Supporting Information to

Europium-Doped NaYF₄ Nanocrystals as Probes for the Electric and Magnetic Local Density of Optical States throughout the Visible Spectral Range

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Fabrication

Materials: yttrium(III) acetate hydrate (YAc$_3$), 99.9%, Sigma-Aldrich; europium(III) acetate hydrate (EuAc$_3$), 99.9%, Sigma-Aldrich; sodium hydroxide (NaOH), 99.99%, Sigma-Aldrich; ammonium fluoride (NH$_4$F), 99.99+%, Sigma-Aldrich; oleic acid, 90%, Sigma-Aldrich; 1-octadecene, 90%, Sigma-Aldrich; methanol, >99.6%, Sigma-Aldrich; Ag pellets, 99.99%, Kurt J. Lesker; Al sputtering target, 99.999%, Plasmaterials.

Nanocrystal synthesis: The NaYF$_4$ nanocrystals (NCs) doped with 5% Eu$^{3+}$ were synthesized following a procedure modified from Refs. S1 and S2. A mixture of YAc$_3$ (252.7 mg; 0.95 mmol) and EuAc$_3$ (16.5 mg; 0.05 mmol) in oleic acid (6 mL) and 1-octadecene (17 mL) was degassed at 120°C under vacuum for 90 min, and then allowed to cool down to room temperature under nitrogen atmosphere. Solutions of NaOH (100 mg; 2.5 mmol) in methanol (2.5 mL) and NH$_4$F (148.4 mg; 4 mmol) in methanol (7.5 mL) were injected directly after each other into the reaction mixture under nitrogen. The reaction mixture was then stirred overnight. Next, the methanol was removed by evaporation at 100°C under vacuum for 90 min. The reaction mixture was heated to 300°C for 2 hours under nitrogen atmosphere while stirring, during which the NaYF$_4$ NCs form. After cooling down, the NCs were washed three times by precipitation with ethanol, centrifugation, and redispersing them in hexane. In the second last redispersing step, pure oleic acid (3 mL) was added to improve the colloidal stability of the NCs. The final product was dispersed in approximately 2 mL of hexane.

Mirror fabrication: Optically thick flat Ag mirrors were thermally evaporated on a Si(100) wafer at a rate of 5 nm/s (Kurt J. Lesker Nano36), and then template-stripped. The Al$_2$O$_3$ spacer layers were deposited on the Ag surface by reactive sputtering of Al in an O$_2$/Ar (10/90) plasma (1 mTorr; 200 W) at a rate of 5.6 nm/min (Kurt J. Lesker PRO Line PVD 75). The NC stock solution (see above) was diluted by a factor 25 in hexane, and then spin-coated on the Al$_2$O$_3$ surface at a rotation speed of 5000 rpm.

Spectroscopic experiments

Excitation: The mirror samples were loaded on a Nikon Ti-U inverted microscope equipped with a 100× air objective with a numerical aperture of 0.9. Measurements in tetradecane solution were done using a thin microscope coverslip with a droplet of NCs in tetradecane (diluted 10× from the stock solution) and an oil immersion objective with a numerical aperture of 1.3. The Eu$^{3+}$ ions of the sample were excited at 395 nm and 20 kHz (or at 100 Hz for Figure 1d in the main text) using the output of a Spectra-Physics Spirit-OPA optical parametric amplifier pumped by a Spectra-Physics Spirit solid state laser (520 nm). For the mirror experiments, the laser power was 45 μW at the position of the sample, focussed to a spot of approximately 1 μm diameter. Assuming that the absorption cross-section of Eu$^{3+}$ at 395 nm is 10$^{-20}$ cm$^2$ (Ref. S4), this would correspond to an excitation rate of approximately 0.1 ms$^{-1}$.

Detection: The emitted light was collected using the same objective, and dispersed on an Andor Shamrock 303i imaging spectrograph, using a 150 lines/mm grating blazed at 500 nm and a 100 μm entrance slit. The emission spectrum was detected on an Andor iXon 888 Ultra electron multiplying charge-coupled device camera (EMCCD) cooled to −75°C and operated at an electron multiplying gain of 1000. The central ~60 rows on the CCD image were then integrated in the vertical direction to obtain the emission spectrum (Figure 1e,f and Figure 2e in the main text). For the fits (Figure 3 in the main text) we took into account the 20% lower detection efficiency of the setup for the near-infrared emission at 690 nm, as determined by comparison to a calibrated spectrometer. The photoluminescence decay traces of Figure 1d in the main text were detected on a Excelitas SPCM-AQRH-14-TR avalanche photodiode, and recorded on a PicoQuant PicoHarp 3000 time-correlated single photon counting module operated in time-tagging mode.
Calculating the radiative decay rate of ED and MD emitters

