Spectral characterization of LiYbF₄ upconverting nanoparticles

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Abstract

In light of the recent developments on Yb³⁺-based upconverting rare-earth nanoparticles (RENPs), we have systematically explored the spectral features of LiYbF₄:RE³⁺/LiYF₄ core/shell RENPs doped with various amounts of Tm³⁺, Er³⁺, or Ho³⁺ ions. Tm³⁺-RENPs displayed photoluminescence from UV to near-infrared (NIR), and the dominant high-photon-order upconversion emission of these particles was tunable by Tm³⁺ doping. Similarly, Er³⁺- and Ho³⁺-RENPs with green and red upconversion showed wide color tuning depending on doping amount and excitation power density. From steady-state power plot and photoluminescence decay studies we have observed respective changes in upconversion photon order and average lifetime that attest to a number of cross-relaxation processes occurring at higher RE³⁺ doping concentration. Particularly in the case of Tm³⁺-RENPs, cross-relaxation promotes four- and five-photon order upconversion emission in UV and blue spectral regions. Quantum yield of higher order upconversion emission was on par with classic Yb³⁺/Tm³⁺-doped systems, yet due to the high number of sensitizer ions in the LiYbF₄ host these RENPs are expected to be brighter and thus better suited for applications such as controlled drug delivery or optogenetics. Overall, LiYbF₄:RE³⁺/LiYF₄ RENPs are promising systems to effectively generate high-

order upconversion emissions, owing to excitation energy confinement within Yb^{3+} network and its efficient funneling to the activator dopants.

Introduction

Favored in biomedical, energy, and anti-counterfeiting sectors, rare earth nanoparticles (RENPs) are at the forefront of multifunctional photoluminescent (PL) nanomaterials. RENPs are intensively researched as temperature and pressure sensors,^[1,2] active media for microscale lasers,^[3,4] optical actuators,^[5–8] and theranostic agents,^[9] to name a few examples. Such diversity is owed to the high degree of freedom in designing these host-guest systems. Host selection, doping type and concentration, or core/shell architecture can all be varied to attain desired RENPs.

A distinctive feature of RENPs is upconversion (anti-Stokes PL): the ability to transform low energy photons into higher energy ones – mostly near-infrared (NIR) excitation to UV, visible and shorter wavelength NIR emission.^[10] Long-lived $4f$ electronic states of RE^{3+} , and their near evenly spaced ladder-like arrangement, enable photon upconversion at low-to-moderate excitation power densities of 10^{-3} - 10^3 W/cm². Yet, the full potential of RENPs is often plagued by their low absorption cross-section and low upconversion quantum yield (*UCQY*). A number of strategies have been proposed to increase *UCQY*,^[11,12] among the simplest and most effective is the growth of an optically inert shell as a final enclosure to the active-core of the RENPs, protecting them from external quenching.^[13–15] Thus, RENPs with *UCQY* approaching the one of their bulk counterpart could be conceived.^[16] Together with new host materials and improved synthesis strategies, use of the active-core/passive-shell architecture enables the engineering of small and bright RENPs, pertinent to the biomedical framework.^[17,18] Despite great strides in improving *UCQY*, low absorption cross-section remains an intrinsic limitation set by the parity forbidden electronic transitions between different RE^{3+} $4f$ states. Dye-sensitization^[19,20] or coupling to plasmonic structures^[21] can greatly improve harvesting of the excitation energy, however, these avenues are still rather complex to execute in real life applications, particularly biomedical.

In fact, the active-core/passive-shell strategy has recently influenced the reevaluation of optimal RENP doping and became a mean to increase excitation light absorption.^[22] Generally, RENPs are doped with RE^{3+} acting as sensitizers (Yb^{3+} , Nd^{3+} , and recently

Tm^{3+})[23–26] and activators (Tm^{3+} , Er^{3+} , Ho^{3+})[27,28], the former being responsible for NIR light absorption and the latter for upconversion emission. In classic $\text{Yb}^{3+}/(\text{Tm}^{3+}$, Er^{3+} or $\text{Ho}^{3+})$ RENPs, the optimization for most intense upconversion emission fixes Yb^{3+} doping to the 18-25 mol% range. Beyond this, the extended Yb^{3+} network facilitates long-scale energy migration to the surface of the RENPs and subsequent PL loss to external quenchers. However, once quenching by surface defects or vibrational modes of the solvent are suppressed by an inert shell, the limits on Yb^{3+} doping can be lifted.[29] RENPs whose hosts are comprised entirely of Yb^{3+} ions (i.e. NaYbF_4 , LiYbF_4 , KYb_2F_7) can absorb significantly more of incoming photons and efficiently funnel that excitation to their higher energy states, due to the close proximity between Yb^{3+} and activator dopants.[30] As such, Yb^{3+} -based RENPs have lately received much attention in terms of their controlled and reproducible synthesis,[17,31,32] but still little is reported on their spectral properties or how those are influenced by different activators and their concentration. Furthermore, among Yb^{3+} -based RENPs, Li^+ -type hosts continue to be largely underrepresented.

