Supporting information

Super Metal-Hydrogels Constructed from Simple Tripodal Gelator with Rare Earth Metal Ions and Its Application in Highly Selective and Ultrasensitive Detection Histidine

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Materials and General Methods:

Materials: 4-aminopyridine, trimesoyl chloride, DMF, triethylamine, ethyl alcohol, Tb^{3+}, Eu^{3+}, La^{3+} and Ce^{3+} and acids were reagent grade and used as received. Solvents were either employed as purchased or dried by $CaCl_2$. Fresh double distilled water was used throughout the experiment. Nuclear magnetic resonance (NMR) spectra were recorded on Varian Mercury 400 instruments. Mass spectra were recorded on a Bruker Esquire 6000 MS instrument. The infrared spectra were performed on a Digilab FTS-3000 Fourier transform-infrared spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Study of scanning electron microscopy (SEM), Determination of the SEM images was performed on a JSM-6701F FE-SEM microscope.

Preparation of water suspension of TP: About 10 mg of **TP** was weighed out in a test bottle. Then, 2.0 mL deionized water was added into that test bottle followed by shaking for 1−3 min at room temperature, producing a viscous and milky suspension (0.5%).

Preparation of hydrogel based on Tb^{3+}, Eu^{3+}, La^{3+} and Ce^{3+}: To a solution of Tb^{3+}, Eu^{3+}, La^{3+} and Ce^{3+} (20 μL, 0.1 M) was added into the emission of **TP** (200 μL, 0.5 %). The mixture of emission and Tb^{3+}, Eu^{3+}, La^{3+} and Ce^{3+} was heated to obtain a colorless solution, cooling the above solution to give white hydrogel.

Fluorescence titration: A serious of the gel with different equivalents guests were prepared by dissolving **TP** (2 mg) and proper equivalent of guest in water (400 μL). Then record their fluorescence intensity at 467 nm.

Calculation formula of LOD:

Linear Equation: y=Ax + B

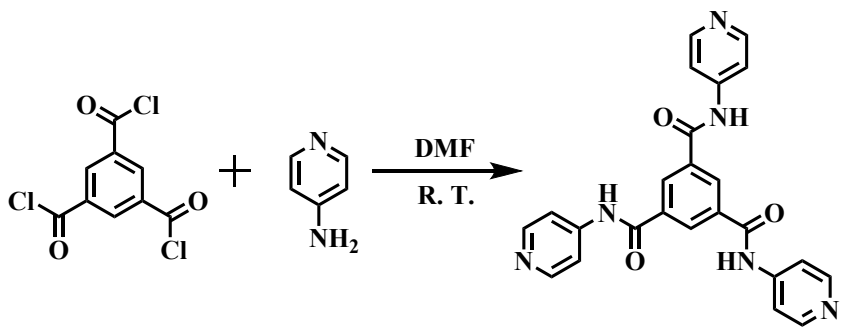
$$\delta = \sqrt{\frac{\Sigma(Fi - F0)^2}{N-1}}(N = 20),$$

S=A×10^6,

$$LOD = K \times \frac{\delta}{s}(K = 3)$$

State, Fi: the fluorescence intensity of **TP-Eu** or **TP-La** with different concentration His at λ_{ex}= 467 nm; F0: the average of 20 times fluorescence intensity of **TP-Eu** or **TP-La** at λ_{ex}= 467 nm; A: Slope of linear fitting of fluorescence titration; B: intercept of linear fitting of fluorescence titration.

Results and Discussion:



Scheme S1. The synthesis of **TP.**

The gelator **TP** was synthesized by simple classical reaction between 4-aminopyridine and trimesoyl chloride. To a solution of mixture of trimesoyl chloride (0.2639 g, 1.0 mmol) and triethylamine (1-2 d) was slowly dropwise added into the solution of 4-aminopyridine (0.3105 g, 3.3 mmol) in DMF (10 mL), the mixture was stirred at room temperature for 12 h, appearing a pale solid. The solid is vacuumed suction filtration and washed with cold ethyl alcohol (10 ml), finally the product solid was followed by drying in a vacuum oven at 40 °C for 24 h. Yield: 0.0421g (96%). M.P.: 167-168 °C.

