Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A highly sensitive near-infrared luminescent metal−organic framework thermometer in physiological range

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1. Materials and characterization.

The ligand 1,3,5-benzenetrisbenzoic acid (H_3BTB) was obtained from Ji'nan Henghua Company and used as received. All other reagents and solvents were commercially available and used without further purification. $Nd(NO_3)_3 \cdot 6H_2O$ (87.6 mg, 0.2 mmol), H_3BTB (87.6 mg, 0.2 mmol) were dissolved in N,N'-dimethylformamide (DMF, 20 mL) in a 25 mL Teflon-lined steel autoclave. The autoclave was sealed and placed in an oven at 120 °C for three days. The resulting crystals were collected by filtration and washed by DMF several times. The other MOFs were synthesized by the same procedure using the corresponding lanthanide nitrate. Powder X-ray diffraction (PXRD) patterns were performed using Cu Kα (λ = 1.542 Å) radiation on an X'Pert PRO diffractometer and recorded in the range of 2θ = 5−50 ° at room temperature. Thermogravimetric analysis (TGA) was carried out on a Netzsch TG209F3 instrument at a heating rate of 5 °C/min under a N_2 atmosphere. Inductively coupled plasma spectroscopy (ICP) was performed on a Thermo IRIS Intrepid II XSP spectrometer. The scanning electron microscopy (SEM) images were obtained using a field-emission scanning electron microscopy (FE-SEM, Hitachi S4800). The temperature dependence of the emission spectra were observed on an Edinburgh Instrument F920 spectrometer with an external NIR laser of 808 nm. The slit width of emission spectra for the MOF samples is 2.0 nm, and the scan speed is 1 nm/s.

2. Excited state calculation

The molecular geometry optimization and frequency analysis of H_3BTB were performed using density functional theory (DFT) at the B3LYP/6-31+G(d,p) level,[1] and the optimized geometry was shown in Figure S1. Based on the optimized result, the energy of the lowest triplet excited state of the H_3BTB were calculated to be 2.8893 eV (23304 cm^{-1}) by the time-dependent DFT approach.[2] All calculations were performed using Gaussian 09 software.[3]

