SUPPORTING INFORMATION

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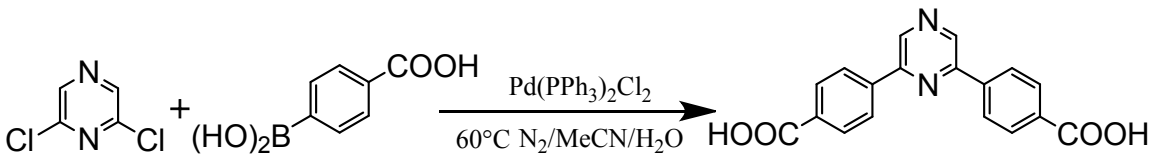
Meterials and General Characterization.

All of chemicals were purchased and used without purification. Elemental analyses for C, H, and N were measured with Perkin-Elmer 2400 elemental analyzer. The TF-IR spectra were measured with a Vertex 70 FTIR on KBr disks on a spectrophotometer (4000–400 cm^{-1}). TGA were measured with NETZSCH TG 209 under heating rate of 10°C min^{-1}. Powder X-ray diffraction measurements were recorded on a PANalytical Empyrean X-ray diffractometer using Mo Kα radiation. The fluorescent spectra were measured on an Edingburage FLS920 spectrophotometer.

S1. Detail experiment procedure for 2,6-Bis(4'-carboxyphenyl)pyrazine[1]

2,6-Dichloropyrazine (0.19 g, 1.269 mmol), 4-carboxyphenylboronic acid (0.45 g, 2.680 mmol), Na_2CO_3 (0.28 g, 2.7 mmol) and $Pd(PPh_3)_2Cl_2$ (0.025 g, 0.035 mmol, 1.3 mol %) were added to a Around bottom flask. H_2O (8 mL) and MeCN (7 mL) were added and N_2 bubbled through the mixture for 20 min. The reaction was heated at 60 °C under a N_2 atmosphere for 48 h later and let cool to room temperature. The MeCN was removed with a rotary evaporator. The precipitate was filtered and the aqueous solution acidified with 4 mL of 1.0 M HCl and a white precipitate formed. The precipitates were combined and dissolved in 1.0 M K_2CO_3. The solution was washed with dichloromethane (2 x 20 mL) and the organic layer discarded. The aqueous phase was reacidified with 1.0 M HCl (5 mL) to precipitate the product that was recrystallized from DMSO as a fine white powder.

S2. Schematic synthetic ligand



S3. Preparation of Mg-MOF

A mixture of H_2pdda (0.064g, 0.2mmol), $Mg(NO_3)_2{\cdot}6H_2O$ (0.0513 g, 0.2 mmol), and 8 mL of distilled water and 8ml DMF were sealed in a Teflon-lined stainless vessel (25 mL) heated at 140 °C for 72 h under autogenous pressure. The vessel was then cooled slowly down to room temperature at 2°C/h. Block crystals were obtained.

S4. Crystallography：

Crystallographic data of Mg-MOF were collected on a SuperNova single crystal diffractometer equipped with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). The data integration and empirical absorption correction were carried out by SAINT program. The crystal was kept at 153(2) K during data collection. Using Olex2,[2] the structure was solved with the XS [3] structure solution program using Direct Methods and refined with the XL [4] refinement package using Least Squares minimization. All hydrogen atoms in these coordination

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polymers were generated geometrically and refine isotropically using the riding model. Crystallographic data and structure refinement parameters for Mg-MOF are listed in Table S1. Selected Distances and Bond Angles for Mg-MOF are listed in Table S2. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1000768 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Table S1 Crystal Data and Structure Refinement for Mg-MOF

	Mg-MOF
Formula	$C_{20}H_{14}MgN_3O_5$
Fw	400.65
Cryst syst	monoclinic
Space group	C2/c
a, Å	16.0685(17)
b, Å	14.6258(12)
c, Å	9.3457(9)
β, deg	117.798(8)
V, Å^3	1942.9(3)
Z	4
$D_υ$ g/cm^3	1.370
F(000)	828.0
Reflections collected/unique	5284/1716
μ, mm^{-1}	0.129
GOF on F^2	1.073
Rint	0.0240
R_1/wR_2 (I>2(I))	0.0654/ 0.1958

