Electronic Supplementary Information

Temperature Dependence of the Local Field Effect in YAG:Ce^{3+} Nanocomposites

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Contents

1. Materials and methods

1A. Materials. Aluminum isopropoxide (≥98%), yttrium(III) acetate tetrahydrate (≥99.9%), and cerium(III) acetate monohydrate (≥99.99%), 1,4 butanediol (≥99%), propanol (≥99.9%), pentanol (≥99%), hexanol (≥99%) and heptanol (≥98%) were purchased from Sigma-Aldrich. The reagents and solvents were used without further purification.

1B. Synthesis of YAG:Ce samples 1 and 2: 1.26±0.01 at.% Ce/Y NPs. The Ce^{3+}-containing YAG nanoparticles were prepared using a modified glycothermal method based on Nyman's work[1]. Aluminum isopropoxide (3.215 mmol), yttrium acetate (1.9097 mmol) and cerium acetate (0.0193 mmol) were placed in a 50 mL round-bottomed flask, and then 30 mL 1,4 butanediol and diethylene glycol (1,4 BD: DEG = 95:5) were added. The mixture was heated in an oil bath at 90 °C for 6 h and the contents

were mixed thoroughly by magnetic stirring. Subsequently, the prepared precursor was transferred into a 50 ml Teflon lined vessel, and it was slowly slid into a stainless steel autoclave and sealed. The autoclave was placed in a furnace and heated up to 280 °C at a heating rate of 3 °C min^{-1}, and then kept at that temperature for 3.5 h. The furnace was then switched off and allowed to cool to room temperature. The yellow reaction products were added to 30 mL of absolute ethanol and centrifuged at 14000 rpm for 40 min to obtain a yellow precipitate and a colorless supernatant. The supernatant was discarded, and the yellow precipitate was repeatedly washed 3 times using ethanol and then dried under vacuum. The amount of cerium acetate was according adjusted for the synthesis of the 0.13 at% Ce/Y sample No. 3.

1C. Experimental procedure. In each case, 100 μL stock solution was diluted to 2.6 mL liquid sample in the appropriate solvent. The Ce^{3+} doped YAG nanoparticle samples 1 and 2 were redispersed in propanol, pentanol, hexanol and heptanol with the concentration of 3.5 mmol (YAG) L^{-1}. The corresponding concentration for sample 3 was 3.0 mmol (YAG) L^{-1}.

Table S1. The concentrations of Y, Al, Ce in the YAG stock solutions as analyzed by ICP-MS.

Sample No.	Y (mol L^{-1})	Al (mol L^{-1})	Ce (mol L^{-1})	Ce/Y at.%
1	0.302±0.007	0.451±0.005	3.77E-3±3E-5	1.25%
2	0.356±0.004	0.535±0.0009	4.533E-3±2E-5	1.27%
3	0.276±0.002	0.388±0.006	3.52E-4±2E-6	0.128%

Two sets of 1.3 at.% Y/Ce samples were prepared using the same synthesis process. Sample 1 was employed to record the photoluminescence spectra and decay curve measurements at different temperatures using different solvents, while sample 2 was used for the filling factor dependence measurements. The sample 3 (0.13 at.% Y/Ce) was employed to record the photoluminescence spectra and decay curve measurements at different temperatures using different solvents.

The cell holder for samples utilized rapid, precise Peltier control over the range of temperatures from 288 K to 318 K. The dispersed NPs in the alcohols were placed in a quartz cell in a qX3/Horiba4 sample holder (Horiba Instruments, Japan). Measurements of spectra and decay curves were taken after 15 minutes equilibration at the desired temperature.

In order to achieve a stable and well dispersed sample in the chosen solvents, the NP concentration used in the experiment was very low (0.0035 mmol mL^{-1} for the 1.3 at.% Ce^{3+} samples), which made it difficult to ensure that the filling factor of the YAG:Ce particle in the four alcohols was exactly the same, due to the existence of weighing errors. A previous study showed that the measured lifetime of the emitter decreases with increasing volume fraction, for media with refractive index less than that of the nanoparticles.[2] In the present study, the decay curves for YAG: Y/Ce 1.3 at.% samples in pentanol were measured at room temperature with filling factors in the range from 2.09×10^{-4} to 4.185×10^{-3}: a factor of 20. However, from the smallest to the largest value of f, the change in n_{eff} in Eq. 2 is only an increase of 0.12%. The data plotted in Figure S3 do not enable a conclusion to be made about the variation in filling factor in the present case.

