

Electronic Supporting Information (ESI)

Dual-Emitting Piezofluorochromic Dye@MOF for White-Light Generating

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S1. Experimental section

S1.1 Materials and Methods

All the reagents and solvents were purchased from commercial sources and used directly without further purification. Infrared (IR) spectra were acquired with KBr discs in the range of 4000 to 400 cm^{-1} on Bruker TENSOR-27 IR spectrometer. Elemental analysis was obtained from Perkin-Elmer 2400 element analyzer. Thermogravimetric analyses (TG) were collected on Perkin Elmer TGA7 micro-analyzer under air stream at a heating rate of 10 $^{\circ}\text{C}/\text{min}^{-1}$. Powder X-ray diffraction (PXRD) data was obtained by using Rigaku MiniFlex 600 X-ray diffractometer, with Cu $K\alpha$ radiation at 40 kV and 15 mA. The solid-state luminescent spectra were collected on a GangDong F-320 fluorescence spectrophotometer at room temperature. Atomic emission spectrometer (ICP) was conducted on an iCAP 7000 Plus Series from Thermo Scientific with a Teledyne CETAC ASX-560 autosampler. The luminescence lifetime decays were measured on an Edinburgh FLS980 fluorescence spectrophotometer equipped with both continuous (450 W) Xenon and pulsed

flash lamps. The absolute external luminescent quantum efficiency was determined employing an integrating sphere (150 mm diameter, BaSO₄ coating) from an Edinburgh FLS980 phosphorimeter. The concentration of RhB was determined by the ultra-violet-spectrophotometric method, which was measured on a UV spectrophotometer (UV-1801, Beijing Beifen Rayleigh Analytical Instruments (Group) Co., Ltd.).

S1.2 X-ray crystallography

The collection of single crystal X-ray diffraction data for **HNU-49** was carried out on graphite monochromator Bruker APEX2 diffraction at 100 K with Mo-K α radiation ($\lambda=0.71073$ Å) using an $\varphi\sim\omega$ -scan technique. The structure was solved by direct method (OLEXS) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL), which the disorder benzene rings are personalized with 'Sadi', 'Flat', 'Dfix', 'Delu', 'Simu', and 'Omit' commands. Nonhydrogen atoms were refined with anisotropic displacement parameters. The highly disordered solvent molecules, which were difficult to model, were removed with the SQUEEZE option of PLATON. The final formula of **HNU-49** was determined by single-crystal structures, elemental analysis and TG. The relevant crystallographic data are shown in Table S1. CCDC numbers are 2031930 for **HNU-49**. Table S1 contains the crystallographic data of **HNU-49**.

S1.3 Computational Details

The frequency analysis of free ligands was performed using density functional theory (DFT) at the B3LYP/6-31+G (d, p) level, and the molecular orbital energies of free ligands are listed in Table S3. Based on the optimized results, the energies of the triplet excited states of the ligands were calculated by the time-dependent DFT approach, and the results are reported in Table S3. All calculations were performed using Gaussian 16 software^{1,2}.

S1.4 Synthesis of HNU-49

Synthesis of $(\text{H}_3\text{O}) [\text{Tb}_3(\text{TCPE})_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (**HNU-49**): A mixture of $\text{Tb}(\text{NO}_3)_3$ (0.2 mmol), H_4TCPE (1,1,2,2-tetra(4-carboxyphenyl)ethylene) (0.05 mmol) is dissolved in 10 mL H_2O in Teflon vessel (25 mL), then acetic acid (150 μL , 98%) was dripped. The mixture was kept at 150 °C for 3 days and cooled to room temperature. After that the colorless block crystals were obtained and collected (yield 38.4% based on TCPE). Elemental analysis calcd (%) for $\text{C}_{64}\text{H}_{49}\text{O}_{25}\text{Tb}_3$ (*Mr*: 1694): C, 45.17; H, 2.75; found: C, 45.36; H, 2.83. IR (KBr, cm^{-1}): 3412 (br), 1647 (s), 1587 (s), 1541 (s), 1419 (s), 1170 (w), 1016 (m), 872 (w), 769 (m), 665 (m).

