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Energy migration up-conversion of Tb³⁺ in Yb³⁺ and Nd³⁺ co-doped active-core/active-shell colloidal nanoparticles

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ABSTRACT: The intentional design of chemical architecture of lanthanide doped luminescent nanoparticles through the proper selection of dopants in core-shell and core-shell-shell structures enables optimization of their optical properties. Such approach allows achieving energy transfer up-conversion (ETU) and energy migration mediated up-conversion (EMU) and green emission from Tb^{3^+} ions with the Yb^{3^+} and Nd^{3^+} sensitizers at 980 and 808 nm photoexcitation respectively. The $[Nd^{3^+}\rightarrow Yb^{3^+}]\rightarrow [Yb^{3^+}\rightarrow Tb^{3^+}]$ EMU phenomenon was significantly enhanced by spatial displacement of the sensitizing Nd₃+ ions from the activator Tb^{3^+} ions by intentionally introducing intermediate Yb^{3^+} sensitizer layer forming $[Nd^{3^+}\rightarrow Yb^{3^+}]\rightarrow [Yb^{3^+}\rightarrow Tb^{3^+}]$ system. Otherwise Tb^{3^+} emission was considerably quenched by Nd³⁺ ions even though they were spitted between core and shell respectively. Moreover, $(Tb^{3^+}, Yb^{3^+})\rightarrow (Tb^{4^+}, Yb^{2^+})$ valence change has been discovered to limit the Tb^{3^+} up-conversion emission. The studies explain how the chemical architecture of the smartly designed active-core @ active-shell luminescent nanoparticles may improve their spectral properties.

Introduction

The demand for enhanced luminescent bio-probes, inspired by numerous new bio-applications, is continuously motivating materials scientists to search for better luminescent materials, new photoluminescence processes and significant progress. Lanthanide doped nanoparticles are good candidates for alternative, not fully explored vet, luminescent bio-labels for innovative bio-sensing and bioimaging.1 These nanomaterials exhibit many interesting photo-chemical properties, out of which efficient anti-Stokes emission (i.e up-conversion UC), long luminescence lifetimes and multicolor narrowband emission are the most prominent, since allows for background free, multi-target-labeling bio-detection and imaging.² While optoelectronic, nano-photonic and biomedical applications of the UC materials gained a lot by co-doping them with sensitizing Yb³⁺ ions, the photoexcitation at 980 nm (suitable to photo excite Yb3+ ions) has been contested recently for bio-application due to the absorption band of water present at this spectral region.^{3,4} The 980 nm excitation energy not only is attenuated, leading to limited penetration depth, but contributes to considerable local elevation of temperature. In the context of bio-imaging, overheating is an undesired side-effect that can affect cell viability and induce tissue damage.⁵ Although weaker absorption side bands of Yb³⁺ at around 915, 940 or 1550 nm were alternatively engaged to improve the penetration depth and reduce the overheating of tissues in the course of prolonged bio- imaging – unfortunately, this becomes possible at the expense of reduced absorption cross section. 5,6

Recently, a new way to circumvent the necessity of using ~980 nm photoexcitation was proposed by replacing Yb3+ sensitizer with Nd³⁺ ions.⁷⁻¹¹ Owing to favorable properties of neodymium ions, such as larger absorption cross section at ~800 nm as compared to the one of Yb3+ at ~980 nm,7 up to 70% quantum efficiency of the $Nd^{3+} \rightarrow Yb^{3+}$ energy transfer with insignificant back energy transfer (BET)^{7,8,12} and water absorption at 800 nm being around 20-fold lower than at ~980 nm excitation, the Nd³⁺ ions were proposed as primary sensitizer to novel $Nd^{3+} \rightarrow Yb^{3+} \rightarrow activator$ energy migration mediated upconversion (EMU).7-10,13,14 The suitability of Nd3+ sensitization for up-conversion has been recognized much earlier,¹³ but actually these are the developments of engineered active-core-active-shell nanostructures and separating primary sensitizing Nd³⁺ ions from activator (e.g. Tm³⁺, Er³⁺) ions, which have enabled to significantly improve the Nd³⁺ sensitized energy transfer up-conversion. Otherwise, when homogenously co-doped, rich energy levels structure of Nd3+ is responsible for parasitic quenching of activating ions through numerous ET and cross-relaxation (CR) processes. Nevertheless, the Yb³⁺ ions remained however important part of the EMU as



