

Supplementary Materials

Novel Photoluminescence and Optical Thermometry of

Solvothermally derived Tetragonal $\text{ZrO}_2\text{:Ti}^{4+},\text{Eu}^{3+}$ Nanocrystals

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Table S1. The assignment of the observed emission lines for Eu^{3+} in the t-ZrO₂ NCs and fluorescence decay constants yielded by bi-exponential fitting

Eu^{3+} type	$^5\text{D}_0 \rightarrow ^7\text{F}_1$ magnetic dipole transition (nm)	$^5\text{D}_0 \rightarrow ^7\text{F}_2$ forced electric dipole transition (nm)	$^5\text{D}_0 \rightarrow ^7\text{F}_3$ forbidden transition by the electric dipole and the magnetic dipole (nm)	$^5\text{D}_0 \rightarrow ^7\text{F}_4$ forced electric dipole transition (nm)	Fluorescence decay constants (ms)
Eu(I)	592.2	607.0, 634.0	628.0, 652.0, 660.0	714.8	$\tau_1 \sim 6.23$, $\tau_2 \sim 2.54$
Eu(II)	591.6, 597.2	614.0, 631.2	626.4, 656.2	713.0	$\tau_1 \sim 6.23$, $\tau_2 \sim 2.54$

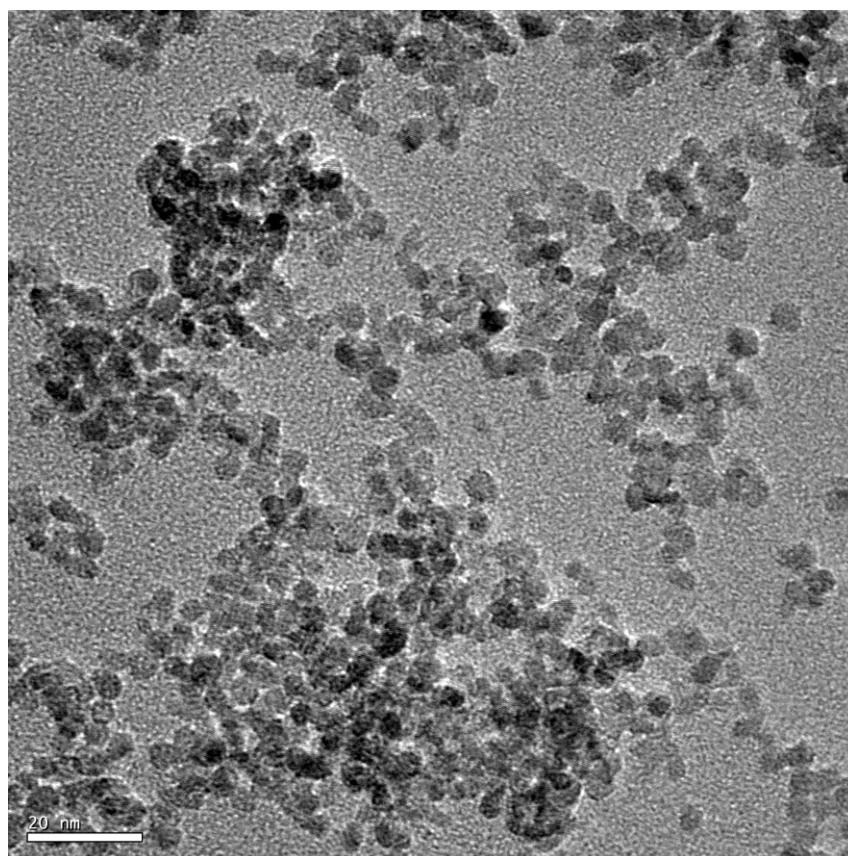


Figure S1. TEM image of t-ZrO₂:4%Ti⁴⁺,1%Eu³⁺ NCs.