S1.5 Preparation of RhB@HNU-49 and piezofluorochromic behavior study of HNU-49 and RhB@HNU-49

The synthesized crystalline **HNU-49** (25 mg) was immersed in 10 mL RhB solution (a drop of triethylamine) with different concentration at room temperature for 12 hours. The soaked sample was washed with water for five times to remove the residual dye from the surface. The adsorption capacity of dye was calculated by the UV absorption-concentration curve.

For the investigation of piezofluorochromic behavior, the synthesized **HNU-49** (30 mg) and RhB@**HNU-49** (30 mg) were firstly dried at 85 °C for 2 h. The dried **HNU-49** and RhB@**HNU-49** were pressed into small tablets (wafer with 7 mm diameter) by an infrared tablet machine at different pressures (pressure=mass*g/area, unit is GPa), and their solid fluorescence was measured by a fluorescence spectrophotometer. Moreover, the **HNU-49** converted to green fluorescence at a pressure of 0.51 GPa and 1 mL DMF were placed in the same device and heated at 100 °C for 30 min, and then the fluorescence changes were observed by ultraviolet lamp irradiation.

S1.6 PXRD and TG of HNU-49

The powder X-ray diffraction (PXRD) pattern of **HNU-49** is completely consistent with simulated spectra, which proves the phase purity and the

structural consistency with the measured single crystal sample (Fig. S1). The thermogravimetric (TG) curve of **HNU-49** shown in Fig. S2 displays a weight loss of about 5.7% (calc. 5.3%) in the range of 30~170 °C, which corresponds to the removal of guest molecules in the channel. With the gradual increasing of temperature, the structure of **HNU-49** collapses due to the decomposition of organic ligands.

S2. Supplementary characterizations

Table S1 Crystallographic data of **HNU-49**

Complex	HNU-49
Formula	$C_{64}H_{38}O_{22}Tb_3$
<i>Mr</i>	1635.73
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	11.1251(4)
<i>b</i> (Å)	11.5573(4)
<i>c</i> (Å)	14.9248(5)
α (°)	68.629(2)
β (°)	78.582(2)
γ (°)	61.274(2)
<i>V</i> (Å ³)	1566.48(10)
<i>Z</i>	1
<i>D</i> _{calc} (gcm ⁻³)	1.734
<i>F</i> (000)	793
<i>R</i> _{int}	0.099
GOF on <i>F</i> ²	1.060
<i>R</i> ₁ ^a [<i>I</i> >2 δ (<i>I</i>)]	0.0971(4537)
<i>wR</i> ₂ ^b (all data)	0.2936(6153)

Table S2 Luminescent lifetime (τ) and absolute quantum yield (ϕ) of the **HNU-49**, **HNU-49-0.51 GPa**, **RhB@HNU-49** and **RhB@HNU-49-0.51 GPa**.

Sample	τ (ns)	ϕ (%)	λ_{ex} (nm)	λ_{em} (nm)
HNU-49	3.57	7.3	393	441
HNU-49-0.51 GPa	4.14	26.7	393	489
RhB@HNU-49	1.02	18.6	393	448
	2.96			583
RhB@HNU-49-0.51 GPa	1.52	24	393	483
	3.02			591

Table S3 Calculated excited state of H₄TCPE.

Basis set	6-31+G(d,p)			
Name	Triplet (eV)			Singlet (eV)
	T ₁	T ₂	T ₃	S ₁
H ₄ TCPE	2.2661 18240 (cm ⁻¹)	3.0883	3.0946	3.2429 (26102 cm ⁻¹)