1D. Instruments. The X-ray diffraction (XRD) patterns of the synthesized nanoparticles were collected on a Bruker AXS D8 Advance X-ray diffractometer at 40 kV and 40 mA with CuKα radiation (λ =1.5418 Å). Transmission electron microscopy (TEM) images were recorded by a Tecnai G2 20 S-TWIN Transmission Electron Microscope. Photoluminescence spectra and decay curves were measured at the appropriate temperatures by a Horiba Fluorolog-3 spectrophotometer using a Hamamatsu R928 photomultiplier as signal detector, a 450 W xenon lamp and 455 nm nano-LED as the continuous light source and pulsed light source, respectively. The concentrations of elements in the YAG:Ce NPs were measured by inductively coupled plasma mass spectrometry using an Agilent 7900 instrument.

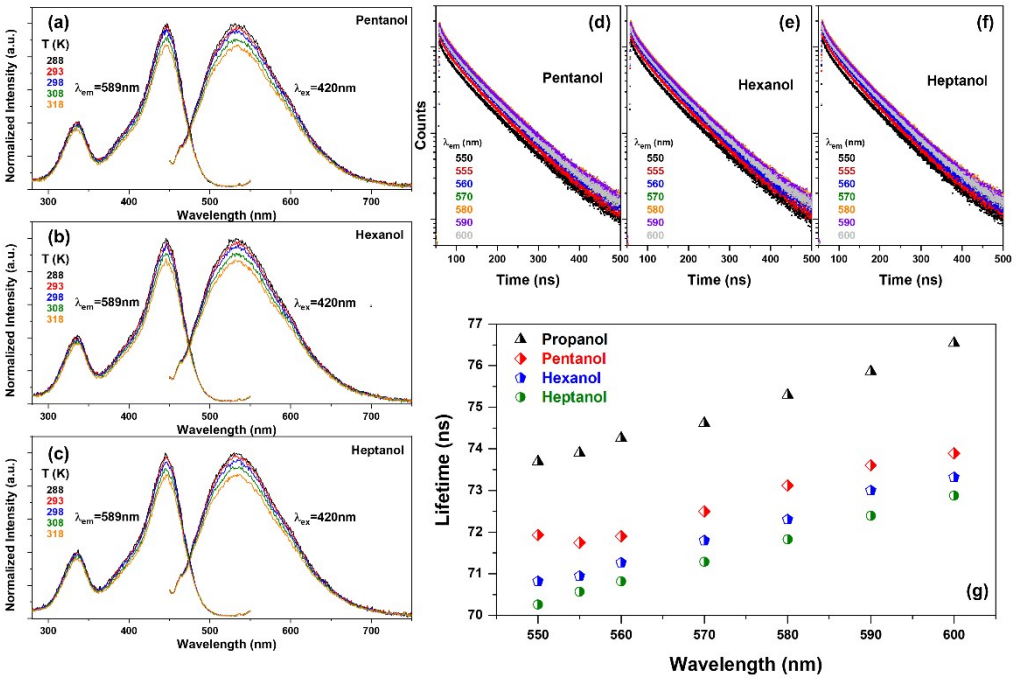

Figure S1. Temperature dependence of emission (λ_{exc} = 420 nm) and excitation (λ_{em} = 589 nm) spectra for the YAG:Ce 1.3 at.% NPs dispersed in pentanol (a), hexanol (b), and heptanol (c). Under 455 nm excitation into $5d_1$, the decay curves for YAG:Ce 1.3 at.% in pentanol (d), hexanol (e), and heptanol (f), were monitored at various emission wavelengths. (g) The plot of fitted monoexponential lifetime versus wavelength of observation for samples dispersed in the four alcohols. The fitted lifetime increases at longer wavelengths.

