Supplementary information

Hydrothermal syntheses, luminescent properties, fluorescence intensity ratio temperature sensing of monodisperse Tb doped NaCeF$_4$ nanocrystals

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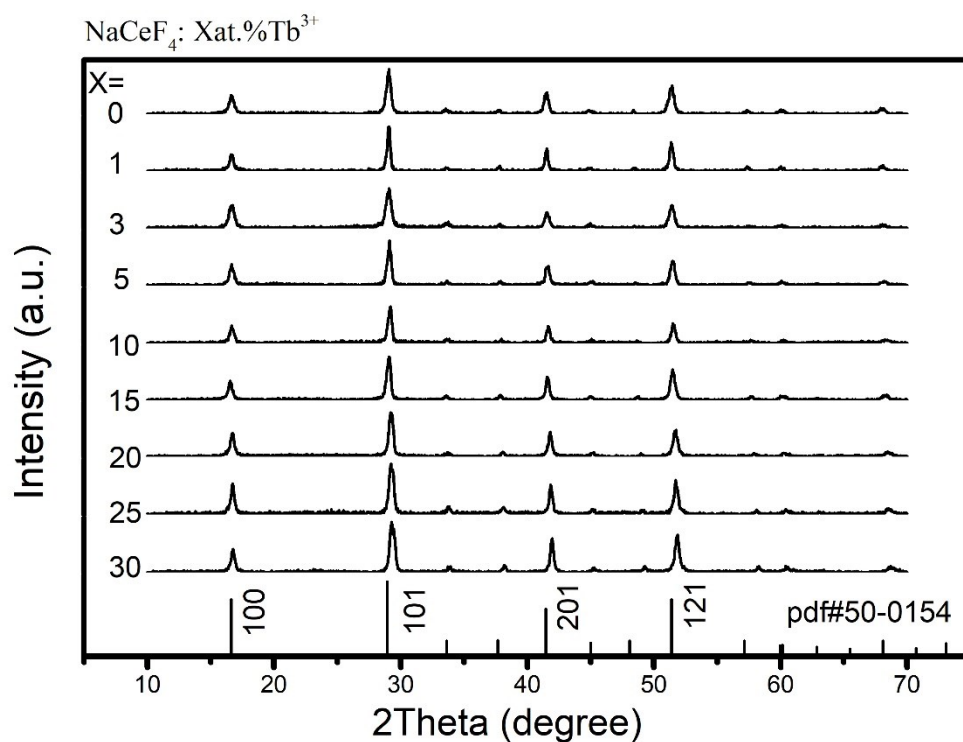b. University of Chinese Academy of Sciences, Beijing 100039, China.