Figure 1. Representative TEM images of (a) the NaYbF₄:60%Tb³⁺ core nanoparticles as well as active-core/active-shell NPs, where shell was co-doped with Nd³⁺ ions. Insets to the TEM images display respective size distributions. Schematic illustration of energy transfer processes in (c) YbTb@NdYb and (d) YbTb@Yb@NdYb core/shell nanoparticles is presented.

While many research have been devoted to ETU and EMU processes with Er³⁺ and Tm³⁺ activators, only limited number of studies was focused on cooperative upconversion processes such as between Yb³⁺ and Tb³⁺.¹⁷⁻ ²⁴ Although the Nd³⁺ \rightarrow Yb³⁺ \rightarrow Tb³⁺ energy transfer (ET) has been reported in homogenously co-doped crystals and glasses,^{17,18} the upconversion of Tb³⁺ was weak due to co-localization of Tb³⁺ activators and Nd³⁺ primary sensitizers. Because homogenous doping (i) requires completely different optimal concentrations of activators, (ii) is much less challenging in terms of materials synthesis but (iii) does not enable deliberate materials' design, our motivation was to study and show the importance of proper composition and chemical architecture of the NPs, to intentionally design and enhance their properties. In the present paper, Nd³⁺ sensitizers and Tb³⁺ activators have been separated into shell and core, respectively, to avoid direct interaction between these ions. The colloidal $Yb^{3+}-Tb^{3+}$ co-doped β -NaYF₄ core and Nd³⁺-Yb³⁺ co-doped β-NaYF₄ shell nanoparticles have been prepared by a sequence of thermal decomposition steps of respective lanthanide precursors in high boiling temperature solvents. For brevity, the core-shell nanoparticles of β -NaYbF₄:60%Tb³⁺ @ β -NaYbF₄: x%Nd³⁺ and β -NaYbF₄:60%Tb³⁺@NaYbF₄@ β -NaYbF₄:x%Nd³⁺ composition were named here YbTb@YbxNd and YbTb@Yb@YbxNd, respectively.

Results and discussion

The obtained materials were pure hexagonal phase NaYF₄ nanoparticles and exhibited narrow ($\pm 2nm$) size distribution (Figure 1, details in SI and Figure S1).

Because of the triple doping, luminescence of the YbTb@ YbNd active-core/active-shell (ACAS) nanoparticles can be excited in three different ways. The 375 nm UV line excites broader and stronger f-d and narrower but weaker high energy f-f electronic transitions of Tb³⁺ ions. Additionally, co-doping the nanoparticles with Yb³⁺ and Nd³⁺ allows for photo-excitation by either ~975 nm (through Yb³⁺ ions) or ~808 nm (through Nd³⁺ ions). In order to understand the actual processes responsible for the up-conversion emission from Tb³⁺ in the presence of Yb³⁺ and Nd³⁺ ions, the studies were carried out for a series of YbTb@YbxNd samples, with the same core nanoparticles (i.e. NaYbF₄: 60% Tb³⁺), and the shell doped with differed content of Nd³⁺ ions (1, 5, 10, 20, 50%).

