Electronic Supporting Information (ESI)

Two Metal-Organic Zeolites for Highly Sensitive and Selective Sensing of Tb^{3+}

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CONTENTS

S1. Experimental section

S1.1 Materials and Methods

S1.2 Synthesis of **HNU-25** and **HNU-26**

S1.3 Luminescence sensing measurements towards Ln^{3+} ions

S1.4 X-ray crystallography

S2. Supplementary characterizations

Table S1 Crystallographic data of **HNU-25** and **HNU-26**

Table S2 Luminescent lifetime (τ) and absolute quantum yield (φ) of MOZs

Fig. S1 The 3D structure of **HNU-25** and **HNU-26**

Fig. S2 PXRD patterns of MOZs

Fig. S3 TGA plots of MOZs

Fig. S4 IR spectra of MOZs

Fig. S5 Excitation spectrum and the emission spectra of MOZs

Fig. S6 The luminescence spectra of MOZs in DMF with different concentration of Tb^{3+} and Dy^{3+} ion

Fig. S7 Luminescence responses of **HNU-25** towards Tb^{3+} ion in the presence of a background of other metal ions

Fig. S8 The luminescence spectra of **HNU-26** in DMF with different concentration of Tb^{3+} ion

Fig. S9 The luminescence spectra of **HNU-25** in DMF with different concentration of Dy^{3+} ion

Fig. S10 The luminescence effect of organic ligands on Tb^{3+} ion.

Fig.S11 HRTEM image, EDS-mapping images and EDX spectrum of MOZs

Fig. S12 Luminescence decay curves of MOZs

Fig. S13 XPS survey spectra of MOZs

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 (TGA) were collected on Perkin Elmer TGA7 micro-analyzer under air stream at a heating rate of 10 $^{o}C/min^{-1}$. Powder X-ray diffraction patterns were collected on Rigaku D/MAX X-ray powder diffractometer (Cu-Kα, 1.5418 Å) at room temperature. The solid state luminescent spectra were collected on a GangDong F-320 fluorescence spectrophotometer at room temperature. XPS measurements were performed in a stainless-steel ultrahigh vacuum chamber (PerkinElmer, model 5500, base pressure <10-10 mbar). ICP was conducted on an iCAP 7000 Plus Series from Thermo Scientific with a Teledyne CETAC ASX-560 autosampler. Tecnai G2 F30 transmission electron microscopy at an acceleration voltage of 300 kV was used to acquire high resolution transmission electron microscopy and EDS mapping images. 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, $BaSO_4$ coating) from an Edinburgh FLS980 phosphor meter.

The synthesis of 5- [bis(4-carboxybenzyl) amino] isophthalic acid (H_4L) was according to literature.[1]

S1.2 Synthesis of HNU-25 and HNU-26

Synthesis of $\{[Zn_2(L)(tta)_2]\cdot 3H_2O\cdot DMF\cdot 2Me_2NH_2^+\}$ (**HNU-25**): A mixture of $Zn(CH_3COO)_2$ solution (0.5 mL, 0.2 M, aq.), H_4L (0.0225 g, 0.05 mmol) and

1H-tetrazole (1H-tta) (0.014 g, 0.2 mmol) was dissolved in 10 mL DMF in glass vial (25mL), then one drop of CH_3COOH (99.5%, aq.) was dripped. After that, it was kept at 85℃ for 3 days and cooled at room temperature, the colorless block crystals were obtained and collected (yield 50% based on 1H-tta). Elemental analysis calcd (%) for $C_{36}H_{57}N_{13}O_{13}Zn_2$ (*M*r: 1013.53): C, 42.42; H, 5.14; N, 18.01; found: C, 42.98; H, 5.622; N, 18.14. IR (KBr, cm^{-1}): 3443 (br), 3155 (w), 2964 (w), 2933 (w), 2805 (w), 2485 (w), 1659 (s), 1608 (s), 1564 (s), 1387 (s), 1251 (m), 1203 (w), 1153 (w), 1106 (m), 1080 (m), 1017 (m), 955 (m), 857 (w), 778 (m).

Synthesis of $\{[Zn_2(L)(mtz)_2]\cdot 4H_2O\cdot DMF\cdot 2Me_2NH_2^+\}$ (**HNU-26**): A mixture of $Zn(CH_3COO)_2$ solution (0.5 mL, 0.2 M, aq.), H_4L (0.0225 g, 0.05 mmol) and 5-Methyl-1H-tertazole (1H-mtz) (0.016 g, 0.2 mmol) was dissolved in 10 mL DMF in glass vial (25mL). After that, it was kept at 85℃ for 3 days and cooled at room temperature, the colorless block crystals were obtained and collected (yield 50% based on 1H-mtz). Elemental analysis calcd (%) for $C_{36}H_{57}N_{13}O_{14}Zn_2$ (*M*r: 1026.64): C, 43.00; H, 5.32; N, 17.20; found: C, 43.00; H, 5.50; N, 17.05. IR (KBr, cm^{-1}): 3439 (br), 2965 (w), 2933 (w), 2806 (w), 2494 (w), 1661 (s), 1610 (s), 1565 (s), 1386 (s), 1252 (m), 1204 (w), 1152 (w), 1102 (m), 1018 (m), 954 (m), 854 (w), 779 (m).