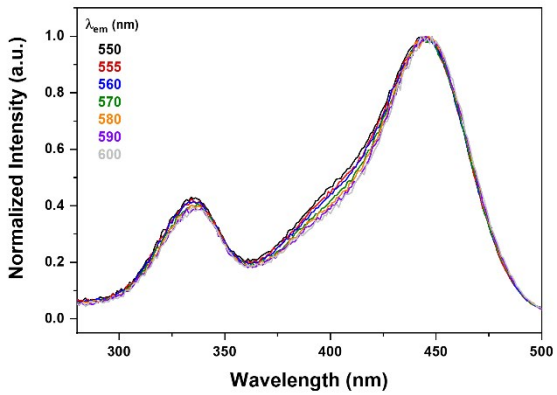

Figure S2. The excitation spectra for Y/Ce 1.3 at.% NPs measured at various emission

wavelengths. The intensity of the band at ~400 nm due to surface species decreases when monitoring at longer wavelengths,

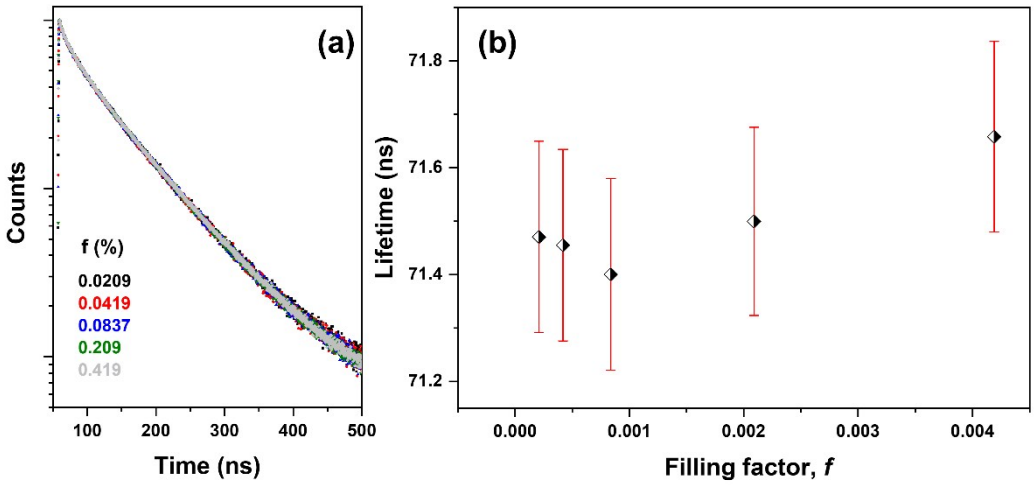

Figure S3. (a) The decay curves for YAG: Ce/Y 1.3 at.% samples in pentanol with different filling factors. (b) The plot of filling factor versus lifetime.

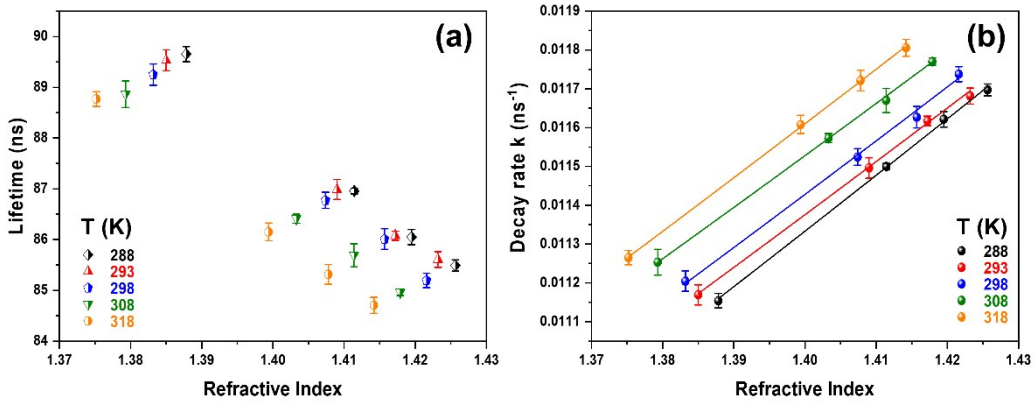

Figure S4. From the biexponential fits to data for the 1.3 at.% Ce/Y samples: (a) Variation of the long lifetime with refractive index. (b) Emission decay rate as a function of refractive index. The lines are fits from Eq. 2.

