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Small Alkaline-Earth-based Core/Shell Nanoparticles for Efficient Upconversion

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ABSTRACT: The optical efficiency of lanthanide-based upconversion is intricately related to the crystalline host lattice. Different crystal fields interacting with the electron clouds of the lanthanides can significantly affect transition probabilities between the energy levels. Here, we investigate six distinct alkaline-earth rare-earth fluoride host materials (M₁−xLnₓF₂±x, MLnF) for infrared-to-visible upconversion, focusing on nanoparticles of CaYF, CaLuF, SrYF, SrLuF, BaYF, and BaLuF doped with Yb³⁺ and Er³⁺. We first synthesize ∼5 nm upconverting cores of each material via a thermal decomposition method. Then we introduce a dropwise hot-injection method to grow optically inert MYF shell layers around the active cores. Five distinct shell thicknesses are considered for each host material, resulting in 36 unique, monodisperse upconverting nanomaterials each with size below ∼15 nm. The upconversion quantum yield (UCQY) is measured for all core/shell nanoparticles as a function of shell thickness and compared with hexagonal (β-phase) NaGdF₄, a traditional upconversion host lattice. While the UCQY of core nanoparticles is below the detection limit (<10⁻⁵%), it increases by 4 to 5 orders of magnitude as the shell thickness approaches 4–6 nm. The UCQY values of our cubic MLnF nanoparticles meet or exceed the β-NaGdF₄ reference sample. Across all core/shell samples, SrLuF nanoparticles are the most efficient, with UCQY values of 0.53% at 80 W/cm² for cubic nanoparticles with ∼11 nm edge length. This efficiency is 5 times higher than our β-NaGdF₄ reference material with comparable core size and shell thickness. Our work demonstrates efficient and bright upconversion in ultrasmall alkaline-earth-based nanoparticles, with applications spanning biological imaging and optical sensing.

KEYWORDS: upconversion, nanoparticles, core/shell, alkaline-earth metals

The crystalline host material of lanthanide-based luminescent materials plays a vital role in their spectroscopic properties and optical conversion efficiency. Because the interaction of 4f electrons with the crystal field of a host material is small, the energy levels of trivalent lanthanide ions are largely unchanged. However, this small interaction can significantly alter the probability of transitions between energy levels by relaxing the selection rules for radiative transitions. Exploring novel host materials has led to breakthroughs in LED phosphors with higher conversion efficiencies, temperature stability, and much desired bright and narrow (∼50 nm) red emission bands. The host material has not yet played a dominant role in research related to upconverting nanoparticles (UCNPs), where multiple low energy photons are converted into one or more higher-energy photons. Indeed, for the past decade, hexagonal-phase sodium rare-earth tetrathalflouride (β-NaLnF₄) has served as the preeminent UCNP host material. This host lattice is known to support relatively low phonon energies as well as two different lattice sites for the lanthanide ions, which experience different crystal fields; accordingly, it sustains highest upconversion quantum yields (UCQYS). The synthesis of β-NaLnF₄ nanoparticles is now well-understood, and many syntheses and shelling procedures have been developed to obtain high quality and monodisperse UCNPs with different shapes and complex multiple shell layers. Accordingly, most attention has been given to optimizing the doping concentrations of optically active dopants, creating various nanoparticle morpholo-
gies,12,13,21,22 and coating the nanoparticle with multiple optically inert11,23−25 or active shells.10,14,26 Recently, other fluoride host materials have received increasing attention, inspired in part by bulk powder studies.19,20,22,27−31 For example, LiLnF4 has received interest because of strong ultraviolet emission in core/shell UCNPs when doped with Yb3+ and Tm3+, which can be used for photodynamic therapy and to initiate drug release.32 Lanthanide fluoride (LnF3)22,31 and lanthanide-doped alkaline fluoride (MF2)33−35 nanoparticles have been researched intensively, but the reported upconversion efficiencies have been lower compared to β-NaLnF4. Alkaline-earth rare-earth fluoride (M1−xLnxF2+x) host lattices, with upconversion studies dating back to 1969,36 promise high radiative efficiencies. For example, in bulk studies, BaYF5 powder was found to have UC power conversion efficiencies rivaling GaP LEDs,37 and monocrystalline Er3+-doped BaY2F8 showed efficient utilization of sub-bandgap photons for silicon solar cells.38 The interchangeability of alkaline-earth and rare-earth elements in the M1−xLnxF2+x system also promises tunable stoichiometry, alloying, and potentially cation doping or exchange with other elements, such as transition metal ions, to alter material and optical properties. A recent study produced monodisperse core/shell SrLuF6 UCNP for multimodal bioimaging with bright upconversion but without any quantitative optical measurements.39 The synthesis of M1−xLnxF2+x core and core/shell nanoparticles has proven challenging, generally producing nanoparticles with broad size distributions, large variations in doping concentrations, and limited colloidal stability.28,40−43 Moreover, M1−xLnxF2+x core/shell nanoparticle performance in comparison to traditional upconverting host materials, such as β-NaGdF4, remains unknown.

