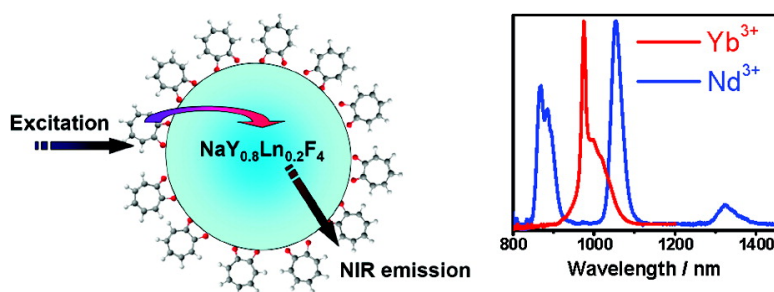


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A Strategy to Protect and Sensitize Near-Infrared Luminescent Nd^{3+} and Yb^{3+} : Organic Tropolonate Ligands for the Sensitization of Ln^{3+} -Doped NaYF_4 Nanocrystals

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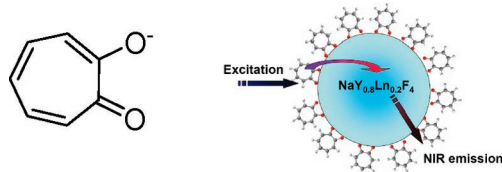
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Lanthanide-based near-infrared (NIR) emitters have a great potential to serve as bioanalytical reporters for several reasons: (i) NIR photons scatter less than visible photons, improving image resolution.¹ (ii) Biological systems have low native autofluorescence in the NIR energy domain,² resulting in higher detection sensitivity due to improved signal-to-noise ratio. (iii) Most luminescent lanthanide complexes are not susceptible to photodecomposition, allowing long or repeated experiments and simplifying sample storage and preparation procedures. Since $f-f$ transitions are Laporte forbidden,³ free Ln^{3+} have low extinction coefficients resulting in low luminescence intensity. Therefore, it is necessary to sensitize these cations through a suitable chromophore (“antenna effect”),⁴ an area of research that has been highly active in recent years.⁵ However, this approach has intrinsic limitations because lanthanide luminescence is easily quenched through nonradiative routes when the cations are in close proximity to the vibrational overtones of -OH, -NH, and -CH groups present in the sensitizing ligand and/or solvent.⁶ This effect is particularly dramatic for NIR emitting Ln^{3+} because of relatively small energy gaps between ground and excited electronic states.⁶ To alleviate this limitation, Ln^{3+} have been incorporated into inorganic matrices, such as LnF_3 ,⁷ Ln_2O_3 ,⁸ LnPO_4 ,⁹ LnVO_4 ,¹⁰ TiO_2 ,¹¹ and Zeolites.¹² These materials protect lanthanide cations from sources of nonradiative deactivation; however, they have either limited (e.g., LnVO_4) or no absorbance in the UV range. Thus, these inorganic materials are not able to sensitize lanthanide luminescence with the efficiency of organic sensitizers.

Here we introduce a strategy to overcome the limited lanthanide sensitization by binding organic tropolonate chromophoric groups to the surface of NaYF_4 nanocrystals (NCs), doped with NIR emitting Nd^{3+} or Yb^{3+} (Scheme 1). Tropolonate (Trop^-) was chosen as a capping ligand since it has been previously demonstrated to be a suitable sensitizer for several lanthanide cations emitting in the NIR range when coordinated in $\text{KLn}(\text{Trop})_4$ complexes.¹³ These novel systems use the NaYF_4 matrix to protect Ln^{3+} from nonradiative deactivations, while a chromophoric coating sensitizes their luminescence.

