

Electronic Supplementary Material (ESI) for

This journal is © The Royal Society of Chemistry 2019

**pH-modulated luminescence switching in a Eu-MOF: rapid
detention of acidic amino acids**

Yifang Zhao, Meng-Yan Wan, Jian-Ping Bai, Heng Zeng, Weigang Lu, Dan Li*

College of Chemistry and Materials Science, Jinan University, Guangzhou 510632, P. R. China

E-mail: danli@jnu.edu.cn

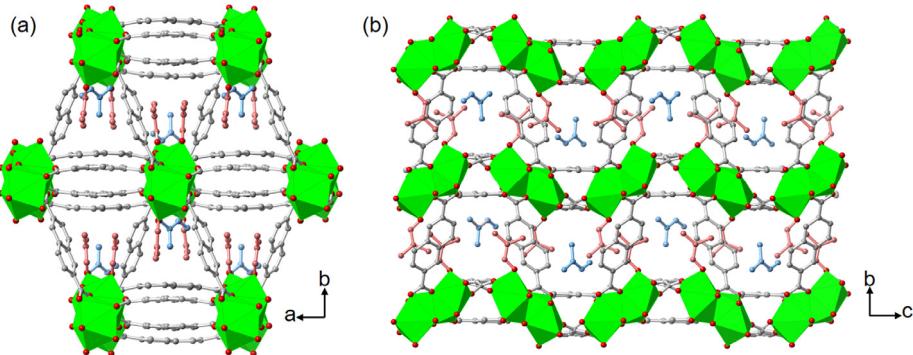


Fig. S1 3D structures of Eu-MOF (**1**) along c axis (a) and a axis (b) of the as-synthesized framework. The red balls represent the coordinated DMF molecules and the blue ones are the non-coordinated DMF molecules.

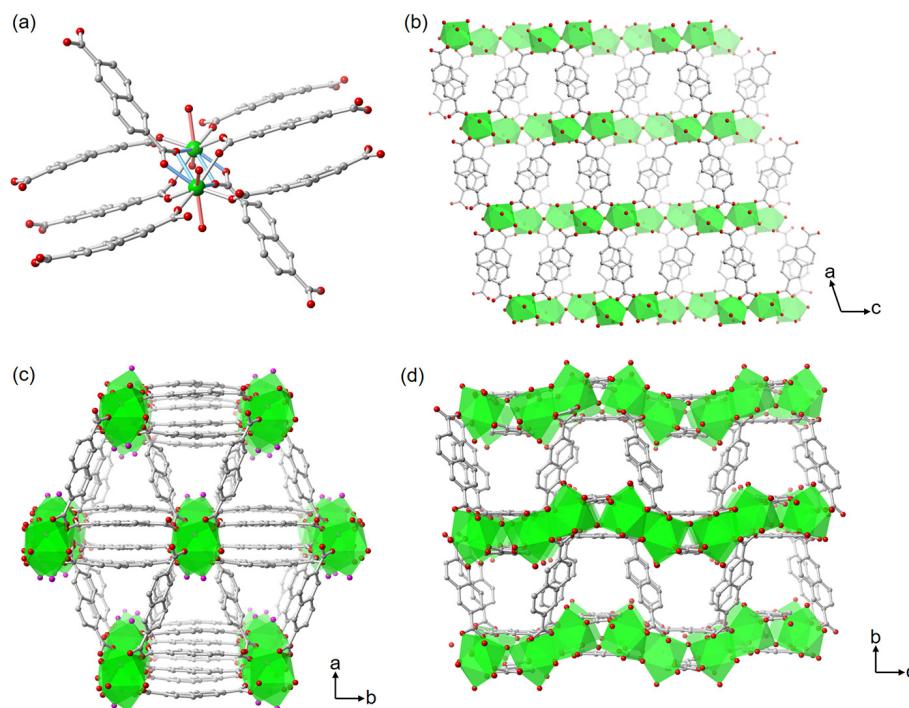


Fig. S2 (a) Coordination environments of a pair of Eu ions; (b) a packed 2D layers along b axis; and perspective view of the channels along c axis (c) and a axis (d) of **2** after the detection experiment. The hydrogen atoms are omitted for clarity. The red balls represent the bridging and terminal water molecules.

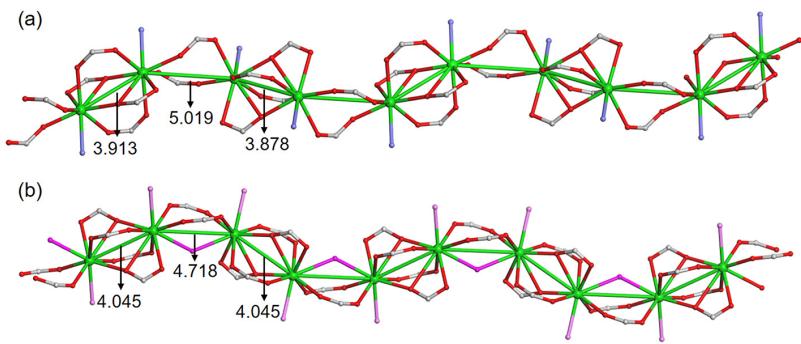


Fig. S3 The Eu chains along c axis before (a) and after (b) detection experiment. The numbers represent the distances between Eu ions in Å.