LiYF_4 , LiLuF_4 , and LiYbF_4 crystals have low phonon energies and high crystal field strengths,[33] favored not only in solid-state lasers, but also when designing bright RENPs with well-resolved spectral signatures.[34–37] Li^+ -based RENPs are also considered to have greater higher-order upconversion capacity (i.e. UV/blue emission of Tm^{3+}) compared to their Na^+ analogs,[32,35] however, rigorous comparative analysis to ascertain this fact is yet to be carried out. Applications requiring high energy photons to initiate secondary photochemical processes *in situ*, like controlled drug release, optogenetics, or photopolymerization are on a constant lookout for RENPs that would effectively satisfy their demands. Ergo, continuously expanding understanding on how to synthesize high-quality Li^+ -based RENPs of various sizes and architectures needs to be complemented with a better grasp on their spectral properties and alteration thereof.

Here, we provide a systematic study on the photophysical properties of $\text{LiYbF}_4:\text{RE}^{3+}/\text{LiYF}_4$ RENPs, laying the foundation to understand their true potential and possible limitations. We focused on the Tm^{3+} -doped RENPs, unveiling how the dopant concentration and excitation power density influence Tm^{3+} upconversion spectrum, excited states' lifetimes, and UCQY. We further expanded the investigation to Er^{3+} - and Ho^{3+} -RENPs, broadening the fan of obtainable emission colors. The library of produced $\text{LiYbF}_4:\text{RE}^{3+}/\text{LiYF}_4$ RENPs,

with their diverse characteristics, is testimony to the flexibility and broad-range applicability of these systems.

Results

Structural characteristics

LiYbF₄: x mol% RE³⁺/LiYF₄ core/shell RENPs (RE³⁺ = Er³⁺, Tm³⁺, Ho³⁺) were prepared *via* the previously reported method.^[17] In brief, first nuclei nanoparticles were prepared from thermally decomposed metal precursors in a mixture of oleic acid and oleylamine, followed by their stabilization in an excess of oleic acid to form the desired LiYbF₄:RE³⁺ cores. Finally, cores were coated with an inert LiYF₄ shell. Three sets of RENPs were synthesized, distinct by the activator ion of varying doping concentration: i) 0.2 to 2 mol% - Tm³⁺, ii) 1 to 10 mol% - Er³⁺, and iii) 1 to 5 mol% - Ho³⁺ (see details in Table S1). LiYbF₄:RE³⁺/LiYF₄ RENPs displayed bi-pyramidal morphology (**Figure 1** and S1-S3), indicative of the tetragonal (*I*₄₁/*a*) crystal structure, which was confirmed by X-ray powder diffraction (Figure S4-S6). All LiYbF₄:RE³⁺ cores were 10-12 nm in size measured along their major axis, subsequently shielded by a LiYF₄ shell of at least 5-nm thickness (Figure S1-S3, Table S1). The final core/shell size of the three sets was: 25-28, 22-23 and 25-27 nm for Tm³⁺-, Er³⁺- and Ho³⁺-RENPs, respectively. (Figure S4-S6, Table S1).

Figure 1. Representative TEM images of core-only (top) and core/shell (bottom) LiYbF₄:RE³⁺/LiYF₄ RENPs, each doped with 1 mol% of Tm³⁺, Er³⁺, or Ho³⁺, respectively.

LiYbF₄:Tm³⁺/LiYF₄

Under 960 nm excitation, the upconversion PL of LiYbF₄: x mol% Tm³⁺/LiYF₄ (x = 0.2, 0.5, 1, 2) RENPs spans the UV, visible, and NIR spectral regions, with major radiative