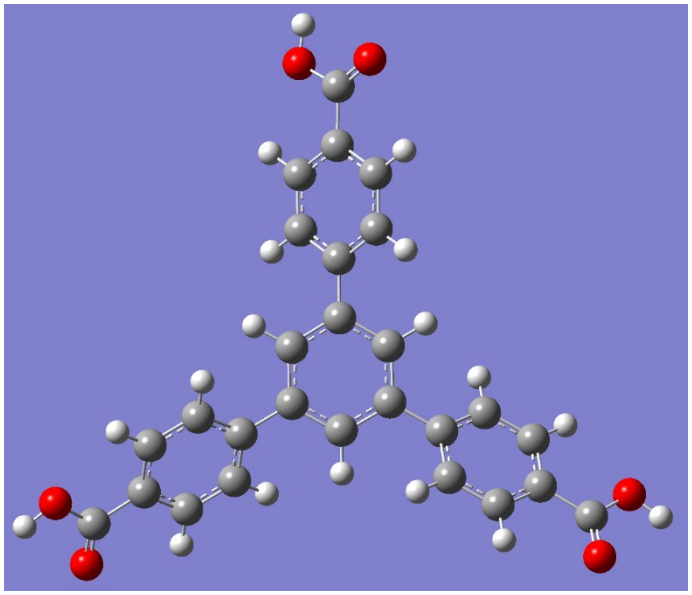


Fig. S1 The optimized geometry of free ligands H_3BTB

3. Cytotoxicity, Imaging of $Nd_{0.866}Yb_{0.134}BTB$:

The MTT assay is an easy and reproducible colorimetric assay for evaluation of cell viability. In this study, rat pheochromocytoma (PC12) cells were incubated in Dulbecco's Modified Eagle's Medium (DMEM, Neuronbc) with 10% fetal bovine serum (FBS) and 1% penicillin/streptomycin (P/S, Boster) for 2-3 days in a humidified incubator (37 °C, 5% CO_2). The cytotoxicity of **$Nd_{0.866}Yb_{0.134}BTB$** was evaluated by using standard MTT assay in a 96-well plate to assess the viability of cultured cells. After 24 h cell incubation in the humidified incubator, **$Nd_{0.866}Yb_{0.134}BTB$** with different concentrations (20, 50, 100, 150, and 200 μg/mL) were added to the wells and incubated with the PC 12 cells for another 24 h in the incubator. After that, 1× MTT solutions were added to each tested wells and incubated for 4 h. All media were removed, and 150 μL of dimethyl sulfoxide was added to the wells. The absorbance of each sample at 490 nm was measured using a microplate reader, and the morphologies of all cells were observed using an optical microscopy. The cell viability was calculated as the ratio of the absorbance of the sample well to that of the cell control and expressed as a percentage. All experiments were sextuplicated, and the results were averaged.

For imaging experiments, the cells (10^4 cells/mL) were seeded in a 24-well plate with a coverslip (0.17 mm in thickness) at the bottom of each well for 24 h incubation. Then 20 μg/mL **$Nd_{0.866}Yb_{0.134}BTB$** probes were added to the wells and incubated with the PC 12 cells for 6 h in the incubator. After that, cells were washed three times with 1× phosphate buffered solution (PBS, pH = 7.4) and fixed with 4% paraformaldehyde for about 15 min at room temperature, followed by DAPI (1 μg/mL, Sigma-Aldrich) staining for 5 min to examine the effect of **$Nd_{0.866}Yb_{0.134}BTB$** on the nuclear DNA. Imaging of cells was carried out using a confocal laser scanning microscopes with a 20× objective at room temperature in a two channel mode of bright-field and laser excitation wavelengths of 405 nm for DAPI.

Table S1. The molar ratio of the starting Nd/Yb salt and that in the synthesized product calculated by ICP analysis

sample	The molar ratio of the starting Nd/Yb salt	The Nd/Yb ratios calculated by ICP analysis
$Nd_{0.866}Yb_{0.134}BTB$	0.90:0.10	0.866:0.134
$Nd_{0.811}Yb_{0.189}BTB$	0.80:0.20	0.811:0.189
$Nd_{0.568}Yb_{0.432}BTB$	0.60:0.40	0.568:0.432

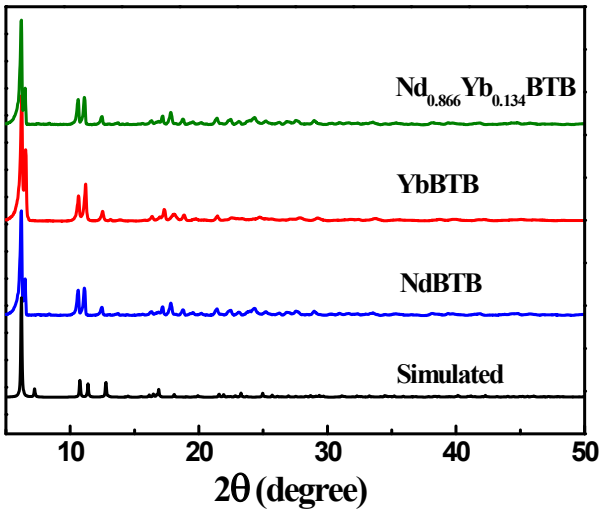


Fig. S2 PXRD patterns of the MOF **NdBTB**, **YbBTB** and **$Nd_{0.866}Yb_{0.134}$BTB.**