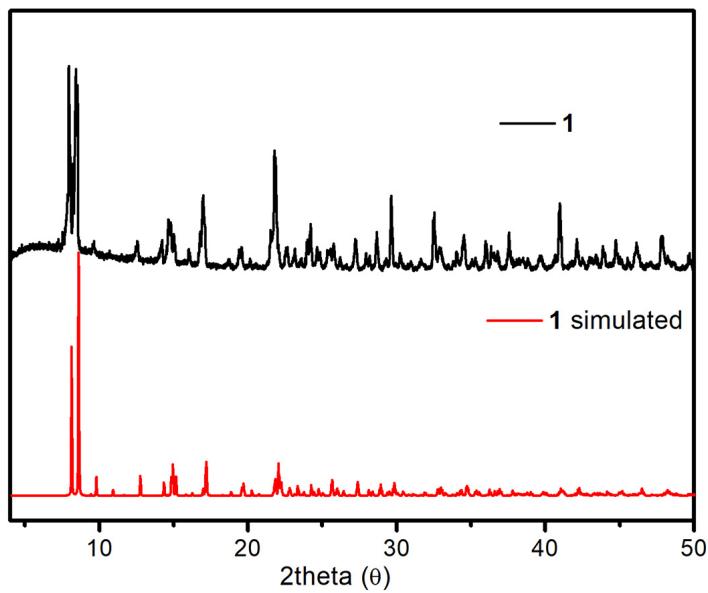


Fig. S4 Simulated and experimental powder X-ray diffraction patterns (PXRD) of the as-synthesized **1**.

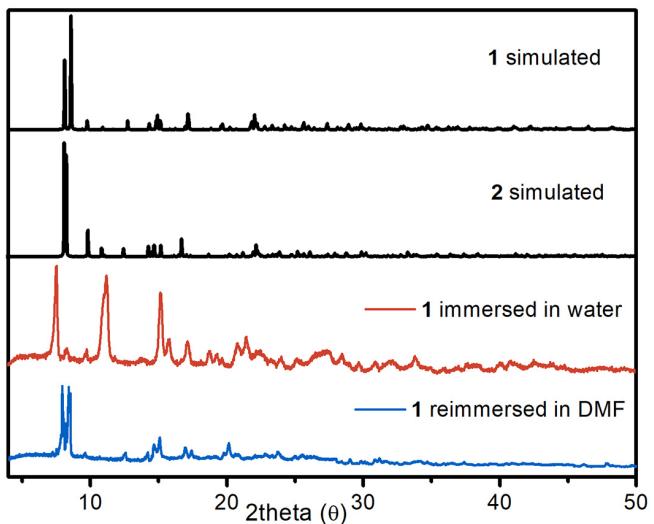


Fig. S5 PXRD patterns of the simulated patterns of **1** and **2**, **1** immersed in water, and **1** reimmersed in DMF solvents.

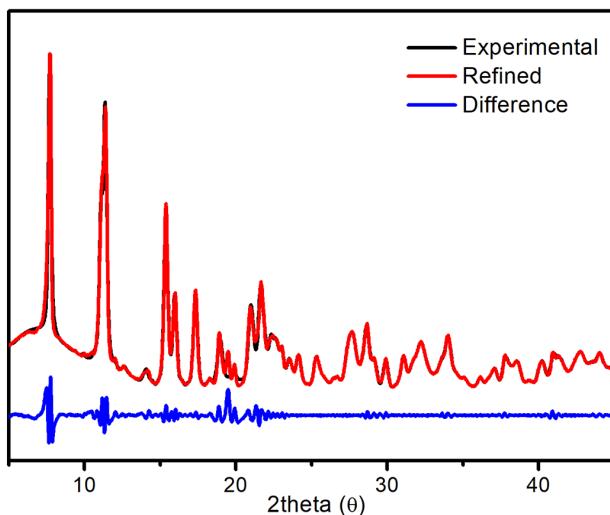


Fig. S6 Pawley refinement of PXRD patterns of **1** immersed in water. Experimental (balck line), refined (red line) and the difference (below) patterns of **1** immersed in water.