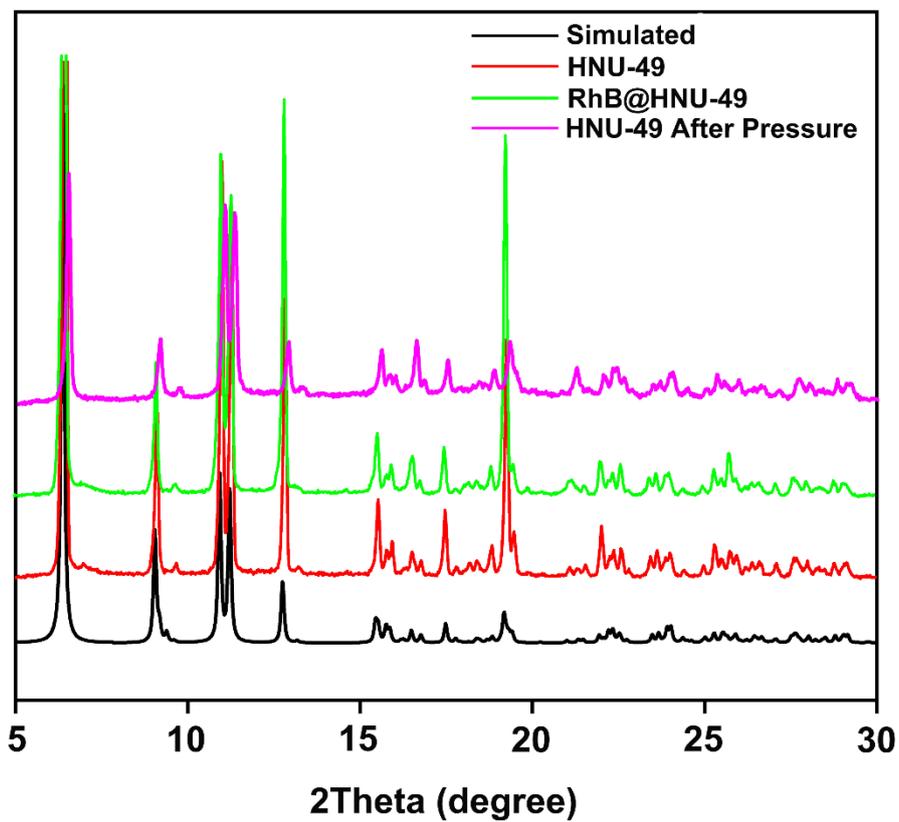


Fig. S1 PXRD patterns of HNU-49, HNU-49 after compression and RhB@HNU-49.

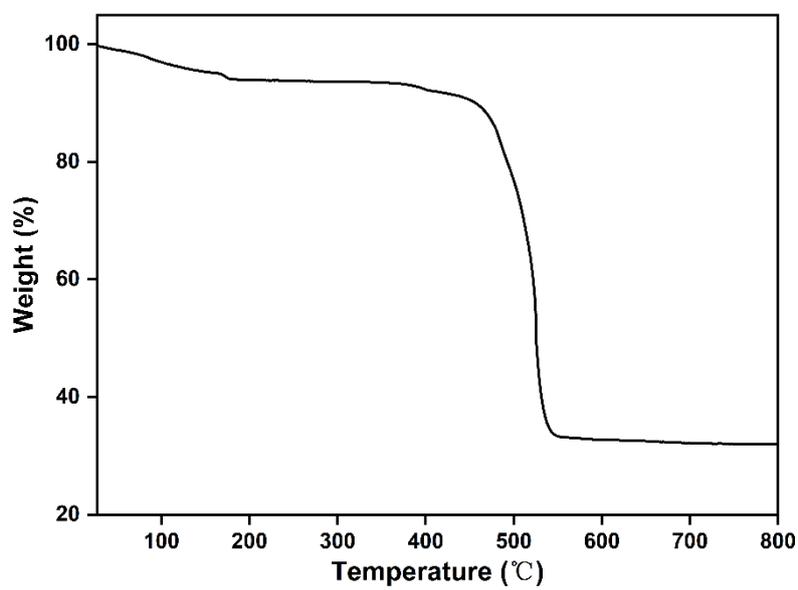


Fig. S2 TG plot of HNU-49.