Table S2 Selected Distances and Bond Angles for Mg-MOF

		Distance/Å	
Mg1–O1	2.044(2)	N3–Mg1^5	2.318(4)
Mg1–O1^1	2.044(2)	O2–Mg1^2	2.065(2)
Mg1–O2^2	2.065(2)	Mg1–N3^4	2.318(4)
Mg1–O2^3	2.065(2)	Mg1–O5	2.052(5)
		Angles/°	
O1^1–Mg1–O1	171.41(2)	O11–Mg1–O5	85.71(8)
O1–Mg1–O2^6	88.16(1)	O1–Mg1–O5	85.71(8)
O1^1-Mg1-O2^2	88.16(1)	O2^6–Mg1–O2^2	171.95(2)
O1–Mg1–O2^2	92.45(1)	O2^6–Mg1–N3^4	85.97(8)
O1^1–Mg1–O2^6	92.45(1)	O2^2–Mg1–N3^4	85.97(8)
O1^1–Mg1–N3^4	94.29(8)	O5–Mg1–O2^6	94.03(8)
O1–Mg1–N3^4	94.29(8)	O5–Mg1–O2^2	94.03(8)

Symmetry code: ^{1}1–*X*, +*Y*, –1/2–*Z*; ^{2}1–*X*, 2–*Y*, –*Z*; ^{3}+*X*, 2-*Y*, –1/2+*Z*; ^{4}–1/2+*X*, 1/2+*Y*, –1+*Z*; ^{5}1/2+*X*, –1/2+*Y*, 1+*Z*; ^{6}+*X*, 2–*Y*, –1/2+*Z*

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S5. Preparation of Eu^{3+}@Act-MOF, Dy^{3+}@Act-MOF and Tb^{3+}@Act-MOF

Mg-MOF was first treated by a process of the activation 300°C 0.5 h under N_2 atmosphere. Then the Act-MOF (0.02 g) soaked in $LnCl_3$ aqueous solution (Ln = Eu, Dy, Tb) (10 mL, 100 ppm) and treated by ultrasonic wave (30 s) and the solution was removed by centrifuge.

S6. Detail experiments for investigating the sensoring feature under different concentrations of Eu^{3+} ions, various pH condition and mixture cations system

1. Detail experiments for the sensing feature under different concentrations of Eu^{3+} ion.

The activated sample (Act-MOF) (10 mg) and distalled water (3 mL) were added to a cuvette. Then, 3 μl $EuCl_3$ solution (200 ppm) was introduced to the above solution and luminescence measurement followed after being treated by ultrasonic wave (30 s). For increasing the concentrations of Eu^{3+} ion in the measurement system, 3 μL $EuCl_3$ solution was added each time.

2. Detail experiments for the sensing feature under various pH values.

A mixture of Act-MOF (0.01 mg), distilled water (3 mL) and $EuCl_3$ solution (1 ml, 50 ppm) were sealed in a cuvette and luminescence measurement was carried on the mixture. The pH values of the mixtures were adjusted from 3 to 9 by HCl (0.1 M) and KOH solution (0.1 M).

3. Detail experiments for the sensoring feature under mixture cations system.

4 mL Eu^{3+}@Act-MOF solution (consists of Act-MOF (0.01 mg), distilled water (3 mL) and $EuCl_3$ solution (1 mL, 50 ppm)) was added 1 mL aqueous solution (50ppm) of MCl_n (M = Cd, Ni, Mn, Cu, Fe, Tb, Dy). Then the luminescence density was measured.

S7. Elemental analysis (ICP):

According to the ICP result for Eu^{3+}@Act-MOF, the content of Eu^{3+} presenting in the pore of the Act-MOF is 0.53, therefore, the sample should be expressed as $Eu^{3+}_{0.53}$@Act-MOF($C_{20}H_{14}N_3O_5MgEu_{0.53}$).

Scheme S1. Coordination mode of H_2L

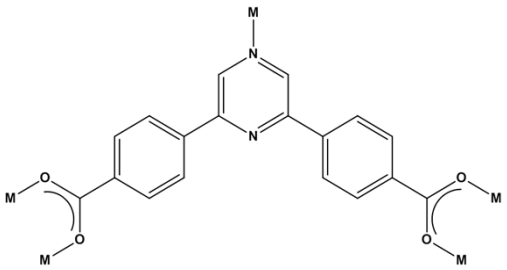

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Figure S1 Morphology of crystal activation process

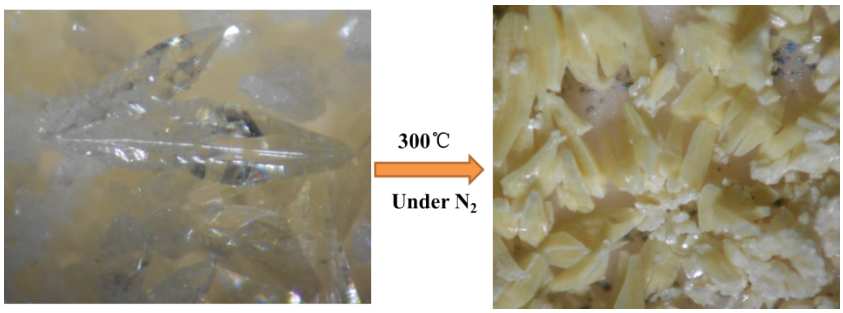

Figure S2 In aqueous solutions, samples were illuminated with 254 nm laboratory UV light.