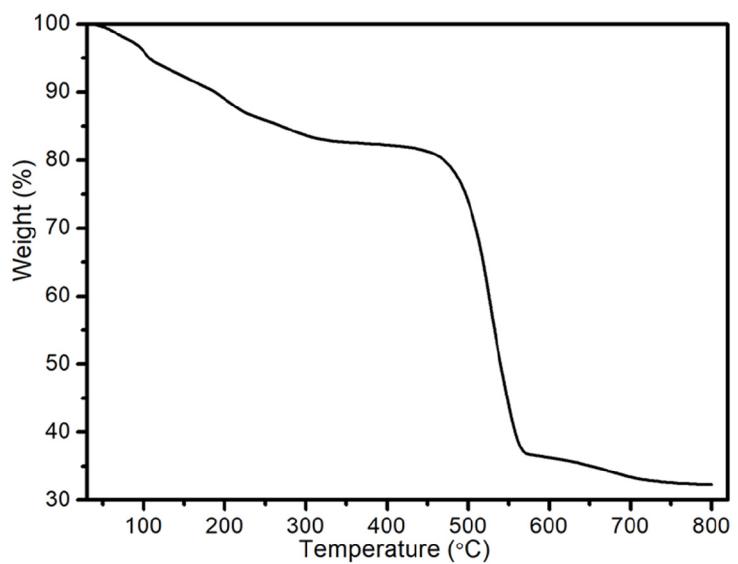


Fig. S7 The TG curve of **1** in a N₂ flow from 40 °C to 800 °C.

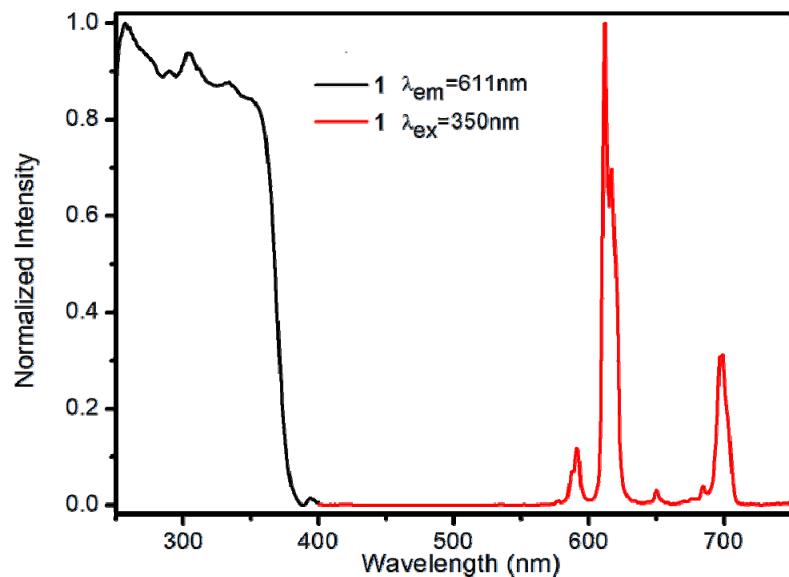


Fig. S8 The excitation (black line) and emission spectra (red line) of **1** in the solid state.

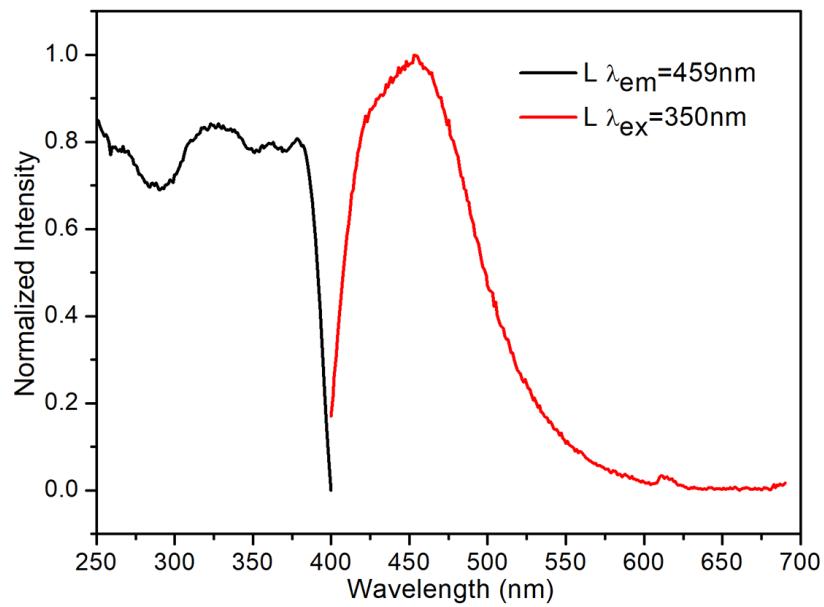


Fig. S9 The excitation (black line) and emission spectra (red line) of ligands H₂NDC in the solid state.