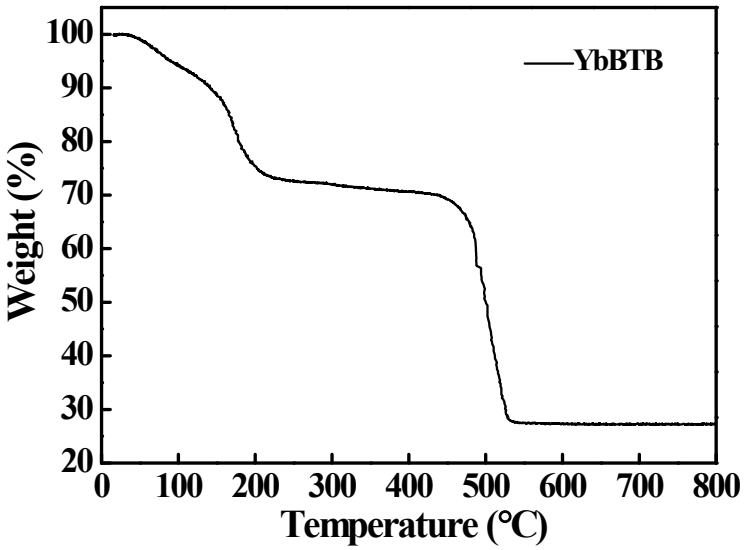


Fig. S3 TGA curve of **YbBTB.**

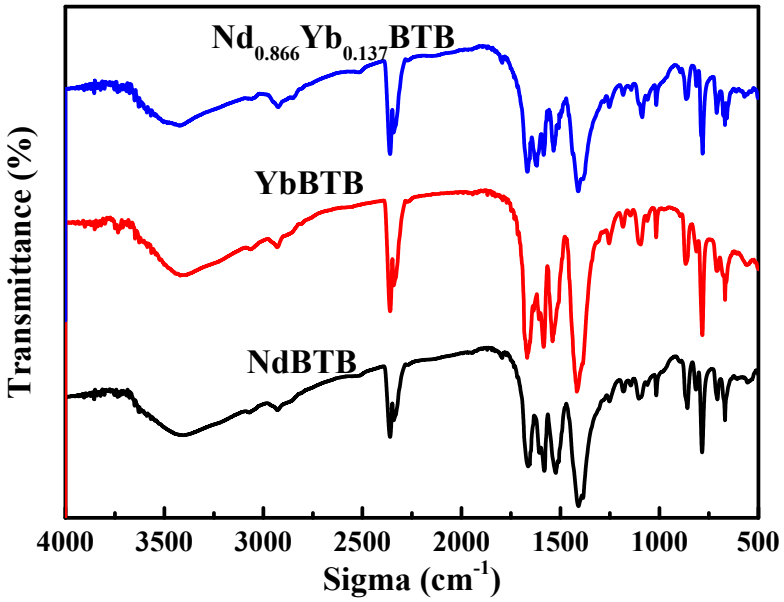


Fig. S4 FTIR spectra of **NdBTB**, **YbBTB**, **$Nd_{0.866}Yb_{0.134}$BTB**.

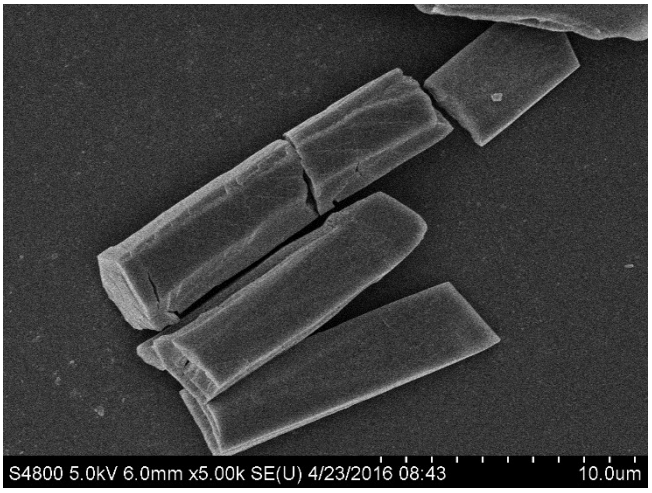


Fig. S5 SEM image of **$Nd_{0.866}Yb_{0.134}$BTB**.

