Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Excitation efficiency determines the upconversion luminescence intensity of β-$NaYF_4$:Er^{3+},Yb^{3+} nanoparticles in magnetic fields up to 70 T

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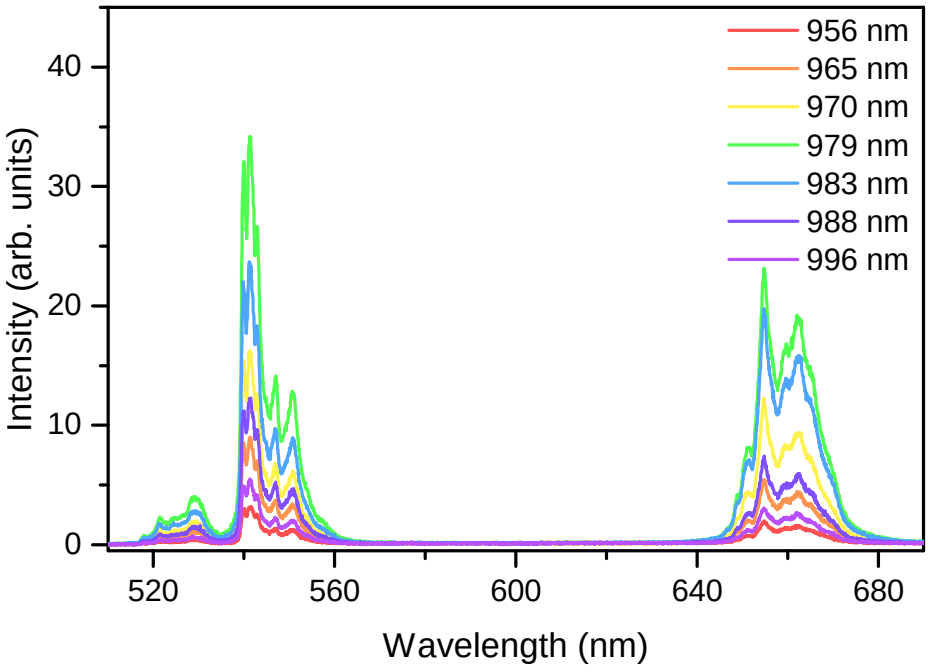

FIG. S1. UCL spectra for selected excitation wavelengths.

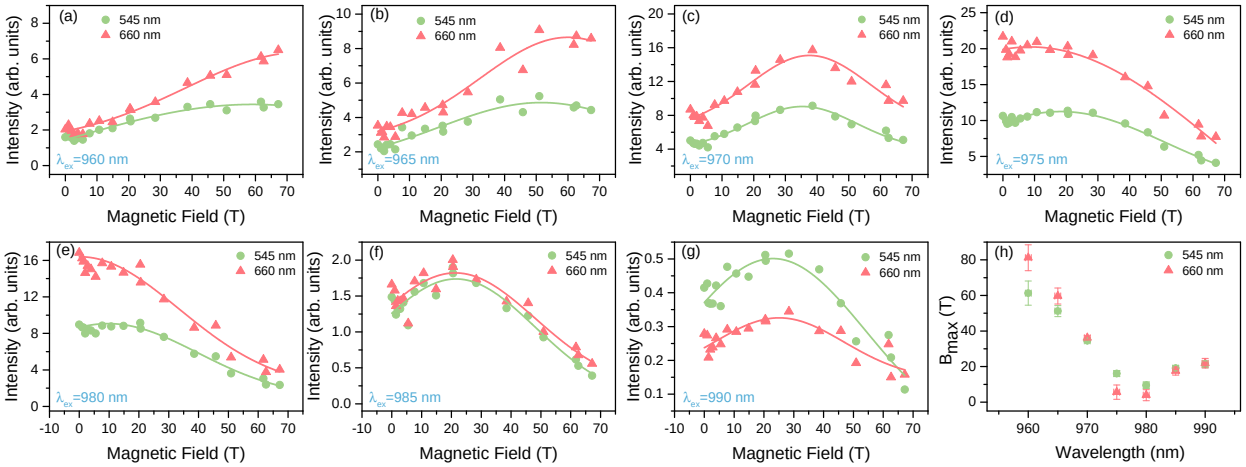

FIG. S2. (a)–(g) Magnetic field dependence of upconverted luminescence intensity integrated in the green and red spectral bands for excitation wavelengths given in the panels. Lines are guides to eye (fitted Gaussian functions). (h) Excitation wavelength dependence of the magnetic field $B_{\max}$, corresponding to the maximum luminescence intensity for the two spectral bands.

