

supplementary information

Monazite $\text{LaPO}_4:\text{Eu}^{3+}$ Nanorods as Strongly Polarized Nano-Emitters

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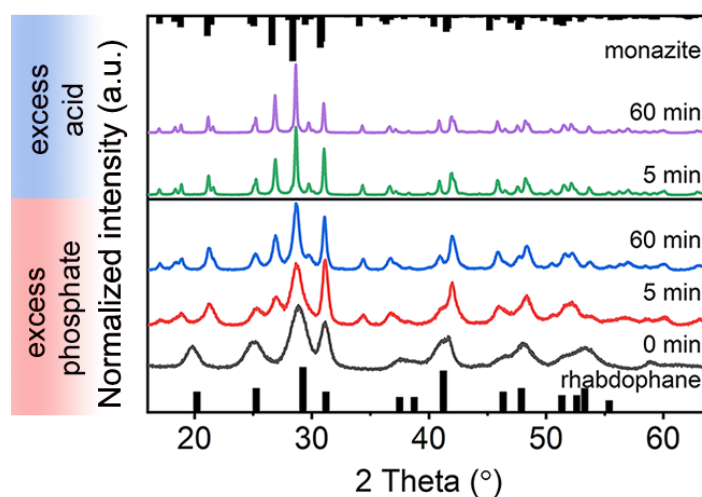


Figure S1. Time-dependent XRD patterns for the monazite $\text{LaPO}_4:5\%\text{Eu}^{3+}$ synthesized in the presence of excess acid and phosphate under microwave heating at 160 °C with standard references.

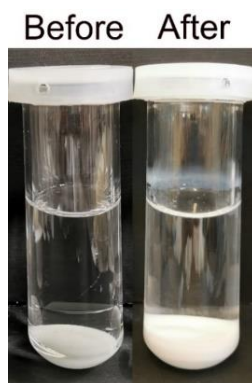


Figure S2. Solution in a glass tube with mixing the precursors in 0.4 M acid before and after the microwave heating (160 °C for 2 h). Notice that the white bottom part in the left image is only an oval stirring bar.

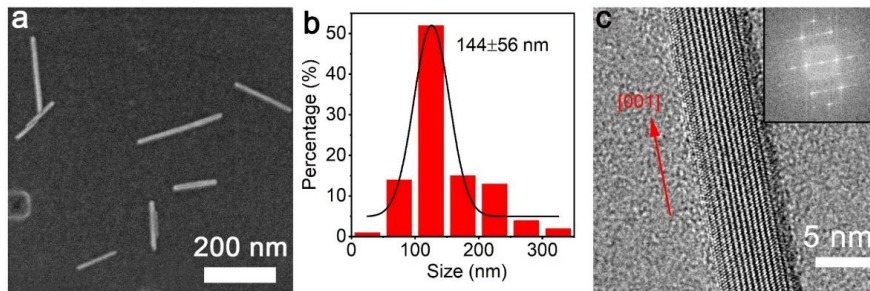


Figure S3. (a) SEM image, (b) histogram of length distribution, and (c) HR-TEM image (inset: FFT analysis) for the rhabdophane nanorods synthesized at 160 °C for 2h.

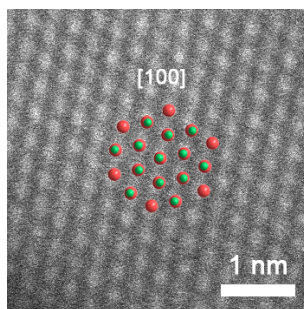


Figure S4. HAADF-STEM image overlapped with La/Eu and P atoms in the monazite crystal structure viewed along the [100] direction. The bright dots correspond to the La/Eu atom columns overlapping with P atom columns viewed along the a axis. The perfect arrangement of atoms further confirms the absence of defects.