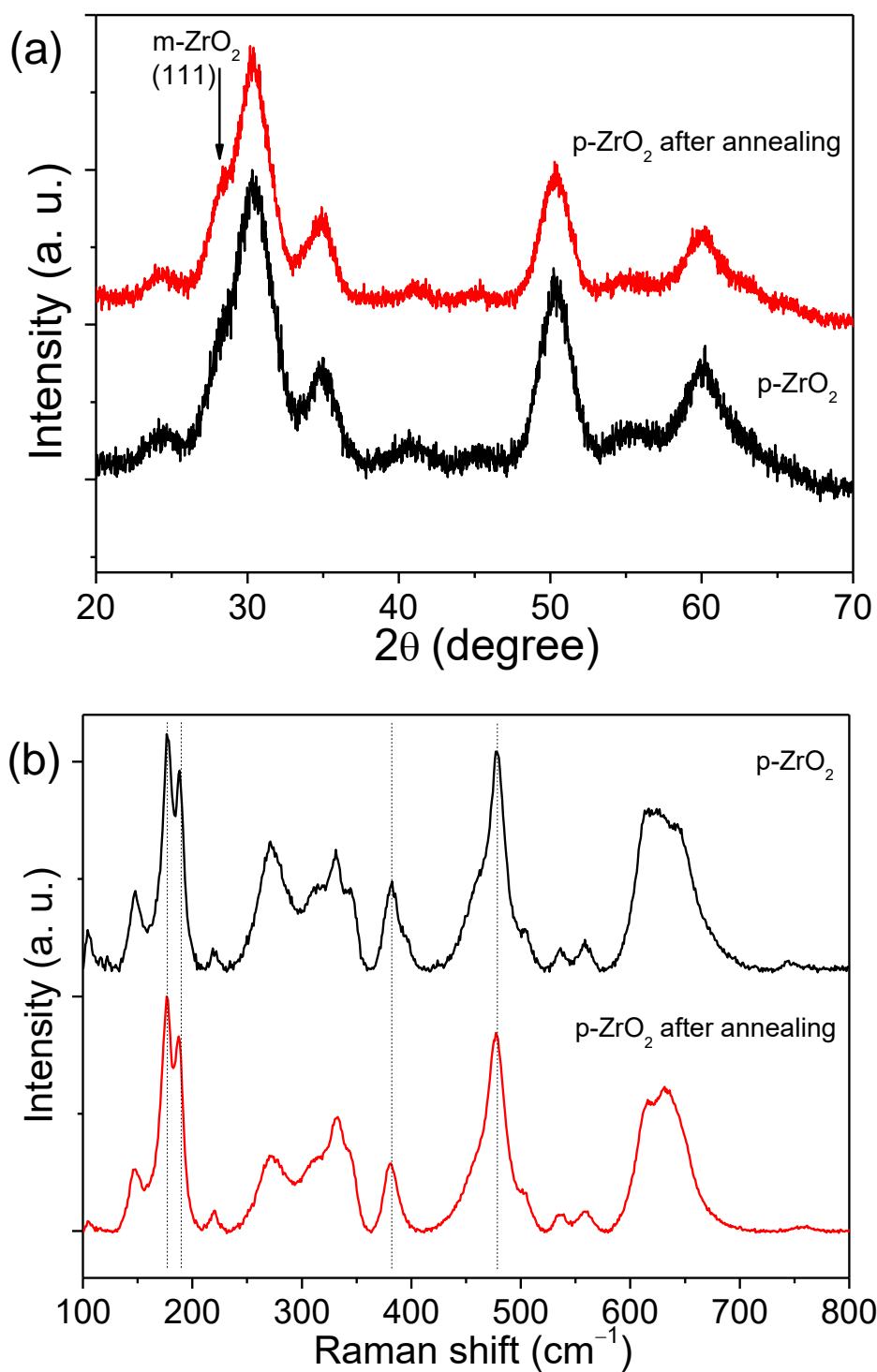


Figure S2. (a) Powder XRD patterns and (b) Raman spectra of p-ZrO₂ NCs before and after annealing at 400 °C; the dash lines in (b) indicate the modes of m-ZrO₂.

