Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for:

Synthesis and Near-infrared Fluorescence of $K_5NdLi_2F_{10}$ Nanocrystals and Its Dispersion with High Doping Concentration and Long Lifetime

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S1. Fitting curve of refractive index

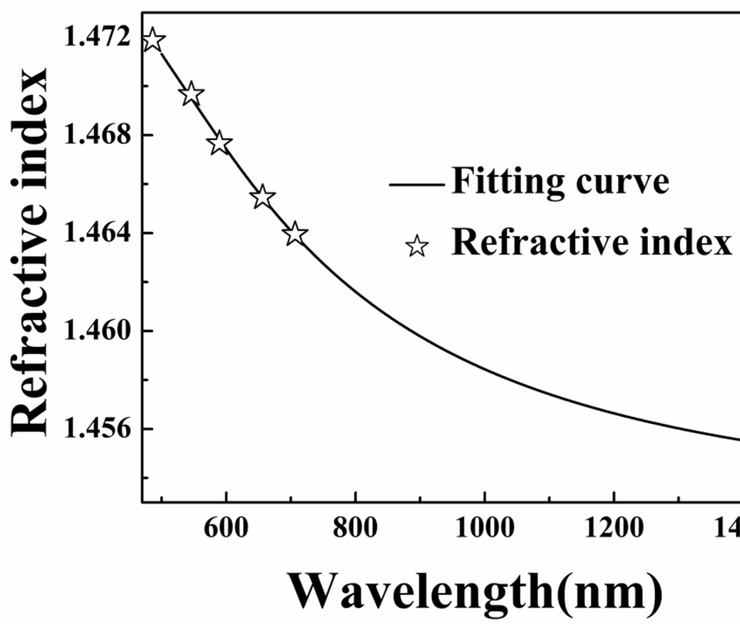

Figure S1. fitting curve of refractive index for $K_5NdLi_2F_{10}$ nanocrystals dispersion in PEG400

Figure S1 shows the fitting curve of refractive index for $K_5NdLi_2F_{10}$ nanocrystals dispersion in PEG-400, which was measured on WYV-V-prismrefractometer. The experimental data was analyzed by soft of MATrix LABoratory. We could get the refractive index at 1048 nm was 1.4579.

S2. Judd-Ofelt calculation

Based on the absorption spectrum which was shown in the inset picture of Figure 7, there are five transitions corresponding to transitions from $^4I_{9/2}$ ground state manifold to various excited states. The experimental oscillator strengths (f_{exp}) of each electronic transition of Nd^{3+} can be evaluated by the following Equation S1[1]:

$$f_{\exp} = \frac{mc^2}{\pi e^2 N \lambda^2} \int \alpha(\lambda) d\lambda \tag{1}$$

Where m and e are electron mass and charge, c is the velocity of light, N is the number density of Nd^{3+} ions, and α (λ) is the absorption coefficient. According to Judd–Ofelt theory, the calculated oscillator strengths (f_{cal}) of electronic transitions from the ground state (aJ) level to the excited state (bJ') level are given by the Equation S2 [2]:

$$f_{cal}(aJ, bJ') = \frac{8\pi^2 mc}{3h\lambda(2J+1)} \frac{\left(n^2+2\right)^2}{9n} \sum_{t=2,4,6} \Omega_t \left| \left\langle aJ \left\| U^{(t)} \right\| bJ' \right\rangle \right|^2 \tag{2}$$

Where n is the refractive index of the host, h is the Planck constant, $2J+1$ is the degeneracy of the ground state. $|\langle aJ\|U(t)\|bJ'\rangle|^2$ represents the reduced matrix elements that are insensitive to the local environment, and those values for Nd^{3+} ions given by *Carnall et al* were used in the calculations[3,4]. The values of three Judd-Ofelt parameters $\Omega_{t\,(2,\,4,\,6)}$ were provided by a least-squares fitting of f_{exp} to f_{cal}. According to the Judd-Ofelt formulae described, measured oscillator strengths (f_{exp}), calculated oscillator strengths (f_{cal}) and Judd-Ofelt parameters Ω_t of $K_5NdLi_2F_{10}$ nanocrystals were determined (Listed in Table S1).