Fig. S1. XRD pattern of NaCeF$_4$ with different Tb doping concentration. All peaks of the synthesized NCs are matched well with the standard pattern of hexagonal β-NaCeF$_4$ (pdf#50-0154, black lines) and no other impurity peaks were detected.
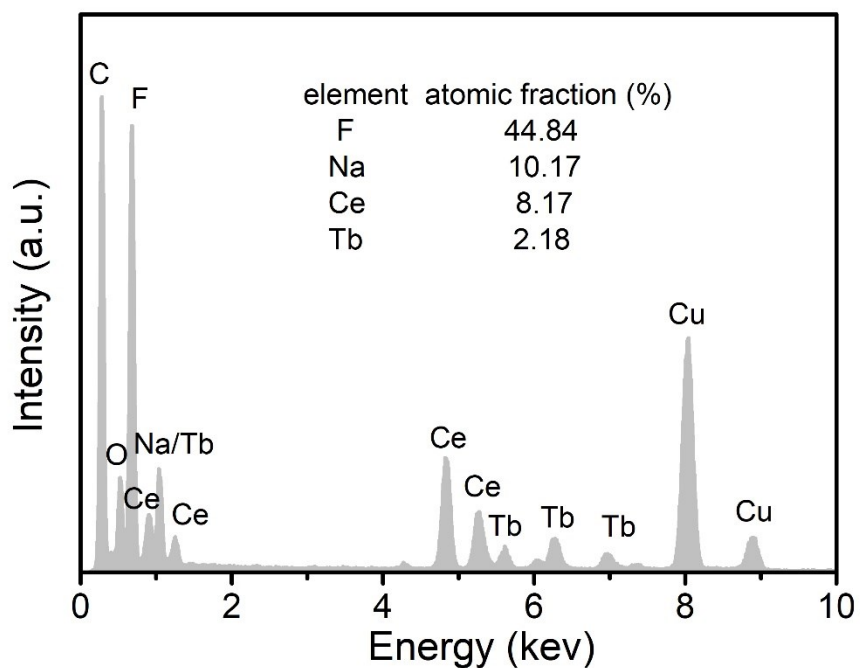
Fig. S2. EDS analysis of NaCeF$_4$:20at%Tb NCs. Elements of C, O, Cu, F, Na, Ce, and Tb were observed in the spectrum, and no other elements were found. Copper element originate from the substrate. Oxygen and carbon elements originate from the capping agent of NCs. The atomic fraction of Na/(Ce+Tb) and Ce/Tb ratio are calculated to be 0.98 and 3.75, respectively, which are roughly in accordance with the stoichiometric ratio of NaCeF$_4$:20at%Tb.