^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ (ppm): 11.78 (s, 3 H), 8.99 (s, 3 H), 8.68 (m, 6 H), 8.25 (m, 6 H); ^{13}C NMR (DMSO-d_6, 150MHz): 165.68, 149.58, 135.07, 131.36, 114.75; ESI-MS m/z: [M]+ Calcd: $C_{24}H_{18}N_6O_3$: 439.14, found 439.19; IR (anhydrous KBr, cm^{-1}) v: 3421 (w) (N-H), 3080 (w) (C-H on pyridyl and phenyl group), 1710 (w) (C=O), 1508 (w) (C=N on pyridyl).

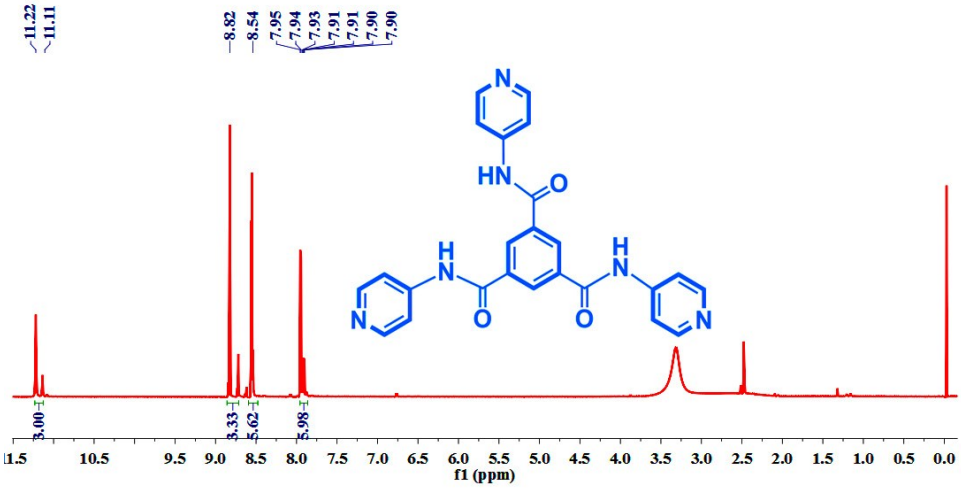


Figure S1. The ^{1}H NMR Spectrum of **TP**.