transitions located at roughly: 340 ($^1I_6 \rightarrow ^3F_4$), 360 ($^1D_2 \rightarrow ^3H_6$), 450 ($^1D_2 \rightarrow ^3F_4$), 480 ($^1G_4 \rightarrow ^3H_6$), 660 ($^1G_4 \rightarrow ^3F_4$) and 790 nm ($^3H_4 \rightarrow ^3H_6$; $^1G_4 \rightarrow ^3H_5$) (**Figure 2A, B**). Note that the NIR upconversion of Tm^{3+} originates from two- and three-photon processes that populate either 3H_4 or 1G_4 energy levels, respectively. To individually assess emission from the 1G_4 state, we have spectrally deconvoluted the $^3H_4 \rightarrow ^3H_6$ and $^1G_4 \rightarrow ^3H_5$ transitions at 790 nm (Figure S7).^[38] For steady-state spectral analysis, different Tm^{3+} emissions were grouped by energy states (1I_6 , 1D_2 , 1G_4 and 3H_4) from they originate (Figure 2A, B). The relative contribution of each of those states varied considerably with both Tm^{3+} concentration and excitation power density (P_d) (Figure 2C). For 0.2 and 0.5 mol% Tm^{3+} , emissions from 1G_4 and 1I_6 states quickly surpassed NIR PL from the 3H_4 energy level at increasing P_d . In contrast, at 1 and 2 mol% Tm^{3+} , upconversion emission was mostly in the NIR, stemming from the 3H_4 energy level. Overall, increasing Tm^{3+} concentration led to diminished spectral contribution from the 1G_4 state, while that of 3H_4 , 1D_2 and 1I_6 increased. Repopulation of these states is indicative of a number of cross-relaxation processes that appear with increasing number of Tm^{3+} dopants (Figure S8). The influence of cross-relaxation was observed from intensity interplay between emissions stemming from neighboring energy levels of n and $(n+1)$ photon order population. As the Tm^{3+} concentration increased, the contribution from the 1G_4 state to the 790 nm NIR emission band was reduced and the $^3H_4 \rightarrow ^3H_6$ radiative transition became dominant (Figure S9). Concomitantly, depopulation of the 1G_4 energy level was reflected in the higher excitation occupancy at the 1D_2 state; the $^1D_2 \rightarrow ^3F_4$ radiative transition became more pronounced with higher Tm^{3+} concentration and excitation P_d (Figure S10). As a consequence, greater 1D_2 population facilitates $^2F_{5/2}$ (Yb^{3+}) $\rightarrow$ 3P_2 (Tm^{3+}) energy transfer upconversion (ETU) and subsequent population of the 1I_6 energy level.^[39] Yet, the intensity between the two UV-emitting states, 1D_2 and 1I_6 , was not constant either (Figure S11). In contrast with the study by Wang et al.,^[39] we observed the $^1D_2 \rightarrow ^3H_6$ radiative transition to be increasingly dominant with greater Tm^{3+} concentration and excitation P_d . We speculate that this is governed by the $^1I_6 \rightarrow ^1D_2$: $^1G_4 \rightarrow ^1D_2$ cross-relaxation, which becomes more relevant as the average distance between neighboring Tm^{3+} ions is reduced.

Figure 2. Spectral characteristics of LiYbF_4 : x mol% $\text{Tm}^{3+}/\text{LiYF}_4$ ($x = 0.2, 0.5, 1, 2$) RENPs. A – upconversion spectra of RENPs under 960 nm excitation at $P_d \sim 200 \text{ W/cm}^2$. Major transitions are labeled above each PL band and are color-coded to the other plots in the figure. Intensity of PL bands for 2 mol% Tm^{3+} -RENPs below 700 nm is magnified by 5 for clarity. B – simplified $\text{Yb}^{3+}/\text{Tm}^{3+}$ upconversion excitation-emission scheme. C – relative contribution of $1\text{I}_6 \rightarrow 3\text{F}_4$ (burgundy), $1\text{D}_2 \rightarrow 3\text{H}_6+3\text{F}_4$ (purple), $1\text{G}_2 \rightarrow 3\text{H}_6+3\text{F}_4+3\text{H}_5$ (blue) and $3\text{H}_4 \rightarrow 3\text{H}_6$ (brown) radiative transitions as a function of P_d and Tm^{3+} doping. D – upconversion photon order, n , as a function of Tm^{3+} concentration, extracted for each PL band from the $\log(I)/\log(P_d)$ (Figure S12). E – average lifetime, τ , of Tm^{3+} excited states as a function of Tm^{3+} concentration, estimated from decay curves of each radiative transition (Figure S13). Lines in D and E serve as guides to the eye.

We then calculated the illustrative value of the minimum photon number (order), n , required to populate each excited state *via* a multiphoton process. For all samples and PL bands, n is given as the slope of a linear fit of $\log(I)/\log(P_d)$ plot in the low P_d regime (Figure 2D and S12). An apparent increase of n with higher spectral energy emissions confirmed the multiphotonic nature of upconversion process, although n values were lower than the theoretically expected ones (5, 4, 3 and 2 for 1I_6 , 1D_2 , 1G_4 and 3H_4 excited states, respectively). Deviation of experimentally obtained n is anticipated due to the more complex nature of the upconversion process in reality compared to simplified multilevel

excitation description.^[40] We observed an increase in n values for the upconversion emissions stemming from the 1D_2 and 1I_6 excited states with increasing Tm^{3+} concentration from 0.2 to 1 mol%, after which, the n values decreased. Similar trends were found for $n(^1G_4)$. These results indicate that cross-relaxation combined with Yb^{3+} excitation energy being distributed among a larger number of Tm^{3+} ions, alleviate saturation of the excited states. However, as seen from the n values of 2 mol% Tm^{3+} -RENPs, cross-relaxation becomes deleterious further increasing the Tm^{3+} concentration. Photoluminescence decay measurements (Figure 2E and S13) further supported the conclusions drawn from steady-state experiments. The average lifetime of each excited state decreased with increasing Tm^{3+} concentration, as non-radiative energy losses became pronounced. The sharpest change in excited state lifetime could be observed for the 1G_4 energy level, signifying its importance as an intermediate state for higher-order upconversion excitation, either through ETU or cross-relaxation-promoted population redistribution among the Tm^{3+} electronic states. In addition to decay time shortening, rise times required to populate the 1I_6 , 1D_2 and 1G_4 energy levels also decreased with increasing Tm^{3+} doping amount (Figure S14).