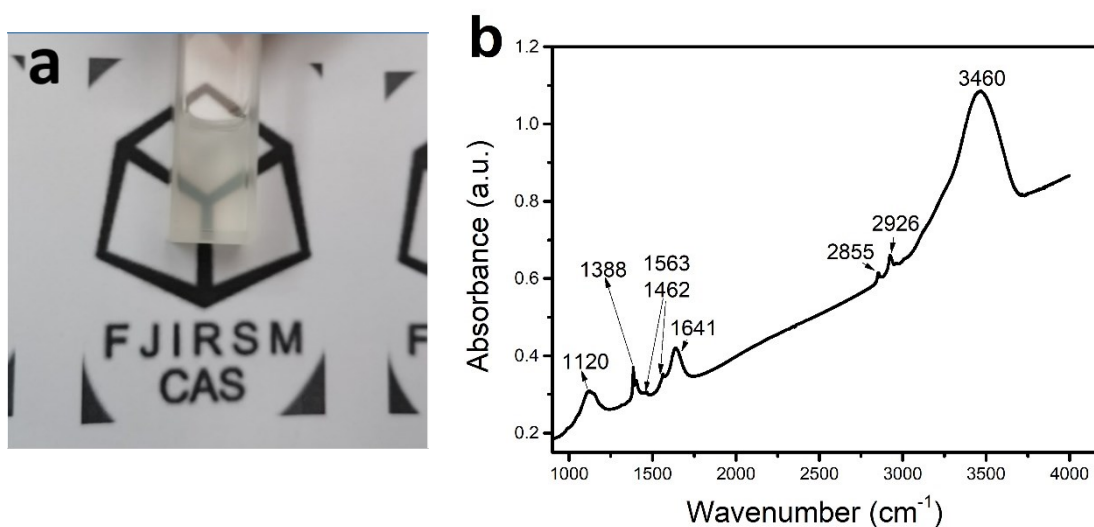Fig. S3. (a) Photograph of NaCeF$_4$:20at%Tb NCs dispersed in cyclohexane solution. (b) The FTIR spectrum of NaCeF$_4$:20at%Tb NCs. The peak around 3460 cm^{-1} can be ascribed to the O-H stretching and bending vibration modes. The peaks around 2926 and 2855 cm^{-1} can be ascribed to the asymmetric and symmetric stretching vibration modes of -CH$_2$- in OA, respectively. The peak centered at 1641 cm^{-1} can be ascribed to the stretching vibration mode of C=C in OA. The peaks centered at 1563 and 1462 cm^{-1} can be attributed to the asymmetric and symmetric stretching vibration modes of -COOH in OA, respectively. The peak centered at 1388 cm^{-1} can be ascribed to the bending vibration mode of -CH$_3$ in OA. The peak around 1120 cm^{-1} can be ascribed to the stretching vibration mode of C-F. The results of FTIR analysis reveal the presence of capping OA on the surfaces of the NCs.
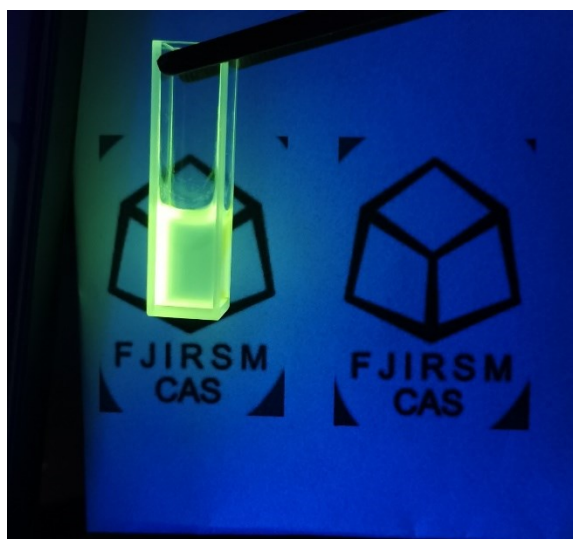
Fig. S4. Luminescence paragraph of NaCeF$_4$: 20at%Tb NCs dissolved in cyclohexane under commercial 254 nm UV lamp excitation.
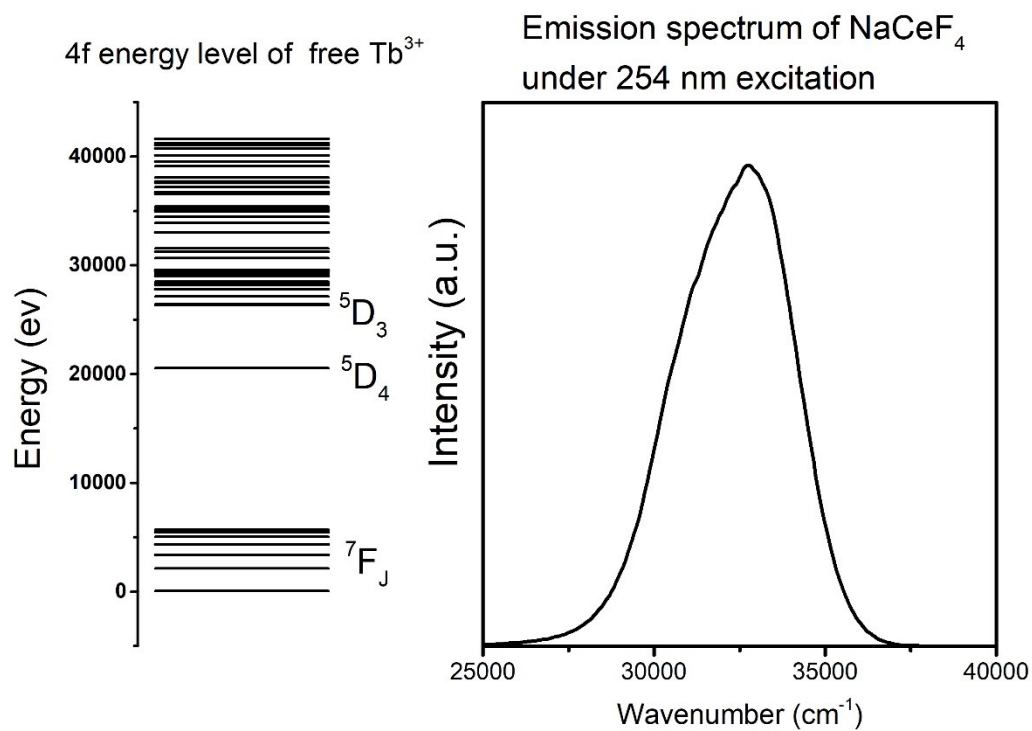
Fig. S5. Left: Energy level diagram of free Tb^{3+}. Right: Emission spectrum of $NaCeF_4$ NCs under 254 nm excitation. Obviously, the emission of Ce^{3+} overlaps with some excited energy levels of Tb^{3+}.
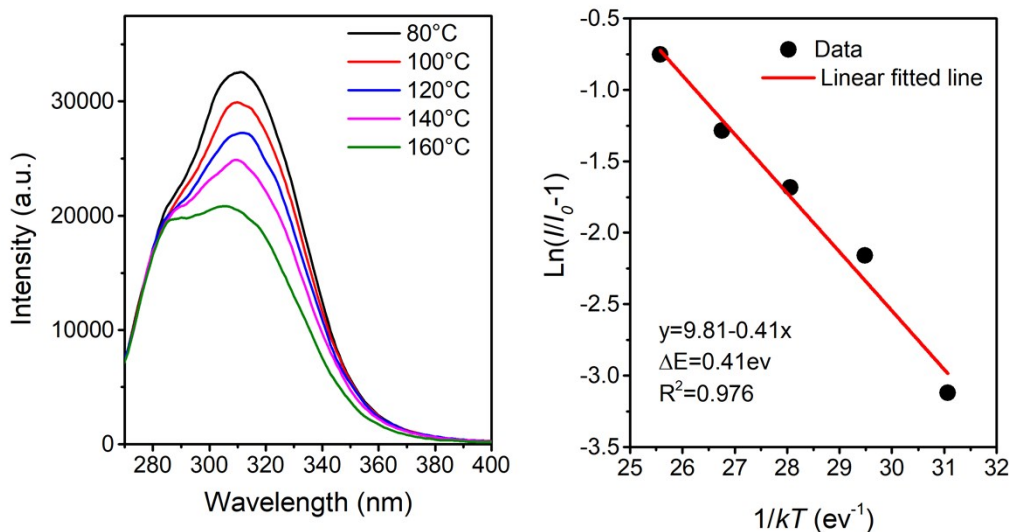
Fig. S6. Left: Temperature dependent luminescent spectra of NaCeF$_4$:5at%Tb NCs.