Here, we synthesize and characterize ultrasmall M1−xLnxF2+x core/shell UCNPs and benchmark their upconversion quantum yield (UCQY) and time-dependent luminescence as a function of shell thickness against the standard material system, β-NaGdF4. We consider UCNPs across the alkaline-earth series (M = Ca, Sr, and Ba) in combination with Y3+ and Lu3+ as host materials for the dopants Yb3+ and Er3+. Our alkaline-earth-based UCNPs show mostly green and red upconversion emission under 980 nm laser illumination as illustrated by the energy level diagram in Figure 1a. The dominant upconversion mechanism is based on Förster resonant energy transfer (FRET), which depends on the inverse distance between the dopants to the power of 6. Therefore, the dynamics of the nonlinear upconversion processes and consequently the optical properties of the UCNPs depend significantly on the distance between the dopants.

We match the average distance between dopants of face-centered cubic-phase M1−xLnxF2+x to β-NaGdF4 with 20% Yb3+ and 2% Er3+, where the highest UCQY values have been reported.7,9 For a given crystal structure and lattice parameters, the average distance translates to an equivalent doping concentration, which we use for the synthesis of the M1−xLnxF2+x UCNP. The alkaline-earth rare-earth fluoride (MLnF) material system is based on the MF2 crystal structure and every alkaline-earth cation position can be exchanged with rare-earth cations. This cation interchangeability makes the M1−xLnxF2+x quite complex but also very interesting and
versatile. A detailed discussion on equivalent doping of rare-earth cations versus all cations, M and Ln, is given in the Supporting Information (SI). In the following, we use the abbreviations MLnF for M_{1−x}Ln_xF_{2+x} and NaGdF for β-NaGdF_4.

The six different MLnF UCNP core samples—CaYF, CaLuF, SrYF, SrLuF, BaYF, and BaLuF—are synthesized by thermal decomposition of alkaline-earth (M) and rare-earth (Ln) trifluoroacetate salts in a 1:1 molar ratio in oleic acid (OA), 1-octadecene (ODE), and oleylamine (OLA) at 300 °C under inert atmosphere using a Schlenk line. We adopt this core synthesis from a recent report of monodisperse SrLuF_3 UCNPs (see SI).^{39} We target doping concentrations of 28.4% Yb^{3+} and 2.8% Er^{3+} based on equivalent doping considerations. We then develop a hot injection shelling method to grow the corresponding inert MYF layers around the upconverting cores. The cores are shed by dropwise injection of shelling precursor solutions into the 300 °C mixture of washed UCNP cores in OA and ODE (see Figure 1b). Yttrium oleate and alkaline-earth trifluoroacetate salts dissolved in OA and ODE are mixed with a 1:1 molar ratio and used as shelling precursor solutions. Using the core diameter, we calculated the amount of shell precursor to be added to obtain shell thicknesses of 1, 2, 3, 5, and 7 nm. After injection of the corresponding shell precursor amount, we wait 5 min before taking an aliquot using a glass syringe and continuing the shelling procedure for the next sample. The NaGdF core and core/shell UCNPs are prepared as reported in the literature,^{25} apart from washing the core UCNPs before shelling to reduce possible intermixing due to potentially unconsumed rare-earth cations in the core synthesis mixture. All UCNPs are dispersed in toluene for characterization.