S1.3 Luminescence sensing measurements towards Ln^{3+} ions

20 mg finely grounded powder of **HNU-25** or **HNU-26** was dispersed in 20 mL of DMF sonicated for 30 min forming a suspension, then different Ln^{3+} ions solutions with concentration of $1x10^{-3}$ M was prepared using DMF and nitrate salts. 1 mL sample suspension was added into glass bottle containing 10 mL Ln^{3+} ions solution and then the luminescent spectra of suspension were tested after ultrasonic treatment for 1 min.

On the other hand, 1 mL sample suspension was added into DMF solution of Tb^{3+} or Dy^{3+} ions with different concentration for further studying the sensing ability. For selectivity experiments, test solution was prepared by adding Tb^{3+} ion and other metal ions (Na^+, Mg^{2+}, Ca^{2+}, Cd^{2+}, Pb^{2+} Eu^{3+}, Sm^{3+}) with the same concentration (1x10^{-3} M), and then the luminescence of the suspensions was recorded after ultrasonic treatment for 1 min.

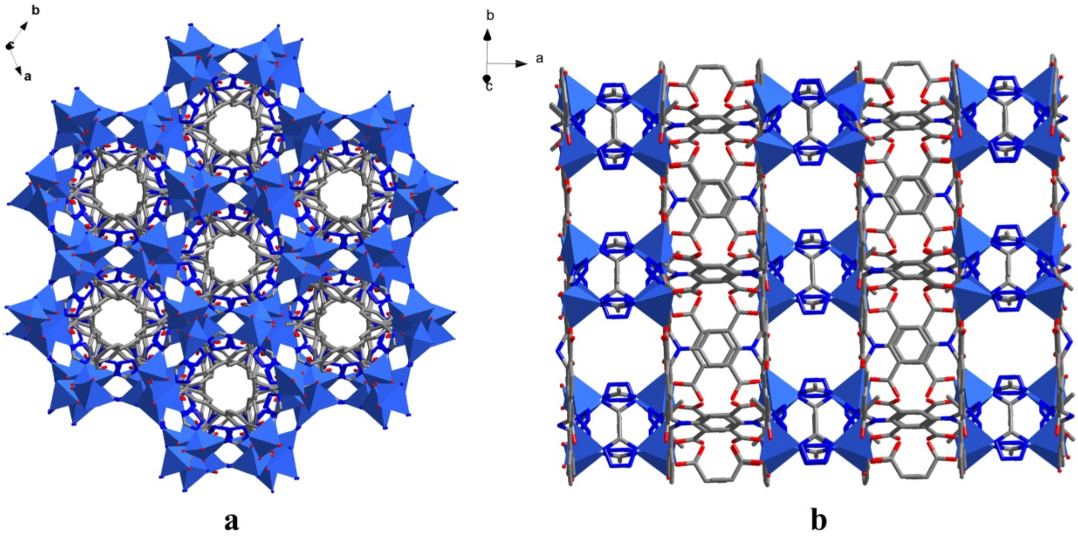
S1.4 X-ray crystallography

Single crystal X-ray diffraction data for **HNU-25** and **HNU-26** collection were carried out on Rigaku XtalAB PRO MM007 DW at 120 and 100 K with Cu-Kα radiation (λ=1.54184 Å) using an φ~ω-scan technique. The program CryAlisPro 1.171.39.9d was used for integration of the diffraction profiles. The structures were solved by direct methods (SHELXS) and refined by a full-matrix least-squares procedure based on F^2 (SHELXL).[2, 3] Nonhydrogen atoms were refined with anisotropic displacement parameters. The final formulae of **HNU-25** and **HNU-26** were determined by single-crystal structures. The highly disordered solvent molecules, which were difficult to model, were removed with the SQUEEZE option of PLATON.[4] The 'sadi' 'flat' 'dfix' 'delu' 'simu' 'omit' instructions were applied to the L^{4-} and tta ligands in **HNU-25**. The relevant crystallographic data are shown in Table S1. CCDC numbers are 1884335, 1884348 for **HNU-25** and **HNU-26**, respectively.

S2. Supplementary characterizations

Table S1 Crystallographic data of **HNU-25** and **HNU-26**

Complex	**HNU-25**	**HNU-26**
Formula	$C_{36}H_{57}N_{13}O_{13}Zn_2$	$C_{36}H_{57}N_{13}O_{14}Zn_2$
Mr	1013.53	1026.64
Crystal system	Trigonal	Orthorhombic
Space group	*R-3c*	*C/m*
a(Å)	21.5586	27.5369
b(Å)	21.5586	24.6251
c(Å)	62.2218	20.1958
α(°)	90	90
β(°)	90	90
γ(°)	120	90
V(Å^3)	25044.6	13694.8
Z	18	8
D_{calc}(gcm^{-3})	0.850	0.720
F(000)	6479	2840
R_{int}	0.066	0.031
GOF on F^2	1.102	1.100
$R_1{}^a$[I>2δ(I)]	0.0961	0.0723
$wR_2{}^b$(all data)	0.3234	0.2949



a b

Fig. S1 The 3D structure of **HNU-25** (a) and **HNU-26** (b).