2. Results for YAG: Ce/Y 0.13 at.% samples

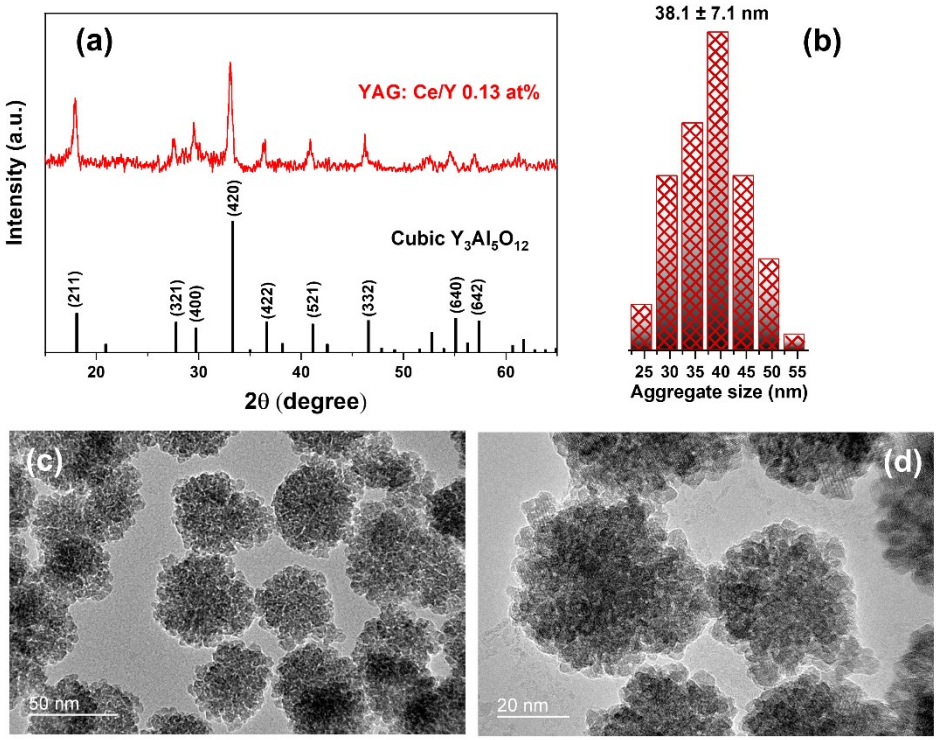

Figure S5. Sample structure determination and morphology. (a) XRD pattern of YAG: Ce/Y 0.13 at.% NPs; (b) size distribution of the Ce^{3+} doped YAG NP aggregates; (c-d) the TEM images of the same sample.

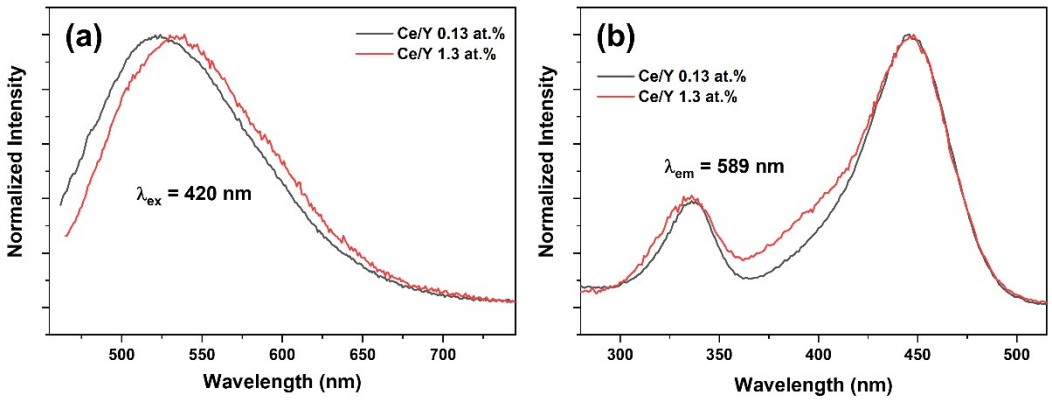

Figure S6. Comparison of the emission and excitation spectra of the YAG: Ce/Y 1.3 at.% and 0.13 at.% samples dispersed in propanol at 288 K.