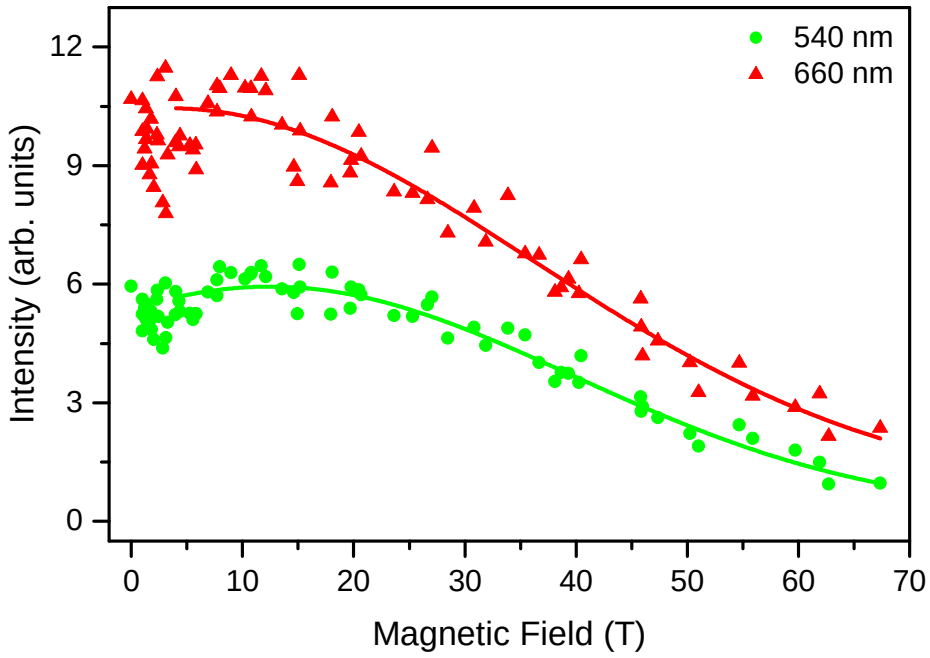

FIG. S3. Detailed measurement of the magnetic field dependence of the UCL intensity under quasi-resonant excitation at 980 nm. Green circles and red triangles denote the intensities of the green and red UCL bands centered, respectively, at 540 nm and 660 nm. Lines are guides to eye.

MODEL CALCULATIONS

In order to calculate the UCL intensities of the green band I_{Green}, we assume that

$$I_{\mathrm{Green}} = A \cdot p_{\mathrm{exc}}^2(B), \tag{1}$$

where $p_{\mathrm{exc}}(B)$ is the probability of Yb^{3+} ion excitation dependent on the magnetic field B. The field-independent proportionality factor A encompasses all other factors influencing UCL such as the efficiency of the energy transfer between Yb^{3+} and Er^{3+} ions, probabilities of various upconversion paths, non-radiative and radiative relaxation rates, etc. We assume that these processes are unaffected by the magnetic field. To calculate the field dependent excitation probabilities $p_{\mathrm{exc}}(B)$, we simplify the energy structure of the absorbing Yb^{3+} ions. Namely, as mentioned in the main text, we neglect all but the lowest Kramers doublets from the $^2F_{7/2}$ and $^2F_{5/2}$ manifolds. This leaves us with a pair of pseudospin-1/2 states. We assume that the optical transitions occur without changing the z-component of this pseudospin and, thus, the transition line energy E_L depends on magnetic field B as

$$E_L = E_0 + 1/2 g \mu_B B, \tag{2}$$

where E_0 is the transition energy at zero field and g and μ_B denote the effective Landé g-factor and the Bohr magneton, respectively. The excitation efficiency $p_{\mathrm{exc}}(B)$ is proportional to the overlap of the laser spectrum and the absorption line:

$$p_{\mathrm{exc}}(B) = \int_0^\infty L(E, E_L, \Gamma_L) G(E, E_G, \Gamma_G) dE. \tag{3}$$

In the above equation, $L(E, E_L, \Gamma_L)$ is the absorption spectrum given by the Lorentzian lineshape: $L(E, E_L, \Gamma_L) = \Gamma_L^2/((E - E_L)^2 + \Gamma_L^2)$, where Γ_L is the transition linewidth, full width at half maximum (FWHM). The laser spectrum is given by a Gaussian function $G(E, E_G, \Gamma_G) = \exp(-4\ln(2)(E - E_G)^2/\Gamma_G)$, where Γ_G is the FWHM laser linewidth and E_G is the central energy related to the excitation wavelength λ_{exc} by $E_G = hc/\lambda_{\mathrm{exc}}$, where h and c are the Planck's constant and the speed of light, respectively.