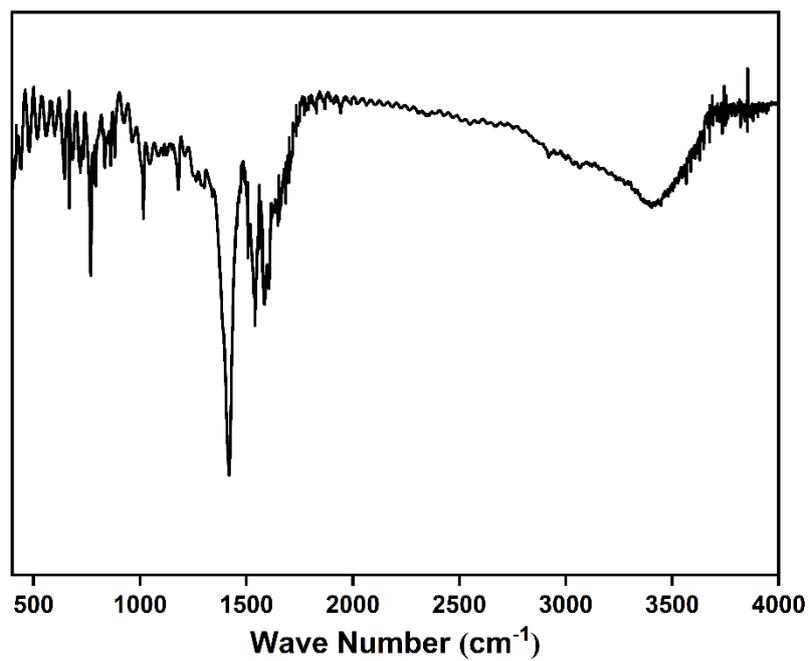


Fig. S3 IR spectrum of **HNU-49**.

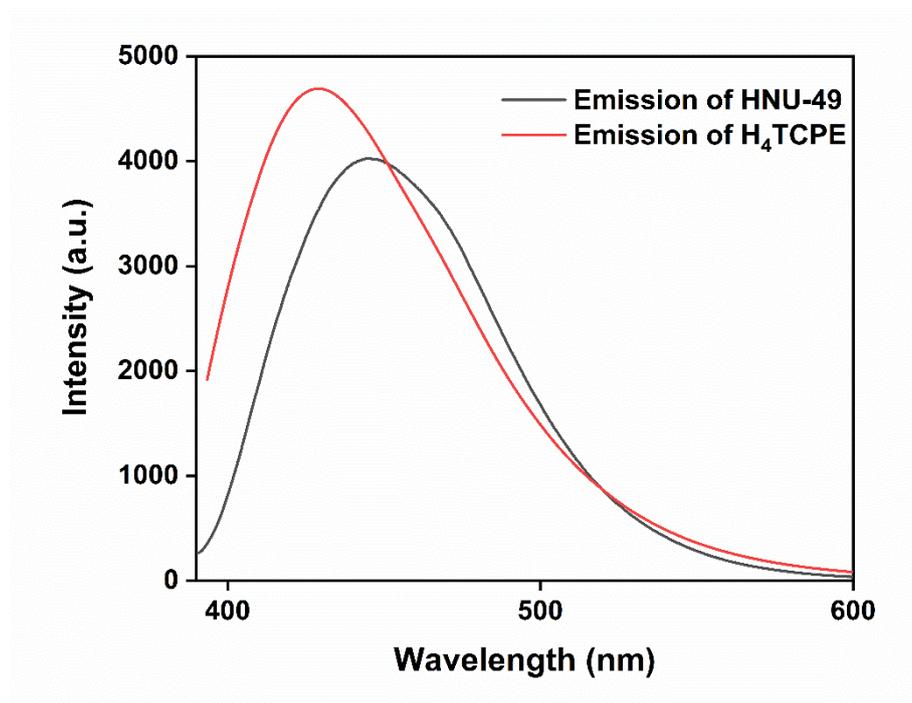


Fig. S4 Excitation and emission spectra of **HNU-49** and **H₄TCPE**, ($\lambda_{\text{ex}} = 393$ nm, $\lambda_{\text{em-HNU-49}} = 441$ nm, $\lambda_{\text{em-H₄TCPE}} = 429$ nm).