On top of a mirror: We consider a three-layer mirror geometry as depicted in Figure 2a of the main text: layer 0 is air with dielectric constant \( \varepsilon_0 = 1 \) containing NCs with refractive index \( n = 1.48 \) (Ref. S5) doped with emitters, layer 1 is Al\(_2\)O\(_3\) with dielectric constant \( \varepsilon_1 = 2.82 \), and layer 2 is Ag with frequency-dependent dielectric constant \( \varepsilon_2 \) (Ref. S3). The radiative decay rate for a MD or ED transition in this geometry is:

\[
y_{\text{ED}}(d) = \frac{\gamma_{\text{bulk}}}{N_{\text{NC}}} \chi_{\text{ED}}^2 \int_0^{u^*} \Im \left\{ \left[ 1 + \left( \frac{1}{2} r_s + \frac{1}{2} r_p - u^2 \right) \right] e^{-2 i k_0 h} \right\} \frac{\mu}{\nu} \, du \quad (S1)
\]

\[
y_{\text{MD}}(d) = \frac{\gamma_{\text{MD}}}{N_{\text{NC}}} \chi_{\text{MD}}^2 \int_0^{u^*} \Im \left\{ \left[ 1 - \left( \frac{1}{2} r_s + \frac{1}{2} r_p - u^2 \right) \right] e^{2 i k_0 h} \right\} \frac{\mu}{\nu} \, du \quad (S2)
\]

Here \( \gamma_{\text{bulk}} \) and \( \gamma_{\text{MD}} \) are the radiative decay rates in the corresponding bulk material, \( n_{\text{NC}} = 1.48 \) is the refractive index of the NC host material, \( \chi_{\text{ED}} = 3/(2 + n_{\text{NC}}^2) \) and \( \chi_{\text{MD}} = 1 \) are the local-field factors for ED and MD transitions, \( k_0 = 2\pi/\lambda \) is the free-space wavevector of the light emitted in the transition, and \( u^* = -i \sqrt{1 - u^2} \). The dependence of the radiative decay rates on the spacer thickness \( d \) is contained in the reflection coefficients \( r_s \) and \( r_p \):

\[
\begin{align*}
  r_s &= \frac{\gamma_{\text{D}}}{r_s} + \frac{\gamma_{\text{P}}}{r_s} e^{-2 i k_0 d} \\
  r_p &= \frac{\epsilon_l - \epsilon_i l_s}{\epsilon_l + \epsilon_i l_s} \quad (S4)
\end{align*}
\]

with \( l_i = -i \sqrt{\varepsilon_i - u^*} \).

The upper limit of integration can be set to \( u^* = \text{NA} \) to calculate the rate \( \gamma_{\text{det}} \) of radiative decay into photon modes that can be collected by an objective with finite numerical aperture (NA), or to \( u^* = \infty \) for the total rate \( \gamma_{\text{tot}} \) of radiative decay including energy transfer to the metal, plasmons and photons that are not collected by the objective.

Dispersed in a solvent: The radiative decay rate of ED and MD transitions for NCs dispersed in a homogeneous solvent of refractive index \( n \) (where we use tetradecane with \( n = 1.429 \) in the main text) is:

\[
y_{\text{ED}}(n) = \frac{\gamma_{\text{ED}}}{N_{\text{NC}}} n_{\text{NC}} \chi_{\text{ED}}^2 n^2 \quad (S6)
\]

\[
y_{\text{MD}}(n) = \frac{\gamma_{\text{MD}}}{N_{\text{NC}}} n_{\text{NC}}^3 \chi_{\text{MD}}^2 n^2 \quad (S7)
\]

where \( \chi_{\text{ED}} = 3 n^2 / (2 n^2 + n_{\text{NC}}^2) \) and \( \chi_{\text{MD}} = 1 \) are the local-field factors. For this situation, since the emission is isotropic, there is a constant factor between \( \gamma_{\text{MD}} \) and \( \gamma_{\text{det}} \) that does not depend on emission wavelength or dipole character of the transition but only on the experimental geometry.

