cm^{-2}, unless indicated otherwise.

References

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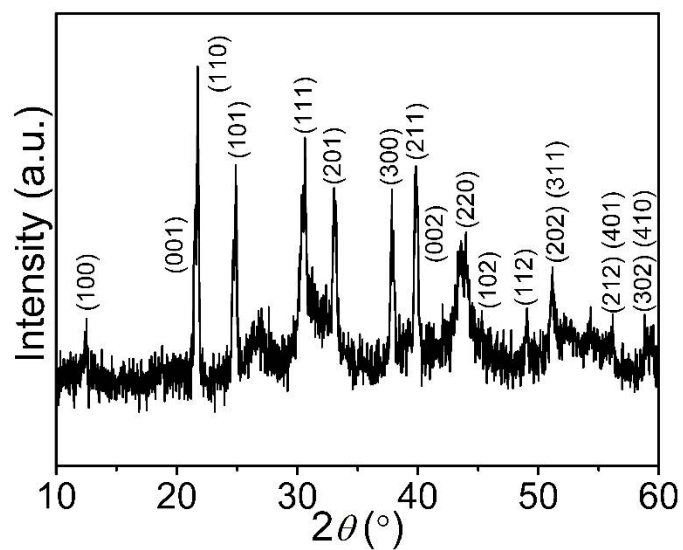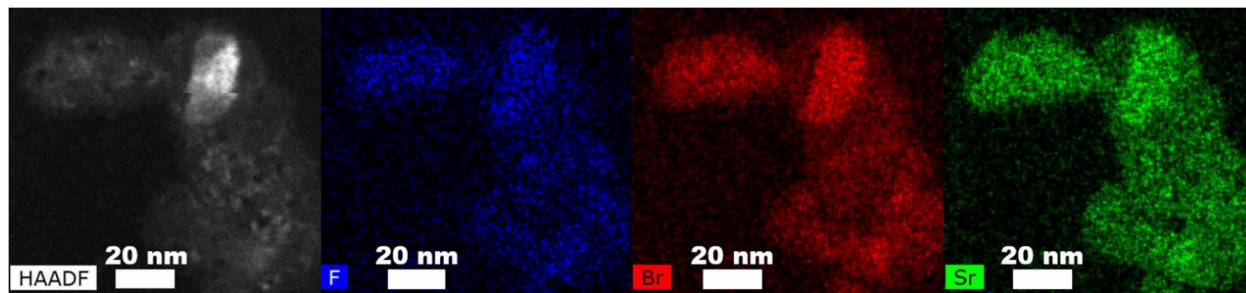
Figure S1. XRD pattern of the product obtained after decomposing 1 mmol of CBr_3COOH in the presence of $Er:Yb:SrF_2$ nanocrystals at 175 °C for 0.5 h. All the diffraction maxima can be indexed to the $SrBr_2 \cdot 6H_2O$ phase (PDF No. 06–0176).
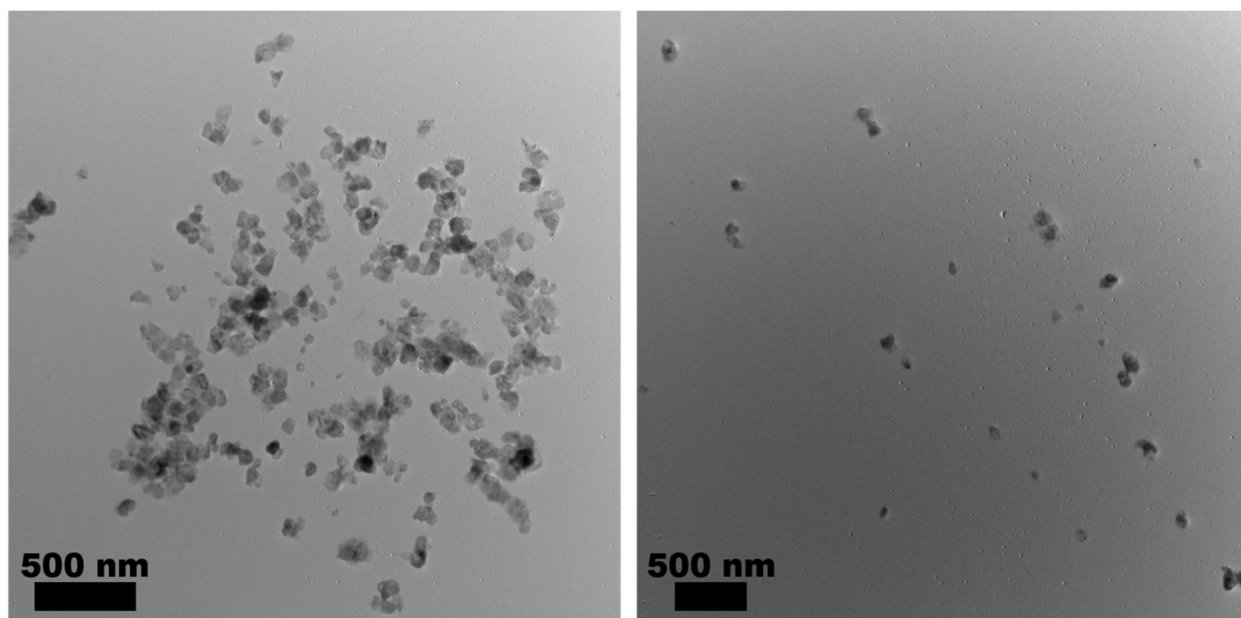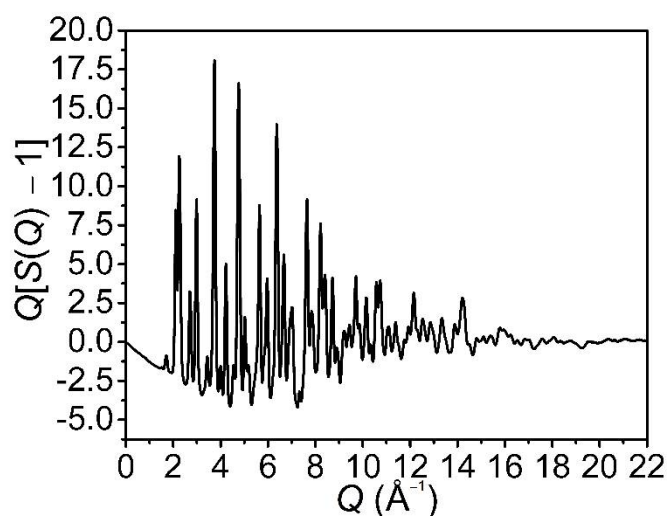
Figure S2. TEM images of Er:Yb:SrFBr nanocrystals.

Figure S3. STEM image of Er:Yb:SrFBr nanocrystals collected with a high-angle annular dark field detector (HAADF), and corresponding fluorine, bromine, and strontium STEM–EDS maps.

Figure S4. Structure function of Er:Yb:SrFBr nanocrystals.