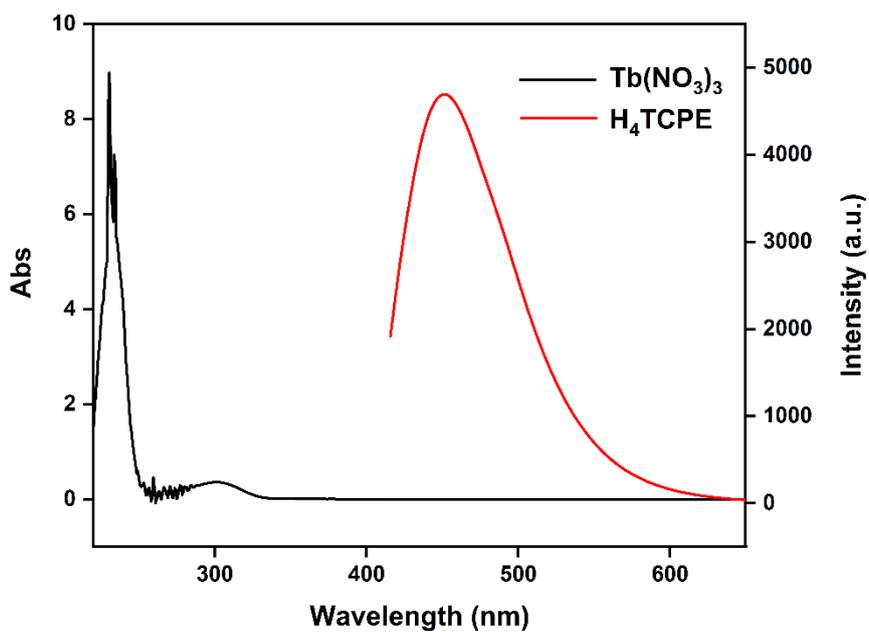


Fig. S5 The UV-Vis absorption spectrum of $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and the fluorescence emission spectrum of H_4TCPE ligand.

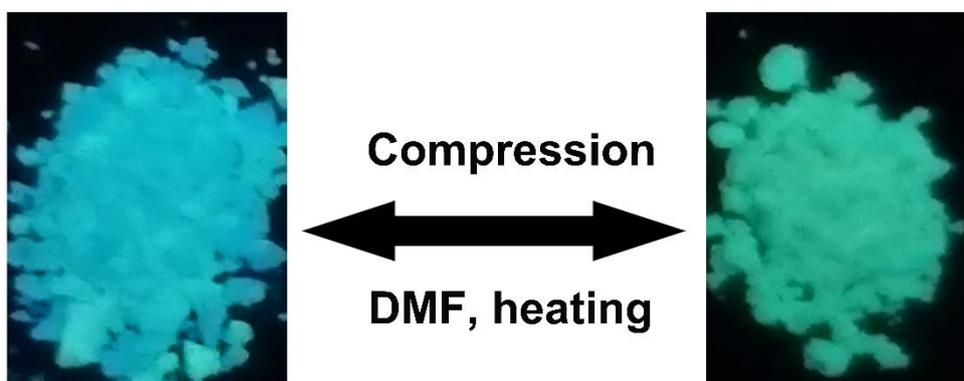


Fig. S6 The luminescence of **HNU-49** recovery treated in DMF vapor (100 °C, 30 min) under UV light (365 nm).

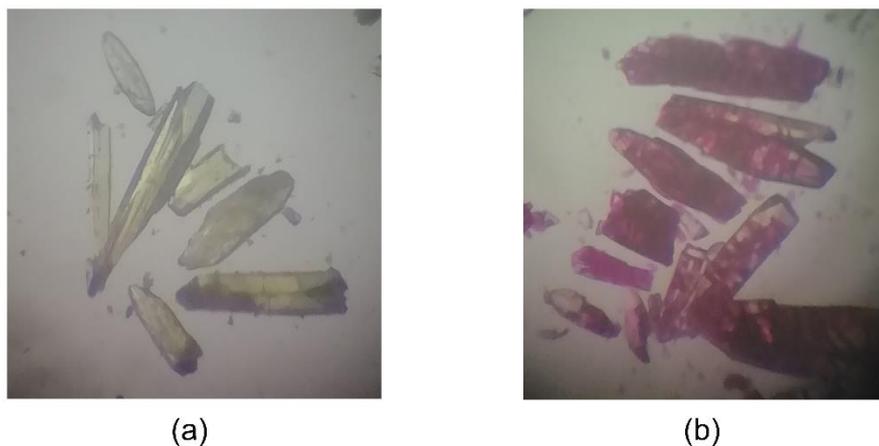


Fig.S7 Optical images of **HNU-49** before (a) and after (b) RhB adsorption.