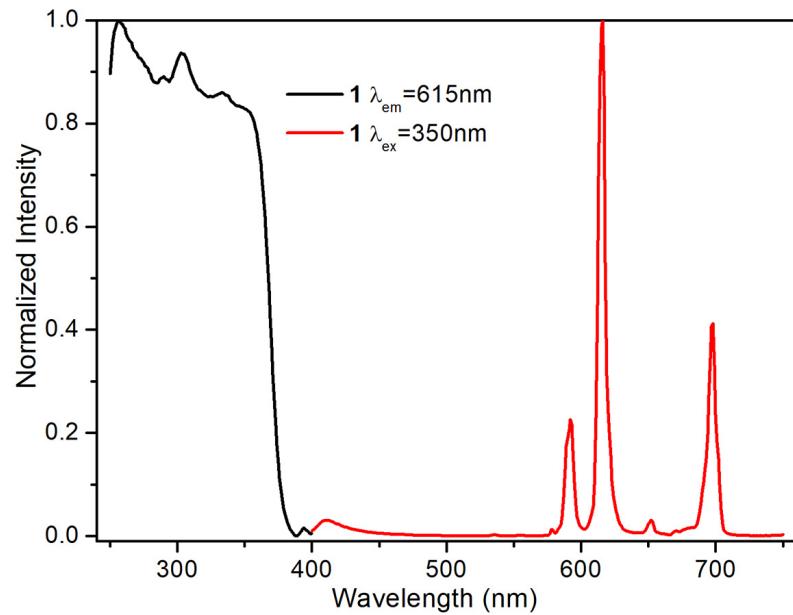


Fig. S10 The excitation (black line) and emission spectra (red line) of **1** dispersed in water (pH 7).

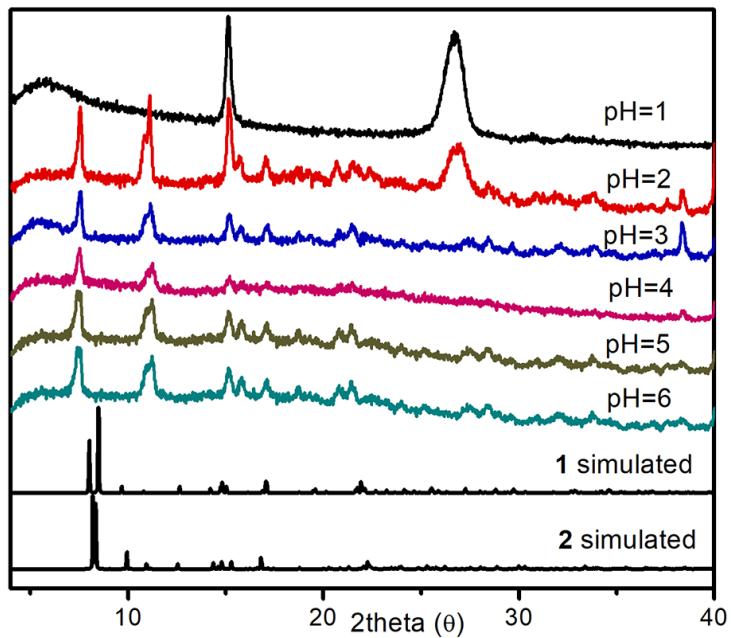


Fig. S11 PXRD patterns of **1** after treated with HCl solutions at different pH (1 to 6) for 24 hrs and the simulated patterns of **1** and **2**.

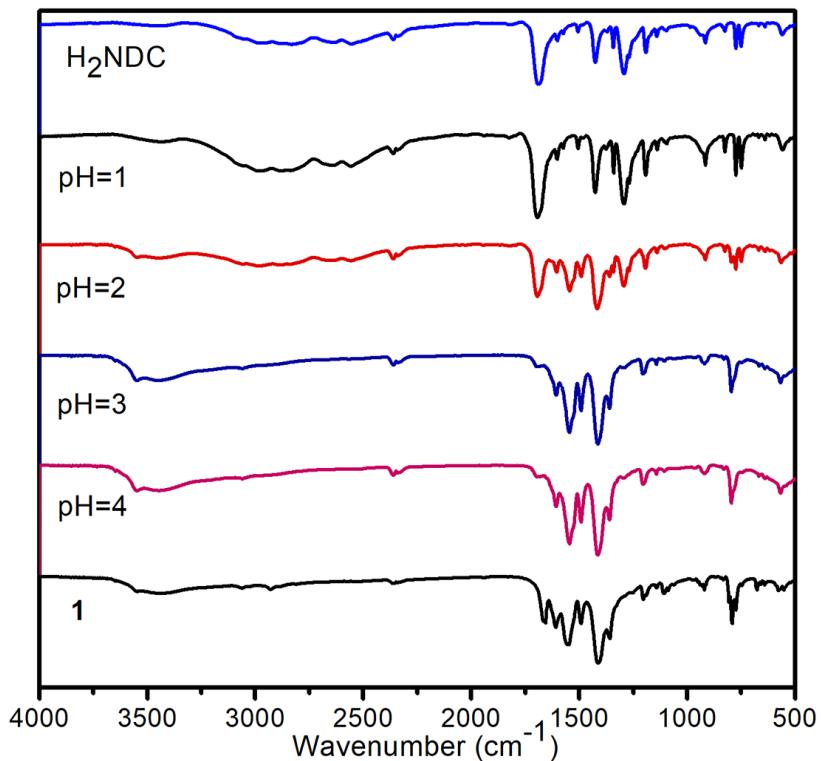


Fig. S12 IR spectra of **1**, the HCl-treated **1** (immersed in HCl solutions with pH from 1 to 4) and the ligand.