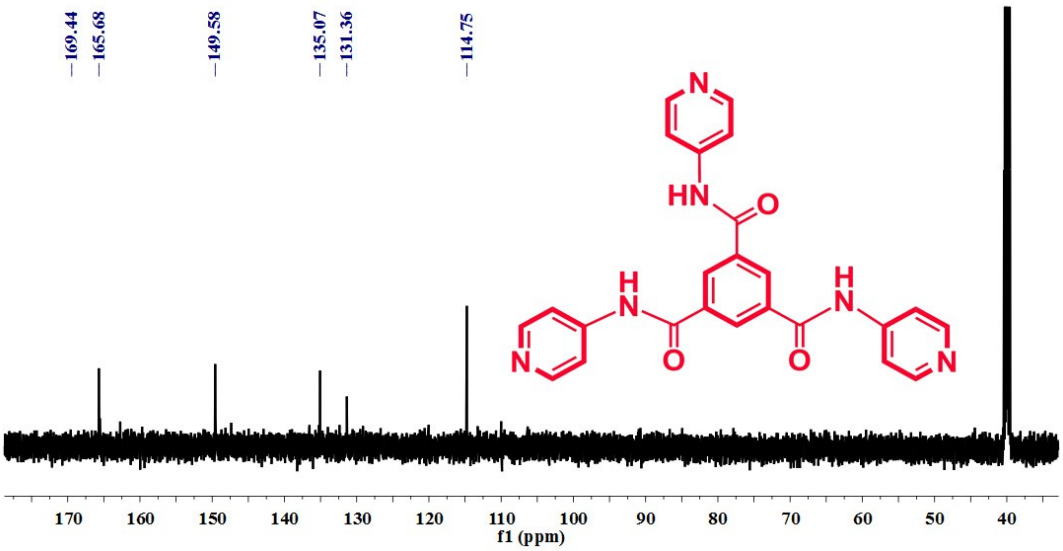


Figure S2. The ^{13}C NMR spectrum of **TP**.

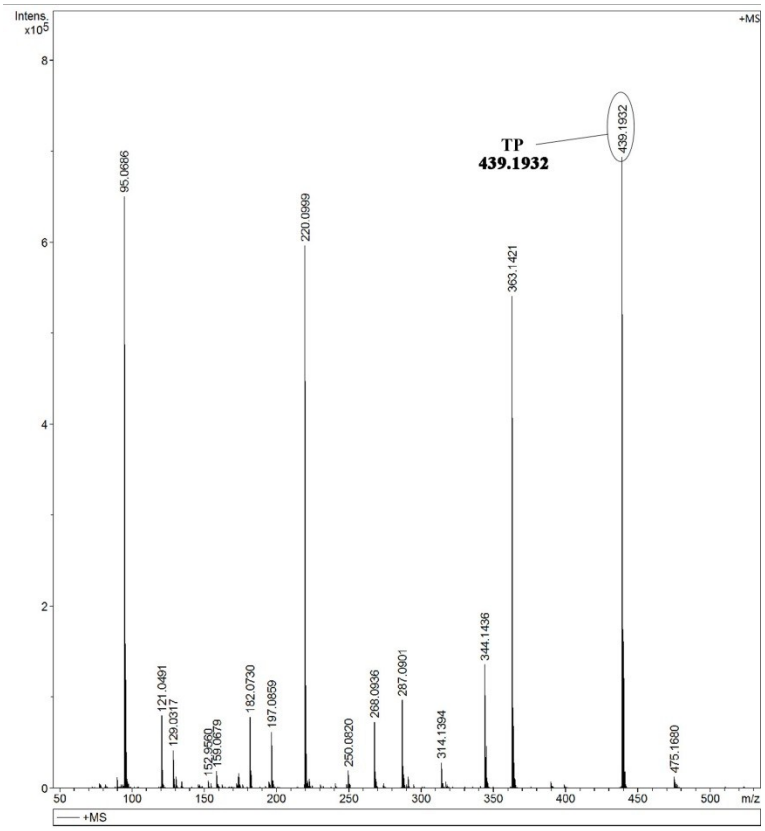


Figure S3. Mass spectrum of **TP.**

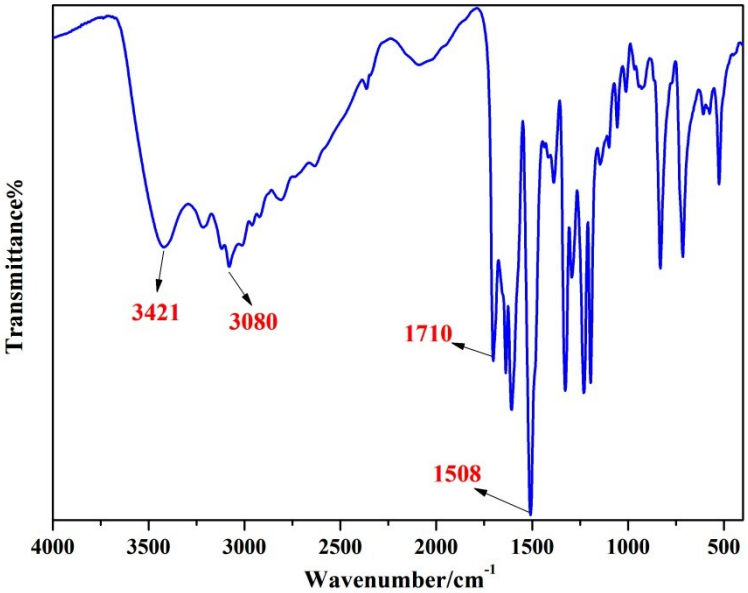


Figure S4. IR spectrum of **TP**.