Even though the Tb³⁺ and Nd³⁺ ions were designed to stay spitted in the core and shell, respectively, thus were separated from each other, we have observed Tb³⁺ up conversion intensity decrease and luminescence lifetimes drop upon increase of Nd³⁺ doping in the shell. Moreover, detailed studies of Stokes emission under UV photoexcitation demonstrated unexpected behavior and shed new light on the chemistry and spectroscopy of active-core/active-shell NPs, which has not been studied so far. The gradual increase of the Nd3+ ions concentration within shell layer, resulted in gradual decrease in the Stokes ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$ (J= 3, 4, 5, 6) emission intensities from Tb³⁺ (Figure 2). This is most probably the result of interaction between Tb³⁺ and Nd³⁺ or Yb³⁺ ions, which stayed in shell layer, because 5- up to 40fold up-conversion enhancement has already been demonstrated in the Yb3+-Tb3+ up-converting NPs upon covering them with un-doped passive shell, which was moreover proportional to the shell thickness.^{20,25} There are two possible explanations for the observed behavior, i.e. spectroscopic and chemical. The first hypothesis suggests, that from the Tb³⁺: ⁵D₄ level, part of the energy can be transferred to two neighboring Yb3+ ions through quantum-cutting process or to ${}^{4}G_{7/2} + {}^{4}G_{9/2}$ levels of Nd³⁺ in the BET process.²² The other possible explanation relates to the observation that the ${}^{5}D_{4} \rightarrow {}^{7}F_{1}$ emission intensity correlates inversely with appearance of broad band at 450 nm (Figure 2) Although lanthanide elements exhibit the oxidation state +3, some trivalent lanthanide ions, such as $RE_1 = Pr^{3+}$, Tb^{3+} and Ce^{3+} , 1

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59 60 have a tendency to become oxidized with ions which have tendency to become reduced ($RE_2 = Yb^{3+}$ or Eu^{3+}). Such ions pair, would then be responsible for either charge transfer (CT-temporal) or valence change (VC) denoted as $(RE_1^{3+}; RE_2^{3+}) \rightarrow (RE_1^{4+}; RE_2^{2+})$. This phenomenon results in appearance of tetravalent states of terbium ions by moving an electron to Yb³⁺, which due to its 4f¹³ electron shell structure, tends to arrest this electron to the full f-shell structure. Such charge transfer process between Tb⁴⁺ and Yb²⁺ has been already shown for yttrium oxide phosphor doped with Tb³⁺ and Yb³⁺ ions.²² Due to non-linear dependence between the broad emission band intensity and the ytterbium content (inset Figure 2), we hypothesize that both, the $Tb^{3+} \rightarrow Yb^{3+}/Nd^{3+}$ energy transfer as well as $(Tb^{3+}, Yb^{3+}) \rightarrow$ (Tb⁴⁺,Yb²⁺) valence change (VC) may occur. Simultaneously, the ~10-fold Tb³⁺ emission quenching upon Yb³⁺-Nd³⁺ co-doped shell deposition on the Yb³⁺-Tb³⁺ codoped core suggest also c.a. ~90 % of total amount of terbium ions are susceptible to VC, which implicates that terbium ions display non-statistical distribution within core NPs volume and are most probably localized in the superficial layers of the core.



Figure 2. The down-conversion spectra of colloidal core (blue) and core/shell nanoparticles doped with different amount of Nd^{3+} in shell (1 - violet, 5-black, 10orange, 20-green, 50%-red) under 370 nm excitation; Nd^{3+} absorption spectrum (grey) is provided for comparison at the top axis. The inset shows terbium and ytterbium emission intensity as a function of ions concentration in the shell.

It has been recognized already that the distribution of Ln³⁺ activators in the nanoparticles may depend on the synthesis procedure, type and ionic radius of doping ions.²³ Therefore, the nanoparticles may reveal non-homogeneous and gradient composition, which is most probably due to the difference in the reactivity and nucleation speed of precursors used in the synthesis.²³ It is interesting to note, the Yb-Tb co-doped core NPs did show insignificant broad band of Yb²⁺ emission (Figure 2) which suggests that Ln³⁺ doped shell sup-