TEM images of our UCNP cores are shown in Figure 1c–i. The cores are monodisperse and around 5 nm in diameter. During the shelling procedure of each MLnF combination, we extract aliquots at different times to obtain a series of five core/shell UCNP samples (CS1–CS5). The UCNPs with the thickest shell (CS5) are shown in Figure 1j–p, while CS1–CS4 are shown in the SI. All samples are of high crystalline quality and monodisperse with standard deviation around 10%. The measured shell thicknesses vary between the samples due to uncertainty in the core diameter, unequal amounts of aliquots taken out of the hot solution, and varying stoichiometric ratios of the different MLnF UCNPs. Detailed material characterization and size distributions of all samples are compiled in the SI. Shape transformation from spherical to cubic is observed after the first or second aliquot when the nanoparticle size exceeds approximately 7 nm. Ca-based nanoparticles, however, remain more spherical. This morphology could be related to a kinetically dominated shell growth regime, due to the lower decomposition temperature of Ca trifluoroacetate compared to the other alkaline-earth trifluoroacetates. To compare the cubic-morphology MLnF samples to the spherical NaGdF particles, we calculate an effective diameter by equating the cube volume to a spherical volume (see SI). For example, the sample SrLuF CS5 with edge length of 11 ± 1 nm converts into an effective diameter of 13.6 ± 1.2 nm (see SI).

We use X-ray powder diffraction (XRD) to assign all MLnF samples to face-centered cubic structure with space group Fm3m. We note, however, that reference XRD patterns are at different contributions from the green (4I_{15/2} \rightarrow 4F_{9/2}) and red (4F_9/2 \rightarrow 4I_{13/2}) transitions, evidenced by changes to the relative green and red intensities in upconversion spectra (Figure 3b). In comparison to the NaGdF reference, all MLnF samples show stronger red
emission. We measured the upconversion quantum yield (UCQY) as a function of irradiance and shell thickness using 800 nm continuous-wave (cw) laser excitation. The UCNPs also emit around 980 nm from Er^{3+} \rightarrow 3I_{11/2} \rightarrow 3H_{15/2} \rightarrow 3F_{7/2} transition, which overlaps with the laser excitation. We subtract this emission in our UCQY analysis to accurately estimate the UCQY values (see SI). The UCQY of all cores was below our setup detection limit of \( \sim 10^{-5} \)%. 

Typically, thicker shells increase UCQY values by reducing surface quenching effects, which can be minimized at shell thicknesses of \( 4 \sim 10 \) nm.\(^{25,45-48} \) For a meaningful comparison between the samples, we factor out the effect of shell thickness by fitting the data to a simple model described by eq 1.\(^{46,47} \) The effect of surface quenching can be described by Förster-type energy transfer from a donor to a plane acceptor, the surface, by

\[
\text{UCQY}(d) = \frac{\text{UCQY}(d \to \infty)}{1 + (d_d/d)^\delta}
\]

(1)

Here, \( d \) is the shell thickness, \( d_d \) is the Förster distance, and UCQY\((d \to \infty)\) is the UCQY for infinite thick shells; \( d_d \) and UCQY\((d \to \infty)\) are fitting parameters.\(^{46,47} \) Figure 3c shows the UCQY trend as a function of shell thickness for an UCQY\((d \to \infty)\) of \( \sim 80 \) W/cm\(^2\).

Table 1. Atomic Composition between Alkaline-Earth Ions (M = Ca, Sr, Ba) and Rare-Earth Ions (Ln = Lu, Gd, Y, Yb, Er) of the Core UCNPs and Figures of Merit from Optical Characterization

