SUPPLEMENTARY INFORMATION

A ratiometric fluorescent pH sensor based on nanoscale metal-organic frameworks (MOFs) modified by europium (Ⅲ) complex

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Experiment

Chemicals. Chemicals were purchased from commercial sources. All solvents were analytical grade and without further purification. $Eu(NO_3)_3 \cdot xH_2O$ were prepared by dissolving oxides Eu_2O_3 in concentrated nitric acid (HNO_3). MOF-253 (Al(OH)(bpydc)) is synthesized according to the references.[S1]

Physical characterization. X-ray diffraction patterns (SAXRD) are recorded on a Rigaku D/ max-Rb diffractometer equipped with a Cu anode in a 2θ range from 5 to 45 °. Transmission electron microscope (TEM) experiments were conducted on a JEM-4000EX microscope operated at 400 kV. Nitrogen adsorption/desorption isotherms are measured by using a Nova 1000 analyzer under the liquid nitrogen temperature. Luminescence excitation and emission spectra are obtained on Edinburgh FLS920 spectrophotometer. Luminescence lifetime measurements are carried out on an Edinburgh FLS920 phosphorimeter using a microsecond pulse lamp as excitation source. The data of life time is achieved from fitting the experiment luminescent decay. The measurement of metal ion was performed on Agilent 7700X inductively coupled plasma-mass spectrometer (ICPMS). UV-Vis spectra are record on Agilent 8453. Scanning electronic microscope (SEM) was measured on Hitachi S-4800. Absolute quantum yield (QY) measurements is made by exciting the samples with diffuse light within an integrating sphere.

MOF-253. MOF-253 was prepared from hydrothermal reaction of $AlCl_3 \cdot 6H_2O$ (151 mg, 0.625 mmol), 2,2'-bipyridine-5,5'-dicarboxylic acid (153 mg, 0.625 mmol) and 10 mL N,N'-dimethylformamide (DMF) at 120 °C for 24 hrs. The resulting white microcrystalline powder was then collected with by centrifugation and washed with DMF. The solid products were washed with methanol viasoxhlet extraction for 24 hrs, and then was collected by filtration and finally dried at 200 °C under vacuum for 12 hrs to give [Al (bpydc)(OH)], MOF-253 (165 mg, 92.5 %).

MOF-253-Eu. The compound Al(OH)(bpydc) (28.6 mg, 0.10 mmol), solution of $Eu(NO_3)_3 \cdot xH_2O$ in the acetonitrile (10 mL, 10 mmol/L) and acetonitrile (5 mL) were added to a Tefloncapped 20 mL scintillation vial and heated on a hotplate at 65 °C for 24 hrs. The resulting white solid product was washed with acetonitrile by

ultrasonic three times and dried at 65 °C under vacuum for 12 hrs to give MOF-253-Eu (58.2 mg, 94.1 %). ICP analysis showed that the molar ration of Al^{3+}/Eu^{3+} was 1:0.99.

MOF-253-Eu-TTA. The MOF-253-Eu (62 mg, 0.1 mmol), solution of TTA in the acetonitrile (0.5 mL, 50 mmol/L), thriethylamine in the acetonitrile (0.5 mL, 50 mmol/L) and acetonitrile (15 mL) were added to a Tefloncapped 20 mL scintillation vial and heated on a hotplate at 65 °C for 24 hrs. The resulting white solid product was collected by centrifugation and washes with acetonitrile by ultrasonic three times and dried at 60 °C under vacuum for 12 hrs to give MOF-253-Eu-TTA (69 mg, 89.1 %).

MOF-253-Eu@TTA. The preparation of MOF-253-Eu@TTA is the same as the MOF-253-Eu-TTA, except for no thriethylamine added in the process. The amounts of MOF-253-Eu and TTA are the same as the MOF-253-Eu-TTA, too.

pH-dependence luminescent studies. The method of studying pH-dependence luminescence is referred to the reported work.[S2] 1 mg of MOF-253-Eu-TTA was dispersed in 5 mL of Milli-Q water by and sonicated for 10 min. 100 μL of this solution was added to the correspondent cuvettes containing 800 μL of Milli-Q water in the range of pH from 5.0 to 7.7 (adjusted using HCl or NaOH). The fluorescence spectra (λ_{ex} = 330 nm and 375 nm) were recorded after 5 min of equilibration time.