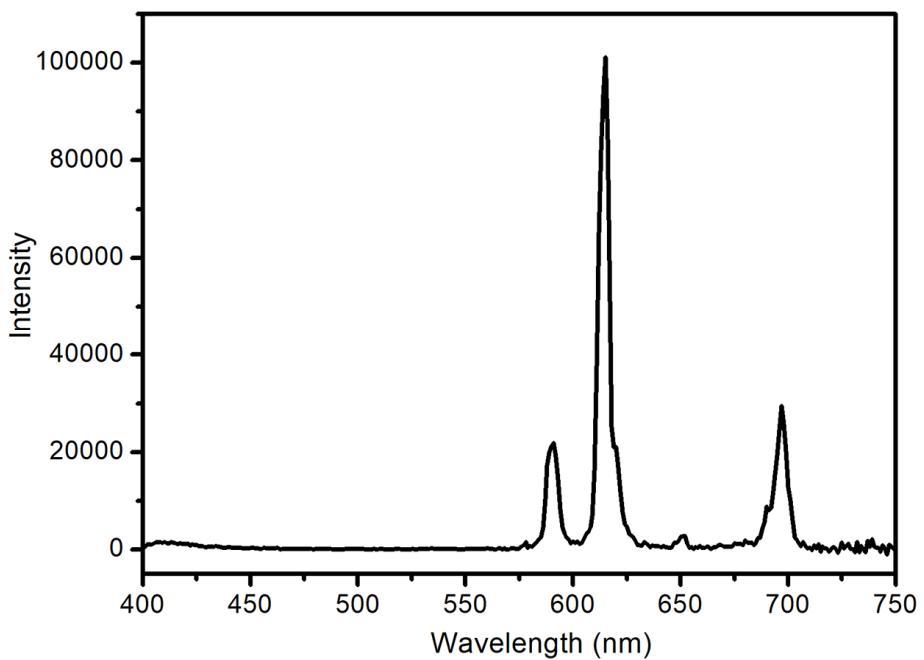


Fig. S13 Emission spectra of **1** after immersed in water for half a year.

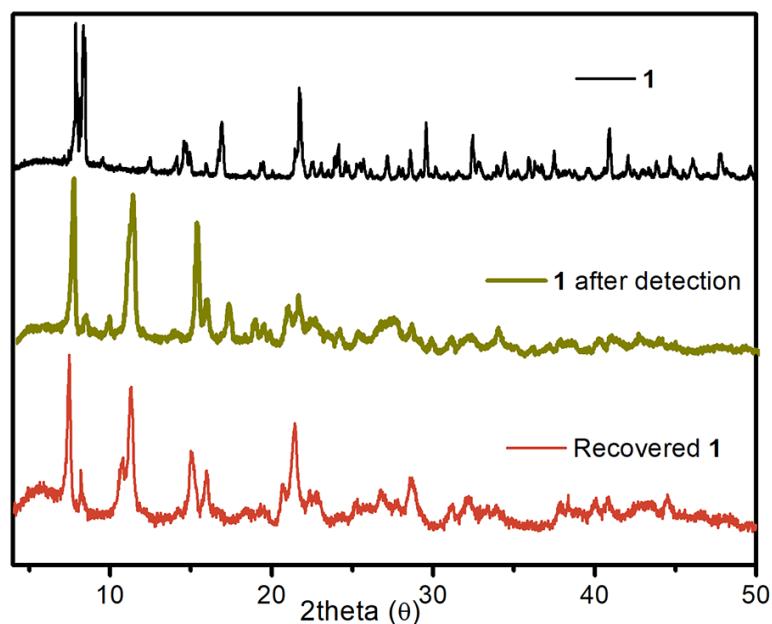


Fig. S14 PXRD patterns of as-synthesized **1**, **1** after detection experiment, and **1** immersed in ethanol.