ports the VC process already at the initial stage of coreshell NPs formation. If Tb ions stay deeply within the NP's volume, such phenomenon would probably not be observed. The observed broadband emission is wider than typically found for Yb²⁺,^{26,27} which could potentially indicate fluorescence of ligand molecules, however in such a case there would be no relation to the shell composition. Therefore, an important question rises about the origin of oxidation of Tb³⁺ to Tb⁴⁺ and reduction of Yb^{3+} to Yb^{2+} in materials such NaYF₄. One should keep in mind that although the matrix does not need charge compensation, the significant surface to volume ratio in nanoparticles may be a sufficient reason for uncompensated charges of lanthanide ions at the border between crystalline host and the environment (i.e. ligands and solvents). Based on spectroscopic studies, we therefore hypothesize the charge uncompensated terbium ions, which are present at the surface of the solid core NPs, are exposed to Ln³⁺ precursors aimed to be deposited as shell layer. This hypothesis was further supported by the EDX studies (Figure 3a-c), which suggested, that Tb³⁺ migrates into outer part of the core NPs during the core formation or shell deposition. This is evidenced by the overlap of some nonzero Tb signal within shell and supports the idea about non-homogenous distribution of Tb in the volume of UCNPs.



Figure 3. STEM image of NaYbF₄: 60% Tb³⁺@NaYbF₄: 50% Nd³⁺ (a) and NaYbF₄: 60% Tb³⁺@NaYbF₄@NaYbF₄: 50% Nd³⁺ (d) nanoparticles showing Yb³⁺ inside and Tb³⁺ outside the core of the particle, as well as Yb³⁺-Nd³⁺ localized in the shell. The corresponding distribution of Tb, Yb and Nd atoms (b,e) and EDX Tb,Yb and Nd line scans across single NP (c,f) of the core/shell and core/shell nanoparticles are shown.

The up-conversion spectra of colloidal NaYbF₄ nanoparticles doped with 60% Tb³⁺ ions coated with NaYbF₄:Nd³⁺ shell are presented in Figure 4. Both Tb³⁺ and Nd³⁺ up-conversion emission can be observed under 975 nm diode excitation of Yb³⁺ ions. Weak Nd³⁺ up-conversion in Yb³⁺-Nd³⁺ system has been already observed under high power density of 980 nm laser excitation.²³

Alternatively, the visible Nd³⁺ emission may also occur from the excited ⁵D₄ level of Tb³⁺ which originates from cooperative energy transfer (CET) up-conversion in Yb³⁺-Tb³⁺ system under 980 nm.¹⁹ Therefore both scenarios, i.e.Yb³⁺ \rightarrow Nd³⁺ ETU and (Yb³⁺,Yb³⁺) \rightarrow Tb³⁺ \rightarrow Nd³⁺ ETU are probable but it is difficult to quantitatively judge which mechanism is more probable. Moreover the Yb³⁺ \rightarrow Nd³⁺ ETU followed by Nd³⁺ \rightarrow Tb³⁺ ET is possible as well.



Figure 4. (a) A comparison of up-conversion spectra of the colloidal nanoparticles doped with 1% of Nd³⁺ in shell under 975 nm excitation (red line) and 808 nm (blue line); (b) Dependence of green • emission of Tb³⁺ (${}^{5}D_{4}\rightarrow{}^{7}F_{4}$ at 540 nm), • visible Nd³⁺ (${}^{4}G_{9/2}\rightarrow{}^{4}I_{13/2}$ + ${}^{4}G_{7/2}\rightarrow{}^{4}I_{11/2}$ at 575 nm) and • NIR Nd³⁺ (${}^{4}F_{5/2}\rightarrow{}^{4}I_{9/2}$ at 800 nm) up-conversion emission intensities on the concentration of Nd³⁺ ions for YbTb@YbNd core/shell nanoparticles under 975 nm excitation; (c) The respective relative comparison of •Nd³⁺ (${}^{4}G_{9/2}\rightarrow$) and •Yb³⁺ (${}^{2}F_{5/2}\rightarrow{}^{2}F_{7/2}$) emission intensity under 808nm photoexcitation with respect to the concentration of Nd³⁺ ions (bottom axis) and Yb³⁺ ions (top axis) in the shell