Finally, the $UCQY$ of Tm^{3+} -doped RENPs was measured (**Figure 3**). For all the samples, $UCQY$ increased with increasing excitation P_d , as expected for multiphoton processes. For 0.2 and 0.5 mol% Tm^{3+} samples $UCQY$ rapidly approached saturation, in contrast to the continuous rise of $UCQY$ in the case of 1 and 2 mol% Tm^{3+} doping (Figure 3A). $UCQY$ measurements emphasize the high intensity of the Tm^{3+} NIR emission ($^3H_4 \rightarrow ^3H_6$), which grew from ~0.10 to 1.38% (at $P_d \sim 90 \text{ W/cm}^2$) increasing Tm^{3+} doping from 0.2 to 2 mol%, respectively (Figure 3B). Although RENPs doped with the lowest Tm^{3+} amount (0.2 mol%) had greatest spectral contribution from the 1G_4 excited state, the maximum $UCQY$ for 1G_4 radiative transitions was achieved at 0.5 mol% Tm^{3+} , with approximate values of 0.049% for $^1G_4 \rightarrow ^3H_6$ and 0.021% for $^1G_4 \rightarrow ^3F_4$ at $P_d \sim 90 \text{ W/cm}^2$. Further increase in Tm^{3+} concentration reduced the $UCQY$ of these emissions, giving way to radiative transitions from 1D_2 and 1I_6 excited states, with a maximum $UCQY$ at 1 mol% Tm^{3+} – 0.010% ($^1I_6 \rightarrow ^3F_4$), 0.006% ($^1D_2 \rightarrow ^3H_6$) and 0.021% ($^1D_2 \rightarrow ^3F_4$) at $P_d \sim 90 \text{ W/cm}^2$. It is obvious that the optimal activator doping in $LiYbF_4:Tm^{3+}/LiYF_4$ RENPs depends strongly on the preference for desired upconversion emission. For most intense UV and blue PL, a balance has to

be made between increasing the total number of emitters (Tm^{3+}) and activation of cross-relaxation in a manner that supports population of higher lying energy levels. Whereas cross-relaxation processes began to quench higher order upconversion at the highest Tm^{3+} doping studied, the NIR ($^3\text{H}_4 \rightarrow ^3\text{H}_6$) PL remained unaffected by it and reached above 1% UCQYs for $P_d > 20 \text{ W/cm}^2$. The total UCQY of $\text{LiYbF}_4:\text{Tm}^{3+}/\text{LiYF}_4$ RENPs across all upconversion emissions at $P_d \sim 90 \text{ W/cm}^2$ was measured to be 0.13, 0.60, 0.64 and 1.41% for 0.2, 0.5, 1 and 2 mol% Tm^{3+} , respectively.

Figure 3. UCQY values for $\text{LiYbF}_4: x \text{ mol\% Tm}^{3+}/\text{LiYF}_4$ ($x = 0.2, 0.5, 1, 2$) RENPs. A – change of UCQY of individual Tm^{3+} emission bands as a function of excitation P_d . B – UCQY for each of Tm^{3+} emission band as a function of Tm^{3+} concentration at $P_d \sim 90 \text{ W/cm}^2$. Color coding of experimental points in A and B corresponds to legend below, representing radiative transitions of Tm^{3+} for which UCQY was measured.

$\text{LiYbF}_4:\text{Er}^{3+}/\text{LiYF}_4$ and $\text{LiYbF}_4:\text{Ho}^{3+}/\text{LiYF}_4$

In addition to Tm^{3+} -doped RENPs, we also studied $\text{LiYbF}_4:\text{RE}^{3+}/\text{LiYF}_4$ doped with Er^{3+} or Ho^{3+} ions as activators. $\text{LiYbF}_4: x \text{ mol\% Er}^{3+}/\text{LiYF}_4$ ($x = 1, 2, 5, 10$) RENPs displayed PL around 380, 420, 525/545 and 660 nm, attributed to radiative transitions to the $^4\text{I}_{15/2}$ ground state from the $^4\text{G}_{11/2}$, $^2\text{H}_{9/2}$, $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ excited states, respectively (**Figure 4A, B**). We observed that as the Er^{3+} doping level increased, the relative contribution of the green ($^2\text{H}_{11/2}/^4\text{S}_{3/2}$) emission to the PL spectrum of RENPs also increased (Figure 4C, S15). Nonetheless, the red emission ($^4\text{F}_{9/2}$) was dominant across all samples with increasing P_d , except for the 10 mol% Er^{3+} -doped RENPs, which at $P_d < 2 \text{ W/cm}^2$ featured more green ($^2\text{H}_{11/2}/^4\text{S}_{3/2}$) emission. UV ($^4\text{G}_{11/2}$) and blue ($^2\text{H}_{9/2}$)