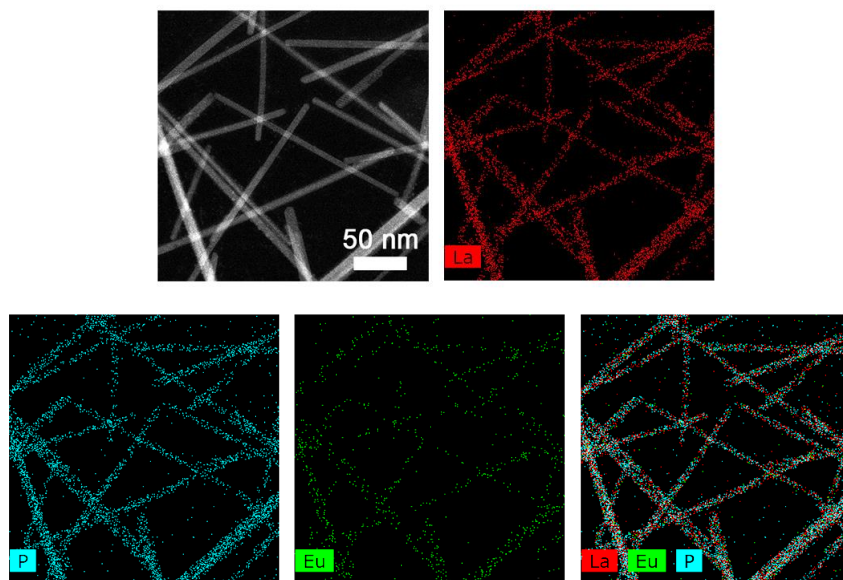


Figure S5. Composite color maps by EDX analysis showing the distribution of La (red), P (blue), and Eu (green) elements. The chemical maps correspond to the electron intensities due to the inelastic scattering of the source electrons with lanthanum L, phosphorus K, and europium L electrons.

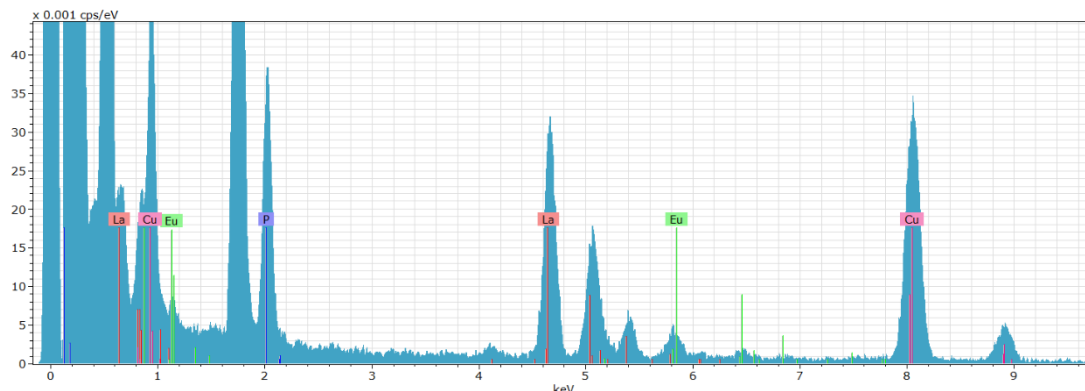


Figure S6. EDX spectrum for the monazite nanorods synthesized with excess phosphate. The experimental ratio of La:Eu:P is determined to be 0.932:0.068:1, which is close to the nominal ratio.

Colloidal dispersion

The process conditions during and after the synthesis have been optimized to control the crystal growth at a minimum level of irreversible aggregations. During the synthesis, rapid heating of microwave (few mins to ~ 200 °C) is applied, in which chemical reactions are volumetrically heated with minimized thermal gradients and rapid reaction rates.^{1, 2} Besides, a low concentration of precursors (0.05 M) ensures the nucleation and crystal growth in a relatively controlled way. Thus, the ionic strength in solution is low to minimize the probability of aggregations during the crystal formation. Note that a high concentration of precursors increases not only the ionic strength but also the acidity as the chemical reaction produces nitric acid. Then, reaction temperature is chosen as low as 160 °C. We studied the influence of reaction temperature on crystal phase, particle size, and optical property. In a wide range of reaction temperatures (120-200 °C with 20% excess phosphate), the particles retain the monazite phase (**Figure S7**) and the nanorod shape (**Figure S8**). Increasing the temperature from 120 to 160 °C, Eu^{3+} emission intensity is maximized (116-fold, **Figure S9**). Rising temperature to 200 °C increases slightly the length of nanorod (1.7-fold). Note that the monazite phase cannot be obtained at 120 °C in a conventional hydrothermal synthesis, verifying the role of the microwave to boost the phase transition.