<table>
<thead>
<tr>
<th>Material</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>Lu</th>
<th>Y</th>
<th>Yb</th>
<th>Er</th>
<th>M/Ln</th>
<th>( x^d )</th>
<th>Cation Doping Yb/Er (%)</th>
<th>UCQY((d \to \infty)) (%)</th>
<th>Q</th>
<th>( \tau(d \to \infty) ) (( \mu ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaYF</td>
<td>99.6</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
<td>75.3</td>
<td>22.4</td>
<td>2.2</td>
<td>1.69</td>
<td>0.37</td>
<td>8.3/0.8</td>
<td>0.21 ± 0.03</td>
<td>20990</td>
<td>998</td>
</tr>
<tr>
<td>CaLuF</td>
<td>99.7</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>66.7</td>
<td>30.3</td>
<td>2.9</td>
<td>1.83</td>
<td>0.35</td>
<td>10.7/1.0</td>
<td>0.43 ± 0.09</td>
<td>42300</td>
<td>1053</td>
</tr>
<tr>
<td>SrYF</td>
<td>1.9</td>
<td>98.1</td>
<td>0.0</td>
<td>0.0</td>
<td>74.1</td>
<td>23.6</td>
<td>2.3</td>
<td>1.51</td>
<td>0.40</td>
<td>9.4/0.9</td>
<td>0.27 ± 0.03</td>
<td>27400</td>
<td>1945</td>
</tr>
<tr>
<td>SrLuF</td>
<td>0.2</td>
<td>99.8</td>
<td>0.0</td>
<td>0.1</td>
<td>30.6</td>
<td>2.9</td>
<td>2.9</td>
<td>1.52</td>
<td>0.40</td>
<td>12.1/1.1</td>
<td>0.94 ± 0.22</td>
<td>94300</td>
<td>1391</td>
</tr>
<tr>
<td>BaYF</td>
<td>2.4</td>
<td>0.8</td>
<td>96.9</td>
<td>0.0</td>
<td>74.8</td>
<td>22.9</td>
<td>2.3</td>
<td>1.20</td>
<td>0.45</td>
<td>10.4/1.1</td>
<td>0.37 ± 0.09</td>
<td>36500</td>
<td>828</td>
</tr>
<tr>
<td>BaLuF</td>
<td>0.1</td>
<td>0.8</td>
<td>99.1</td>
<td>0.1</td>
<td>30.6</td>
<td>2.9</td>
<td>2.9</td>
<td>1.70</td>
<td>0.46</td>
<td>13.8/1.3</td>
<td>0.45 ± 0.07</td>
<td>44500</td>
<td>473</td>
</tr>
<tr>
<td>NaGdF</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>100</td>
<td>80.0</td>
<td>17.9</td>
<td>2.1</td>
<td>1.19</td>
<td>0.46</td>
<td>9.3/1.1</td>
<td>0.19 ± 0.04</td>
<td>18700</td>
<td>973</td>
</tr>
</tbody>
</table>

\( ^{d} \)Ratios of alkaline-earth to rare-earth metals (M:Ln) as determined form the ICP-OES data show the large stoichiometric range in the \( \text{M}_{1-x}\text{Ln}_{x}\text{F}_{24-x} \) material system. Cation doping of \( \text{Yb}^{3+} \) and \( \text{Er}^{3+} \) considering the sum of all M and Ln elements from ICP-EOS measurements. Calculated UCQY for infinite shell thickness \( (d \to \infty) \) at 80 W/cm\(^2\) derived from eq 1 and lower limit of the estimated enhancement factor \( Q \) compared to the core UCNPs. The decay time \( \tau(d \to \infty) \) of the \( \text{Yb}^{3+}\rightarrow\text{F}_{5/2} \rightarrow \text{F}_{7/2} \) transition (excitation at 980 nm, emissions at 1000 nm) was determined by fitting eq 2 to the decay times as a function of shell thickness. Stoichiometry \( x \) in \( \text{M}_{1-x}\text{Ln}_{x}\text{F}_{24-x} \) is the lower limit of estimated enhancement of UCQY\((d \to \infty)\) compared to core at \( \sim 80 \) W/cm\(^2\).
samples are generally more efficient than the MYF ones, which may be related to the closer value of the cation doping concentration to the hypothesized optimum in MLnF. SrLuF is the most efficient upconverter with an UCQY of 0.53 ± 0.07% at 80 W/cm² for nanoparticles with an edge length of 11.0 ± 1.0 nm. This efficiency translates into an enhancement of >52800× from the SrLuF cores of 4.9 ± 0.4 nm in diameter to core/shell UCNPs with thickest shell, considering our UCQY detection limit of ∼10⁻⁵% for the core UCNPs. Accordingly, the UCQY(d → ∞) is >94300× higher than the core UCQY value. The UCQY of all samples is far from saturation, and higher efficiencies can be reached at higher irradiances (Figure 3d).