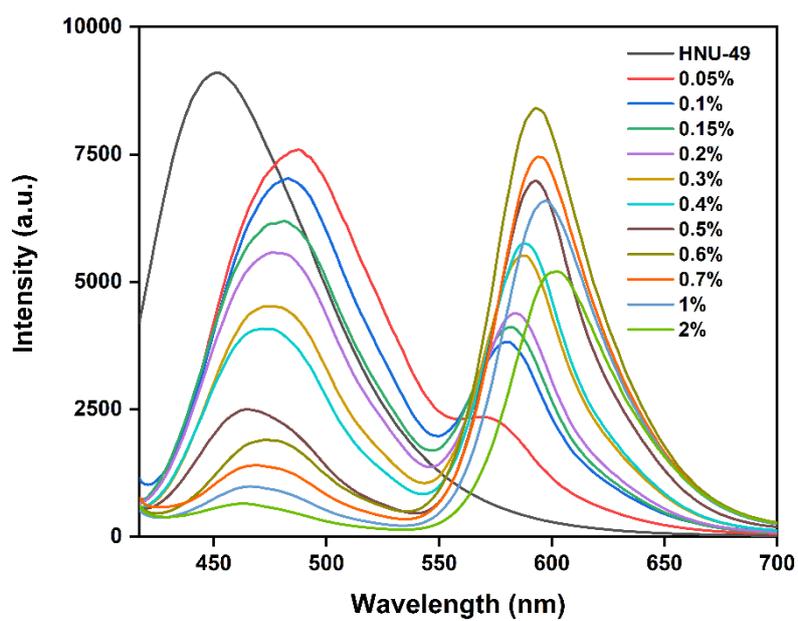


Fig. S8 The emission spectra of RhB@HNU-49 with different content of RhB encapsulation ($\lambda_{ex}=393$ nm).

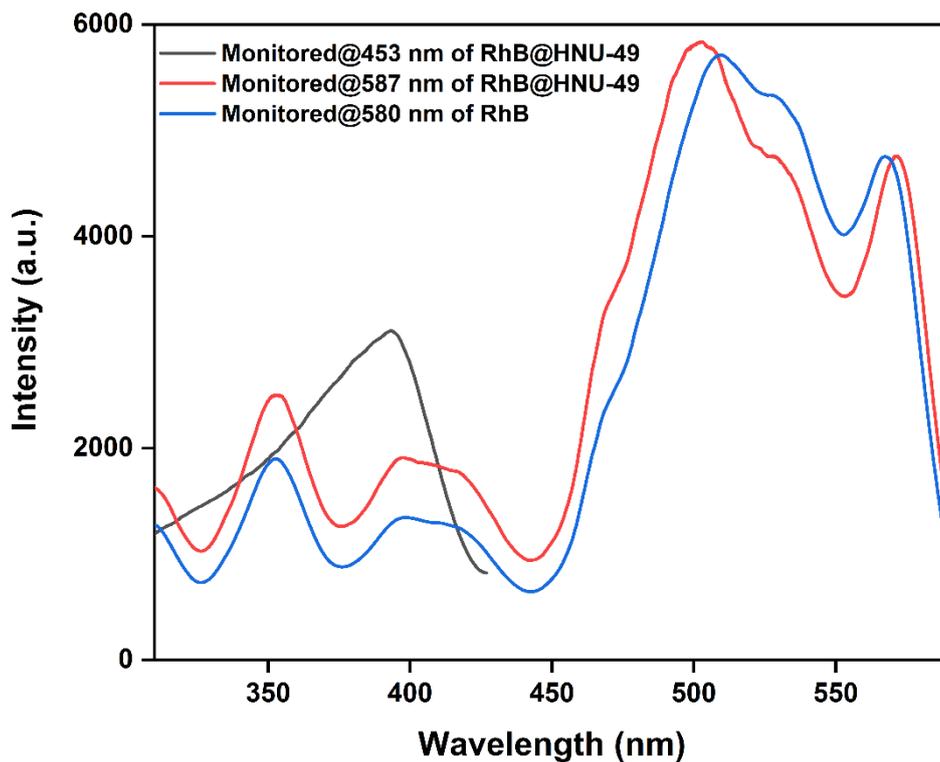


Fig. S9 Overlap between excitation spectra of RhB@HNU-49 (monitored at 453 nm and 587 nm, respectively) and RhB monitored at 580 nm.