UV-Vis spectra for studying the amounts of TTA in the solution. The UV-Vis spectra of the amount of TTA before adding MOF-253-Eu is recorded on a solution with 15 ml acetonitrile and 0.5ml TTA solution in the acetonitrile (50 mmol/L). After adding MOF-253-Eu and reacting 24h, the resulting white solid product was collected by centrifugation (16000 rpm, 5 mins). The filtrate after centrifugation is used to measure the amount of TTA by the UV-Vis spectra, and record as the UV-Vis spectra of the amount of TTA after adding MOF-253-Eu.

The luminescent recover experiment of MOF-253-Eu-TTA after soaked in pH= 5 aqueous solution. The MOF-253-Eu-TTA which have been soaked in pH= 5 aqueous solution is collected by centrifugation and cleaned by water and acetonitrile. The dried produce is soaked in the solution with triethylanmine and heated on a hotplate at 65 °C for 24 hrs. The resulting white solid product was collected by centrifugation and washes with acetonitrile by ultrasonic three times and dried at 60 °C under vacuum for 12 hrs

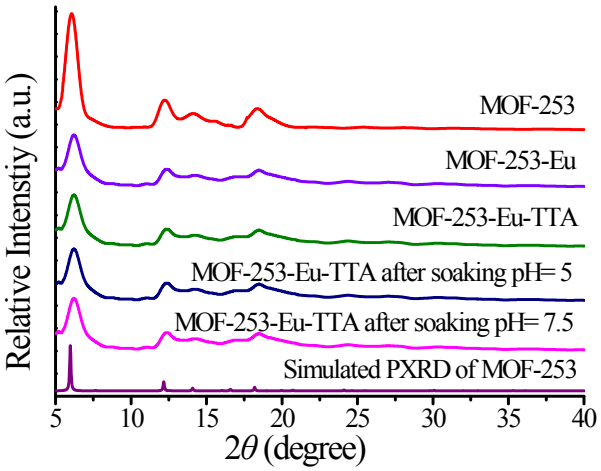

Figure S1. PXRD for MOF-253, MOF-253-Eu, MOF-253-Eu-TTA, MOF-253-Eu-TTA after soaking pH = 5 and MOF-253-Eu-TTA after soaking pH = 7.7, the PXRD of MOF-253 is consistent with reported literature.[S1]

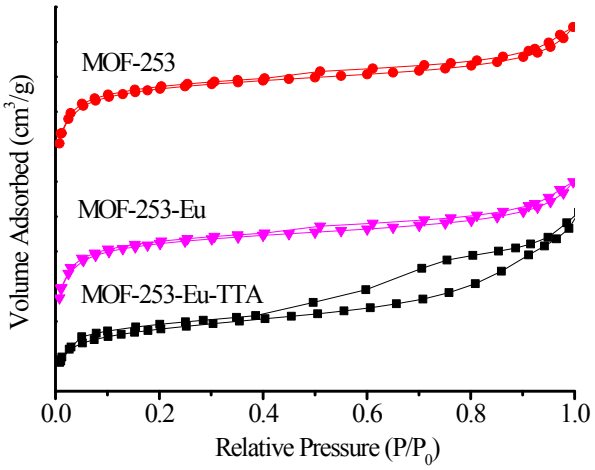

Figure S2. N_2 adsorption-desoption isotherms of MOF-253, MOF-253-Eu and MOF-253-Eu-TTA, the Langmuir surface areas of MOF-253, MOF-253-Eu and MOF-253-Eu-TTA were calculated to be 1188, 728 and 287 m^2/g, the Langmuir surface areas of MOF-253 is consistent with reported literature[S3]