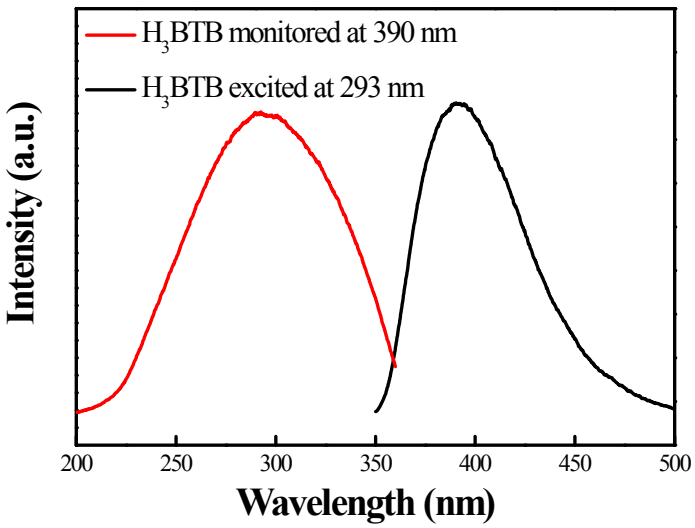
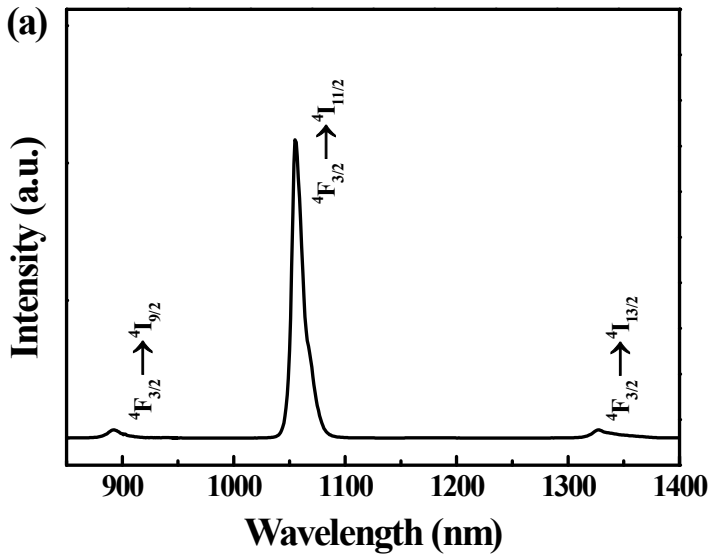


Fig. S6 Excitation and emission spectra of the ligand **H_3BTB.**



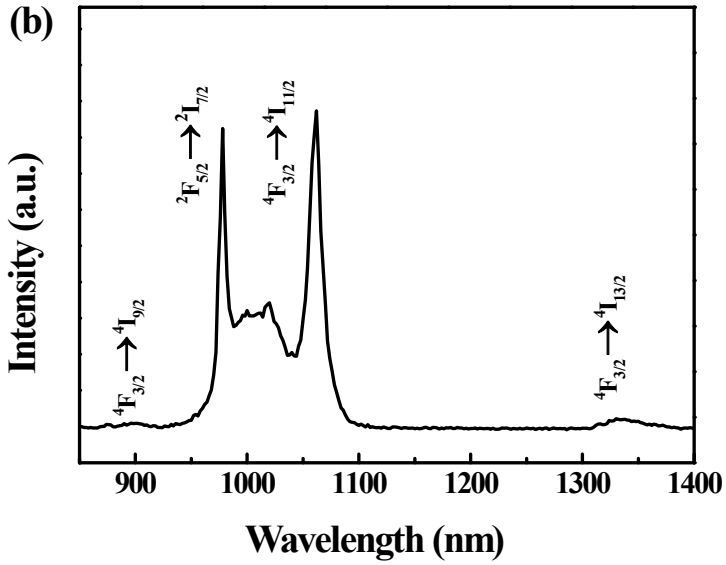


Fig. S7 Emission spectra of **NdBTB** (a) and **$Nd_{0.866}Yb_{0.134}$BTB** (b) at room temperature excited at 808 nm