These conclusions have led us to the optimized design of nanoparticles (Figure 1d, 3d-f), where Tb^{3+} and Nd^{3+} ions were further spatially displaced by $NaYbF_4$ intermediate shell. Such approach, i.e. the intermediate Yb^{3+} co-doped layer between Nd^{3+} doped harvesting layer and e.g. Yb^{3+}/Er^{3+} co-doped core was also proven to enhance the up-conversion by almost 8-fold owing to weakening of the BET from activators to Nd^{3+} sensitizer.¹² Even though the Tb^{3+} and Nd^{3+} could not interact directly in such core/shell/shell NPs, the intermediate Yb³⁺ co-doped shell was capable to transfer energy from Nd³⁺ to the interior of the UCNPs (Figure 5). Therefore, the YbTb@Yb@YbNd core/shell/shell structures were designed (Figure 3d-f), investigated and compared to the original YbTb @ YbNd core/shell NPs, owing to critical role of the intermediate layer in diminishing Tb³⁺ \rightarrow Nd³⁺ back ET and valence change of Tb³⁺ ions. To further confirm the core-shell-shell design, we have performed TEM-EDS studies, whose interpretation is however not always straightforward (Figure 3df). This is because the composition of the materials under studies is complex (Nd, Tb and Yb atoms display similar Z-number, 6o, 65 and 70 respectively) and the materials are susceptible to knock-on damage caused by collisions of beam electrons with specimen atoms.

The up-conversion mechanisms have been proposed for both types of materials (Figure 5). The most important difference between these designs comes from the fact, the back energy transfer (BET) is occurring only for TbYb@NdYb NPs (Figure 5a) due to short distance between Tb³⁺ and Nd³⁺/Yb³⁺, while intermediate Yb shell prevents such parasitic processes (Figure 5b).



Figure 5. Schematic comparison of UC emission mechanism in (a) TbYb@NdYb and (b) TbYb@Yb@NdYb core/shell nanoparticles under 980 nm and 808 nm 1a excitation.

These new designs has led to almost 10- up to 100-fold enhanced up-conversion of Tb^{3+} ions under both direct

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59 60 CET mechanism at ~980 nm (through Yb³⁺) or indirectly through EMU mechanism under ~808 nm (through Nd³⁺ primary sensitizer) as presented in Figure 6. Interestingly, also the luminescence lifetimes of the upconverted and Stokes signal were enhanced significantly (Figure S8 and S9), which shall be considered as the proof for substantial reduction of parasitic quenching processes in the pristine nanoparticles. Moreover, the Stokes emission of these newly synthesized and enhanced ACAS NPs, as compared to some of pristine samples, revealed the coexisting Yb²⁺ emission under short wavelength excitation (Figure S₅). These features have not been recognized in the literature for ACAS NPs and confirm that depositing the Ln³⁺ co-doped shell on the YbTb co-doped core, modifies significantly not only the anti-Stokes and Stokes spectral properties of such NPs, but probably modifies permanently the valence of the composing lanthanide ions. In consequence, the Stokes studies of UCNPs, which are usually disregarded, could be another way to optimize and enhance the spectral properties for those of lanthanide ions, which are prone to arrest or release electrons from their f-shell. These new discoveries require further studies to answer many of the raised questions on the nature of such variation in Stokes properties.



Figure 6. The impact of intermediate Yb^{3^+} doped shell and Nd^{3^+} concentration on spectral properties (a,b) and intensities (c,d) of Tb^{3^+} and Nd^{3^+} emission at 540, 585 and 805 nm under (a,c) 980 nm and (b,d) 808 nm photoexcitation for the three TbYb @ 50%Yb50%Nd (red), TbYb @ 100%Yb@ 50%Yb50%Nd (green) and TbYb @ 100%Yb @ 95%Yb5%Nd (black) samples.