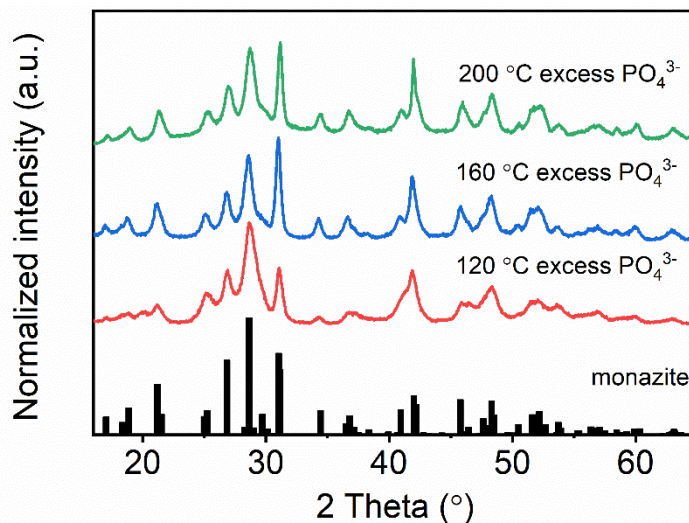


Figure S7. XRD patterns for the nanorods synthesized with excess phosphate under microwave heating at 120, 160, and 200 °C for 2h.

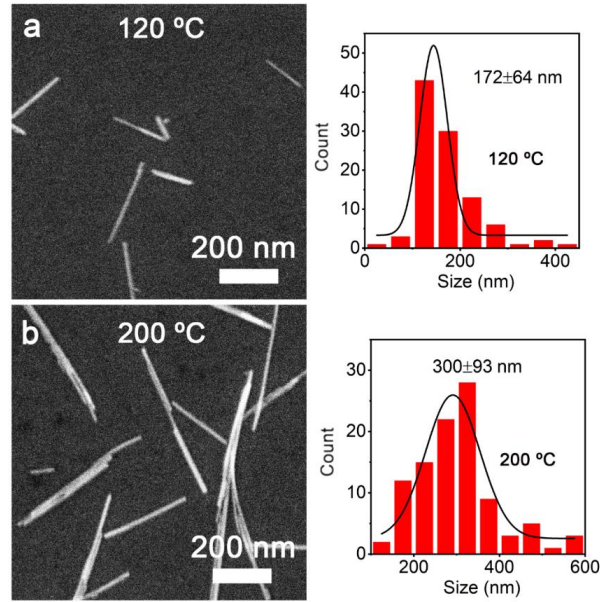


Figure S8. SEM images and histograms of length distribution for the monazite nanorods synthesized with excess phosphate under microwave heating at (a) 120 and (b) 200 °C for 2h.

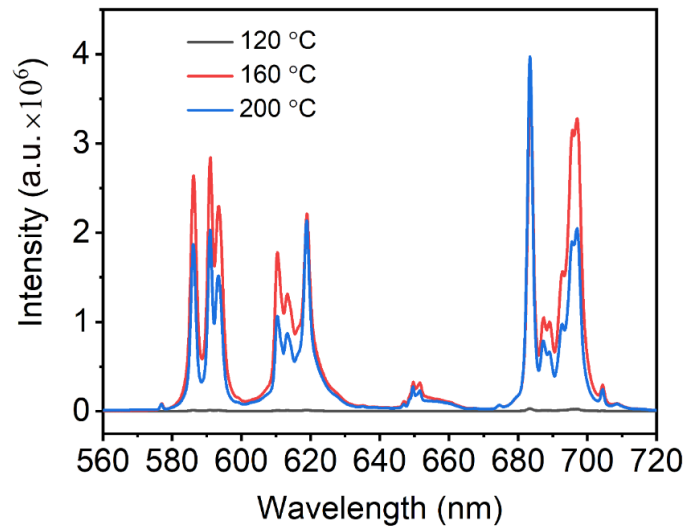


Figure S9. Emission spectra under 394 nm excitation for the monazite nanorods synthesized with excess phosphate under microwave heating at 120, 160, and 200 °C for 2h.

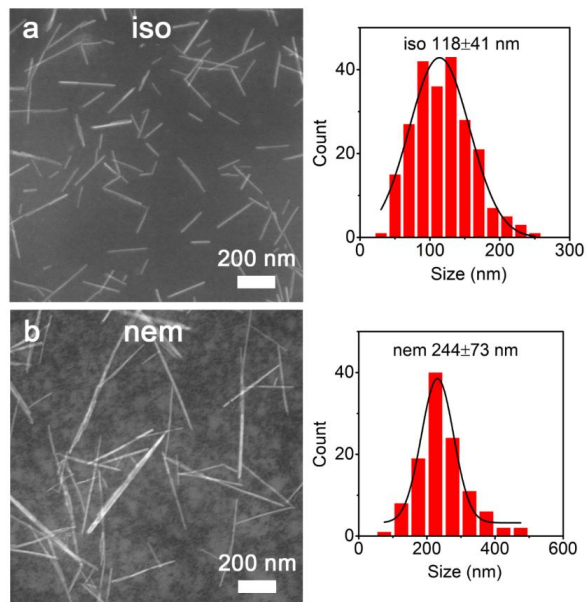


Figure S10. SEM images and histograms of length distribution for the monazite nanorods in (a) the upper isotropic phase and (b) the bottom nematic phase.