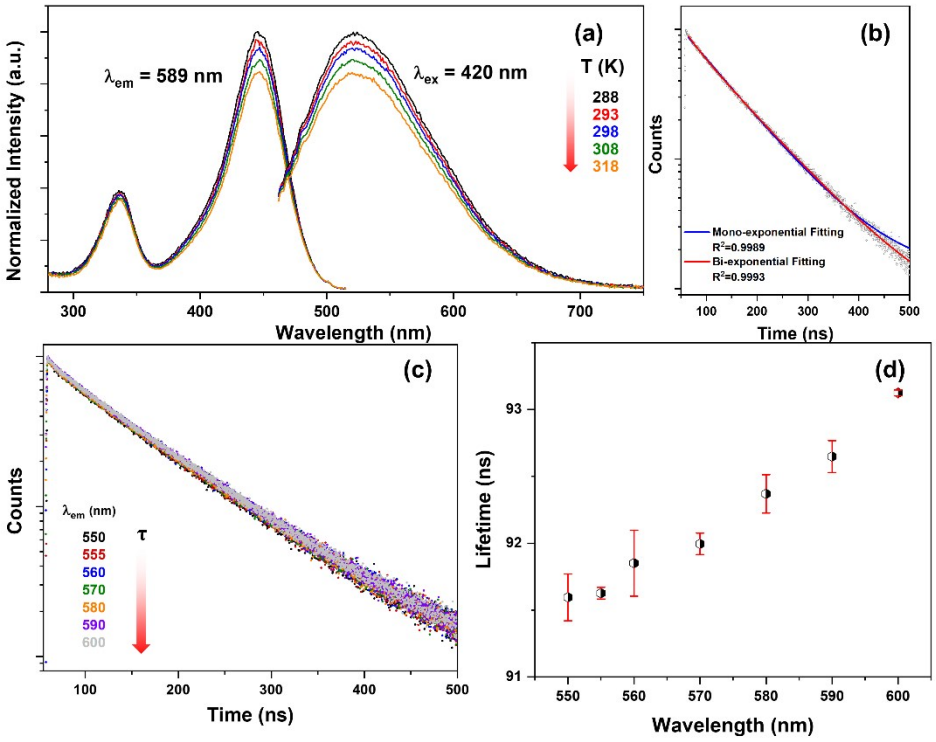

Figure S7. (a) Temperature dependence of emission (λ_{exc} = 420 nm) and excitation (λ_{em} = 589 nm) spectra for YAG: Ce/Y 0.13 at.% NPs dispersed in propanol. (b) The decay curves under 455 nm excitation. (c) The decay curves, λ_{exc} = 455 nm, when monitoring different emission wavelengths. (d) Variation of the fitted monoexponential lifetime with emission wavelength. In Figures S6 – S8 the filling factor (volume fraction = volume of NPs/volume of medium) of the NPs in the media is 3.89×10^{-4}.