The fitting procedure: A model equation for the branching ratios was generated using Equation 2 of the main text, by evaluating the integrals of Equations S1 and S2 in Wolfram Mathematica. This yields model expressions for the branching ratios \( \beta_{J_{\text{upper}} \rightarrow J_{\text{lower}}}^{\text{model}} \) as a function of the bulk decay rates \( \{ \gamma_{J_{\text{upper}} \rightarrow J_{\text{lower}}} \} \) (where \( J \) and \( f \) are labels for the \( ^2D_f \) excited states and the \( ^3F_f \) ground states). Next, a best fit with the experiment is found by minimizing

\[
f \left( \{ \gamma_{J_{\text{upper}} \rightarrow J_{\text{lower}}} \} \right) = \sum_{J_{\text{lower}},d} \left( \beta_{J_{\text{lower}} \rightarrow J_{\text{upper}},d}^{\text{model}} - \beta_{J_{\text{lower}} \rightarrow J_{\text{upper}},d}^{\text{exp}} \right)^2 \quad (S8)
\]

with respect to the bulk decay rates \( \{ \gamma_{J_{\text{upper}} \rightarrow J_{\text{lower}}} \} \), in Wolfram Mathematica. Here \( \beta_{J_{\text{lower}} \rightarrow J_{\text{upper}},d}^{\text{exp}} \) denotes the experimental branching ratios, and the index \( d \) runs over the \( 11 \) measurements at different emitter–mirror separations.
Figure S1 | The X-ray diffraction pattern of NaYF₄:Eu³⁺ NCs. The X-ray diffraction pattern of NaYF₄:Eu³⁺ NCs synthesized according to our method (but not the exact same batch as used for the spectroscopic experiments), recorded using a Co Ka source ($\lambda = 1.79$ Å). The crystal structure matches the reference data for hexagonal $\beta$-NaYF₄ (JCPDS 00-028-1192; red bars).

Figure S2 | Excitation spectrum of Eu³⁺ in NaYF₄ NCs. The excitation spectrum of NaYF₄:Eu³⁺ NCs, detected at 616 nm. Several excitation lines are observed in the visible range of the spectrum from the lowest-energy $^7F_0$ state or from the thermally populated $^7F_1$ state, to the $^5D_J$ excited states. Some excitation lines have MD character, as indicated with an asterisk. The excitation transitions to the $^5D_1$ state are used in Ref. S9 (labeled in yellow). The UV spectral range shows several excitation lines close to each other occur, corresponding to a series of closely-spaced excited states. The strongest excitation line, for the transition to the $^7L_6$ excited state, lies at 395 nm and is used to excite for the experiments presented in the main text. This measurement was done on an Edinburgh Instruments FLS980 spectrofluorometer equipped with a 450 W Xe arc lamp.

Figure S3 | The optical properties of the mirror in the spectral range investigated. The calculated reflection coefficient $R$ on the interface between Al₂O₃ and Ag (blue) or Au (yellow) for light at normal incidence. S5 Ag (used in this work), in contrast to Au (not used), makes a good mirror throughout the visible spectral range.
Figure S4 | The independent electric and magnetic local density of optical states. Theoretical radiative decay rates of (a) the electric-dipole transitions, and (b) the magnetic-dipole transitions of NaYF₄:Eu³⁺ NCs. Solid lines: the decay rate $\gamma^{\text{det}}$ into 'detectable' photon modes that can be collected by our microscope objective (NA 0.9), as a function of separation from the Ag mirror as in the geometry of Figure 2a in the main text. Dashed lines: the total decay rate $\gamma^{\text{tot}}$, including photon emission at angles grazing over the mirror surface, plasmon emission, and energy transfer to the metal. Circles: $\gamma^{\text{det}}$ (closed symbols), and $\gamma^{\text{tot}}$ (open symbols) for NCs in vacuum, NCs in tetradecane, and bulk NaYF₄:Eu³⁺. All decay rates are normalized to the total decay rate $\gamma^{\text{tot}}$ of the transition in NCs in vacuum.

Figure S5 | The emission intensity from higher-energy excited states of Eu³⁺ in NaYF₄ NCs. The fraction of Eu³⁺ emission coming from the $^5D_2$ excited state (yellow) and the $^5D_1$ excited state (green) as a function of excitation power at 395 nm, and normalized to the lowest power. The NCs are dispersed in tetradecane. The emission is collected with an oil-immersion objective (NA 1.3) to allow more accurate detection of the intensity from the $^5D_2$ and $^5D_1$ states at low excitation power.
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