Right: $ln\left(\dfrac{I_0}{I(T)} - 1\right)$ variation with $\dfrac{1}{kT}$.

The emission spectra of NaCeF$_4$ NCs under 254nm excitation were plotted in Fig. S6 left, the Ce^{3+} fluorescence intensity decrease with temperature increasing. The variations of fluorescence intensity with temperature can be expressed by Arrhenius formula:[1, 2]

$$I(T) = \frac{I_0}{1 + Cexp\left(-\dfrac{\Delta E}{kT}\right)}$$

Where T is temperature (K), C is a constant, k is the Boltzmann constant (8.63×10^{-5}ev/K), I is integrated fluorescence intensity (270-380 nm) of Ce^{3+}, ΔE is the activation energy. The above formula can be transferred into:

$$ln\left(\frac{I_0}{I(T)} - 1\right) = A - \frac{\Delta E}{kT}$$

where A is a constant. Let $\dfrac{1}{kT}$ be x and $ln\left(\dfrac{I_0}{I(T)} - 1\right)$ be y, we can plot Fig. S6 right, the dots can be linear fitted and the ΔE is therefore calculated to be 0.41eV.

References

1 Y. Zhang, L. Li, X. Zhang and Q. Xi, J. Rare Earth., 2008, **26**, 446-449.

2 K. Jyothi, K. Bhagya, H. Nagabhushana, M. Murugendrappa, A. Prakash, V. Hegde and N. Nagabhushana, Ceram. Int., 2020, **46**, 9706-9713.