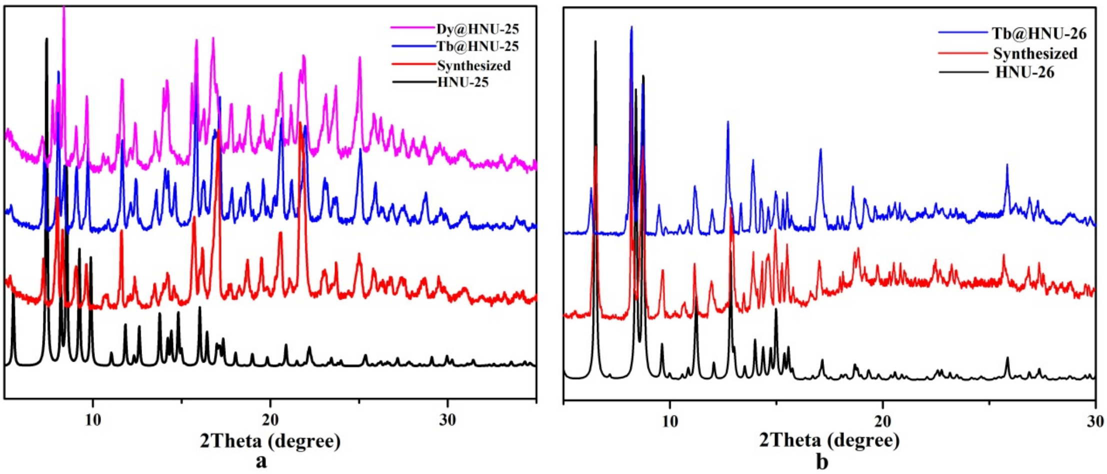


Fig. S2 (a) PXRD patterns of MOZs **HNU-25**, Tb@**HNU-25**, Dy@**HNU-25;** (b) **PXRD** patterns of the MOZs **HNU-26**, Tb@**HNU-26**.

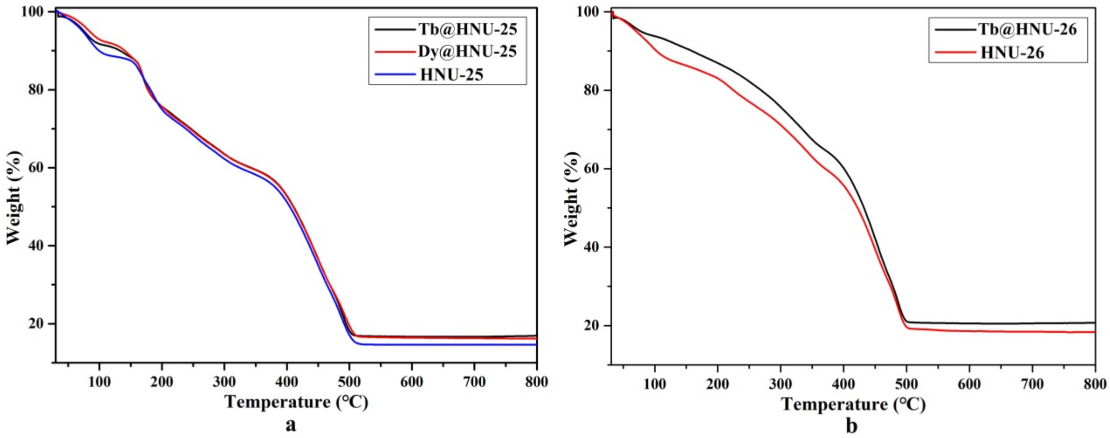


Fig. S3 (a) TGA plots of **HNU-25**, Tb@**HNU-25**, Dy@**HNU-25;** (b) TGA plots of **HNU-26**, Tb@**HNU-26**.

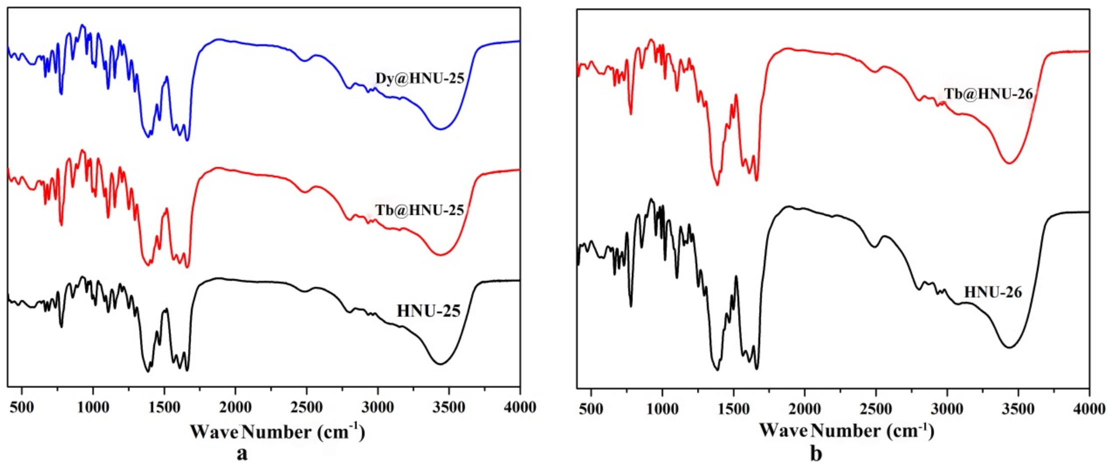


Fig. S4 IR spectra of **HNU-25**, Tb@**HNU-25**, Dy@**HNU-25**; (b) IR spectra of **HNU-26**, Tb@**HNU-26**.