Table S1. Gelation property of super supramolecular metallo-hydrogels**.**

Ion	Solution	State	CGC(%)	Tgel(℃)
Tb^{3+}	H_2O	G	0.5%	57-59 (0.5%)
Eu^{3+}	H_2O	G	0.5%	75-77 (0.5%)
La^{3+}	H_2O	G	0.5%	55-57 (0.5%)
Ce^{3+}	H_2O	G	0.5%	52-54 (0.5%)

G=gelation

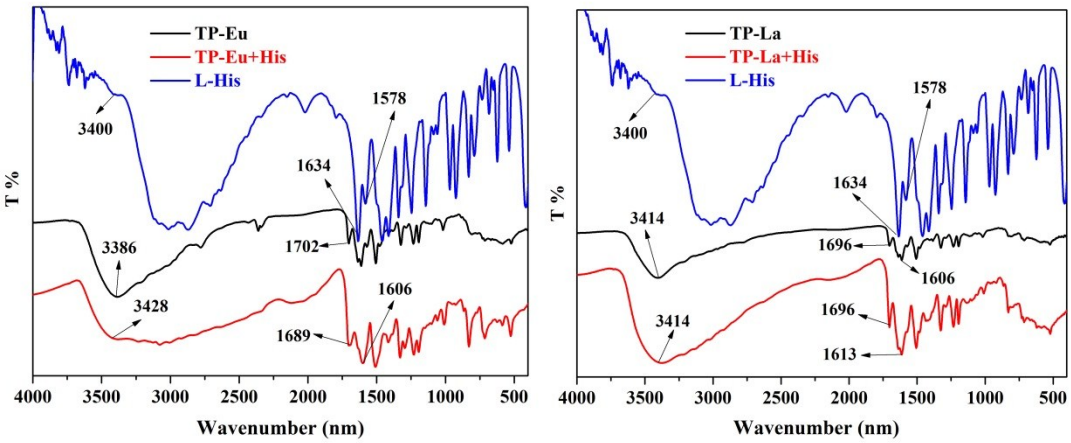


Figure S5. FT-IR spectra of His, xerogel of **TP-Ms** and **TP-Ms**+ His (**TP-Ms**: **TP-Eu**, **TP-La**).

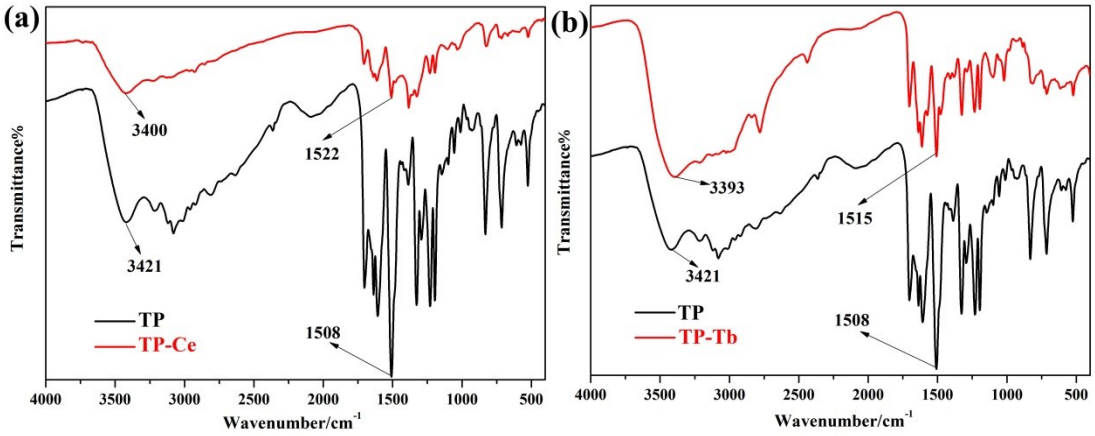


Figure S6. FT-IR spectra of **TP** and xerogel of **TP-Ms:** (a) **TP-Ce**, (b) **TP-Tb**.

