Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Measuring the Internal Quantum Yield of Upconversion Luminescence for Ytterbium-Sensitized

Upconversion Phosphors Using the Ytterbium(III) Emission as an Internal Standard

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I.) Absorbance spectrum of Yb^{3+}:$^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of β-$NaYF_4$:2%Er, 18%Yb nanocrystals in CCl_4

The absorbance spectrum below was used to determine the relative absorbance values 976 nm and 936 nm. CCl_4 was chosen for the dispersion medium because of its excellent transparency in the NIR spectral region. Dispersions used for upconversion experiments were at lower concentrations with peak absorbance, A(976 nm) < 0.004.

$$\frac{A(936nm)}{A(976nm)} = 0.143$$

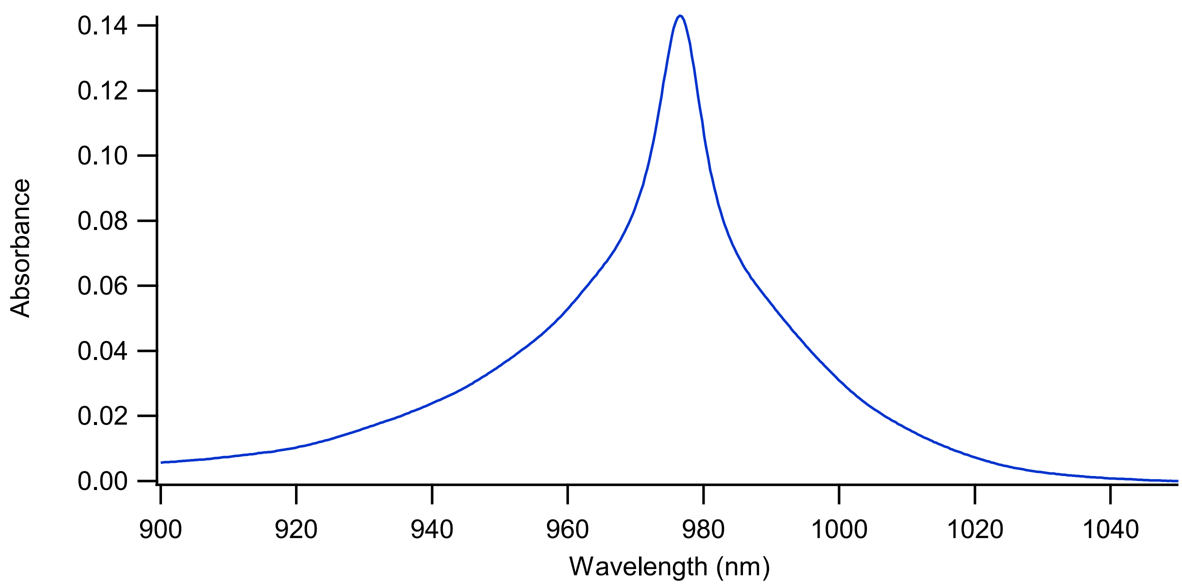

Figure S1. Absorbance spectrum of Yb^{3+}:$^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of β-$NaYF_4$:2%Er, 18%Yb nanocrystals in CCl_4

II.) Tabulated Results of the IQY measurements.

Table S1. IQY (%) values vs irradiance for β-$NaYF_4$: 0.5%Tm, 25%Yb@ $NaYF_4$ core-shell nanoparticles dispersed in toluene

Irradiance 936 nm (W/cm^2)	Equivalent Irradiance at 976 nm (W/cm^2)	%IQY 450nm	%IQY 474nm	%IQY 800nm	%IQY 1µm
547	78.2	0.127	0.135	10.44	38.9
221	31.6	0.041	0.074	9.45	41.6
148	21.2	0.021	0.052	8.43	44.6
59	8.5	0.005	0.025	6.26	52.0
28	4.0	0.000	0.000	4.57	53.1
7.1	1.0	0.000	0.000	2.66	58.6
3.8	0.54	0.000	0.000	2.24	60.7

Table S2. IQY (%) values vs irradiance for β-$NaYF_4$: 0.5%Tm, 25%Yb core nanoparticles dispersed in toluene