emissions had no clear dependence on the Er^{3+} concentration, having minimal relative contributions to the luminescence spectrum in general. The asymptotic saturation of green and red PL continuously shifted to higher P_d with increasing Er^{3+} concentration, indicative of cross-relaxation between Er^{3+} ions. The photon number, n , of Er^{3+} -RENPs showed a decreasing trend for all upconversion bands as Er^{3+} doping increased, with an unexpected jump of n values at 10 mol% Er^{3+} for certain emissions (Figure 4D, S16). The n values confirmed the three-photon excitation of the UV ($^4\text{G}_{11/2}$) and blue ($^2\text{H}_{9/2}$) emissions. On the other hand, the green ($^2\text{H}_{11/2}/^4\text{S}_{3/2}$) emission of Er^{3+} -RENPs was clearly of two-photon order and $n > 2$ values for the red ($^4\text{F}_{9/2}$) emission suggest that it is populated *via* three- and two-photon processes. The higher-order population of the red ($^4\text{F}_{9/2}$) energy state compared to that of the green ($^2\text{H}_{11/2}/^4\text{S}_{3/2}$) could be anticipated from the previously proposed back energy transfer (BET) $^4\text{G}_{11/2}(\text{Er}^{3+}) \rightarrow ^2\text{F}_{5/2}(\text{Yb}^{3+})$,^[14] which is likely considering the host matrix of our RENPs is solely comprised of Yb^{3+} sensitizer ions. In fact, it appears that within 1 to 5 mol% Er^{3+} , excitation of $^4\text{F}_{9/2}$ energy level gradually drifts towards a two-photon process evident from the decrease of $n(^4\text{G}_{11/2})$ and $n(^4\text{F}_{9/2})$. Following the estimation proposed by Kaiser et al.,^[41] we calculated that the relative contribution of the three-photon excitation of $^4\text{F}_{9/2}$ state decreased roughly from 97 to 67%, moving from 1 to 5 mol% Er^{3+} , respectively. However, the sudden increase of $n(^4\text{F}_{9/2})$ at 10 mol% Er^{3+} suggests that the three-photon excitation of this state by BET could be complemented with the $^4\text{G}_{11/2} \rightarrow ^4\text{F}_{5/2}; ^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ cross-relaxation (Figure S16), however more detailed examination is necessary to ascertain this. Lifetimes of the Er^{3+} excited states decreased almost linearly with increasing Er^{3+} concentration, confirming the growing influence of cross-relaxation and non-radiative depopulation of the excited states (Figure 4E, S17). Average rise times for the excitation of higher energy states also decreased with Er^{3+} concentration, and those of the red ($^4\text{F}_{9/2}$) emission were considerably longer than those observed from other transitions (Figure S18). This, together with the average decay time of the green ($^2\text{H}_{11/2}/^4\text{S}_{3/2}$) emission being systematically longer than that of the red ($^4\text{F}_{9/2}$) emission, attests to mostly three-photon excitation of $^4\text{F}_{9/2}$ excited state *via* BET. In addition, we measured the UCQY of 5 mol% Er^{3+} -doped RENPs and found the total UCQY to be 0.78% at $P_d \sim 90 \text{ W/cm}^2$ where the

UV ($^4G_{11/2}$), blue ($^2H_{9/2}$), green ($^2H_{11/2}/^4S_{3/2}$) and red ($^4F_{9/2}$) emissions contribute 0.001, 0.014, 0.17 and 0.59%, respectively (Figure S19).

Figure 4. Spectral characteristics of $\text{LiYbF}_4: x \text{ mol\% Er}^{3+}/\text{LiYF}_4$ (x = 1, 2, 5, 10) RENPs. A – upconversion spectra of RENPs, under 960 nm excitation at $P_d \sim 200 \text{ W/cm}^2$. Major transitions are labeled above each PL band and are color-coded to other plots in the figure. Intensity of the PL bands below 540 nm is magnified by 5 for clarity. B – simplified $\text{Yb}^{3+}/\text{Er}^{3+}$ upconversion excitation-emission scheme. C – relative contribution of $^4G_{11/2}$ (purple), $^2H_{9/2}$ (blue), $^2H_{11/2}+^4S_{3/2}$ (green) and $^4F_{9/2} \rightarrow ^4I_{15/2}$ (red) radiative transitions as a function of P_d and Er^{3+} doping. D – upconversion photon order, n , as a function of Er^{3+} concentration, extracted for each PL band from the $\log(I)/\log(P_d)$ plot (see Figure S16). E – average lifetime, τ , of Er^{3+} excited states as a function of Er^{3+} concentration, estimated from decay curves of each radiative transition (see Figure S17). Lines in D and E serve as guides to the eye.