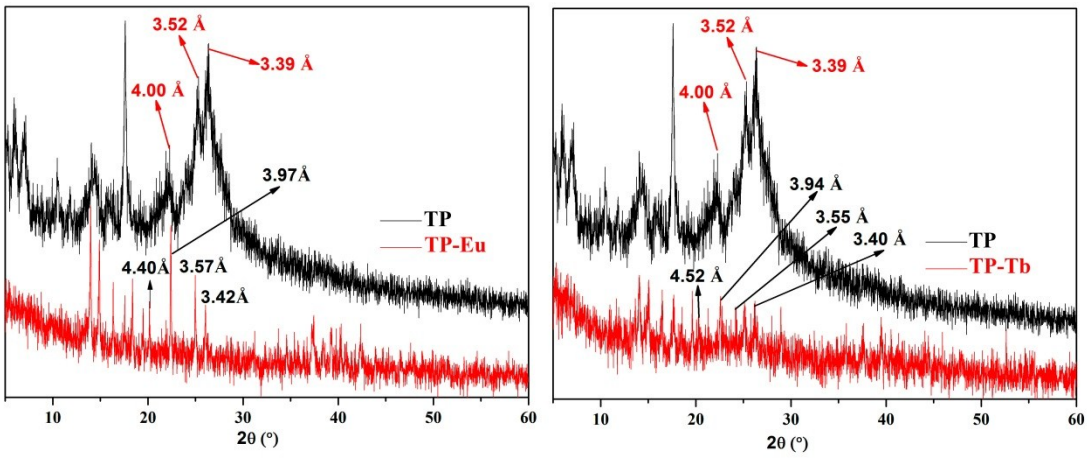


Figure S7. The Powder XRD spectra of **TP** and xerogel of **TP-Eu** and **TP-Tb**.

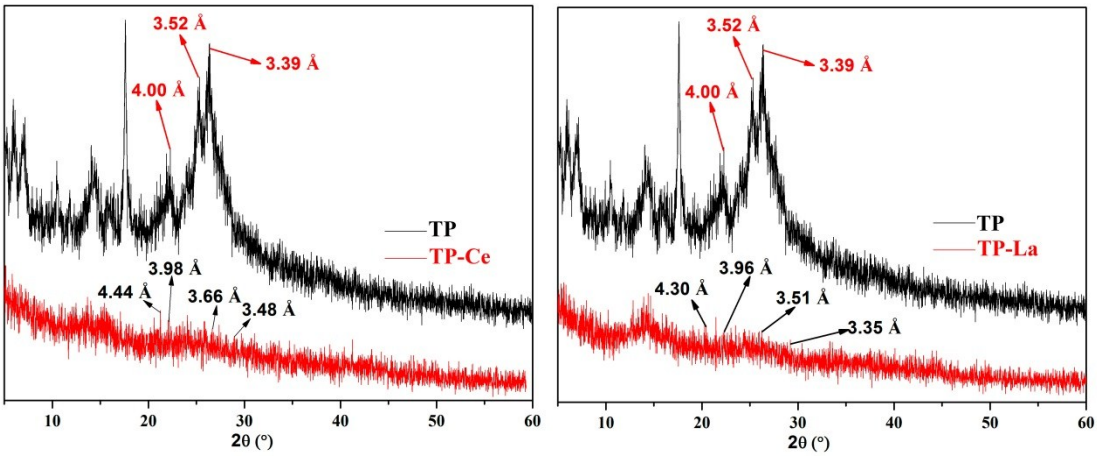


Figure S8. The Powder XRD specta of **TP** and xerogel of **TP-Ce** and **TP-La**.