A synthetic method to prepare Nd^{3+} or Yb^{3+} doped NaYF_4 NCs was developed on the basis of a recently reported synthesis of NaYF_4 NCs (see Supporting Information).¹⁴ The Trop^- capped NCs were synthesized using the following procedure. Tropolone was dissolved in methanol, then deprotonated with an equimolar amount of KOH in methanol. Chloroform was added to obtain a 1/1 (v/v) MeOH/ CHCl_3 solvent mixture. This solution was added to a purified solution of NCs dispersed in chloroform. The resulting mixture was sonicated for 2 h, and the solvent was removed under vacuum. The resulting solid was washed with ethanol and DMSO and dried under vacuum for 24 h. The binding of the Trop^- groups to the surface of nanocrystals was monitored through FT-IR spectroscopy (Figure S1, Supporting Information). Upon reaction, the absorption bands

Scheme 1. Molecular Structure of Tropolonate and Schematic Illustration of Tropolonate Capped Nd^{3+} - or Yb^{3+} -Doped NaYF_4 Nanocrystals and the Energy Transfer Process



assigned to the original capping ligands of the NCs (oleic acid, oleylamine, and octadecene) present at 2924 and 2854 cm^{-1} disappear and are replaced by the characteristic absorption bands of Trop^- at 1595 and 1510 cm^{-1} .

The XRD patterns (Figure 1, right) of the uncapped and capped $\text{NaY}_{0.8}\text{Ln}_{0.2}\text{F}_4$ NCs (Ln: Nd or Yb) reveal the formation of cubic $\alpha\text{-NaYF}_4$ (space group: $Fm\bar{3}m$). All diffraction peak positions and intensities agree well with calculated values.¹⁵ Transmission electron microscopy (TEM) images (Figure 1, left) of both uncapped and capped NC samples also indicate that the obtained nanocrystals are of single-crystalline nature with high crystalline size uniformity. They are relatively monodisperse with roughly spherical shape. The average sizes are 6.1 ± 0.6 nm, 6.0 ± 0.6 nm, 5.3 ± 0.7 nm, and 5.3 ± 0.6 nm for $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, Trop^- capped $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4$ NCs, and Trop^- $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, respectively (Figure S3, Supporting Information). Such relatively small sizes are compatible for use in many bioanalytical applications.

The UV-vis absorption spectra (Figure 2) of Trop^- capped NCs in DMSO reveal the presence of two bands with apparent maxima centered around 323 and 384 nm, similar to those observed for $[\text{Ln}(\text{Trop})_4]^-$ confirming the presence of Trop^- on the surface of NCs. Upon excitation at 340 nm, the characteristic sharp NIR emission bands arising from Nd^{3+} or Yb^{3+} were observed (Figure 2). The excitation profiles of lanthanide luminescence in both Nd^{3+} and Yb^{3+} doped NCs are similar (Figure S3), demonstrating that the lanthanide cations are sensitized through the same source: the electronic structure of the Trop^- ligand. For Yb^{3+} , there is a significant energy gap between the energy donating levels of Trop^- and its accepting levels. Energy transfer over this large gap could be explained by phonon-assisted or electron-transfer mechanisms.¹⁶

The lifetimes of the luminescence arising from Nd^{3+} and Yb^{3+} in Trop^- capped NCs and in $[\text{Ln}(\text{Trop})_4]^-$ complexes were determined in DMSO and are reported in Table 1. It is important to note that the Nd^{3+} and Yb^{3+} luminescence decays in $[\text{Ln}(\text{Trop})_4]^-$ complexes are best fit as monoexponential decays, indicating a unique coordination environment around the central Ln^{3+} .¹³ Since there should be more than one coordination environment for Ln^{3+} in the NCs (i.e., core and surface), multiexponential decay profiles are expected. The experimental results reflect this hypothesis. For Yb^{3+} in the NCs, the experimental decay was best fitted as a

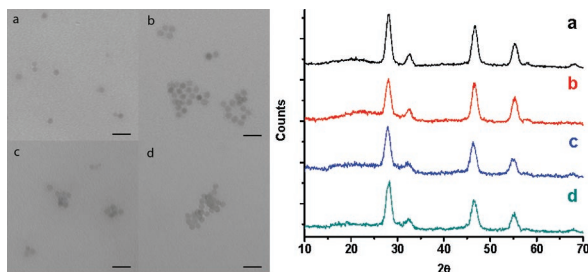


Figure 1. Transmission electron microscopy images (left, scale bar: 20 nm) and the X-ray diffraction patterns (right) of uncapped and capped NCs. (a) $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, (b) Trop^- capped $\text{NaY}_{0.8}\text{Yb}_{0.2}\text{F}_4$ NCs, (c) $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4$ NCs, (d) Trop^- capped $\text{NaY}_{0.8}\text{Nd}_{0.2}\text{F}_4$ NCs.