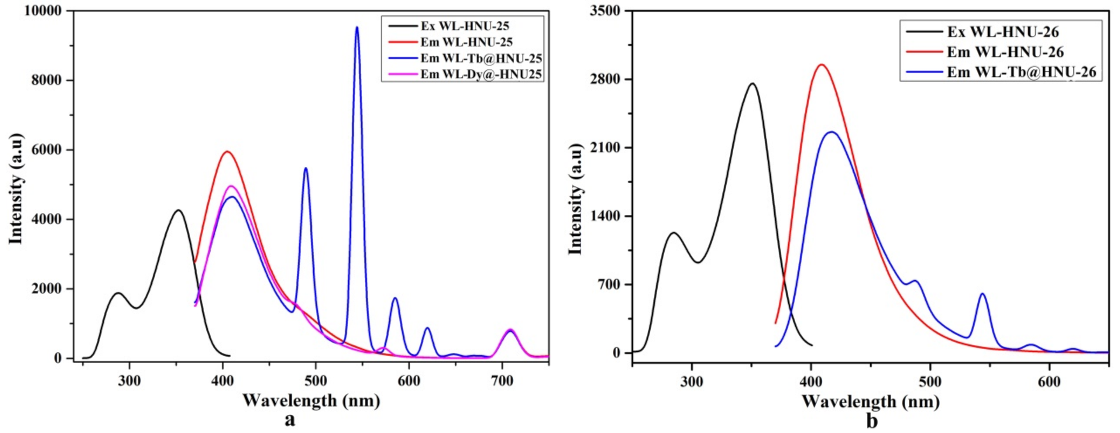
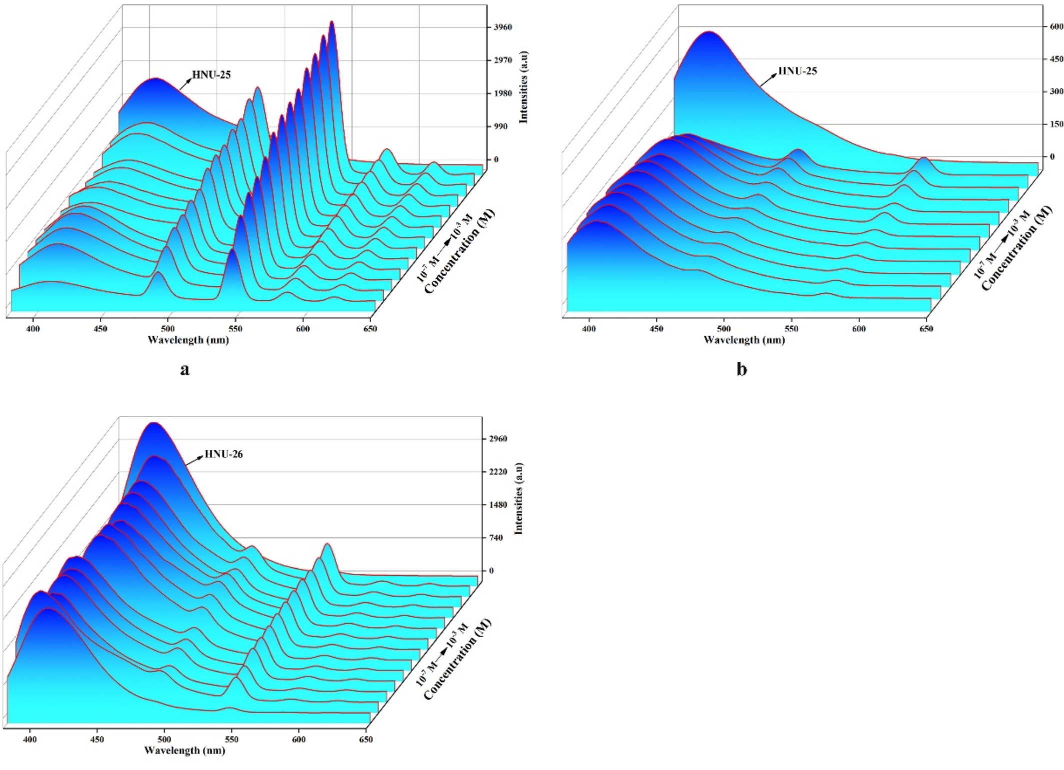


Fig. S5 (a) Excitation spectrum (λ_{ex} = 351nm) and the emission spectra of **HNU-25** with Tb^{3+} ion and Dy^{3+} ion in DMF; (b) Excitation spectrum (λ_{ex} = 353nm) and the emission spectra of **HNU-26** with Tb^{3+} ion in DMF.



a

b

c

Fig. S6 (a) The luminescence spectra of **HNU-25** in DMF with different concentration of Tb^{3+} ion from $1x10^{-7}$ to $1x10^{-3}$ M; (b) The luminescence spectra of **HNU-25** in DMF with different concentration of Dy^{3+} ion from $1x10^{-7}$ to $1x10^{-3}$ M; (c) The luminescence spectra of **HNU-26** in DMF with different concentration of Tb^{3+} ion from $1x10^{-7}$ to $1x10^{-3}$ M.