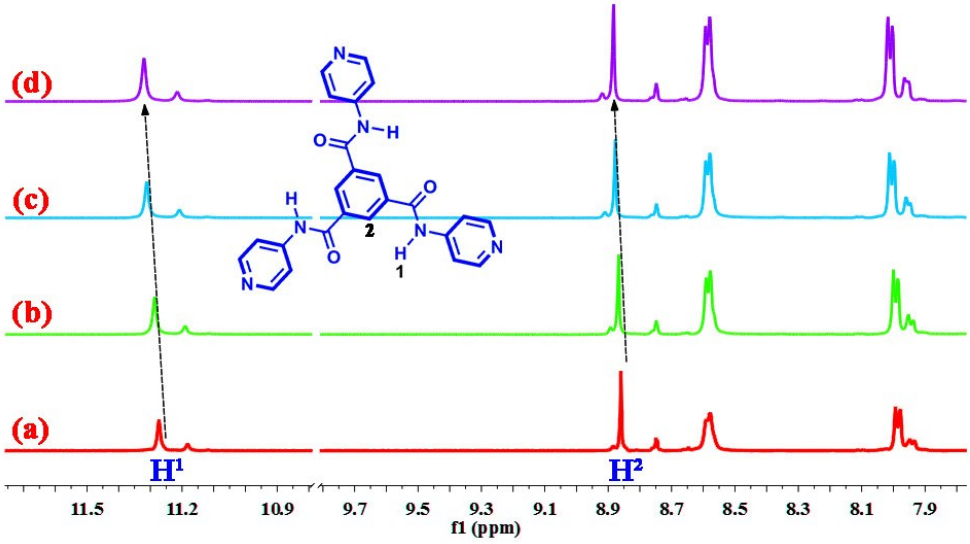


Figure S9. Partial concentration-dependent ^{1}H NMR spectra of the mixture of **TP** in DMSO-d_6: (a) 1.37 × 10^{-2} M; (b) 1.82 × 10^{-2} M; (c) 2.28 × 10^{-2} M; (d) 2.73 × 10^{-2} M.