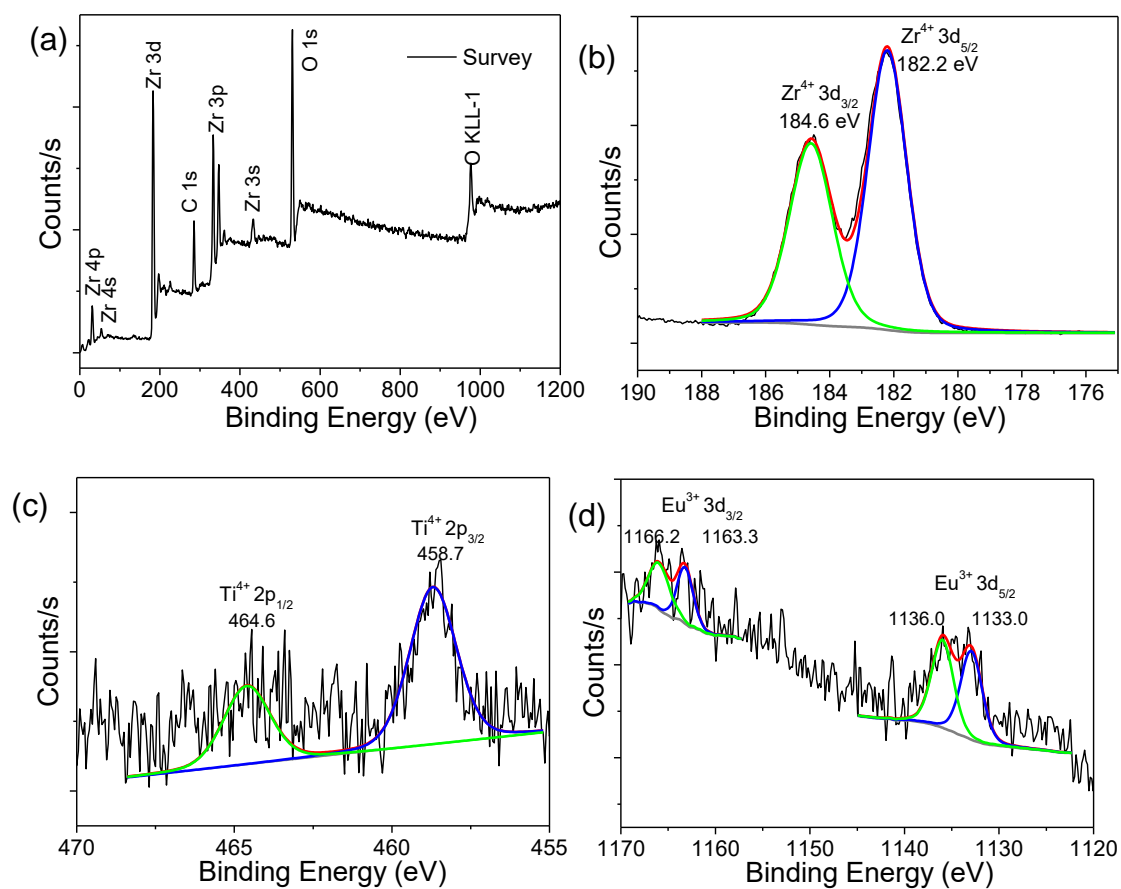


Figure S3. (a) XPS survey spectrum of t-ZrO₂:4%Ti⁴⁺,1%Eu³⁺ NCs and XPS high resolution spectra of (b) Zr 3d, (c) Ti 2p and (d) Eu 3d in t-ZrO₂:4%Ti⁴⁺,1%Eu³⁺ NCs.

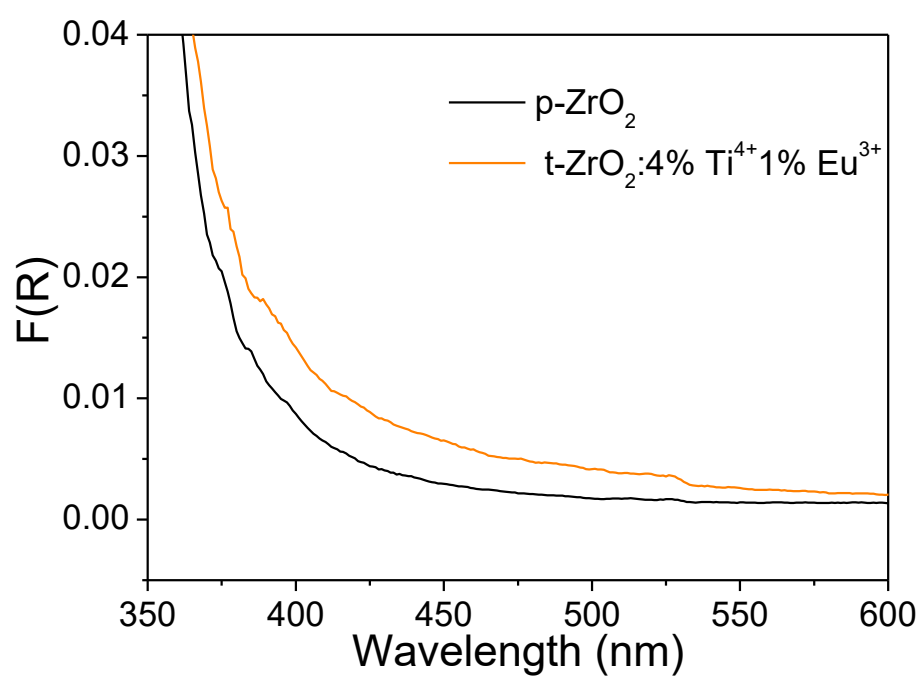


Figure S4. The enlarged diffuse reflection-UV-visible spectra of the as-synthesized $p\text{-ZrO}_2$ and $t\text{-ZrO}_2:4\% \text{Ti}^{4+}, 1\% \text{Eu}^{3+}$ NCs in the $F(R)$ range of 0.0–0.04.