The Act-MOF (0.02g) soaked in the solution of $LnCl_3$ (Ln=Eu, Dy, Tb) (100ppm) and treated by ultrasonic wave (30s) and their photographs under a standard UV lamp.

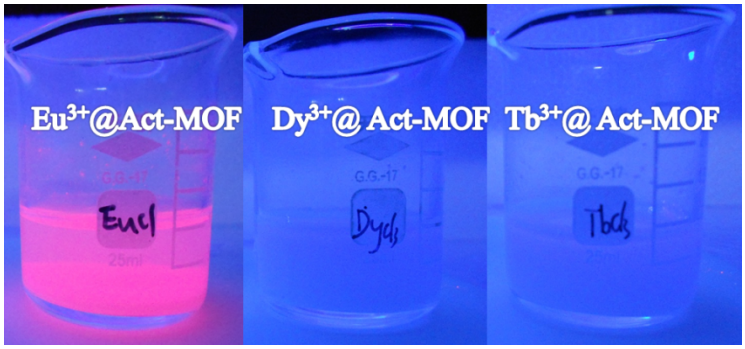

Figure S3 Photoluminescences of H_2L (left) ligand and Act-MOF (right) (Emission spectra (black) and Excitation spectrum (red)).

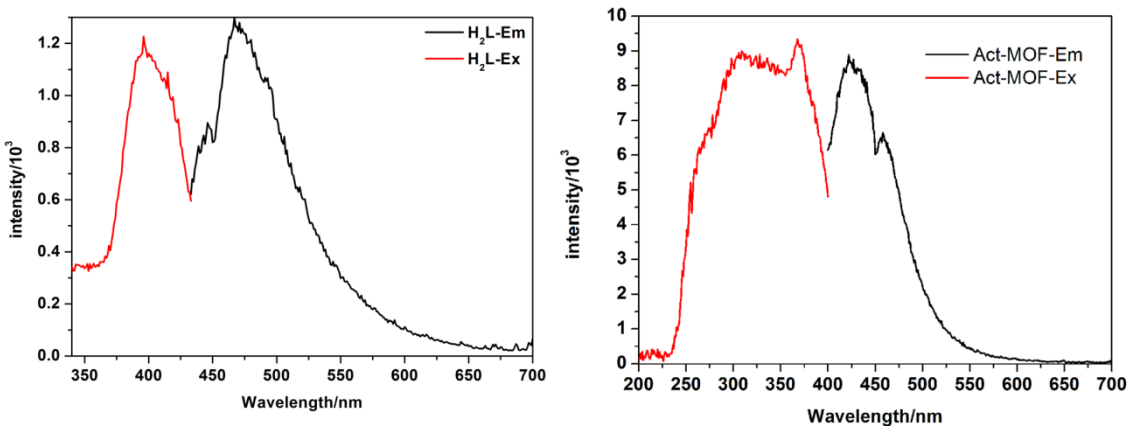

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Figure S4 The emission spectra of $EuCl_3$ (black), a thoroughly ground mixture of $EuCl_3$ and Act-MOF (blue), Act-MOF (red) and Eu^{3+}@Act-MOF (pink) excited at 393 nm in the solid state at room temperature.