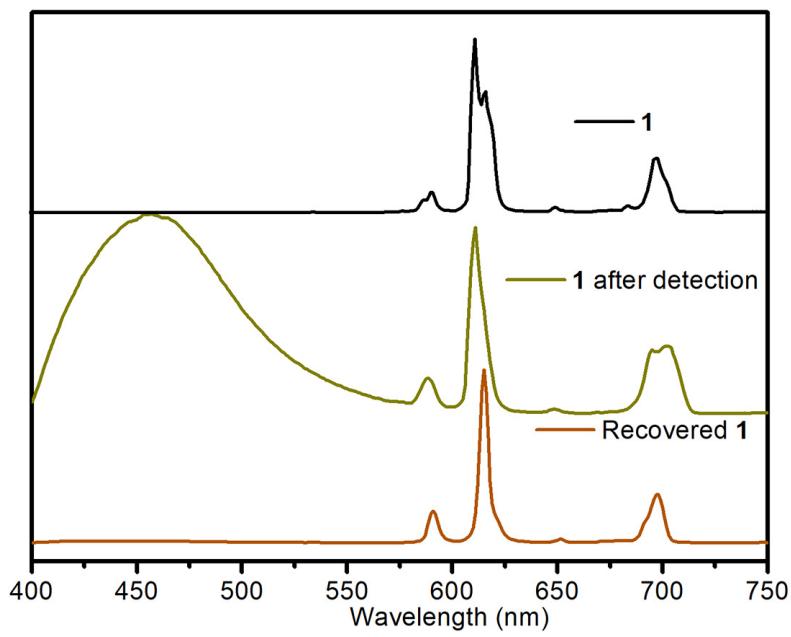


Fig. S15 Solid state emission spectra of **1**, **1** after detection experiment, and recovered **1** (immersed into ethanol and filtered).

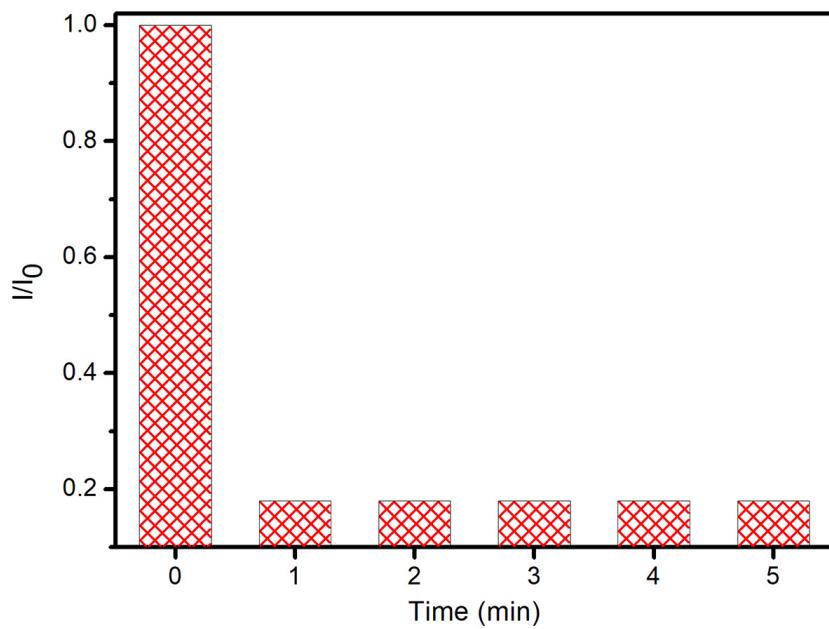


Fig. S16 Quenching efficiency of emission at 615 nm for **1** as a function of time when immersed in HCl solution (pH = 3.2).



Fig. S17 The photographs of **1** in aqueous Asp solutions with different concentrations under the irradiation of 365 nm UV light.