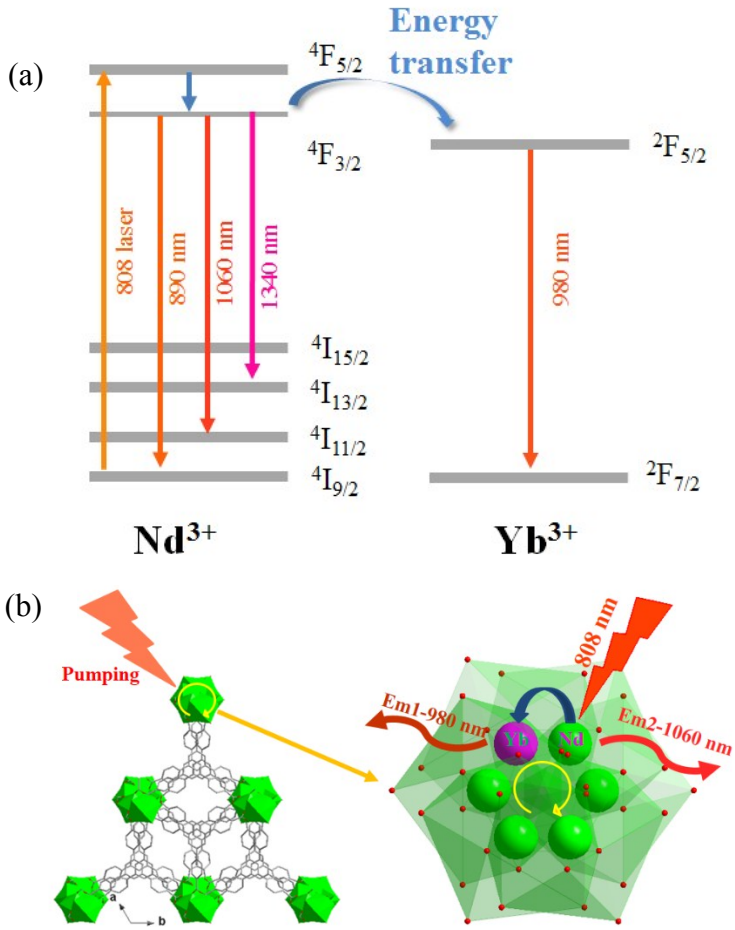
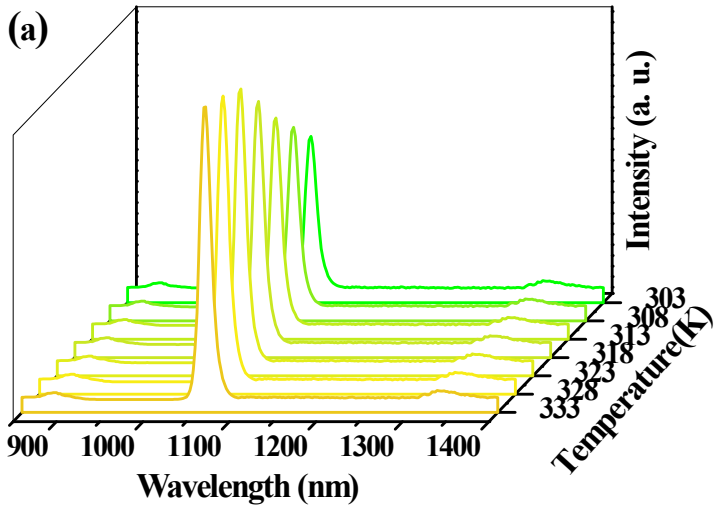


Fig. S8 (a) Schematic energy-level diagrams of Nd^{3+} and Yb^{3+}. (b) Illustration of energy transfer process from Nd^{3+} to Yb^{3+} in **$Nd_{0.866}Yb_{0.134}BTB$** (excited at 808 nm).