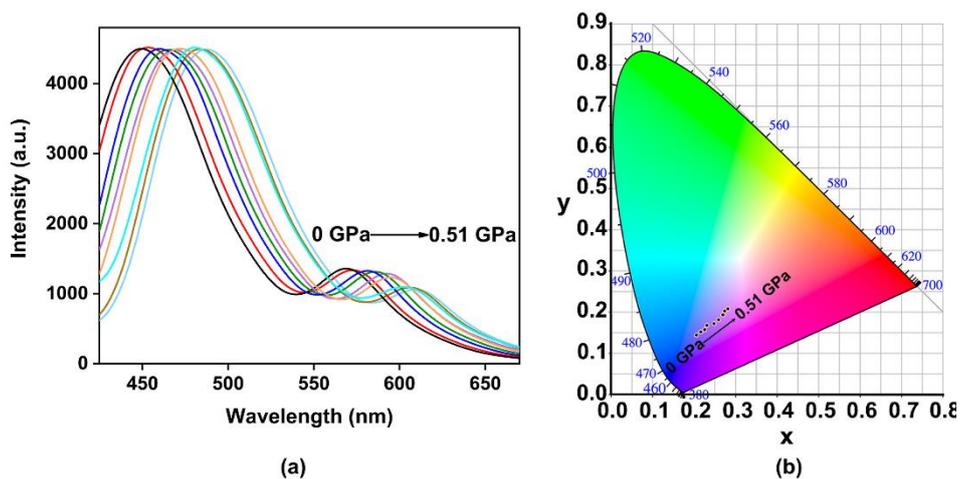


Fig. S10 Emission spectra ($\lambda_{\text{ex}}=393$ nm) (a) and CIE coordinates (b) of RhB@HNU-49-0.05% after exerting different pressure.

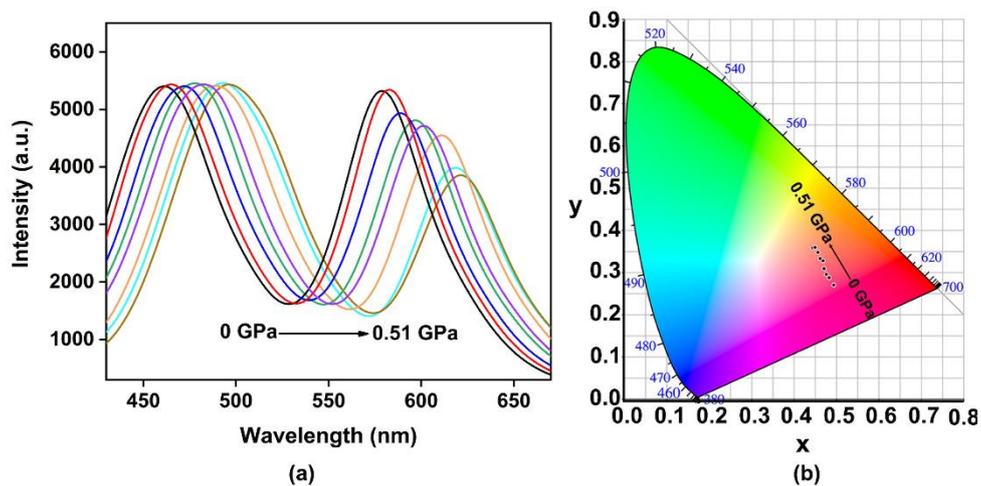


Fig. S11 Emission spectra ($\lambda_{\text{ex}}=393$ nm) (a) and CIE coordinates (b) of RhB@HNU-49-0.7% after exerting different pressure.

1. J. Yao, Y.-W. Zhao and X.-M. Zhang, *ACS Omega*, 2018, **3**, 5754-5760.
2. D. Zhao, X. Rao, J. Yu, Y. Cui, Y. Yang and G. Qian, *Inorganic chemistry*, 2015, **54**, 11193-11199.