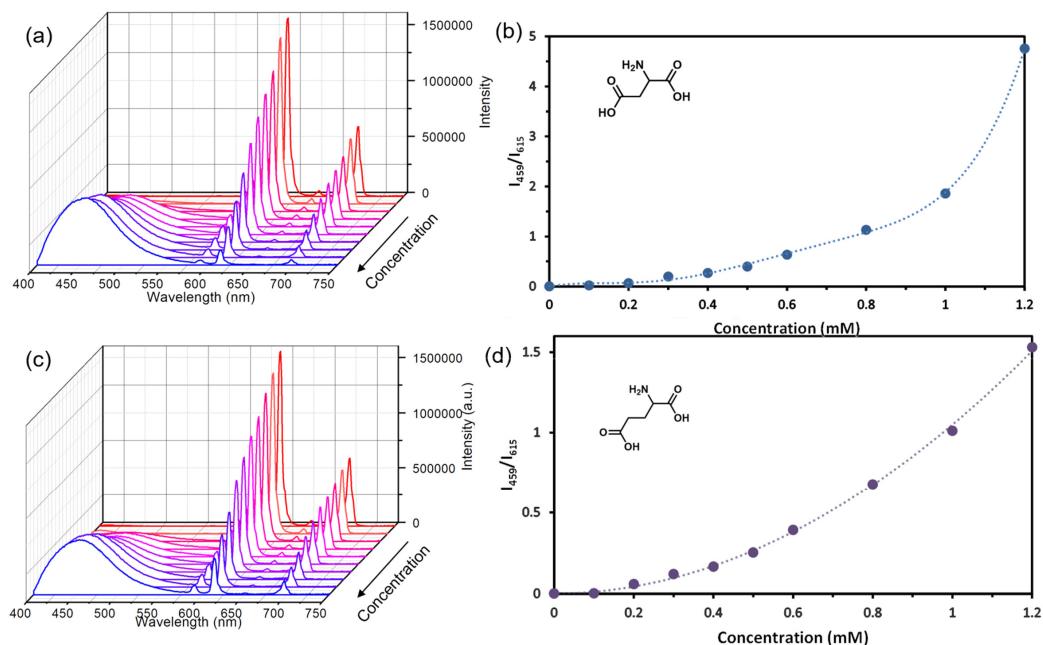


Fig. S18 The emission spectra of **1** in aqueous Asp solutions at different concentrations (a, b) and Glu (c, d) and the corresponding plots of the relative intensity I_{459}/I_{615} and the concentration.

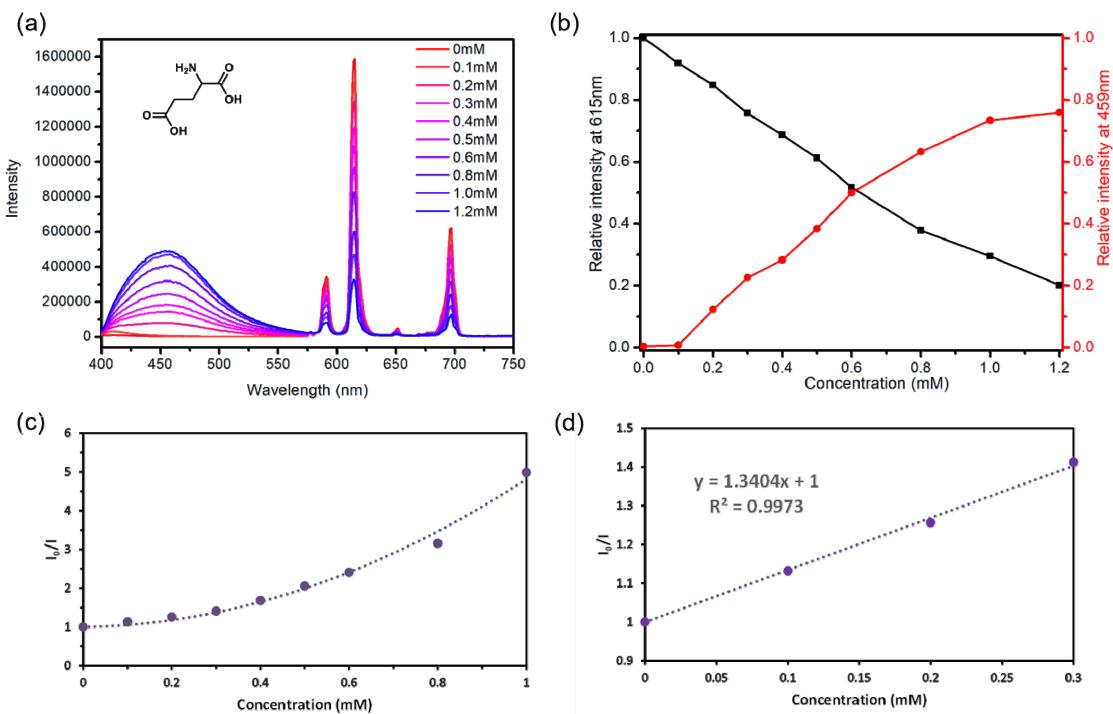


Fig. S19 Emission spectra of **1** in aqueous solutions of Glu at different concentrations; (b) the corresponding plot of the relative intensity at 615 nm and 459 nm as a function of concentrations. The relative intensity at 615 nm is calculated by I/I_0 (I_0 is the peak intensity at 615 nm of the as-synthesized sample). The relative intensity at 459 nm is calculated by $I/I_{3.00}$ ($I_{3.00}$ is the peak intensity at 459 nm of the HCl-treated samples at pH 3.00). (c) S-V plot of **1** in Glu and (d) the corresponding linear fitting at low concentrations.

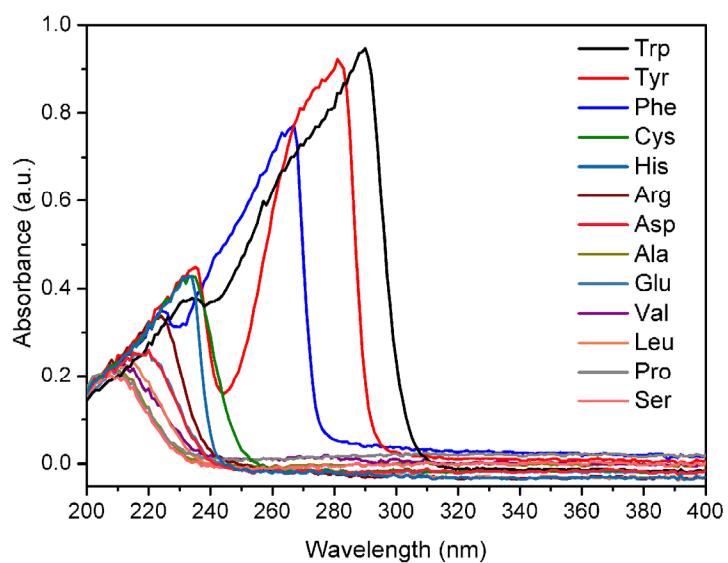


Fig. S20 UV-vis absorption spectra of various amino acids.