Conclusions

Concluding, we have successfully synthesized 1, 5, 10, 20, 50% Nd^{3+} co-doped $NaYbF_4$:60% Tb^{3+} @ $NaYbF_4$: x% Nd^{3+} active-core/active-shell nanoparticles in order to study the possibility to get visible Tb₃₊ up-conversion under 980 or 808 nm photoexcitation. Terbium ions displayed non-homogenous distribution within the core NPs, which interacted with Yb³⁺ and Nd³⁺ present

in the shell, leading to either $Tb^{3+} \rightarrow Tb^{4+}$ valence change and appearance of broad emission spectrum of Yb^{2+} , or to $Tb^{3+} \rightarrow Nd^{3+}$ back energy transfer and Tb^{3+} quenching. The Tb³⁺ up conversion emission and luminescence lifetimes have been significantly enhanced, by introduction of intermediate shell between the YbTb doped core and YbNd doped shell in order to form YbTb @ Yb @ YbNd core/shell/shell NP. Such approach disabled Tb ions from direct chemical and energy transfer interactions with respectively Yb and Nd ions being deposited in the shell. Simultaneously the intermediate layer allowed for back-and-forth energy migration through Yb³⁺ migration network. Moreover, the observed valence change at the edge of core and shell, and inverse relation between amount of Yb²⁺ emission vs Tb³⁺ as relationships complex found well as for NdYb@Yb@YbTb emission indicates the need for further studies of the ACAS UCNPs to advance in understanding and optimisation of their properties.

Three important phenomena have been studied in this paper. Firstly, using Nd³⁺ sensitizer offers numerous advantages, but as we show in our work, brings also some pitfalls owing to back energy transfer from activators to the sensitizer, when the NPs chemical architecture is not optimized. While existing $(Nd \rightarrow Yb) \rightarrow$ (Yb→Er) systems in YbEr@YbNd C-S upconverting nanoparticles have been extensively described, the nonstatistical distribution of dopants (here Tb³⁺ ions) and parasitic phenomena resulting from the interaction between Tb³⁺ activator and Nd³⁺ sensitizer were not studied so far in great details. In particular, in opposite to our initial presuppositions, splitting these ions into two neighbour parts of the NPs was not sufficient to achieve intense Tb³⁺ up-conversion. We therefore put attention to the proper design of the core-shell NPs, in order to obtain the engineered UCNPs and enhance their properties. Secondly, we were intrigued to study the possibility to engage Nd \rightarrow Yb \rightarrow Tb UC to increase the UC efficiency of Tb³⁺ upconversion, which, due to cooperative sensitization, is significantly lower than in conventional up-converting luminescent nanoparticles. Thirdly, the Tb³⁺ up-conversion phosphors are promising for biological applications due to their long luminescence lifetimes and their spectral fingerprints being different from commonly known materials co-doped with Yb³⁺/Er³⁺ and Yb³⁺/Tm³⁺. The major motivation behind increased number of possible choice of spectral signatures (out of the paper scope) is the feasibility to label more biological species (e.g. proteins, antibodies etc.) within the same biological sample. This is problematic when the labels are co-localized and relay on color (e.g. ratiometric) only. For these reasons, the Tb^{3+} up-conversion emission must be enhanced in order to meet the high sensitivity requirements indispensable for bioassays and bioimaging.

Although NdYb@YbTb are not as efficient as NdYb@YbTm or NdYb@YbEr, these new UC material demonstrated the feasibility to obtain Tb₃₊ emission under either 808 nm or 980 nm excitation as well as showed Nd₃₊ visible up-conversion emission under 980 nm photoexcitation. These spectral features have important meaning for the possibility to design multiple spectral codes and multiplexed bio-detection of multiple targets within the same biological sample. The work is also important from fundamental perspective, since demonstrates and explains how the chemical architecture of the engineered active-core/active-shell nanoparticles may improve, modulate and optimize its spectral properties.