In the case of $\text{LiYbF}_4: x \text{ mol\% Ho}^{3+}/\text{LiYF}_4$ (x = 1, 2, 5) RENPs, under 960 nm excitation we observed upconversion emissions around 485, 540, 650 and 750 nm, corresponding to the $^5F_3 \rightarrow ^5I_8$, $^5S_2/^5F_4 \rightarrow ^5I_8$, $^5F_5 \rightarrow ^5I_8$ and $^5S_2/^5F_4 \rightarrow ^5I_7$ radiative transitions, respectively (Figure 5A, B). Many higher-order upconversion lines could also be seen, however, due to their low emission intensity they were excluded from further analysis (Figure S20). For all Ho^{3+} -doped RENPs, the emission was mainly composed of green/NIR (both stemming

from $^5S_2/^5F_4$ states) and red (5F_5) upconversion. In addition to change in relative intensities of these bands with Ho^{3+} doping and excitation P_d , an inversion point could be clearly discerned (Figure 5C). At first, increasing excitation P_d resulted in a growing contribution of emissions belonging to the $^5S_2/^5F_4$ energy levels, however, it subsequently saturated making the red (5F_5) emission more pronounced again.^[42] The saturation point shifted to higher P_d values for higher Ho^{3+} concentration, leading to a decrease in the relative difference between green ($^5S_2/^5F_4$) and red (5F_5) emissions (Figure S21). The power plots of Ho^{3+} -RENPs indicated an increase in $n(^5S_2/^5F_4)$ seen from the NIR emission and a decrease in $n(^5F_3)$ of the blue band (centered at 485 nm) at higher Ho^{3+} concentration (Figure 5D and S22). Similar to the case of Tm^{3+} -RENPs, the increasing $n(^5S_2/^5F_4)$ indicates lessened saturation of this state at greater Ho^{3+} doping, as the excitation energy is shared between more activator ions. Green ($^5S_2/^5F_4$) and red (5F_5) upconversion emissions also appeared to have a three-photon population component, having $n > 2$ for each doping. Given the observed decrease in $n(^5F_3)$ values, we assume that the feeding of $^5S_2/^5F_4$ might proceed from cross-relaxation processes depopulating the 5F_3 and 5G_5 energy levels (Figure S22), which would account for the three-photon component in the excitation of green and red upconversion emission.^[43] Average lifetime values, τ , were similar for blue (5F_3), green and NIR ($^5S_2/^5F_4$) emissions (Figure 5E and S23). While τ of the 5F_5 energy level was greater than that of other levels, it rapidly diminished with increasing Ho^{3+} concentration. The longest rise time was also measured for the 5F_5 state, indicating that this energy level can be quickly depleted and does not suffer from excitation saturation (Figure S24). Furthermore, average rise time values had a maximum point at 2 mol% Ho^{3+} . We believe that the rise time increase between 1 and 2 mol% Ho^{3+} is a result of reduced $^5S_2/^5F_4$ excitation saturation due to increased number of activators that can receive energy from Yb^{3+} , and shorter rise times at even greater Ho^{3+} concentration is a consequence of cross-relaxation among Ho^{3+} themselves. The measured UCQY of 5 mol% Ho^{3+} -doped RENPs at $P_d \sim 90 \text{ W/cm}^2$ was 0.074%, with the 5F_3 (blue), $^5S_2/^5F_4$ (green+NIR) and 5F_5 (red) energy levels, respectively contributing 0.0009, 0.039 and 0.035% (Figure S25).

Figure 5. Spectral characteristics of LiYbF_4 : x mol% $\text{Ho}^{3+}/\text{LiYF}_4$ ($x = 1, 2, 5$) RENPs. A – upconversion spectra of RENPs under 960 nm excitation at $P_d \sim 200 \text{ W/cm}^2$. Major transitions are labeled above each PL band and are color-coded to other plots in the figure. Intensity of the PL bands below 500 nm is magnified by 10 for clarity. B – simplified $\text{Yb}^{3+}/\text{Ho}^{3+}$ upconversion excitation-emission scheme. C – relative contribution if $5\text{F}_3 \rightarrow 5\text{I}_8$ (blue), $5\text{S}_2/5\text{F}_4 \rightarrow 5\text{I}_8+5\text{I}_7$ (green) and $5\text{F}_5 \rightarrow 5\text{I}_8$ (red) radiative transitions as a function of P_d and Ho^{3+} doping concentration. D – upconversion photon order, n , as a function of Ho^{3+} concentration, extracted for each PL band from the $\log(I)/\log(P_d)$ plot (see Figure S21). E – average lifetime, τ , of Ho^{3+} excited states as a function of Ho^{3+} concentration, estimated from decay curves of each radiative transition (see Figure S22). Lines in D and E serve as guides to the eye.