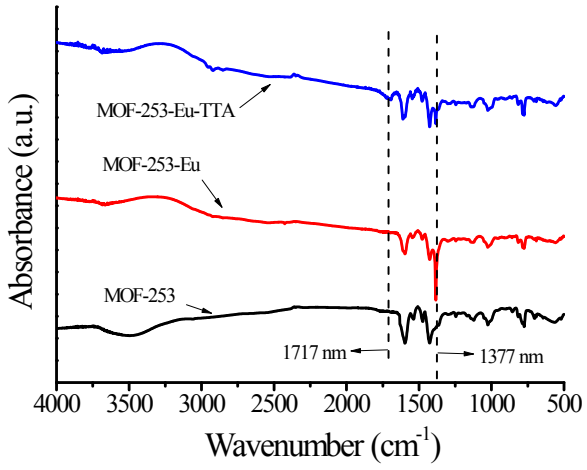

Figure S3. FT-IR spectra of MOF-253, MOF-253-Eu and MOF-253-Eu-TTA.

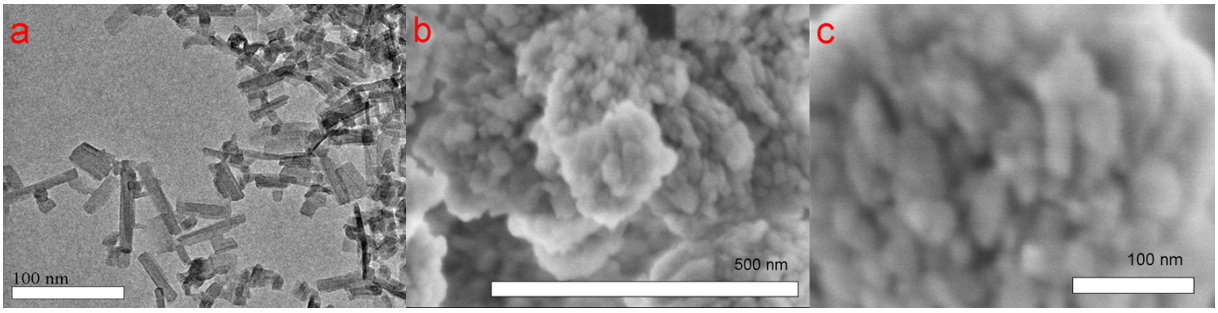

Figure S4. The TEM (a) and SEM (b and c) of MOF-253-Eu-TTA.

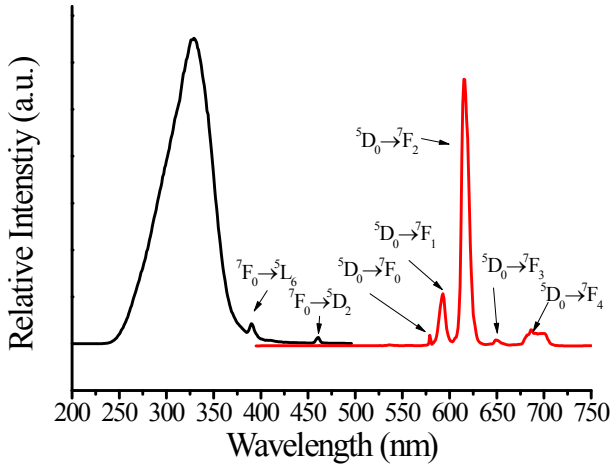

Figure S5. The excitation (black) and emission spectra (red) of MOF-253-Eu (the λ_{em} = 614 nm and the λ_{ex} = 330 nm).

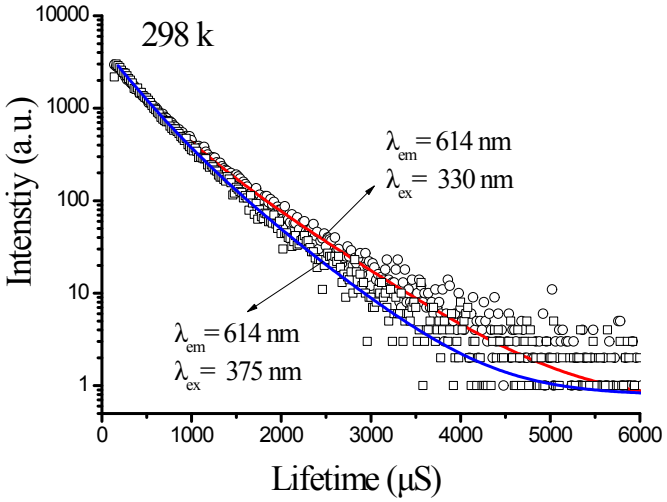

Figure S6. The decay curve of MOF-253-Eu-TTA, the red is obtained under λ_{em} = 614 nm and the λ_{ex} = 330 nm, the blue is obtained under λ_{em} = 614 nm and the λ_{ex} = 375 nm, which is record under 298 k.