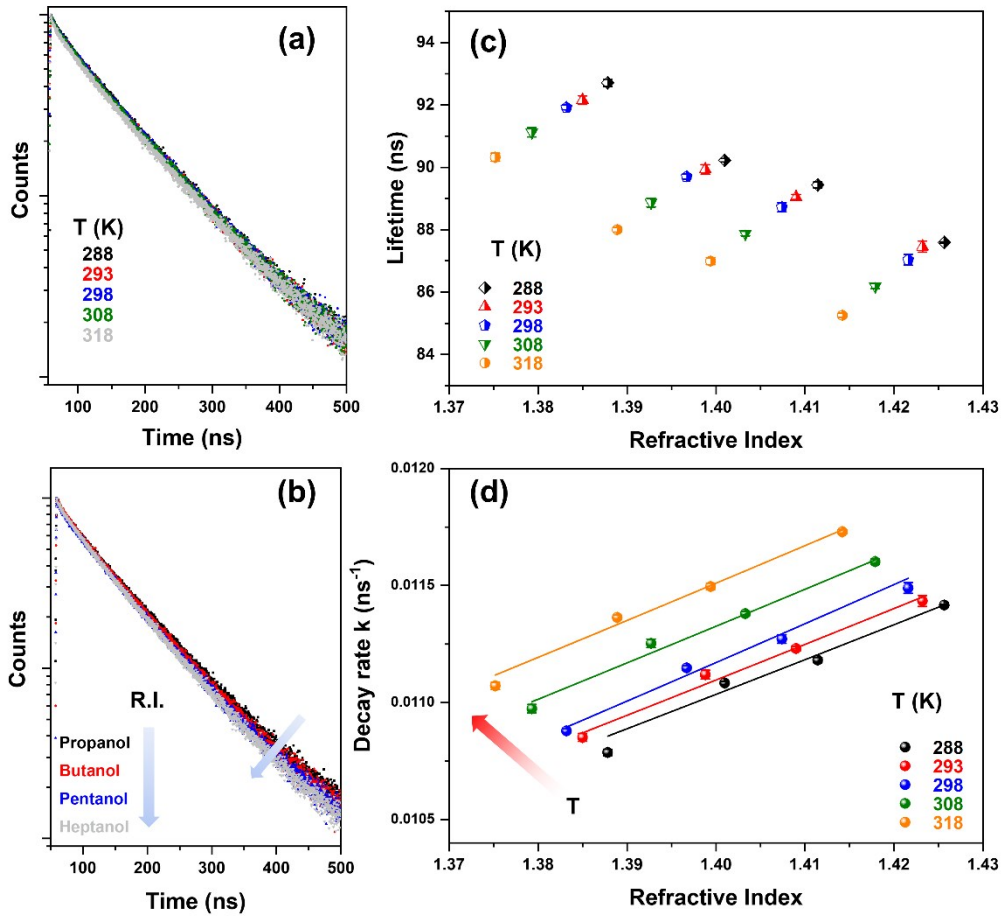

Figure S8. (a) Temperature dependence the emission decay of YAG: Ce/Y 0.13 at.% NP sample in propanol; (b) refractive index dependence of the decay curves of the sample dispersed in different alcohols at 288 K. Both (a) and (b) employed λ_{exc} = 455 nm, λ_{em} = 589 nm. The plot of fitted monoexponential lifetime (c) and decay rate (d) of Ce^{3+} in the YAG host versus refractive index of the medium at temperatures from 288 K to 318 K. The values in c and d are from 4 separate measurements. The lines are fits according to Eq. 2.

Table S2. Derived parameters k_{nr} and A_{bulk} using Eq. 2 for the YAG: Ce/Y 0.13 at.% samples.

Temperature (K)	Monoexponential fits			Biexponential fits		
	k_{nr} (ns^{-1})	A_{bulk} (ns^{-1})	R_{adj}^2	k_{nr} (ns^{-1})	A_{bulk} (ns^{-1})	R_{adj}^2
288	3.78E-3±6.31E-4	1.46E-2±1.21E-3	0.9794	2.61E-3±3.80E-4	1.55E-2±7.39E-4	0.9932
293	3.64E-3±6.15E-4	1.50E-2±1.22E-3	0.9802	2.70E-3±2.60E-4	1.54E-2±5.10E-4	0.9967
298	3.04E-3±7.95E-4	1.63E-2±1.61E-3	0.9712	3.71E-3±5.88E-4	1.34E-2±1.16E-3	0.9775
308	3.59E-3±5.20E-4	1.55E-2±1.03E-3	0.9868	3.03E-3±1.84E-4	1.49E-2±3.63E-4	0.9982
318	3.65E-3±6.24E-4	1.58E-2±1.26E-3	0.9812	2.81E-3±3.52E-4	1.55E-2±7.29E-4	0.9934

3. References

1 M. Nyman, L. E. Shea-Rohwer, J. E. Martin and P. Provencio, *Chem. Mater.*, 2009, *21*, 1536–1542.

2 Y. Luo, L. Li, H. T. Wong, K. L. Wong and P. A. Tanner, *Small* 2020, *16*, 1905234.