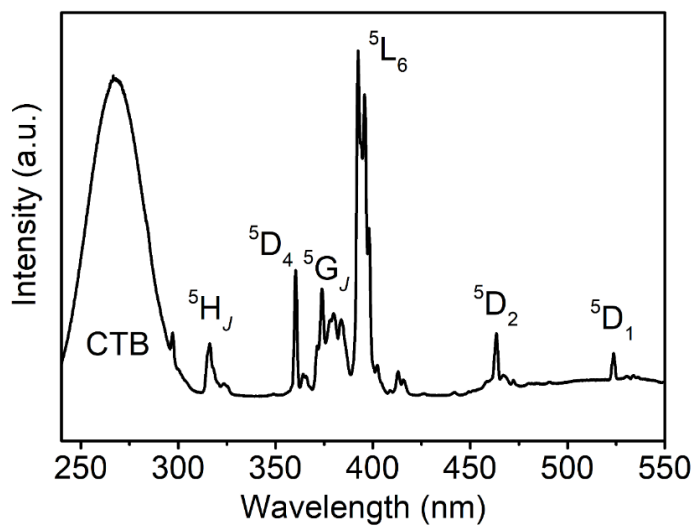


Figure S11. Excitation spectrum monitoring 591 nm emission for the monazite nanorods. The excitation lines are labeled by the final states for the excitations from the 7F_0 ground state. The broad band at ~ 270 nm is an O^{2-} - Eu^{3+} charge transfer band (CTB).

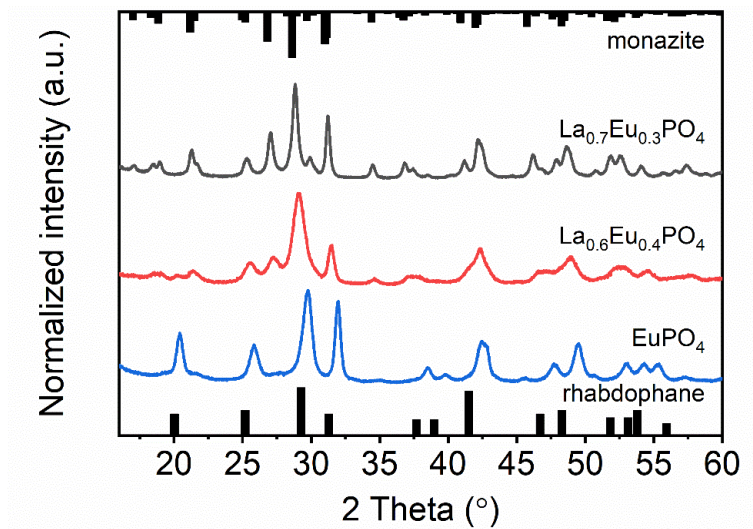


Figure S12. Eu³⁺ concentration-dependent XRD patterns for the LaPO₄:5%Eu³⁺ samples synthesized in the presence of excess phosphate under microwave heating at 200 °C with standard references.

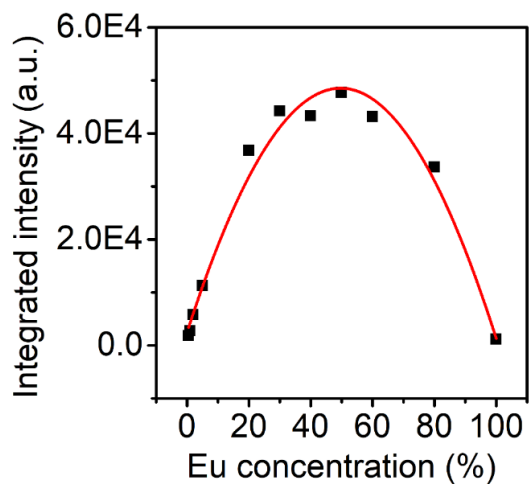


Figure S13. Concentration quenching for monazite LaPO₄ doped with different concentrations of Eu³⁺. The microwave synthesized nanoparticles with excess phosphate were annealed at 1000 °C for 1 h. The plot shows the integrated emission intensity (derived from emission spectra under 394 nm excitation) versus the Eu³⁺ concentration.