Discussion and outlook

The current library of $\text{LiYbF}_4\text{:RE}^{3+}/\text{LiYF}_4$ RENPs, where $\text{RE}^{3+} = \text{Tm}^{3+}, \text{Er}^{3+}, \text{and Ho}^{3+}$, was created to provide a more accurate picture of the spectral characteristics of LiYbF_4 -type RENPs. Our RENPs featured a Yb^{3+} -based core, with an average separation between neighboring RE^{3+} ions of around 0.41 nm (see Supporting Information for inter-ion distance calculation), and a thicker-than-5 nm inert shell. This architecture ensures that the absorbed excitation energy is strictly confined to the core of the RENPs and absorption saturation among Yb^{3+} ions is reached quickly. Introduction of activator ions

allows Yb^{3+} to relax from the excited state *via* non-radiative energy transfer, i.e. ETU, and even co-operative sensitization.^[32] As we observed from Tm^{3+} - or Ho^{3+} -RENPs at low doping, excitation saturation also affects the lower lying excited states of these dopants, increasing the probability of higher state population *via* ETU. This leads to a greater contribution of higher-order upconversion emissions to the total PL spectrum of the activator ions, however, it is case-by-case specific. In contrast to Er^{3+} - or Ho^{3+} -RENPs where ETU from Yb^{3+} is near-resonant, the $\text{Yb}^{3+} \rightarrow \text{Tm}^{3+}$ ETU processes are highly non-resonant, requiring absorption or emission of a lattice phonon. The largest energy mismatch is present at the $^1\text{D}_2$ excited state of Tm^{3+} , thus to facilitate the four- and five-photon excitation of $^1\text{D}_2$ and $^1\text{I}_6$ energy levels, respectively, additional population pathways are needed. Increasing Tm^{3+} doping leads to a reduced distance between the neighboring Tm^{3+} ions and promotes energy transfer *via* cross-relaxation. In fact, for each activator studied, cross-relaxation processes became quickly apparent with increasing RE^{3+} concentration, as witnessed from the linear decrease in the lifetimes of their excited states.^[44] Thus for higher Tm^{3+} doping, cross-relaxation plays an important role in distributing excitation energy from $^1\text{G}_4$ to $^1\text{D}_2$ states, while the latter then leads to more efficient ETU excitation of the $^1\text{I}_6$ energy level. Overall, higher doping influences PL of the RENPs by: i) exponentially increasing the number of available emissive centers, and ii) reducing the mean distance between them, which has an impact of several orders of magnitude on the non-resonant energy transfer rates for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions (Figure S26).^[45,46]

Cross-relaxation represents an important aspect in color tuning of Yb^{3+} -based RENPs, as shown on the CIE color map (Figure S27-S29). In terms of observable color output Tm^{3+} -RENPs showed only minor change from light to deep blue PL upon increasing Tm^{3+} concentration. Nonetheless, by varying Tm^{3+} doping, RENPs with individually optimized UV, blue, or NIR upconversion could be prepared for applications in photocleavable bond breaking,^[7] optogenetic stimulation,^[5] or NIR imaging applications,^[47] respectively. Er^{3+} -RENPs showed the least color variability with doping concentration, however, the PL color could be varied from green to orange by increasing the P_d , and the dynamic range of this change was narrower at greater concentrations of Er^{3+} . Overall, these RENPs have predominantly red ($^4\text{F}_{9/2}$) upconversion emission, which is sought after in photodynamic

therapy (PDT) to excite photosensitizers in the vicinity of RENPs.^[48,49] Ho³⁺-RENPs also showed intense red emission, however its *UCQY* was an order of magnitude lower than that of Er³⁺-RENPs, making the latter a much better option for PDT. Nonetheless, the color invariability of 5 mol% Ho³⁺-doped RENPs across a broad excitation P_d range could be interesting in lighting and security print applications requiring constant color output. Aside from the color of upconversion PL, the lifetimes of different excited states of Tm³⁺-, Er³⁺-, and Ho³⁺-RENPs varied notably with dopant amount, which can be harnessed in multiplexing and sensing applications.

Our *UCQY* measurements revealed that for Er³⁺- and Ho³⁺-doped RENPs Na⁺-based systems remain unmatched in upconversion efficiency.^[16,50] Yet the presence of high Yb³⁺ content (4-5 times more than if Yb³⁺ are dopants) allows Yb³⁺-based systems to compete in terms of brightness (product of *UCQY* and absorbance of RENPs). A more intriguing case is represented by Tm³⁺-RENPs. Following the discussion of Zhang et al.,^[51] the Tm³⁺ energy levels in Li⁺-based hosts are blue-shifted compared to when Tm³⁺ is present in NaYF₄ or NaYbF₄ matrices. We believe that this slight shift is the contributing factor for Li⁺-based RENPs to generate higher order Tm³⁺ upconversion emission more efficiently, as it reduces energy mismatch between the non-resonant Yb³⁺ → Tm³⁺ ETU. Still, as explored by Meijer et al.,^[52] classic LiYF₄:Tm³⁺, Yb³⁺ RENPs feature orders of magnitude more efficient NIR upconversion (³H₄ → ³H₆) than UV or blue. Similar observations were reported by Kraft et al. for NaYF₄:Tm³⁺, Yb³⁺ RENPs.^[53] In our case, the *UCQY* of transitions stemming from the ¹I₆ (UV), ¹D₂ (UV/blue) and ¹G₄ (blue/red) energy levels was also one or two orders lower than that coming from ³H₄ (NIR) state. However, emissions from these higher excited states were either on par or greater than what was measured for much larger LiYF₄, as well as NaYF₄ RENPs (see Table S8). Coupled with large Yb³⁺ content (hence high light absorption capabilities), this makes LiYbF₄:Tm³⁺/LiYF₄ an overall brighter UV/blue light emitter and a more suitable choice in high photon energy demanding applications. In addition, the total *UCQY* of our Tm³⁺-RENPs was close to few other studies on LiYbF₄:Tm³⁺/LiYF₄ RENPs, where either the same or greater values (possibly due to larger RENP size) were reported.^[32,37,54] LiYbF₄:RE³⁺/LiYF₄ RENPs present an interesting formulation in the development of next generation upconversion probes, but we believe that their full potential remains untapped.