Table S1. Observed absorption peak positions, integrated absorption coefficient, measured oscillator strengths (f_{exp}), calculated oscillator strengths (f_{cal}) and Judd-Ofelt parameters of the $K_5NdLi_2F_{10}$ nanocrystal dispersion [a].

Electronic transition (from $^4I_{9/2}$)	Absorption peak (nm)	Absorption coefficient $\int\alpha(\lambda)d\lambda(10^{-7})$	Oscillator strength $f_{exp}(10^{-6}\ cm^2)$	Oscillator strength $f_{cal}(10^{-6}\ cm^2)$
$^4G_{7/2}+^4G_{9/2}+^2K_{13/2}$	521	14.20691	4.55085	4.45444
$^4G_{5/2}+^2G_{7/2}$	576	19.46721	5.10968	6.70554
$^4F_{7/2}+^4S_{3/2}$	743	23.68136	3.73563	4.27054
$^4F_{5/2}+^4H_{9/2}$	800	24.98455	3.39959	5.33955
$^4F_{3/2}$	866	17.88561	2.07492	2.56509
Ω_2 ($\times10^{-20}$ cm^2)			1.153	
Ω_4 ($\times10^{-20}$ cm^2)			6.174	
Ω_6 ($\times10^{-20}$ cm^2)			2.997	

[a] Based on absorption data from $K_5NdLi_2F_{10}$.

From the Judd–Ofelt parameters Ω_t obtained above, the radiative transition rates for electronic dipole transitions between an excited state and the lower lying levels can be calculated by the following Equation S3 [5]:

$$A(aJ,bJ')=\frac{64\pi^4e^2n^2\chi}{3h\lambda^3\left(2J+1\right)}\sum_{t=2,4,6}\Omega_t\left|\left\langle 4f^N aJ\left\|U^{(t)}\right\|4f^N bJ'\right\rangle\right|^2 \tag{3}$$

The radiative lifetime of the $^4F_{3/2}$ state is related to the radiative decay rate through following Equation S4 [6]:

$$\tau_r(a)=\frac{1}{A_{ed}(a)}=\frac{1}{\sum_b A_{ed}(ab)} \tag{4}$$

The quantum efficiency (φ) of the emission bands can be evaluated from the following Equation S5 [7]:

$$\varphi = \frac{\tau_{mea}}{\tau_{rad}} \qquad (5)$$

The emission spectra of $K_5NdLi_2F_{10}$ nanocrystals in PEG-400 shows three emission bands centered at 865, 1048, and 1332 nm. The fluorescence branching ratios of these bands, radiative transition probability (A_{rad}) between the excited states, and radiative lifetime of an emitting state were presented in Table S2.

Table S2. Observed emission bands, their measured and calculated radiative properties of $K_5NdLi_2F_{10}$ [a]

Transition from $^4F_{3/2}$	Wavelength (nm)	$A_{rad}(s^{-1})$	$\beta_{exp}(\%)$	$\tau_{cal}(\mu s)$
$^4I_{13/2}$	1332	1223.58	5.91774	441.274
$^4I_{11/2}$	1048	908.478	40.0888	
$^4I_{9/2}$	865	134.106	53.9935	

[a] Based on emission data from $K_5NdLi_2F_{10}$ nanocrystals dispersion in PEG400.

In this work, a lifetime of 174.6 μs was measured for the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition of $K_5NdLi_2F_{10}$ nanocrystals dispersion in PEG-400 that was confirmed by the radiative lifetime and the fluorescence branching ratios of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition. According to the function (5), the emission quantum yield is deduced to be as high as 39.57 %.

References

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