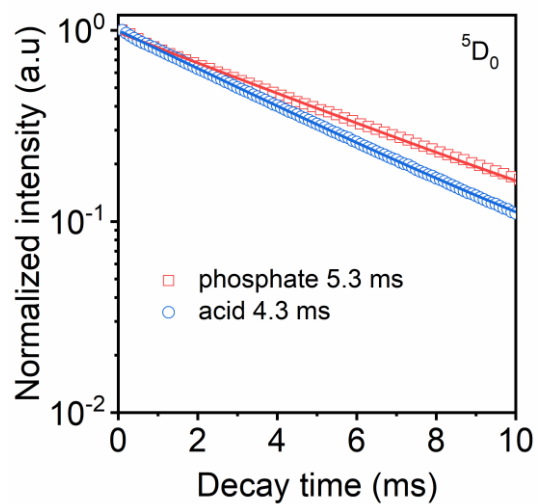


Figure S14. Luminescence decay curves of 5D_0 emission under 394 nm excitation for the monazite nanorods synthesized with excess phosphate and acid after annealing at 1000 °C for 1 h.

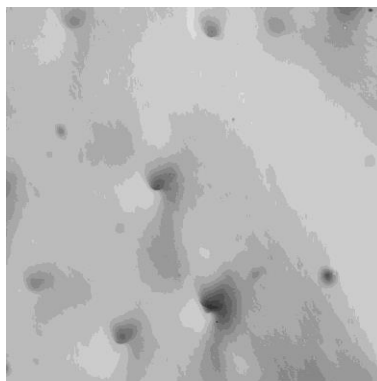


Figure S15. Birefringent texture of the nematic sample in ethylene glycol ($\Phi = 5\%$) observed by a polarizing microscope with crossed polarizers.

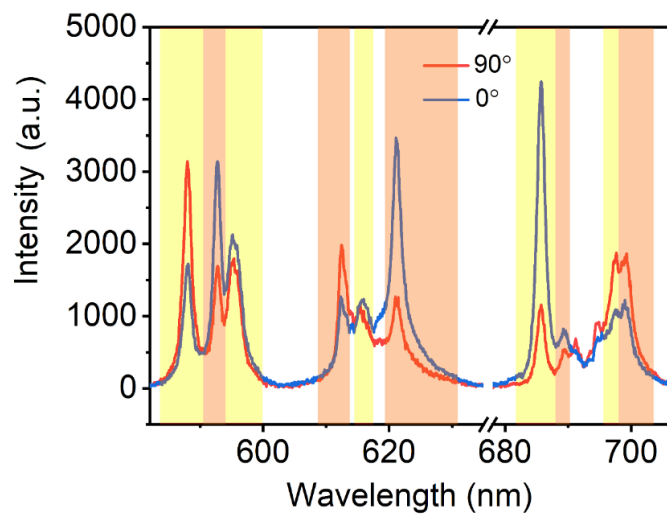


Figure S16. Polarized luminescence of nematic aligned monazite nanorods under 394 nm 5L_6 excitation, showing the chosen wavelength range to integrate the intensity area for the main emission lines.

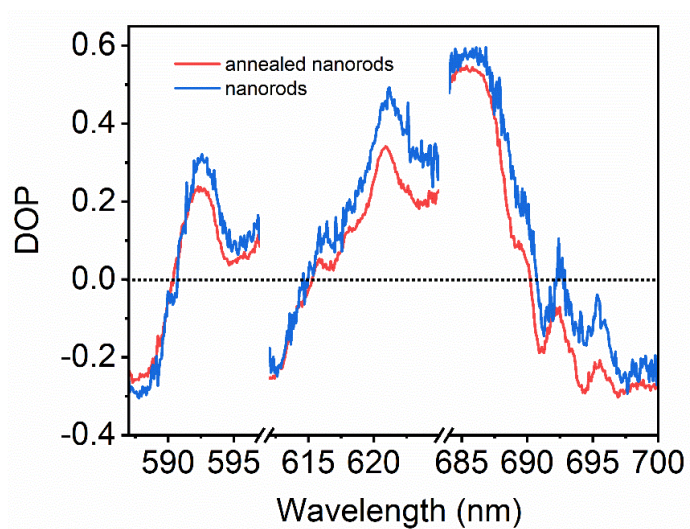


Figure S17. DOP through the whole emission spectrum directly derived from the polarized emission spectra in Figure 4d, e for the nanorods and annealed nanorods.

References

1. J. A. Gerbec, D. Magana, A. Washington and G. F. Strouse, *J. Am. Chem. Soc.*, 2005, **127**, 15791-15800.
2. G. Bühler and C. Feldmann, *Angew. Chem. Int. Ed.*, 2006, **45**, 4864-4867.