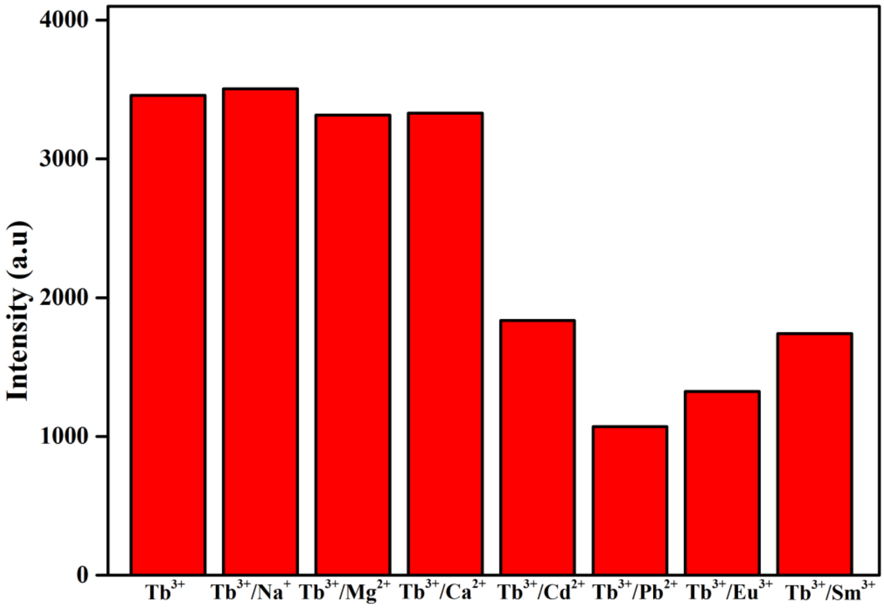
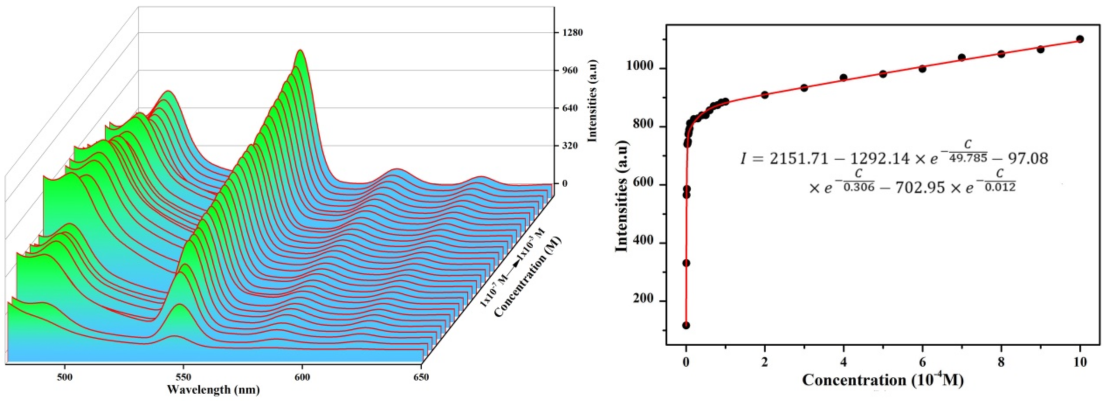


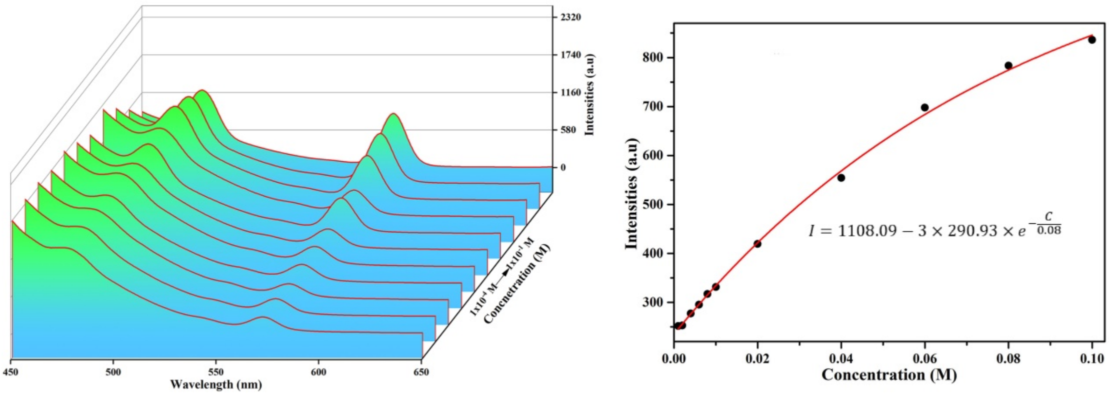
Fig. S7 Luminescence responses of **HNU-25** towards Tb^{3+} ion in the presence of a background of other metal ions (the luminescence emission monitored at 544 nm).