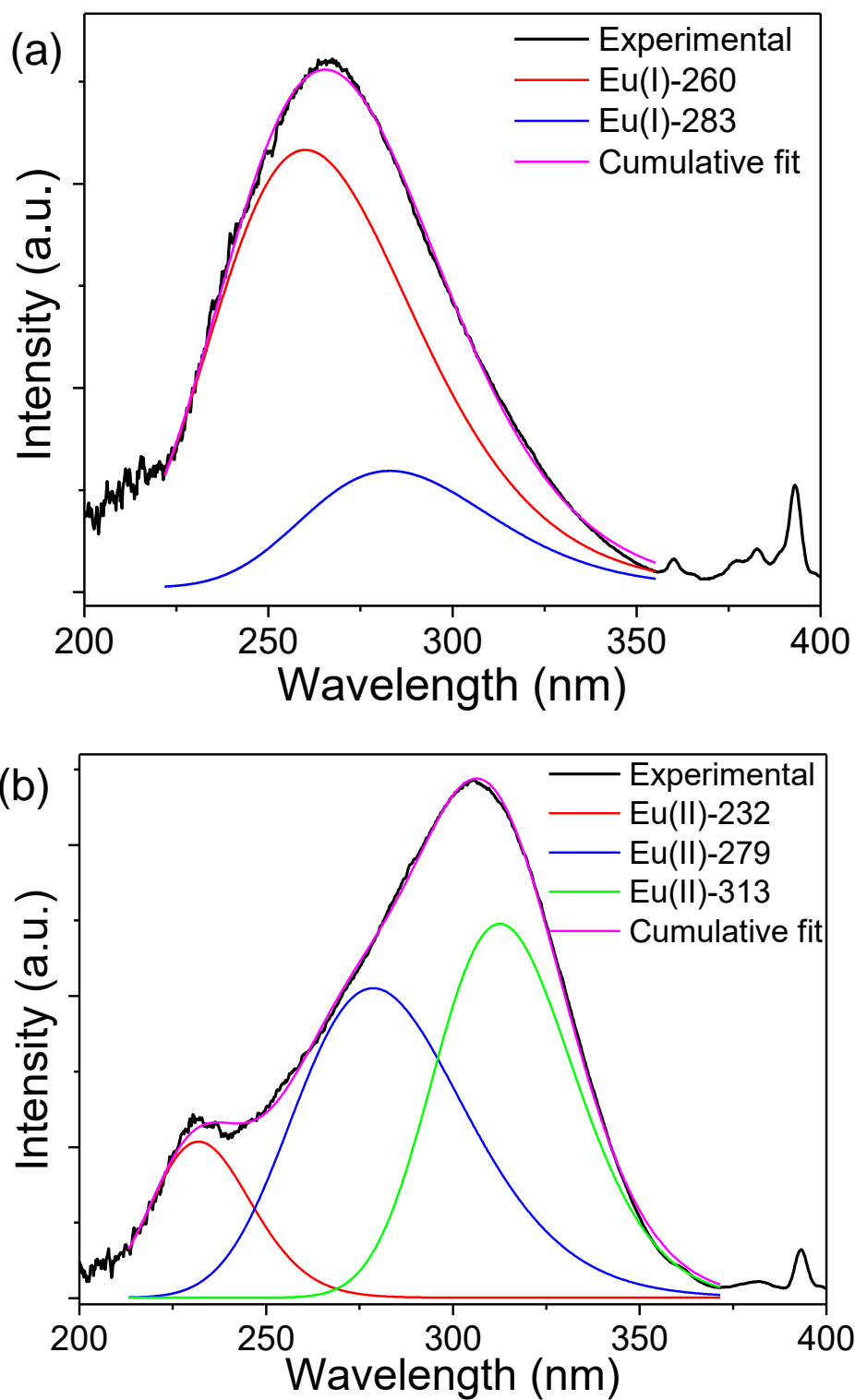


Figure S5. PL excitation spectra of t-ZrO₂:1%Eu³⁺ NCs by monitoring the relative maxima of Eu(I) ((a), λ_{em} =607) and Eu(II) ((b), λ_{em} = 614 nm) and their spectral decomposition of the corresponding broadband with Gauss typed peaks.

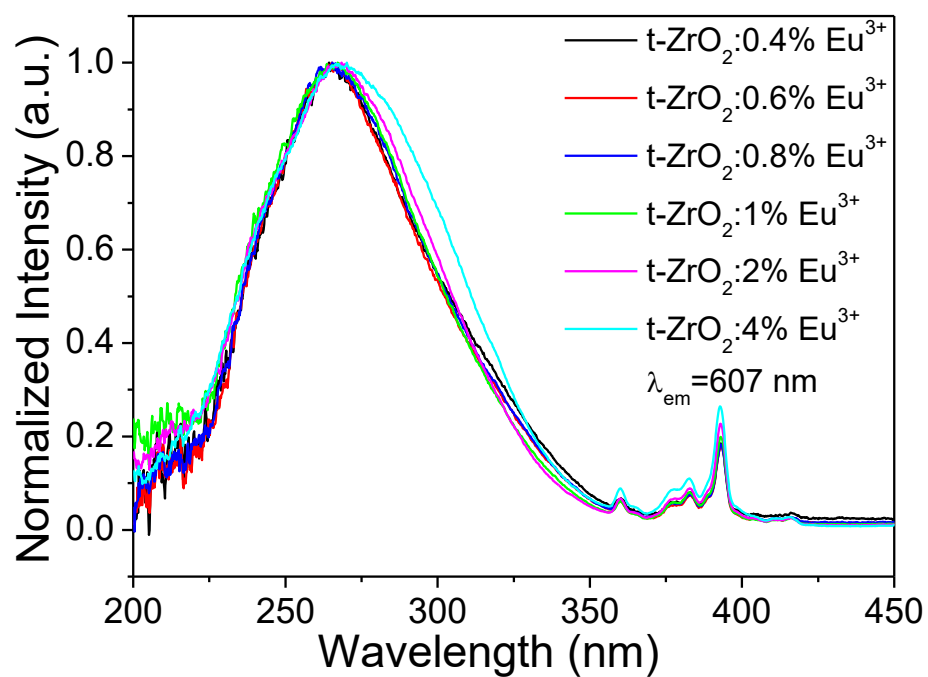


Figure S6. Normalized PL excitation spectra of t-ZrO₂:xEu³⁺ (x=0.4%, 0.6%, 0.8%, 1%, 2% and 4%) NCs by monitoring the relative maxima of Eu(I) (λ_{em} =607).