There are very few reports on UCQY values for ultrasmall core/shell UCNPs. The most comparable studies with similar core size and shell thickness are from Li et al., Hudry et al., and Würth et al. (see also SI).²³,²⁵,⁴⁸ Li et al. reported an UCQY of 0.5% at 100 W/cm² for ∼5 nm β-NaYF₄: 20% Yb³⁺, 2% Er³⁺ core with ∼6 nm β-NaYF₄ shell with a total diameter of 17 nm.²³ Hudry et al. determined an UCQY of ∼0.55% at 100 W/cm² for ∼4.8 nm β-NaGdF₄: 20% Yb³⁺, 2% Er³⁺ core with ∼3.5 nm β-NaYF₄ shell with a total diameter of 11.7 nm.²⁵ Würth et al. measured an UCQY of ∼0.3% at 100 W/cm² for ∼4 nm β-NaGdF₄: 20% Yb³⁺, 2% Er³⁺ core with ∼6 nm β-NaYF₄ shell with a total diameter of 16 nm.²⁵ To be comparable to the literature values, we estimate an UCQY for our SrLuF CS5 sample of 0.66% at 100 W/cm² by extrapolating the irradiance-dependent UCQY shown in Figure 3d. In order to account for the thicker inert shell layers reported by Li et al. and Würth et al., we extrapolate to a shell thickness of ∼5.5 nm using the data shown in Figure 3c,d. For such SrLuF core/shell UCNPs with a total size of ∼16 nm, we estimate an UCQY of ∼1.0% at 100 W/cm². This comparison shows that our SrLuF core/shell UCNPs are as efficient or even better than the best β-NaLnF₄ core/shell UCNPs found in literature when considering equivalent core size, shell thickness, and irradiance. The excellent efficiency of SrLuF is based on equivalent doping considerations to equal β-NaGdF₄ with 20% Yb³⁺ and 2% Er³⁺. The concept of equivalent doping is a reasonable starting point for our investigation of MLnF UCNPs, but it is a simplification.
of the dopant distribution in the crystals. Moreover, it does not account for changes in stoichiometric ratios between the alkaline-earth and the rare-earth cations (see SI). It is expectable that higher UCQY values are possible by optimizing the concentration of the dopants.

We next measure time-dependent luminescence of the most relevant energy levels for direct photoluminescent excitation as well as in upconversion mode using 980 nm excitation for all samples (see SI). As one example, Figure 4a shows the increase of decay time from the core to the core/shell SrLuF samples for the Yb$^{3+}$$^4I_{15/2} \rightarrow ^2F_{7/2}$ transition. The decay curves of the CSS samples of all considered host lattices are shown in Figure 4b–d under 980 nm excitation and emission of the Yb$^{3+}$$^4I_{15/2} \rightarrow ^2F_{7/2}$ transition at 1000 nm, Er$^{3+}$$^4S_{3/2} \rightarrow ^4I_{13/2}$ transition at 540 nm, and Er$^{3+}$$^4F_{9/2} \rightarrow ^4I_{15/2}$ transition at 654 nm, respectively. We use a 1/$\tau$ definition to determine the decay times and quantify the time-dependent photoluminescence dynamics. It is often presumed that longer lifetimes of the sensitizer excited state, here Yb$^{3+}$$^4I_{15/2}$ (Figure 4b), translates into higher UCQY. We did not find a direct correlation between the trend in the decay time of the Yb$^{3+}$ excited state and the UCQY. For instance, if we take CSS samples, BaLuF is more efficient than SrYF although the lifetime of the Yb$^{3+}$ excited state is 3 times shorter. The different crystal fields acting on the electron clouds of lanthanide ions in the different host materials may contribute to this effect of shorter lifetimes and higher efficiency by further relaxing the selection rules of certain transitions, thereby enhancing dipole moments. Altered energy transfer rates between the lanthanides due to changes in the overlap integral of absorption and emission spectra between ground and excited states but also between excited states may be another factor for the great performance of the SrLuF sample.

It is worth noting that the rise time of the upconversion luminescence of NaGdF$\_4$ shown in Figure 4c,d, is the only one to stand out as the longest although the decay time of the Yb$^{3+}$$^4I_{15/2} \rightarrow ^2F_{7/2}$ transition, shown in Figure 4b, is among the three shortest (see also SI). The shorter rise time of MLnF UCNPs may be attributed to a faster depopulation of the Er$^{3+}$$^4S_{3/2}$ energy level or a stronger coupling between the Er$^{3+}$ and Yb$^{3+}$, which could eventually lead to the higher UCQY values measured in this study for MLnF UCNPs.