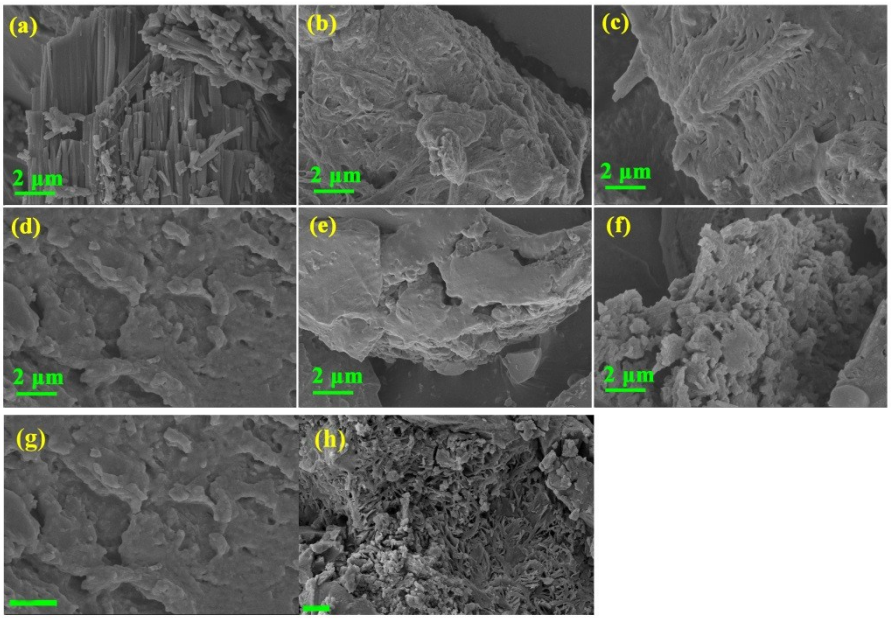


Figure S10. SEM images of (a) **TP** (fibre structure), (b) **TP-Tb** (aggregation structure), (c) **TP-Eu** (aggregation structure), (d) **TP-La** (aggregation structure), (e) **TP-Ce** (aggregation structure), (g) **TP-Eu**+His (aggregation structure), (h) **TP-La**+His (aggregation structure).

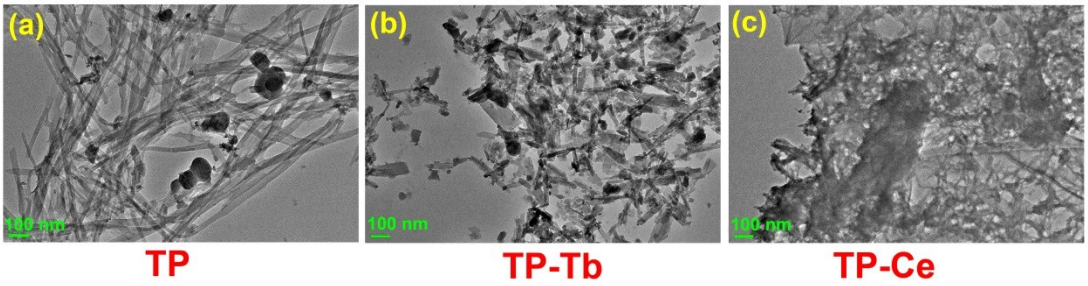


Figure S11. TEM images of (a) **TP**, (b) **TP-Eu** and (c) **TP-Ce.**

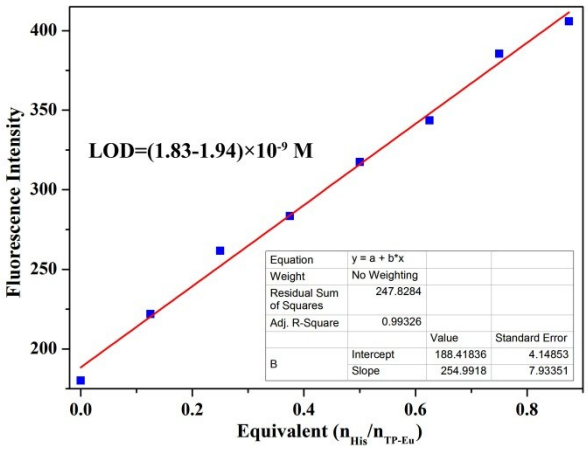


Figure S12. Fluorescence titration linear range of **TP-Eu** for His by addition various concentrations His into **TP-Eu**.

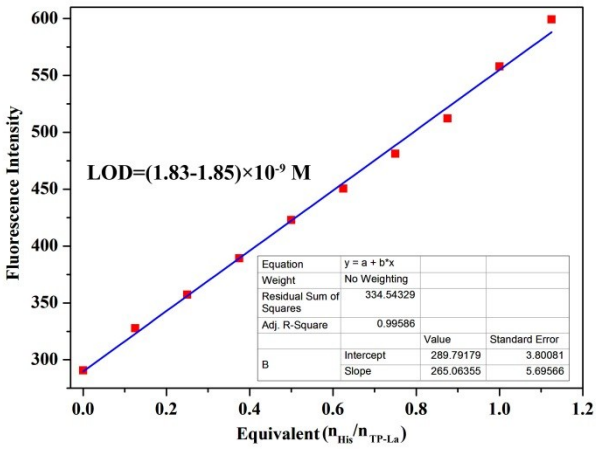


Figure S13. Fluorescence titration linear range of **TP-La** for His by addition various concentrations His into **TP-La**.