Irradiance 936 nm (W/cm^2)	Equivalent Irradiance at 976 nm (W/cm^2)	%IQY 450nm	%IQY475nm	%IQY800nm	%IQY 1µm
534	76.4	0.0343	0.0320	3.71	10.36
220	31.5	0.0100	0.0167	3.09	11.33
145	20.7	0.0053	0.0120	2.71	11.99
55	7.9	0.0005	0.0042	1.56	13.85
25	3.6	0.0000	0.0017	1.02	15.04
7.1	1.0	0.0000	0.0000	0.55	14.86
3.5	0.50	0.0000	0.0000	0.36	15.06

Table S3. IQY (%) values vs irradiance for β-$NaYF_4$: 2%Er, 18%Yb@ $NaYF_4$ core-shell nanoparticles dispersed in toluene

Irradiance 936 nm (W/cm^2)	Equivalent Irradiance at 976 nm (W/cm^2)	%IQY 408nm	%IQY 540nm	%IQY 660nm	%IQY 1 µm	%IQY 1.5 µm
509	72.7	0.126	2.68	3.0	54.4	17.2
214	30.5	0.064	1.96	1.9	58.6	16.0
140	20.0	0.043	1.63	1.4	61.2	16.2
55	7.9	0.013	1.03	0.65	66.5	14.6
29	4.1	0.0000	0.48	0.18	74.0	13.4

Table S4. IQY (%) values vs irradiance for β-$NaYF_4$: 2%Er, 18%Yb core nanoparticles dispersed in toluene

Irradiance 936 nm (W/cm^2)	**Equivalent Irradiance at 976 nm (W/cm^2)**	**%IQY 408nm**	**%IQY 540nm**	**%IQY 660nm**	**%IQY 1 µm**	**%IQY 1.5 µm**
503	71.9	0.0235	0.54	0.72	15.9	7.9
214	30.5	0.0091	0.35	0.36	16.3	7.1
138	19.8	0.0052	0.27	0.24	16.6	7.1
48	6.9	0.0010	0.12	0.07	18.7	7.4
25	3.6	0.0000	0.06	0.02	19.0	8.1

III.) Correlation of radiative rate constants, k_{rad}, for Yb^{3+}:$^2F_{5/2} \rightarrow {}^2F_{7/2}$ emission with the refractive index of the crystal host.

The values of k_{rad} for Yb^{3+} emission doped in a series of crystal hosts has been reported by Krupke,[1] and is tabulated below along with the refractive index of the host. We have omitted the centrosymmetric systems for which the Yb^{3+}:$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition is electric-dipole forbidden.

Table S1. Values of k_{rad} reported by Krupke for Yb^{3+} emission for a series of crystal hosts. The refractive index of the bulk host is also given.

Host	**k_{rad} (s^{-1})**	**n**
$KCaF_3$	370	1.378
$LiYF_4$	452	1.455
KY_3F_{10}	535	1.5
BaY_2F_8	490	1.521
LaF_3	463	1.597
$Ca_5(PO_4)_3F$	769	1.63
Y_2SiO_5	962	1.79
$Y_3Al_5O_{12}$	990	1.82
$LiYO_2$	885	1.82
$LuPO_4$	885	1.83

Assuming a constant dipole strength for the Yb^{3+}:$^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, in bulk materials k_{rad} should scale with the refractive index of the host according to[2,3]

$$k_{rad}(n) = k_{rad}^{0} \cdot n\left(\frac{3n^2}{2n^2+1}\right)^2 \quad (1.)$$

where k_{rad}^{0} is the value of the rate constant in a vacuum. Equation 1 is linear in n, so that k_{rad} should increase linearly with increasing refractive index.

The data in Table S1 is plotted in Figure S2 in two groups, fluorides and oxides, each fit to Eq. 1, with k_{rad}^{0} being the only fit parameter. For the oxides, $k_{rad}^{0} = 301.2 \pm 8.2 s^{-1}$ and, for the fluorides, $k_{rad}^{0} = 206.6 \pm 9.5 s^{-1}$. The higher k_{rad}^{0} for the oxides is indicative of a higher dipole strength relative to the fluorides, which is commonly attributed to a lower-lying ligand-to-metal charge transfer band in the oxides. Using the $k_{rad}^{0} = 206.2 \pm 9.5 s^{-1}$ fit value for the fluorides and the refractive index for $NaYF_4$ (n=1.497), Equation 1 predicts k_{rad} =464 s^{-1} for Yb^{3+} emission in a bulk $NaYF_4$ host.