Table S1. Crystal data and structure refinement parameters for **1** and **2**.

Compound	Eu-MOF (1)	Eu-MOF-H₂O (2)
Empirical formula	[Eu ₂ (NDC) ₃ (DMF) ₂]·DMF	[Eu(H ₂ O) _{0.5} (NDC) _{1.5} (H ₂ O)]
M_r	1165.73	998.45
Temperature(K)	149.99(10)	150.01(10)
Crystal size(mm)	0.08×0.06×0.02	0.08×0.05×0.02
Crystal system	Monoclinic	Monoclinic
Space group	P ₂ ₁ /n	C2/c
a/Å	11.93700(10)	12.4096(5)
b/Å	21.89300(10)	21.3850(8)
c/Å	16.57120(10)	16.2060(6)
α/°	90	90
β/°	100.5340(10)	103.343(4)
γ/°	90	90
V/Å³	4257.68(5)	4184.6(3)
Z	4	4
F(000)	2304.0	1936.0
Reflection collected	8885	3450
Independent reflections	7963	4115
GOF on F²	1.103	1.051
Final R indexes [I>=4σ (I)]	0.0310	0.0509
Final R indexes [all data]	0.0323	0.0575
wR₂	0.0932	0.1318
Largest diff. peak and hole (e.Å⁻³)	0.89/-0.95	1.26/-0.77

Table S2. Bond lengths of Eu ions in **1**.

Eu(00)-O(004)	2.2627(17)	Eu(00)-O(003)	2.3329(16)	Eu(00)-O(00C)	2.3680(18)
Eu(00)-O(008)#1	2.3680(17)	Eu(00)-O(00B)#2	2.3798(17)	Eu(00)-O(00G)	2.4319(18)
Eu(00)-O(006)#1	2.4496(18)	Eu(00)-O(003)#1	2.7518(18)		
Eu(1)-O(00A)	2.2636(16)	Eu(1)-O(005)#3	2.3442(16)	Eu(1)-O(007)#4	2.3600(19)
Eu(1)-O(00F)#5	2.3774(16)	Eu(1)-O(009)#6	2.3873(17)	Eu(1)-O(00D)#3	2.4605(18)
Eu(1)-O(00E)	2.4769(18)	Eu(1)-O(005)#7	2.6836(17)		
Eu(00)-Eu(00)#3	3.9127(2)	Eu(00)-Eu(1)#8	5.0192(2)	Eu(1)-Eu(1)#3	3.8776(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 x-1,y,z #3 -x+1/2,y+1/2,-z+1/2 #4 x,y,z-1 #5 x+1,y,z
#6 -x+2,-y+1,-z+1 #7 x+1/2,-y+1/2,z-1/2 #8 x-1,y,z

Table S3. Bond lengths of Eu ions in **2**.

Eu(01)-O(6)	2.310(5)	Eu(01)-O(2)	2.350(5)	Eu(01)-O(3)	2.366(5)
Eu(01)-O(7)#1	2.367(5)	Eu(01)-O(5)#2	2.428(5)	Eu(01)-O(4)#2	2.471(5)
Eu(01)-O(8)	2.508(7)	Eu(01)-O(1)	2.592 (3)	Eu(01)-O(2)#2	2.750 (5)
Eu(01)-Eu(01)#2	4.0447(7)	Eu(01)-Eu(01)#1	4.7181(7)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2 #2 -x+1,-y+1,-z+1

Table S4. Crystal data and Pawley refinement parameters for **1** immersed in water.

Compound	1 immersed in water
Temperature(K)	293
Space group	<i>P</i> 2 ₁ / <i>n</i>
a/Å	11.08325(7)
b/Å	22.61446(6)
c/Å	16.47657(9)
α/°	90
β/°	95.255(01)
γ/°	90
V/Å ³	4112.20(5)
R _{wp}	0.0378
R _{wp} (w/o bck)	0.0677
R _p	0.021

Table S5. The pH values of different concentration of amino acid solution tested by pH meter.

C (mM)	pH value of Asp solution	pH value of Glu solution
0.05	4.07	4.50
0.1	3.91	4.26
0.2	3.80	4.05
0.3	3.71	3.96
0.4	3.67	3.88
0.5	3.60	3.81
0.6	3.52	3.79
0.8	3.48	3.75
1.0	3.40	3.69
10.0	3.09	3.35