Supplementary Information for:

Luminescence Properties of Nd^{3+}-doped LaF_3 Nanocrystals with a Long Lifetime in Organic Solvents

Wenxiu Sun,[a] Xiaoxia Cui,[b] Zhongyue Wang,[a] Wei Wei*[a,b] and Bo Peng*[a,b]

[a]Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210046, P.R. China.

[b]State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and Precision Mechanics, Chinese Academy of Science (CAS) Xi'an Shaanxi 710119, P.R. China.

Judd-Ofelt calculation

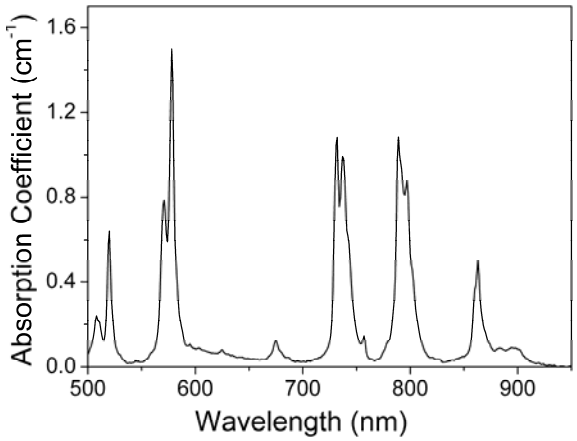

Fig. S1 Absorption spectrum of LaF_3:Nd nanocrystals in DMSO/tetrabromoethane.

Fig. S1 shows the room temperature absorption spectrum of LaF_3:Nd (3 mol%) nanocrystals in DMSO/tetrabromoethane, which was measured on a Unico UV-2000 scanning spectrophotometer. There are five transitions corresponding to transitions from $^4I_{9/2}$ ground state manifold to various excited states. Based on the absorption spectrum, the experimental oscillator strengths (f_{exp}) of each electronic transition of Nd^{3+} can be evaluated by the following expression [1]:

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

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[2]:

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

Where n is the refractive index of the host, h is the Planck constant, $2J + 1$ is the degeneracy of the ground state. $|<aJ\|U(t)\|bJ'>|^2$ represents the reduced matrix elements that are insensitive to the local environment, and those values for Nd^{3+} ions in LaF_3 given by *Carnall et al* were used in the calculations [3, 4]. The values of the 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 LaF_3:Nd 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 LaF_3:Nd nanocrystals [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$^2)$
$^4G_{7/2}+^4G_{9/2}+^2K_{13/2}$	520	5.0182	1.65721	2.24068
$^4G_{5/2}+^2G_{7/2}$	578	14.1402	3.77952	5.37280
$^4F_{7/2} + ^4S_{3/2}$	732	15.62548	2.60404	3.60157
$^4F_{5/2}+ ^4H_{9/2}$	789	15.68613	2.25009	3.33696
$^4F_{3/2}$	863	6.08722	0.72985	0.97020
Ω_2 ($\times10^{-20}$ cm^2)		0.81		
Ω_4 ($\times10^{-20}$ cm^2)		1.78		
Ω_6 ($\times10^{-20}$ cm^2)		2.47		

[a]Based on absorption data from LaF_3:Nd (3 mol%).

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 [5]:

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

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

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

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

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

The emission spectra of LaF_3:Nd nanocrystals shows three emission bands centered at 880, 1060, and 1330 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 LaF_3:Nd[a]

Transition from $^4F_{3/2}$	Wavelength (nm)	$A_{rad}(s^{-1})$	$\beta_{exp}(\%)$	$\tau_{cal}(\mu s)$
$^4I_{13/2}$	1323	511.037	38.49	753
$^4I_{11/2}$	1057	674.332	50.78	
$^4F_{9/2}$	863	142.498	10.73	

[a]Based on emission data from LaF_3:Nd (3 mol%, sample F4).

To compute the quantum efficiency, measured lifetime data was confirmed by the radiative lifetime: In this work, a lifetime of 359 μs was measured for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of LaF_3:Nd nanocrystals dispersed in DMSO/tetrabromoethane. According to the function (5), the emission quantum yield is deduced to be as high as 47.7 %.

References

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