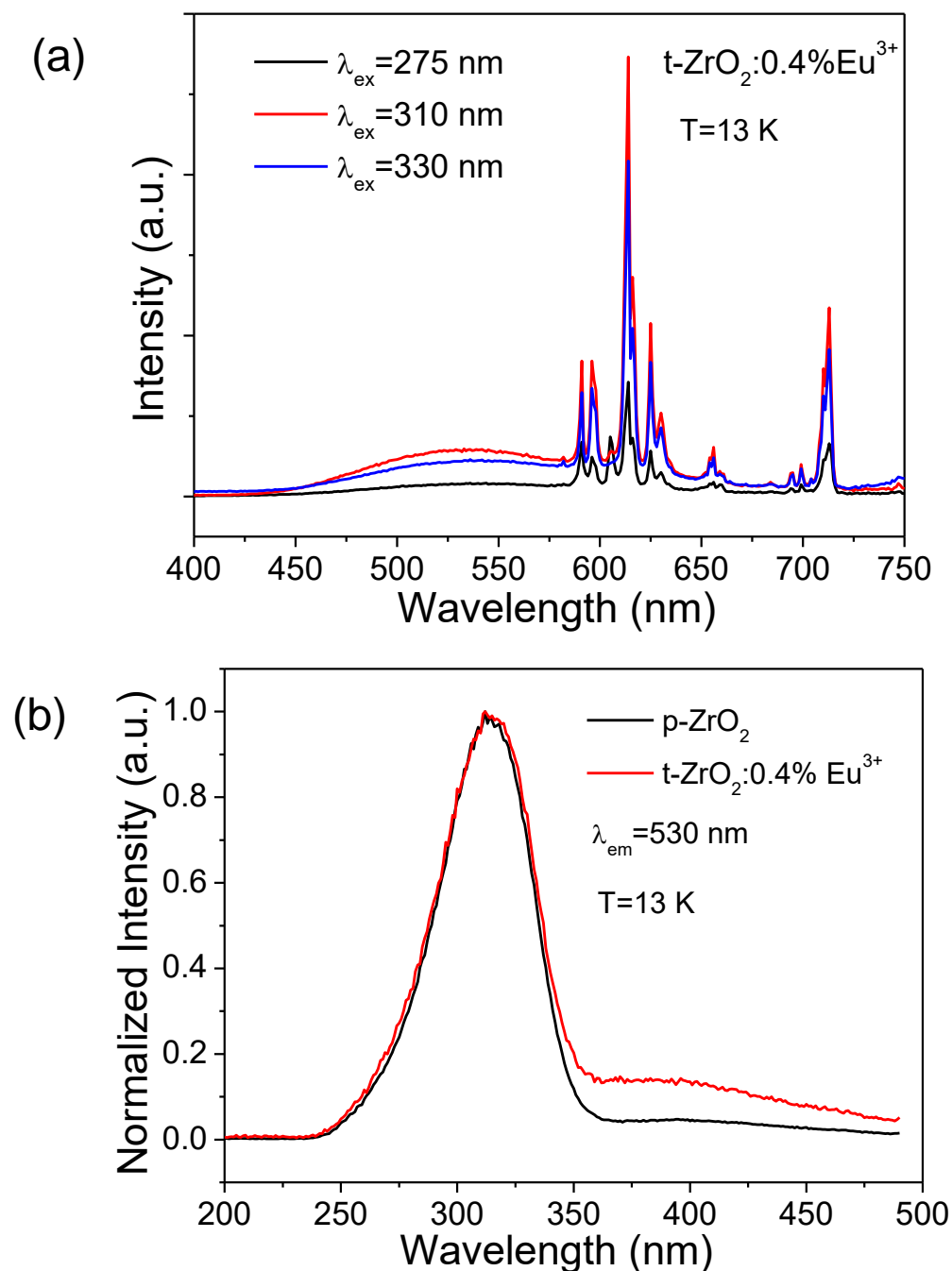


Figure S7. (a) The bright broadband PL emissions of CT ($\text{Ti}^{3+} \rightarrow \text{O}^-$) transitions in $t\text{-ZrO}_2:0.4\%\text{Eu}^{3+}$ NCs upon excitation into titanate groups at 13 K, together with the spectral superimposition of stronger sharp line emissions of Eu^{3+} due to nonradiative energy transfer; (b) Normalized PL excitation spectra of $p\text{-ZrO}_2$ and $t\text{-ZrO}_2:0.4\%\text{Eu}^{3+}$ NCs upon monitoring the peak of the broadband emissions at 530 nm.