a

b

Fig. S8 (a) The luminescence spectra of **HNU-26** in DMF with different concentration of Tb^{3+} ion from 1x10^{-7} to 1x10^{-3} M ($\lambda_{ex} = 353$ nm); (b) Nonlinear fitting of concentration and the intensity of Tb^{3+} ion emission peak at 544 nm.



a

b

Fig. S9 (a) The luminescence spectra of **HNU-25** in DMF with different concentration of Dy^{3+} ion from 1x10^{-4} to 1x10^{-1} M ($\lambda_{ex} = 351$ nm); (b) Nonlinear fitting of concentration and the intensity of Dy^{3+} ion emission peak at 576 nm.

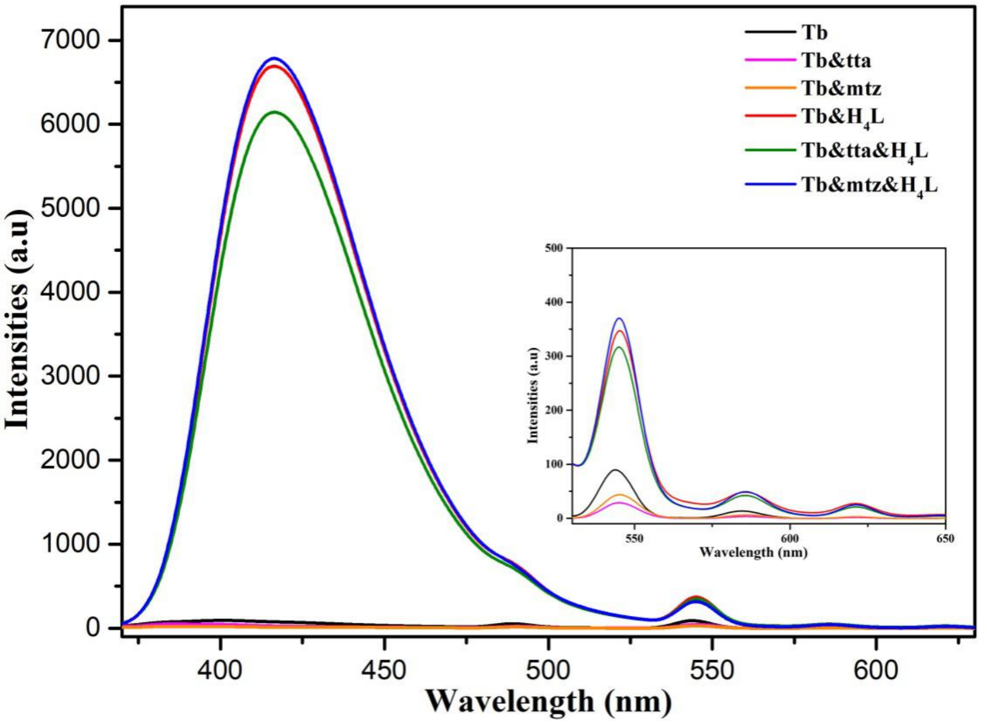


Fig. S10 The luminescence effect of organic ligands on Tb^{3+} ion.