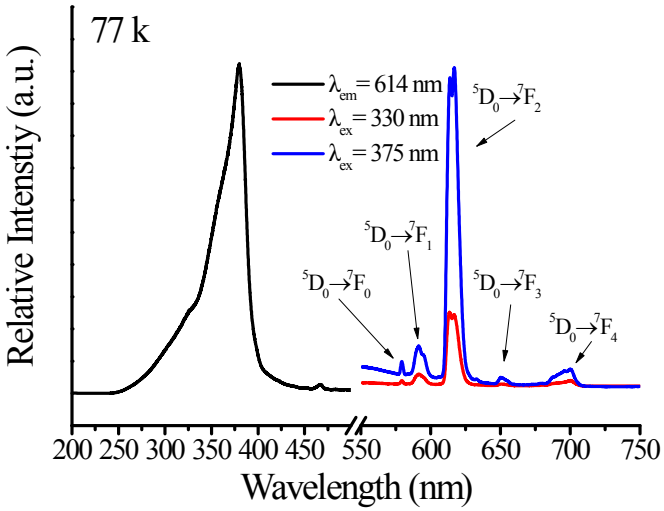

Figure S7. The excitation spectrum (λ_{em} = 614 nm) of MOF-253-Eu-TTA (black) and the emission spectra of MOF-253-Eu-TTA, λ_{ex} = 330 nm (red) and λ_{ex} = 375 nm (blue), which is record under 77 k.

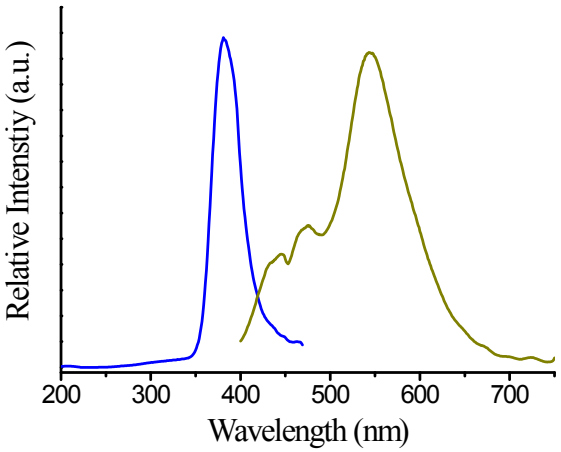

Figure S8. The excitation (blue) and PL spectra (yellow) of MOF-253 (λ_{em} = 550 nm and λ_{ex} = 385 nm).

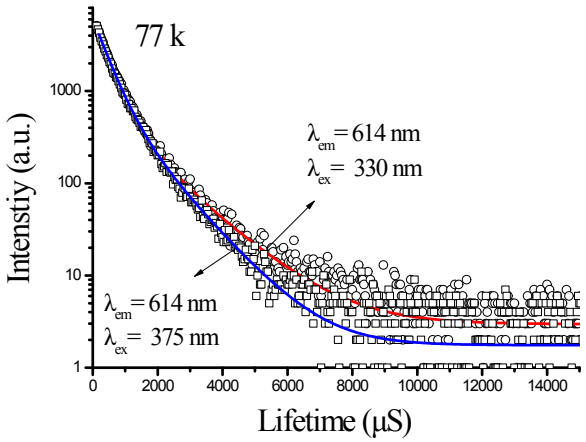

Figure S9. The decay curve of MOF-253-Eu-TTA, the red is obtained under λ_{em} = 614 nm and the λ_{ex} = 330 nm, the blue is obtained under λ_{em} = 614 nm and the λ_{ex} = 375 nm, which is record under 77 k.