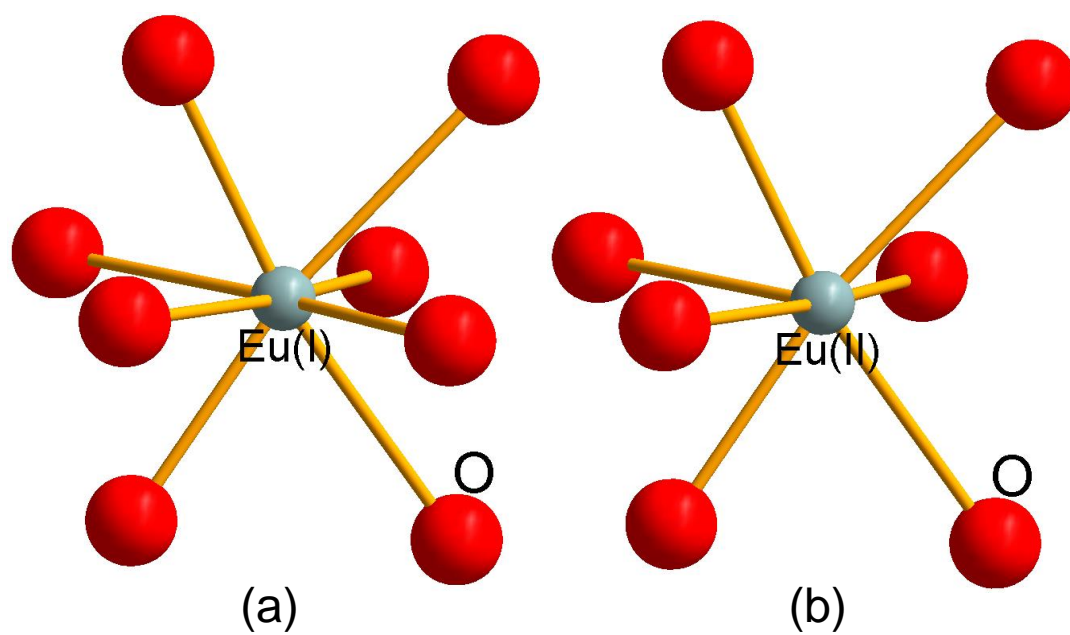


Figure S8. The scheme of oxygen coordination spheres of Eu(I) (a) and Eu (II) (b) in t-ZrO₂ NCs.