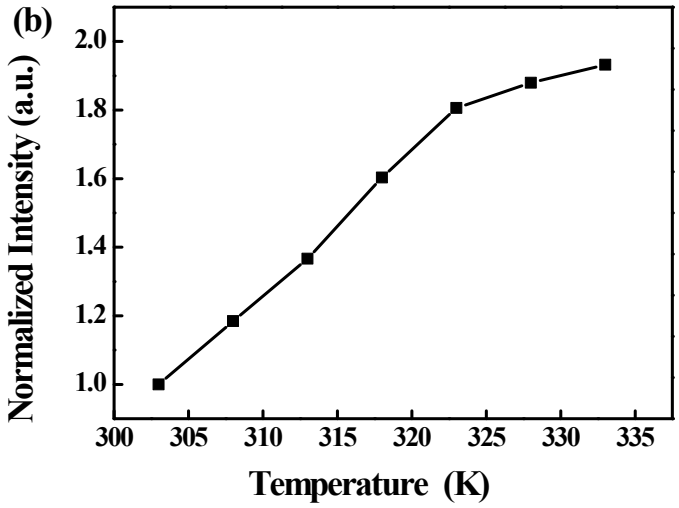


Fig. S9 (a) Emission spectra of **NdBTB** recorded between 303 and 333 K excited at 808 nm; (b) Temperature-dependent intensity of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of **NdBTB.**

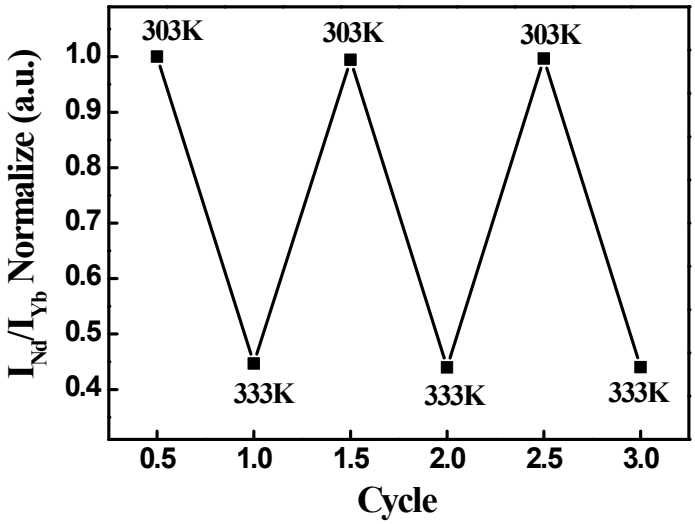


Fig. S10 The normalized intensity ratio of Nd^{3+} (1060 nm) to Yb^{3+} (980 nm) for **$Nd_{0.866}Yb_{0.134}$BTB** in cycles of heating and cooling.