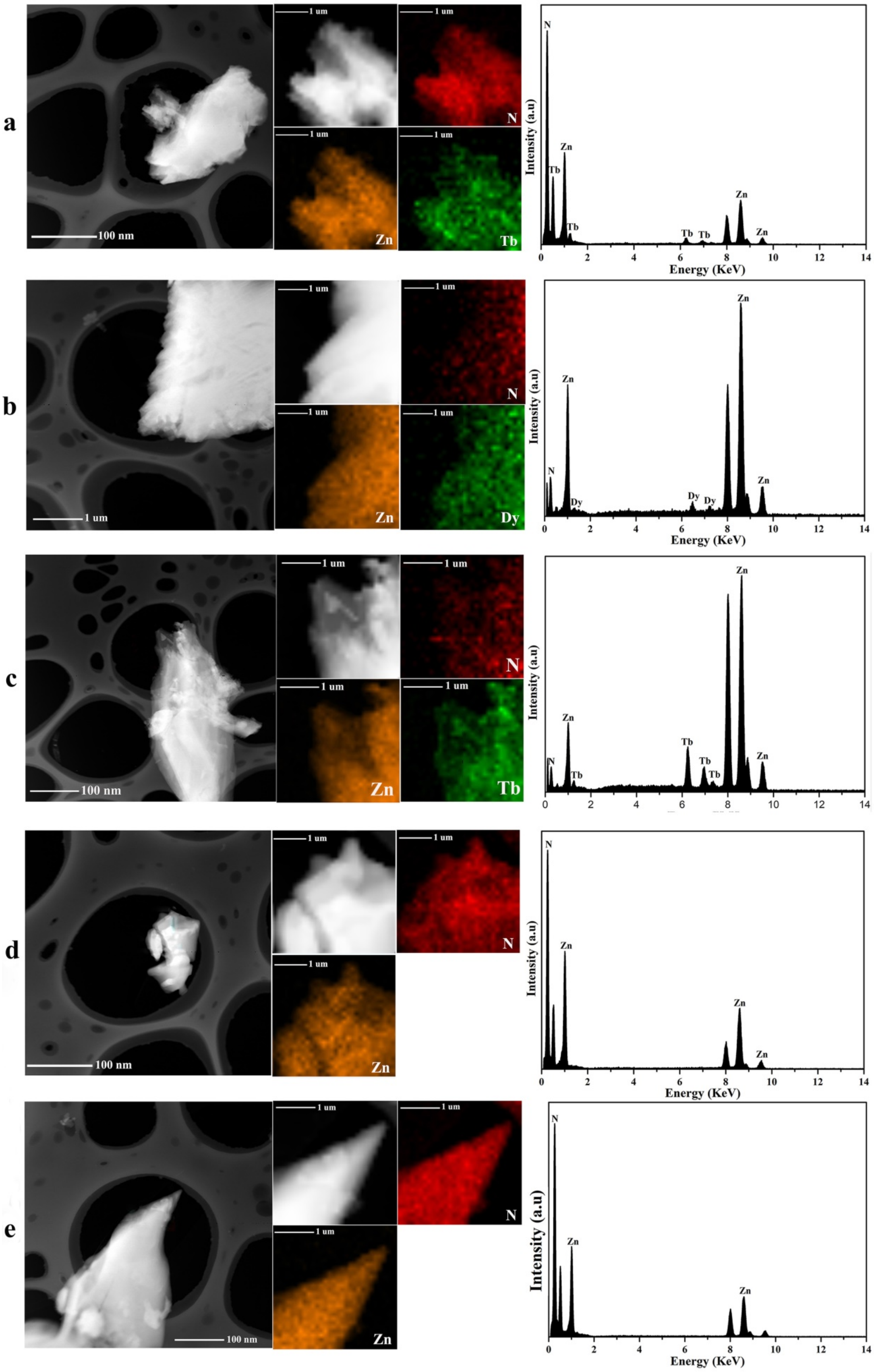


Fig.S11 (a) HRTEM image of Tb@**HNU-25**, EDS-mapping images of Tb@**HNU-25,** EDX spectrum of the Tb@**HNU-25** (from left to right); (b) HRTEM image of Dy@**HNU-25**, EDS-mapping images of Dy@**HNU-25**, EDX spectrum of the Dy@**HNU-25**; (c) HRTEM image of Tb@**HNU-26**, EDS-mapping images of Tb@**HNU-26**, EDX spectrum of the Tb@**HNU-26**. (d) HRTEM image of **HNU-25**, EDS-mapping images of **HNU-25,** EDX spectrum of the **HNU-25**; (e) HRTEM image of **HNU-26**, EDS-mapping images of **HNU-26,** EDX spectrum of the **HNU-26**.

Table S2 Luminescent lifetime (τ) and absolute quantum yield (φ) of the **HNU-25**, Tb@**HNU-25,** Dy@**HNU-25, HNU-26** and Tb@**HNU-26**.

Sample	**τ (μs)**	**φ (%)**
HNU-25	**1.42**	**16.2**
Tb@HNU-25	**2.00**	**28.2**
Dy@HNU-25	**1.53**	**25.7**
HNU-26	**1.03**	**16.2**
Tb@HNU-26	**1.55**	**27.8**

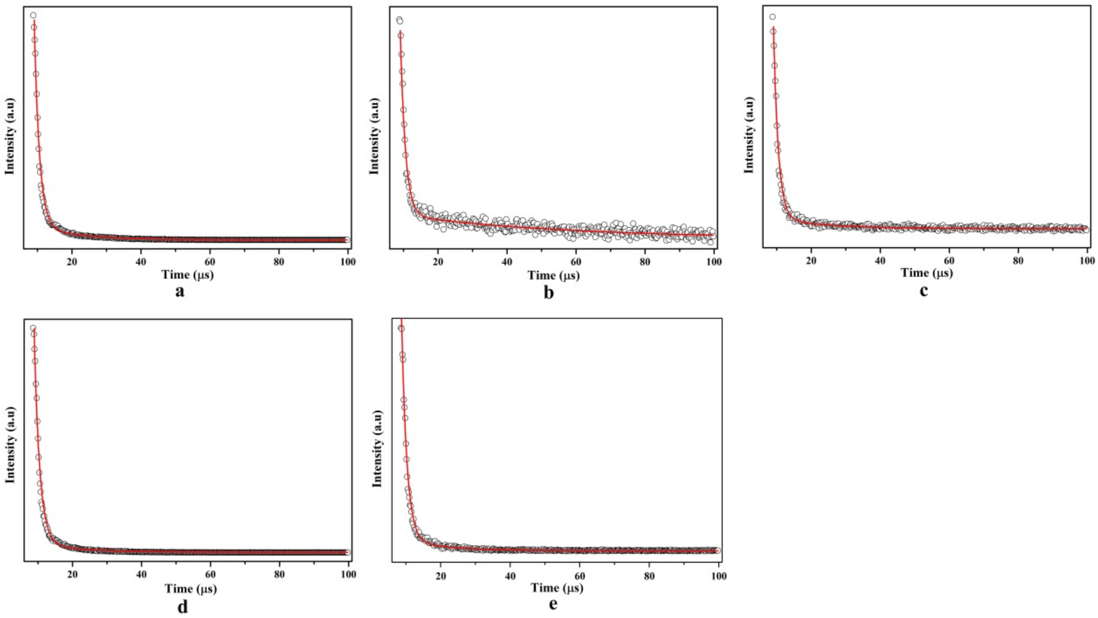


Fig. S12 Luminescence decay curves. (a) τ = 1.42 μs for **HNU-25**, (b) τ = 2.00 μs for Tb@**HNU-25**, (c) τ = 1.53 μs for Dy@**HNU-25**; (d) τ =1.03 μs for **HNU-26**, (e) τ =1.55 μs for Tb@**HNU-26**.