To factor out the different shell thicknesses, we fit the decay times as a function of shell thickness for all material combinations with

$$\tau(d) = \frac{\tau(d \rightarrow \infty)}{1 + (d/d_0)^\beta}$$

in accordance with eq 1. Here, we set the starting value of the function to the decay time of the core UCNPs. The trends in Figure 4e are different to the ones of the UCQY in Figure 3c further highlighting the discrepancy between decay time and UCQY in different host materials. While in Figure 3c Lu-based and Y-based MLnF UCNPs build separate groups, in Figure 4e the different alkaline-earth elements seem to build groups; Ba-based samples show the shortest decay time, Sr-based samples have the longest decay time, and Ca-based samples are in the middle.

To further quantify the differences in the host materials, the same data analysis is performed on the time-dependent luminescence under direct excitation of the measured energy level at center emission wavelength of 540, 654, 1000, and 1530 nm to obtain the $\tau(d \rightarrow \infty)$ values relative to those of NaGdF$\_4$ (Figure 4f). In general, the Er$^{3+}$$^4S_{3/2}$ energy level in MLnF UCNPs have significantly shorter lifetimes in contrast to NaGdF. The reddest samples, CaYF and CaLuF, also have shorter Er$^{3+}$$^4F_{9/2}$ lifetimes suggesting larger dipole moments likely as a result of different crystal field distortion of the electron cloud of erbium ions. The NIR emission from Er$^{3+}$$^4I_{13/2} \rightarrow ^4I_{15/2}$ is quite similar for all samples with ~20% longer decay times for the Sr- and Ba-based samples.

The superior performance of SrLuF could be explained by several factors, including relaxed selection rules, modified phonon modes, or reduced cation intermixing. Detailed spectroscopic analysis including Judd–Ofelt theory could provide insight into the dipole moments of the transitions. Additionally, determining the phonon energy distribution and FRET rates between different energy levels could inform the dynamics of upconversion between the different materials. Finally, we note that cation intermixing at the core/shell interface impacts the performance of the UCNPs. In particular, mixing of rare-earth ions from core and shell layers due to diffusion or incorporation during the shelling procedure can reduce the passivation effect of the shell layer and dilute the active cations in the core. The superior performance of SrLuF may be a result of less pronounced cation intermixing compared to other host materials such as NaGdF$\_4$. All such studies are exciting future directions to explore in pursuit of the next high-efficiency upconverting host.

In conclusion, we have introduced a host material platform for efficient and small lanthanide-doped core/shell nanoparticles. We have synthesized a series of ~5 nm alkaline-earth rare-earth fluorides (MLnF) core UCNPs and developed a hot-injection shelling approach. Inert MYF shell layers with different thickness have been grown around the active cores of the six different MLnF UCNPs. We compared the optical properties of the different MLnF UCNPs to $\beta$-NaGdF$\_4$, a reference upconverting host material, as a function of the shell thickness. Due to reduced surface quenching by the inert shell layers, we measured efficiency enhancements of 4–5 orders of magnitude from the core to the core/shell samples. The host material SrLuF provides the most efficient UCNPs of the samples studied and outperforms the $\beta$-NaGdF$\_4$ reference by a factor of 5 at comparable core sizes and shell thickness. Our SrLuF is also as efficient or better than comparable NaYF$\_4$-based UCNPs reported in the literature. Further optimization of doping concentrations for the alkaline-earth rare-earth fluoride host materials promise even better performance with higher UCQY and brightness. In addition, the interchangeability of alkaline-earth and rare-earth elements in the MLnF system allow strong variations in stoichiometric ratios, alloying, and potentially cation doping or exchange with other elements, such as transition metal ions, to alter material and optical properties. Our results show that MLnF, and in particular SrLuF, are host materials that provide efficient upconversion for ultrasmall UCNPs, which are particularly interesting as multiphoton nanoprobe for applications in biological imaging and sensing, life science, and energy-related applications.

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.9b01057.
Experimental details, synthesis protocols, doping level calculations, discussion on equivalent vs. cation doping, TEM images, size distributions, XRD, time-dependent photoluminescence, absorption correction for UCQY, and power-dependent UCQY. 

APPENDIX

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
UCNP, upconverting nanoparticles; UCQY, upconversion quantum yield; Ln, rare-earth metals; M, alkaline-earth metals; NaGdF₄, β-NaYF₄; MLnF; MₓLₓ−xF₂x; MₓLₓ−xF₂x+.

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