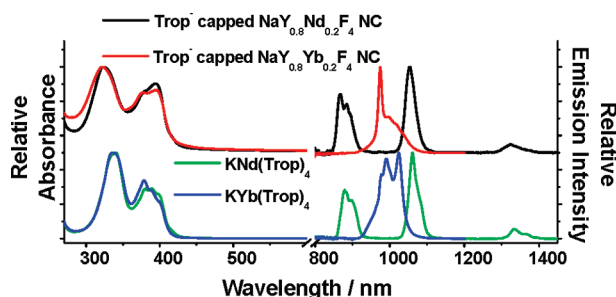


Figure 2. Normalized UV-vis absorption (left) and NIR luminescence emission spectra (right) of the complex (bottom) ($\lambda_{\text{ex}} = 340 \text{ nm}$, 10^{-4} M) and Trop^- -capped NCs (ca. 1 g L^{-1}) in DMSO (top).

Table 1. Luminescence Lifetimes (μs) of the Complexes and Trop^- -Capped NCs and Contribution to Luminescence Intensity in Brackets. $\lambda_{\text{ex}} = 354 \text{ nm}$

	$\text{NaY}_{0.8}\text{Ln}_{0.2}\text{F}_4$ NC	$\text{KLn}(\text{Trop})_4$
Yb^{3+}	68(3), [80(2)%] 4.1(4), [20(2)%]	12.43(9)
Nd^{3+}	12.6(9), [22(1)%] 3.7(2), [63(6)%] 1.1(2), [15(6)%]	1.10(4)

biexponential function. The longest component is attributed to the luminescence decay from cations in the NC core and is the major contribution to the overall intensity. The second component is significantly shorter and can be attributed to Yb^{3+} with a lower level of protection from nonradiative deactivation, likely located at the surface of the nanocrystals. The experimental decay recorded for Nd^{3+} in the NCs is best fit with a triple exponential decay. Similar to Yb^{3+} , there is a long component which corresponds to luminescence decay from Nd^{3+} in the nanocrystal matrix. The two shorter components are assigned to Nd^{3+} at or near the NCs surface in different coordination environments. Since Nd^{3+} , unlike Yb^{3+} , has a large number of excited states, and thus additional routes for nonradiative deactivations, it may be more sensitive to coordinating ligands than Yb^{3+} resulting in additional lifetime components.

Globally, significantly longer luminescence lifetimes were observed for the Trop^- capped $\text{Yb}^{3+}/\text{Nd}^{3+}$ doped NCs than for the corresponding molecular complex $[\text{Ln}(\text{Trop})_4]^-$. The longest components among the luminescence lifetimes were more than 5 times longer for Yb^{3+} and more than 11 times longer for Nd^{3+} . These values prove that our strategy to increase protection around the lanthanide cations through their incorporation in NCs is successful.

In conclusion, we have demonstrated the success of an innovative strategy to protect and sensitize NIR emitting Nd^{3+} and Yb^{3+} cations via doping in NaYF_4 NCs coated with sensitizing tropolonate

chromophores. The NC matrix protects the Ln^{3+} from nonradiative deactivation via high-energy vibrations of solvent molecules and/or of organic ligands, as proven by the longer luminescence lifetimes. Through this work, we have established proof that it is possible to combine the antenna effect provided by organic chromophores with the protection from an inorganic matrix, thereby reducing the usual limitations of NIR lanthanide luminescence in coordination complexes. This is a general strategy that can be expanded for application to different combinations of organic chromophores, lanthanide cations, and inorganic matrices. The NCs have a relatively small size, and combined with the proper choice of ligand system(s) to give the capped NCs water solubility, it will be possible to extend this methodology for bioanalytical applications.

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Supporting Information Available: Chemicals used, instruments, methods, experimental spectroscopic procedures, and synthesis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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