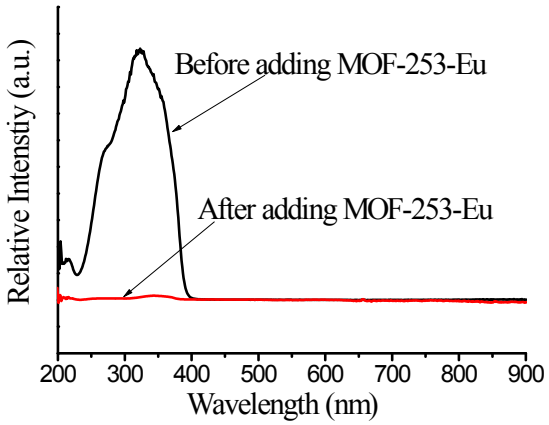

Figure S10. The UV-Vis spectra of the solution before adding MOF-253-Eu and after adding MOF-253-Eu

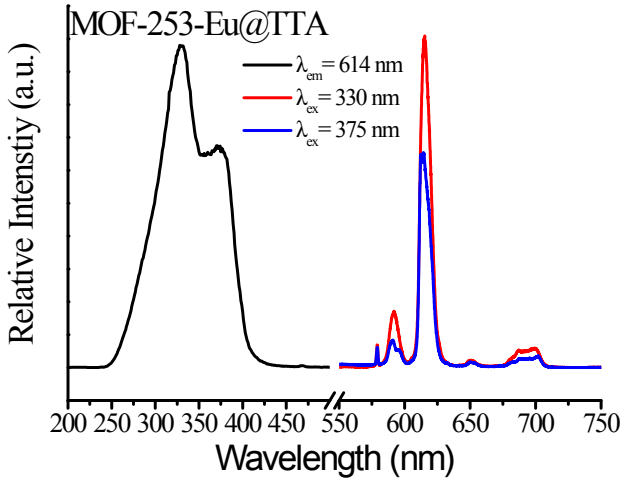

Figure S11. The excitation spectrum (λ_{em} = 614 nm) of MOF-253-Eu-TTA (black) and the emission spectra of MOF-253-Eu-TTA, λ_{ex} = 330 nm (red) and λ_{ex} = 375 nm (blue)

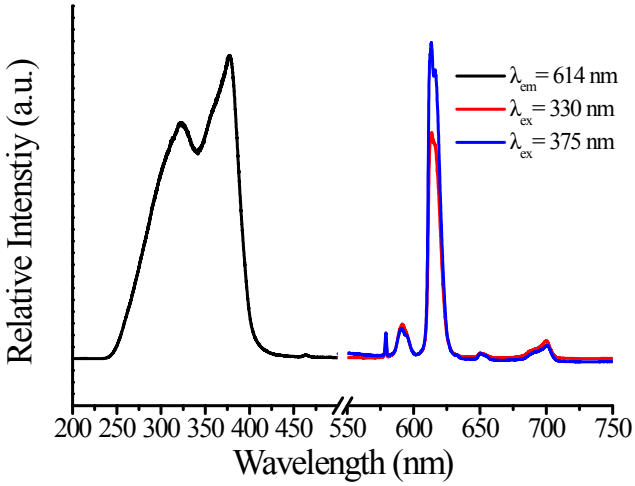

Figure S12. The excitation spectrum (λ_{em} = 614 nm) of MOF-253-Eu-TTA after luminescent recovering (black) and the emission spectra of MOF-253-Eu-TTA after luminescent recovering, λ_{ex} = 330 nm (red) and λ_{ex} = 375 nm (blue)

Table S1. The intensity ration of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ for MOF-253-Eu-TTA (λ_{ex} = 375 nm) in different pH aqueous solution

pH	The intensity ration of $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$ (λ_{ex} = 375 nm)
5.0	8.3
5.5	8.7
5.8	8.9
6.4	9.5
7.2	10.3
7.7	10.2

REFERENCES

S1. E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382.

S2. J. Aguilera-Sigalat and D. Bradshaw, *Chem. Commun.*, 2014, **50**, 4711

S3. F. Carson, S. Agrawal, M. Gustafsson, A. Bartoszewicz, F. Moraga, X. D. Zou, B. Martin-Matute, *Chem-Eur. J.* 2012, **18**, 15337.