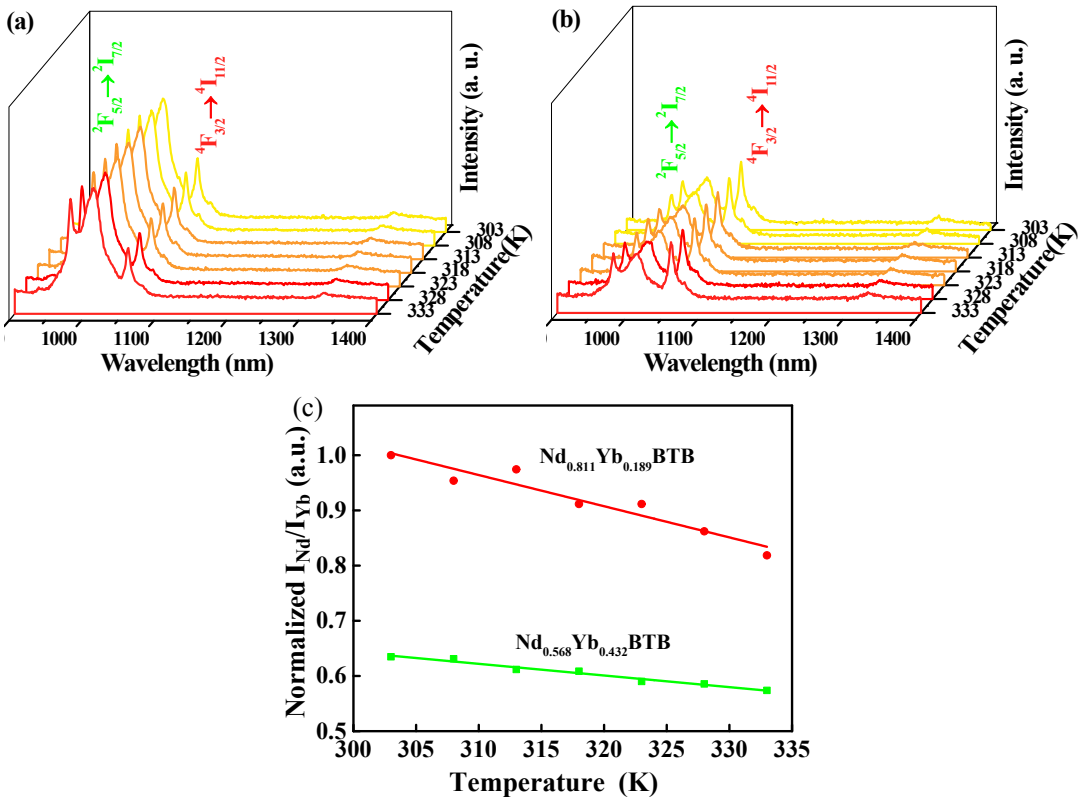


Fig. S11 Emission spectra of (a) **$Nd_{0.568}Yb_{0.432}BTB$** and (b) **$Nd_{0.811}Yb_{0.189}BTB$** recorded between 303 and 333 K excited at 808 nm; (c) Temperature-dependent intensity ratio of Nd^{3+} (1060 nm) to Yb^{3+} (980 nm) and the fitted curve for **$Nd_{0.568}Yb_{0.432}BTB$** and **$Nd_{0.811}Yb_{0.189}BTB$** (excited at 808 nm).

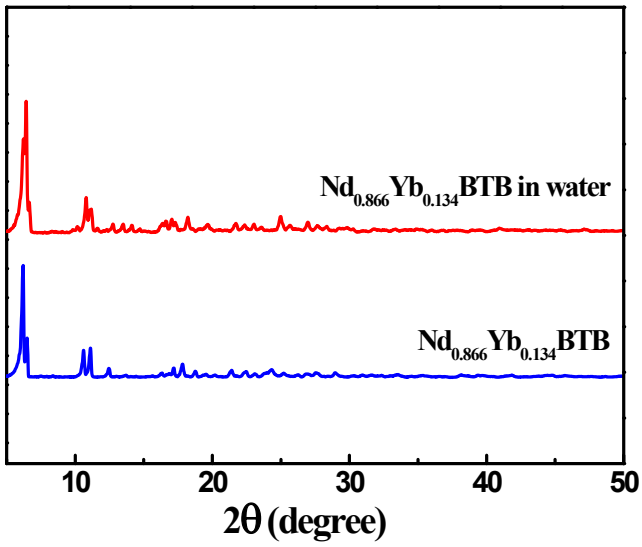


Fig. S12 PXRD patterns of **$Nd_{0.866}Yb_{0.134}BTB$** and **$Nd_{0.866}Yb_{0.134}BTB$** immersed in H_2O for 2 h.

Reference

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3 M. J. Frisch, et al., *Gaussian 09*, revision D.01; Gaussian Inc.: Pittsburgh, PA, 2009.