Recent reports indicate that although RENPs might appear equal in composition and size, a multitude of factors can still affect their PL output. When it comes to the shelling procedures particularly, reducing interlayer ion migration,^[55] optimizing crystallization temperature,^[56] removing hydroxyl groups,^[16] and other factors all alter the upconversion efficiency of RENPs. Besides, novel architectural designs, like limiting inter-ion energy hopping to the 2D plane^[57] or separating activator and sensitizer ions in different layers^[58,59] might prove potent in developing even brighter LiYbF₄ RENPs. Furthermore, complementary theoretical studies would help to interpret energy migration dynamics among the large network of Yb³⁺ and numerous activator excitation processes.

Conclusions

We have synthesized small and highly monodisperse LiYbF₄:RE³⁺/LiYF₄ RENPs. Tm³⁺, Er³⁺ and Ho³⁺, the most relevant upconversion light emitters, were introduced at various concentrations and their photophysical properties were investigated. Through steady-state, time-resolved and quantum yield photoluminescence measurements, we demonstrated that the UV, blue, and NIR upconversion emissions of Tm³⁺-RENPs could be individually optimized by selecting the appropriate Tm³⁺ doping concentration and excitation power. In doing so, the pivotal role of concentration-dependent cross-relaxation processes was unveiled, observing that higher-photon-order UV and blue emissions are favored at greater Tm³⁺ concentration (here, 1 mol%). Calculated UCQYs were in line with previous reports on different Tm³⁺-doped systems; yet, due to high Yb³⁺ content (and thus efficient light absorption), our Tm³⁺-RENPs show greater potential for applications requiring bright UV/blue emission.

The spectral characteristics of Er³⁺- and Ho³⁺-doped LiYbF₄: RE³⁺/LiYF₄ were also investigated. Although Er³⁺-RENPs mainly featured red upconversion emission irrespective of Er³⁺ concentration, Ho³⁺-RENPs had an inversion point between their green and red upconversion emissions upon increasing excitation power density, which also could be altered varying Ho³⁺ doping amount.

Overall, LiYbF₄:RE³⁺/LiYF₄ RENPs were found to be effective upconverting nanomaterials suitable for different lines of research and application, while this comprehensive account of their spectral characteristics is expected to spark more extensive research on bright Yb³⁺-based upconversion systems.

Materials and Methods

For the complete description of RENP synthesis, structural and optical characterization please refer to the provided Supporting Information. Briefly, LiYbF_4 : x mol% RE^{3+} / LiYF_4 RENPs were synthesized *via* the thermal decomposition method, with RE^{3+} doping: i) 0.2, 0.5, 1, 2 mol% Tm^{3+} , ii) 1, 2, 5, 10 mol% Er^{3+} , iii) 1, 2, 5 mol% Ho^{3+} . Core nanoparticles were prepared by first preparing first nuclei nanoparticles from Li^+ , Yb^{3+} and RE^{3+} trifluoroacetate precursors, coordinated with oleic acid and oleylamine at 330 °C under an Ar atmosphere. The first nuclei were then stabilized in excess oleic acid at 315 °C and Ar atmosphere, obtaining the desired LiYbF_4 : x mol% RE^{3+} cores.^[17] Subsequently, Li^+ and Y^{3+} trifluoroacetate precursors were injected into the core solution to grow the LiYF_4 shell; the reaction proceeded at 290 °C and under Ar atmosphere for 2h total. All the RENPs were characterized by X-ray powder diffraction analysis (XRD; Bruker D8 Advance Diffractometer), transmission electron microscopy (TEM; Philips Tecnai 12), and inductively coupled plasma - optical emission spectroscopy (ICP-OES; Agilent Technologies 5100). Steady-state PL of RENPs was recorded with an Avaspec-ULS2048L spectrometer under 960 nm laser diode excitation. Lifetime measurements were performed on an FLS980 spectrometer, using 980 nm pulsed laser diode as the excitation source. *UCQY* measurements were carried out using an Edinburgh Instruments spectrofluorometer (FLS920), equipped with an extended red-sensitive detector (Hamamatsu, PMT, 200-1010 nm), an integrating sphere (Yobin Yvon), and a 960 nm laser diode (BWT).

Associated content

Supporting information. Complete RENP synthesis and characterization description. Additional TEM, XRD, ICP-OES, and spectral data; including Figures S1-S29 and Table S1-S8 (PDF).

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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