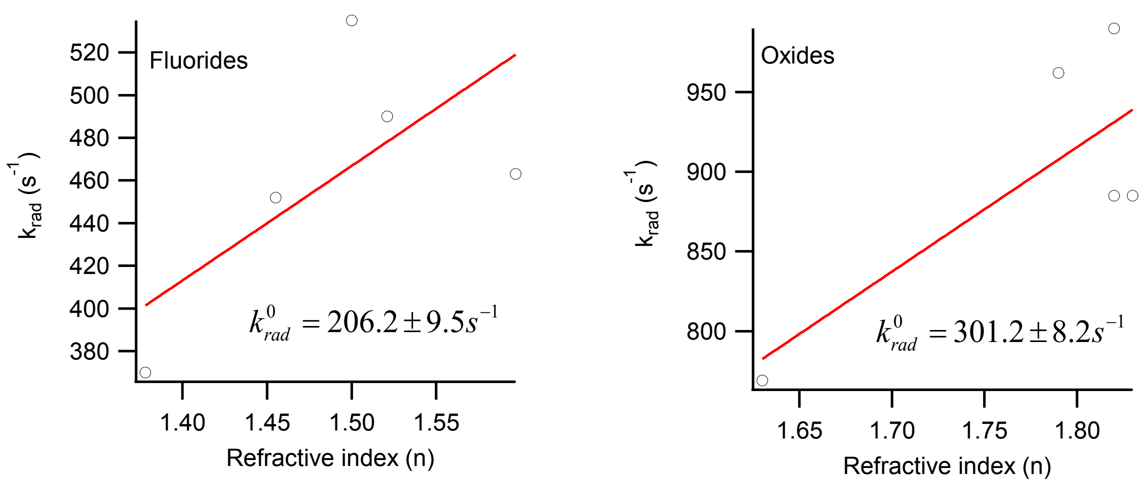

Figure S2. Fits of the fluoride and oxide data in Table S1 to Equation 1.

We note also that the entire data set in Table S1 can be empirically fit to a line function, as shown in Figure S3. The trend shown in Figure S3 would predict k_{rad} =498 s^{-1} for Yb^{3+} emission in a bulk $NaYF_4$ host.

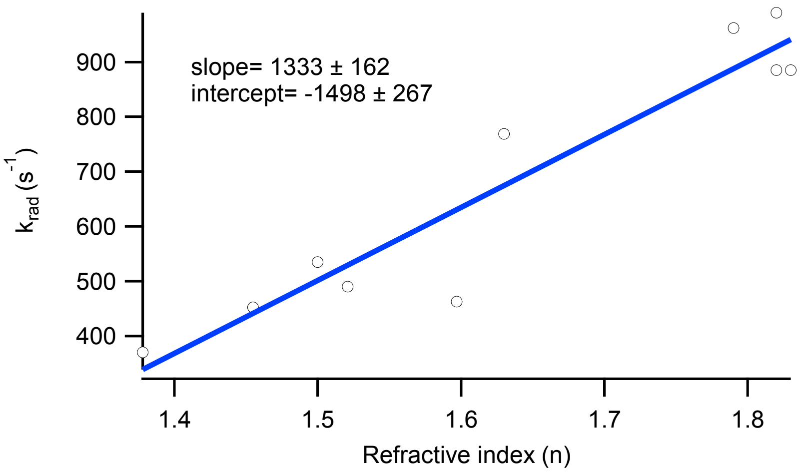

Figure S3. Empirical fit of all the data in Table S1 to a line function.

The preceding discussion applies only to k_{rad} values in bulk materials. For nanomaterials, the effect of solvent on k_{rad} must be considered separately.[2] The solvent effect will only be significant, however, for cases in which the refractive index of the solvent and sample differ markedly.

(1) Page, R. H.; Schaffers, K. I.; Waide, P. A.; Tassano, J. B.; Payne, S. A.; Krupke, W. F.; Bischel, W. K. Upconversion-pumped luminescence efficiency of rare-earth-doped hosts sensitized with trivalent ytterbium. *J Opt Soc Am B* **1998**, *15*, 996-1008.

(2) Senden, T.; Rabouw, F. T.; Meijerink, A. Photonic Effects on the Radiative Decay Rate and Luminescence Quantum Yield of Doped Nanocrystals. *ACS Nano* **2015**, *9*, 1801-1808.

(3) Glauber, R. J.; Lewenstein, M. Quantum optics of dielectric media. *Physical Review A* **1991**, *43*, 467-491.