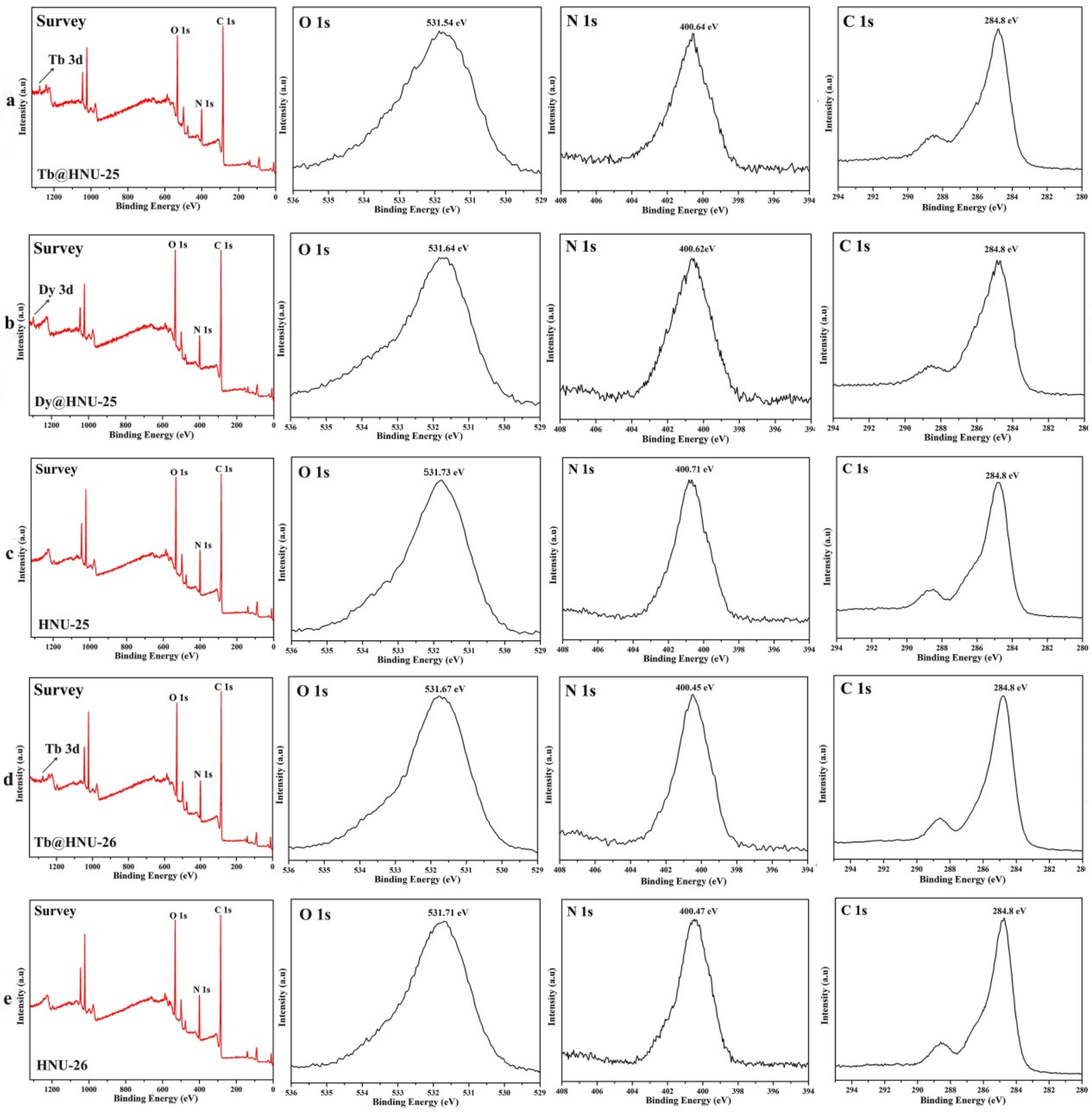


Fig. S13 (a) XPS survey spectra as well as C 1s, N 1s, O 1s spectra of the Tb@**HNU-25**; (b) XPS survey spectra as well as C 1s, N 1s, O 1s spectra of the Dy@**HNU-25**. (c) XPS survey spectra as well as C 1s, N 1s, O 1s spectra of the **HNU-25**. (d) XPS survey spectra as well as C 1s, N 1s, O 1s spectra of the Tb@**HNU-26**; (e) XPS survey spectra as well as C 1s, N 1s, O 1s spectra of the **HNU-26**.

references

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