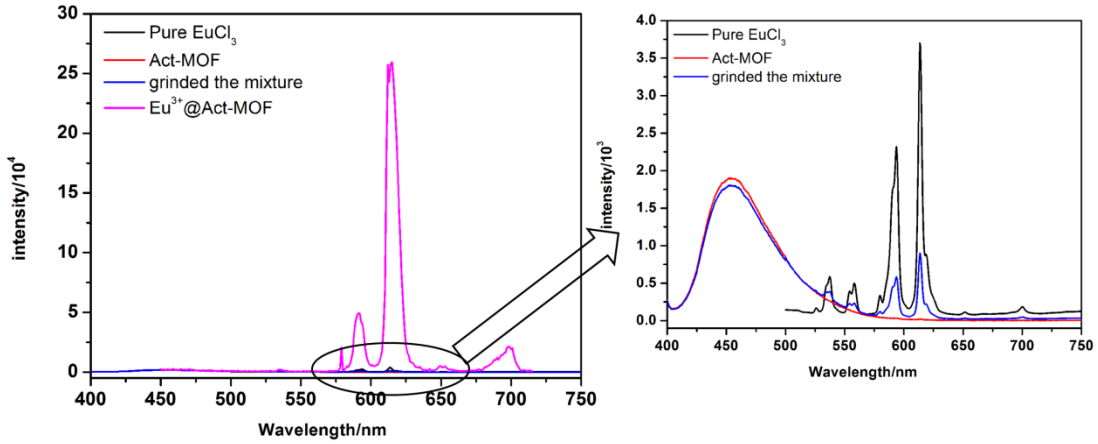

Figure S5 The emission spectra for Act-MOF (left) and Eu^{3+}@Act-MOF (right) excited at different wavelengths in the solid state at room temperature.

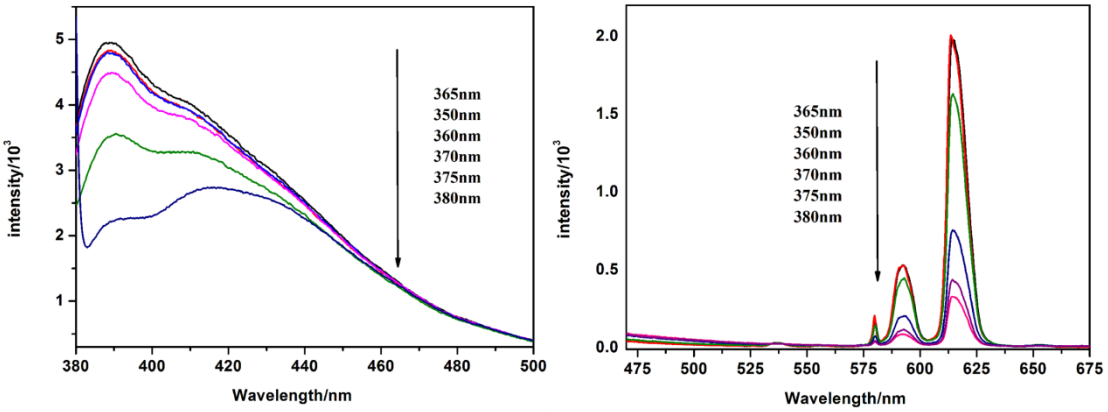

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Figure S6 The test data of absolute quantum yield