Experimental section

The active-core/active-shell (ACAS) β -NaYbF₄:Tb³⁺/ β -NaYbF₄:Nd³⁺ and β -NaYbF₄:Tb³⁺/ β -NaYbF₄:Nd³⁺ nanoparticles were prepared using a modified two- or three- step thermolysis process, which occurs via decomposition of lanthanide oleates.²⁸ The synthesis of core and core/shell nanoparticles was performed based on modified protocol described by K. Abel et.al.²⁸

Materials

Ytterbium oxide (99.99%), terbium oxide (99.99%) and neodymium oxide (99.99%), acetic acid (99%), pure oleic acid and 1-octadecene (90%) were purchased from ALDRICH Chemistry. Sodium trifluoroacetate (99,0%) was purchased from Fluka Analytical. Ethanol (96% pure p.a.), n-hexane (95%) and acetone (pure p.a.) and chloroform were purchased from POCH S.A. (Poland). All of the chemical reagents were used as received without future purification.

Preparation of lanthanide acetate

Stoichiometric amounts of respective Tb_2O_3 , Yb_2O_3 and Nd_2O_3 lanthanide oxides were mixed with 50% aqueous acetic acid. The mixture was stirred and heated up to obtain clear and transparent solution. The final precursor was obtained by evaporation of solvents at pre-vacuum and further drying at 130°C for 24h.

Synthesis of core nanoparticles

The lanthanide acetate- $(CH_3COO)_3$ Yb and $(CH_3COO)_3$ Tb – 2.5 mmol were added to the flask with 15 ml oleic acid and 38 ml octadecene. The solution was stirred and heated up to 140°C under vacuum for 30 min to form Ln(oleate)_3 complex and to remove total oxygen and remaining water. Next the temperature was lowered to 50°C and 10 mmol ammonium fluoride (NH_4F) and 6.25 mmol sodium hydroxide (NaOH) dissolved in 20 ml of methanol was added to the reaction

flask. The resulting cloudy mixture was stirred for 30 minutes at 70°C. Next, the reaction temperature was increased and the methanol was evaporated. After removing methanol, the solution was heated up to 300°C under the nitrogen atmosphere and kept in such conditions for 1 hour. Next, the nanoparticles were precipitated using acetone and n-hexane, centrifuged at 10000 rpm for 10 min and washed with ethanol. Finally, the prepared core NPs were dispersed in chloroform.

Synthesis of core/shell nanoparticles

lanthanide acetate – (CH₂COO)₂Yb The and (CH₃COO)₃Nd - 2.5 mmol were added to the flask with 15 ml oleic acid and 38 ml octadecene. The solution was stirred and heated up to 140°C under vacuum for 30 min to form Ln(oleate)₃ complex and to remove total oxygen and remaining water. The temperature was lowered to 60°C and the reaction flask was places under flow of nitrogen. A solution of core nanoparticles in CHCl₂ was added to the solution. The solution was maintained at 80°C until the all chloroform were removed. Next the temperature was lowered to 50°C and 10 mmol ammonium fluoride (NH₄F) and 6.25 mmol sodium hydroxide (NaOH) dissolved in 20 ml of methanol was added to the reaction flask. The resulting cloudy mixture was stirred for 30 minutes at 70°C. Next, the reaction temperature was increased and the methanol was evaporated. After removing methanol, the solution was heated up to 300°C under the nitrogen atmosphere and kept in such conditions for 1 hour. Next, the nanoparticles were precipitated using acetone and nhexane, centrifuged at 10000 rpm for 10 min and washed with ethanol. Finally, the prepared nanoparticles were dispersed in chloroform.

ASSOCIATED CONTENT

Supporting Information. X-ray powder diffraction patterns, absorption, excitation, and up-conversion spectra, luminescence lifetimes. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest

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