In Fig. 3(c) of the main text, we plot $p_{\mathrm{exc}}(B)$ calculated with eq. (3) for λ_{exc} given in the legend, $\Gamma_G = 100$ cm^{-1} measured directly, $g = 14$, $E_0 = hc/(981\mathrm{nm})$ and $\Gamma_L = 200$ cm^{-1} both consistent with the zero field measurements of the UCL excitation spectrum (Fig. 1(f)).

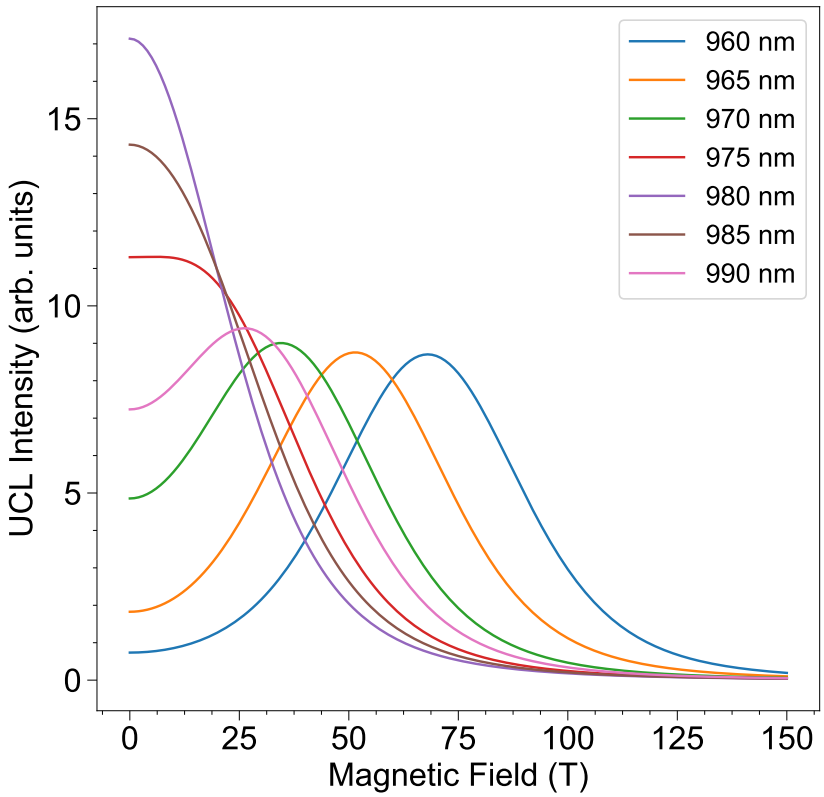

FIG. S4. Results of model calculations for all λ_{exc} used in the experiment and the parameters described in the main text.

The results of model calculations for λ_{exc} values from the experiment and an extended magnetic field range are presented in Fig. S4. The calculation parameters are the same as for the curves displayed in Fig. 4(c) of the main text. The calculations reproduce the decrease of the UCL intensity at zero field as λ_{exc} is progressively detuned from the absorption resonance – an effect observed experimentally and shown in Fig. S2. Simultaneously with increasing detuning, UCL maximum occurs at increasingly large magnetic field. As expected, detuning the excitation laser by a similar energy distance results in a similar field dependence of the UCL intensity: compare, e.g., results for $\lambda_{exc} = 970$ nm and $\lambda_{exc} = 990$ nm. Note also that for large detunings for which the UCL maximum occurs at fields larger than ~ 50 T, the UCL maximum value is half the value for quasi-resonant excitation at $\lambda_{exc} = 980$ nm. This is a consequence of exciting only one of the Zeeman-split branches: at such large fields the

overlap with the other branch is negligible. Note that in the above model, we neglect the spin and energy relaxation between the Zeeman split substates, i.e., assume an infinite spin temperature. The presence of such relaxation maybe one of the reasons that this simple model does not reproduce our data quantitatively.