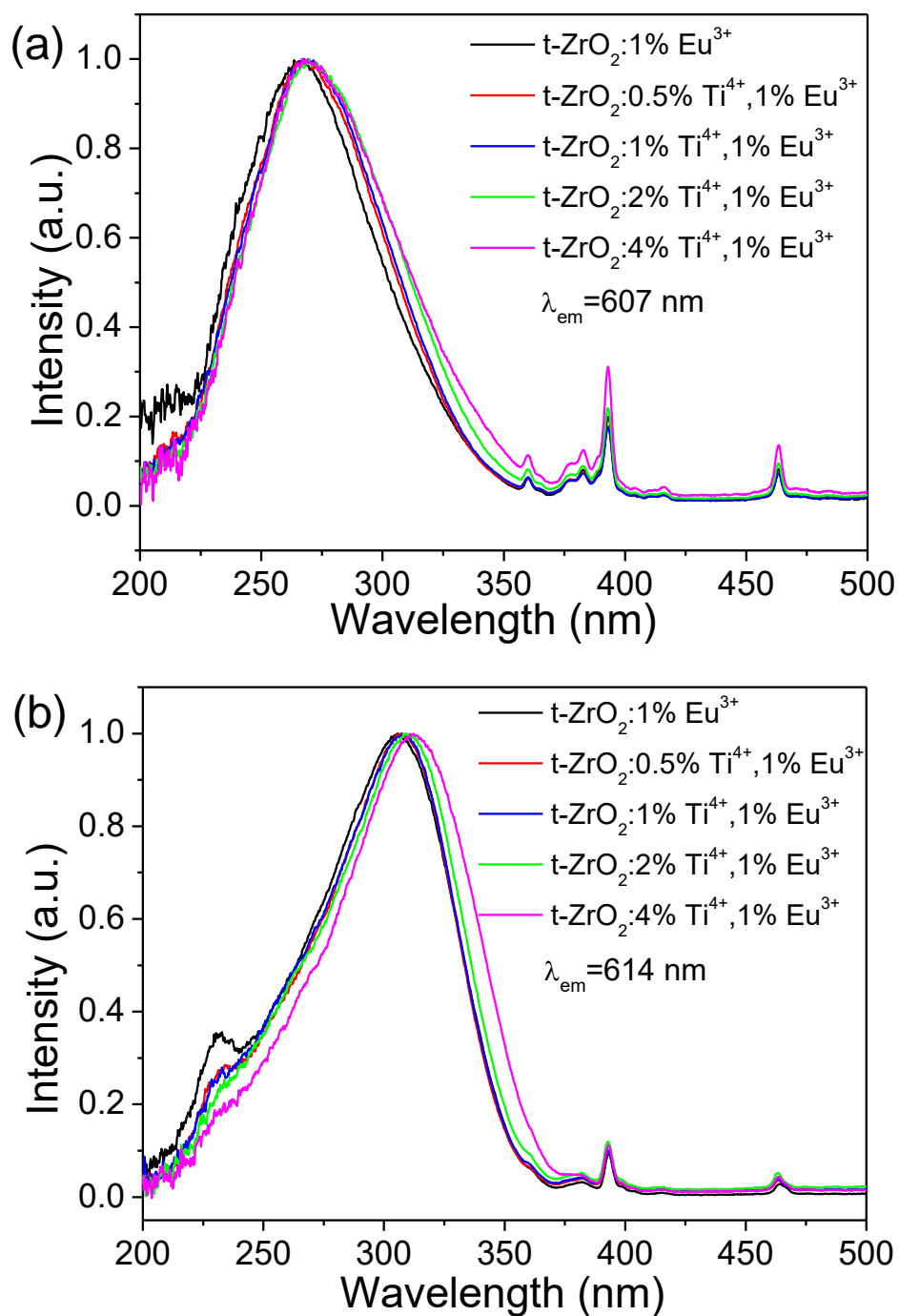


Figure S9. Normalized PL excitation spectra of t-ZrO₂:*x*Ti⁴⁺, 1% Eu³⁺ (*x*=0, 0.5%, 1%, 2% and 4%) NCs by monitoring the relative maxima of Eu(I) ((**a**), λ_{em} =607) and Eu(II) ((**b**), λ_{em} = 614 nm).

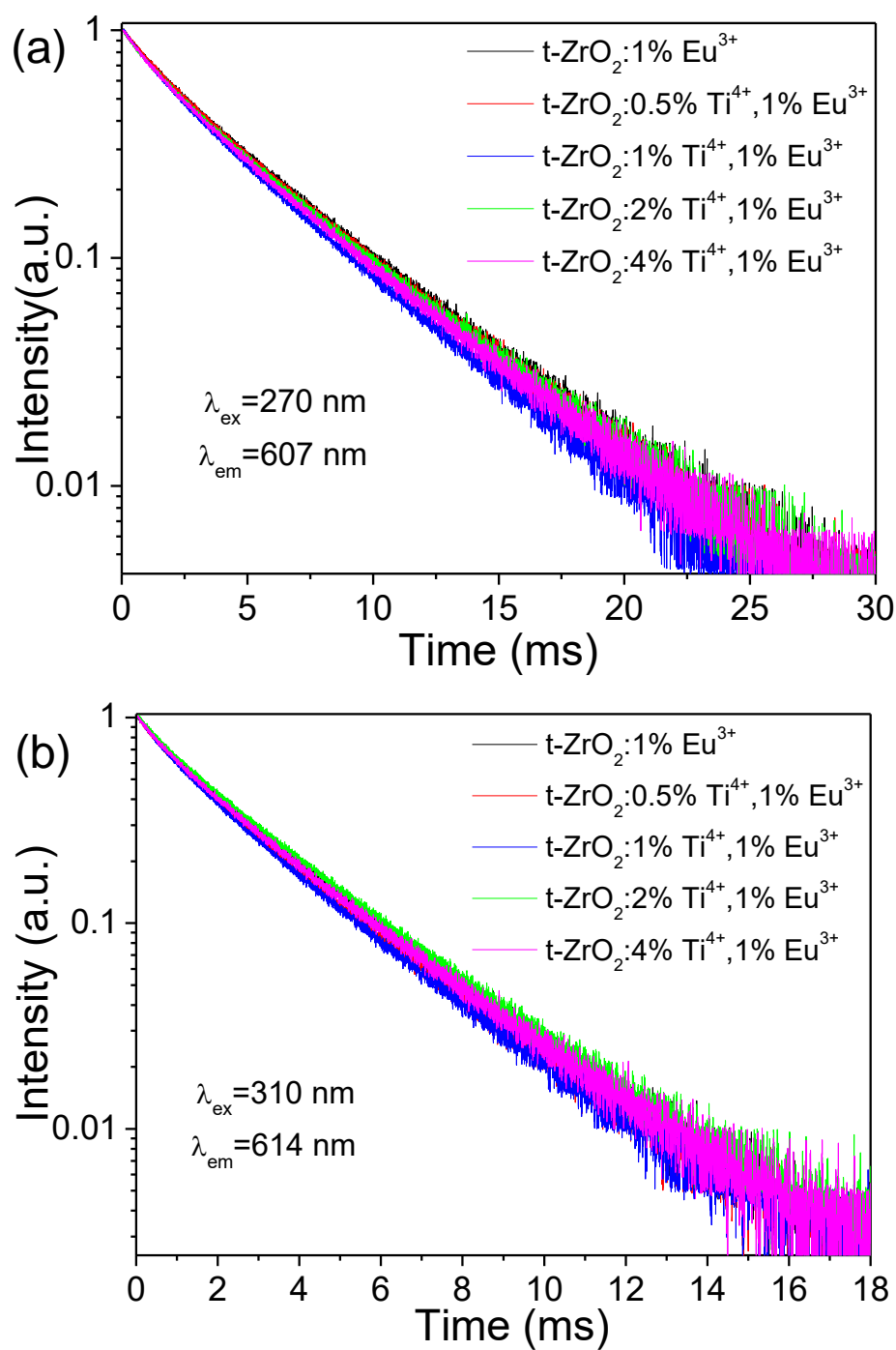


Figure S10. Fluorescence decay traces of t-ZrO₂:xTi⁴⁺,1%Eu³⁺ ($x=0, 0.5\%, 1\%, 2\%$ and 4%) NCs by monitoring the relative maxima of Eu(I) ((a), $\lambda_{\text{ex}}=270$ nm, $\lambda_{\text{em}}=607$) and Eu(II) ((b), $\lambda_{\text{ex}}=310$ nm, $\lambda_{\text{em}}=614$ nm).