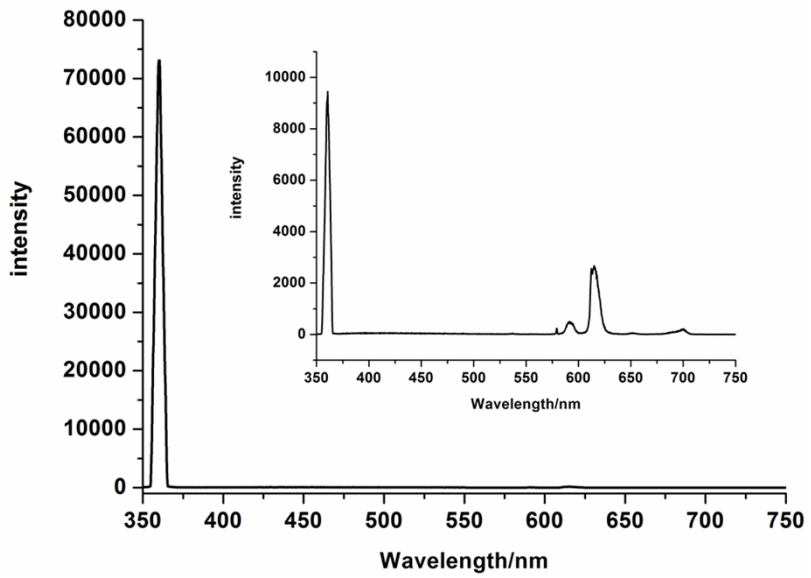
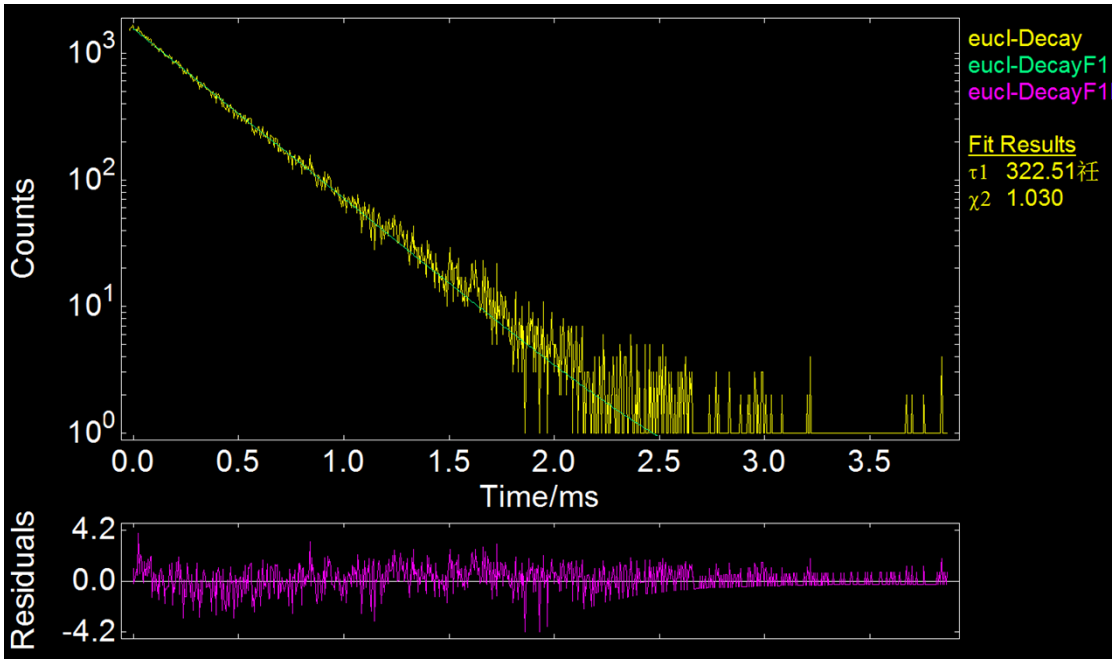


Figure S7 The test data of fluorescence lifetime



$$\tau = \frac{1}{k_f + k_{nr}}$$

(k_f is the rate constant of a radiative process and k_{nr} is the rate constant of a nonradiative process.[2])

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Figure S8 The relationship between the fluorescence intensity (monitored the emission spectra at 618 nm) and $EuCl_3$ concentration in the water solution.

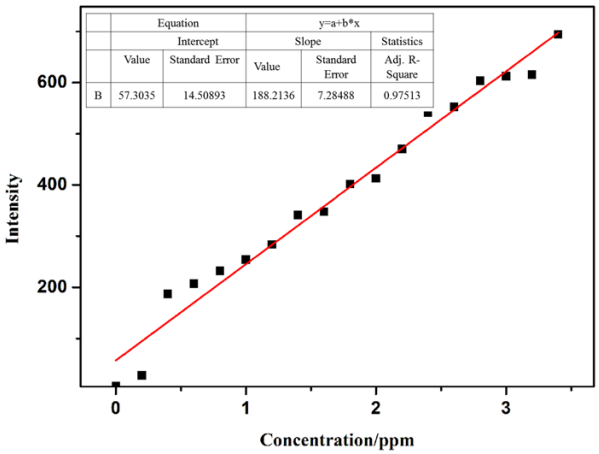
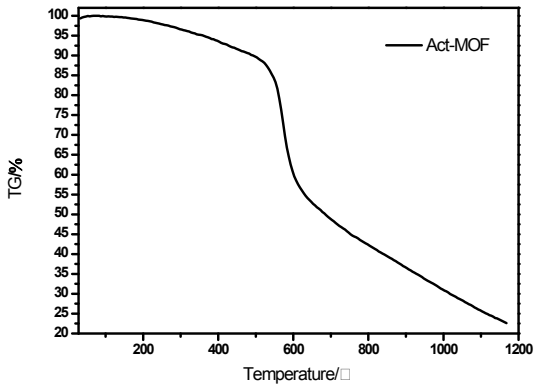


Figure S9 The TGA data of Active MOF.



References:

[1] N. Schultheiss and E. Bosch, *Heterocycles*, **2003**, 60, 1891-1897.

[2] S O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* 2009. **42**, 339-341.

[3] *SHELXS-97.* (Sheldrick, 1990)

[4] XL, G.M. Sheldrick, *Acta Cryst.* (2008). **A64**, 112-122

[5] Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev*, **2011**, 112, 1126-1162.

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