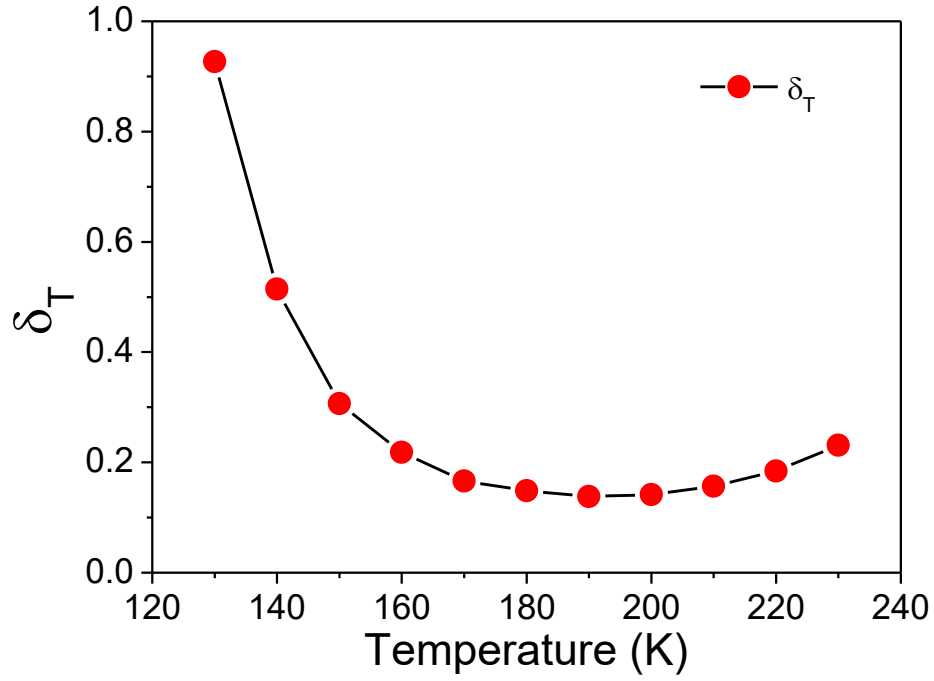


Figure S11. Temperature resolution δ_T of t-ZrO₂:0.4%Eu³⁺ NCs temperature sensing material in the temperature range from 130 to 230 K.

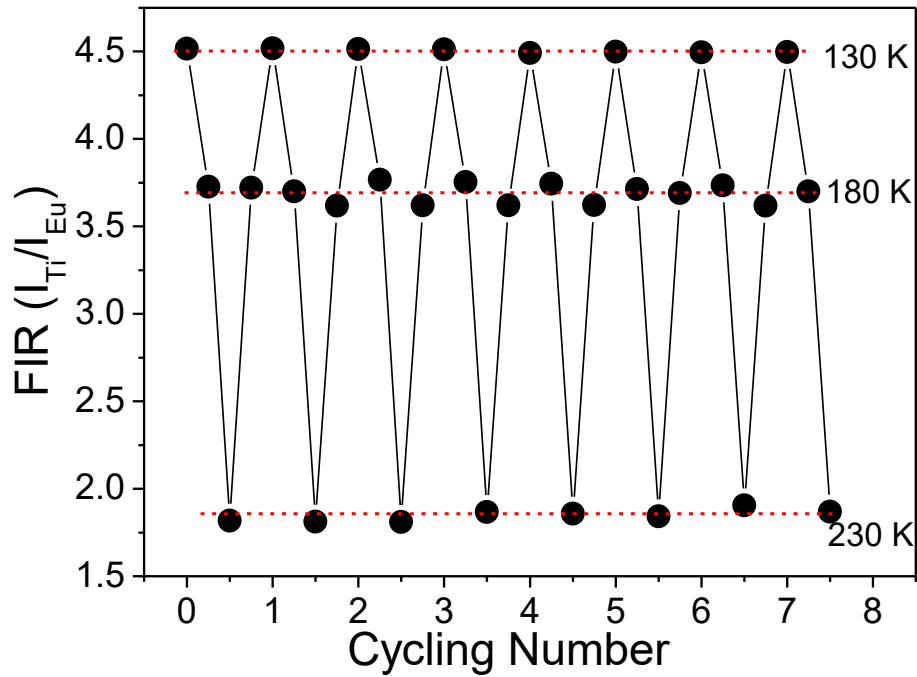


Figure S12. Temperature-induced switching of the FIR between the titanate groups signals (I_{Ti}) (450–580 nm) and Eu³⁺ signals (690–725 nm) (I_{Eu}) (alternating between 130 K and 230 K). The dashed line is drawn to guide the eyes.