Two Novel Zinc-based MOFs as Luminescence Sensors to Detect Phenylglyoxylic Acid

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

1	
Empirical formula	$C_{34}H_{44}N_6O_{14}Zn_2$
Formula weight	891.49
Temperature/K	300
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	16.5723(3)
b/Å	10.68317(15)
c/Å	22.7188(4)
α/°	90
β/°	95.6935(18)
γ/°	90
Volume/Å^3	4002.40(12)
Z	4
ρ_{calc}g/cm^3	1.479
μ/mm^{-1}	2.095
F(000)	1848.0
Radiation	$CuK\alpha$ (λ=1.54184)
2θ range for data collection/°	3.157 to 68.091
Index ranges	-19<=h<=19, -10<=k<=12, -27<=l<=26
Reflections collected	23488
Independent reflections	7221 [R_{int}0.0470]
Data/restraints/parameters	7221/1/508
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1=0.0546, wR_2=0.1538
Final R indexes [all data]	R_1=0.0679, wR_2=0.1616
CCDC	2191737

[a]$R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b]$wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) of the **1**.

Bond	**Length(Å)**	**Bond**	**Length(Å)**
O(1)-Zn(1)	1.951(3)	O(6)-Zn(1)	1.921(2)
O(2)-Zn(2)	2.138(3)	O(7)-Zn(1)	1.938(3)
O(3)-Zn(2)	2.076(3)	O(9)-Zn(2)	2.104(3)
O(4)-Zn(1)	1.947(3)	O(10)-Zn(2)	2.104(3)
O(5)-Zn(2)	2.094(3)	O(11)-Zn(2)	2.077(3)
Angles	**(Å)**	**Angles**	**(Å)**
C(1)-O(1)-Zn(1)	117.2(3)	O(7)-Zn(1)-O(1)	97.19(13)
C(1)-O(2)-Zn(2)	130.3(3)	O(4)-Zn(1)-O(1)	109.52(14)
C(12)-O(3)-Zn(2)	140.6(2)	O(11)-Zn(2)-O(3)	85.68(13)
C(12)-O(4)-Zn(1)	127.5(2)	O(11)-Zn(2)-O(5)	175.27(14)
C(13)-O(5)-Zn(2)	136.7(2)	O(3)-Zn(2)-O(5)	96.23(11)
C(13)-O(6)-Zn(1)	123.5(2)	O(11)-Zn(2)-O(10)	90.17(15)
C(11)-O(7)-Zn(1)	119.3(3)	O(3)-Zn(2)-O(10)	168.66(13)
Zn(2)-O(9)-H(9A)	125.5	O(5)-Zn(2)-O(10)	88.74(12)
Zn(2)-O(9)-H(9B)	125.7	O(11)-Zn(2)-O(9)	93.68(16)
C(28)-O(10)-Zn(2)	126.9(3)	O(3)-Zn(2)-O(9)	87.27(13)
C(25)-O(11)-Zn(2)	124.6(5)	O(5)-Zn(2)-O(9)	90.74(14)
O(6)-Zn(1)-O(7)	106.34(12)	O(10)-Zn(2)-O(9)	82.46(14)
O(6)-Zn(1)-O(4)	115.16(13)	O(11)-Zn(2)-O(2)	84.60(14)
O(7)-Zn(1)-O(4)	106.09(12)	O(3)-Zn(2)-O(2)	103.34(12)
O(6)-Zn(1)-O(1)	119.95(13)	O(5)-Zn(2)-O(2)	90.74(11)
O(10)-Zn(2)-O(2)	86.74(12)	O(9)-Zn(2)-O(2)	169.05(12)

Table S3. Crystal data and structure refinement for **2**.

	2
Empirical formula	$C_{74}H_{100}N_{14}O_{29}Zn_4$
Formula weight	1911.15
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.4312(3)
b/Å	21.5199(3)
c/Å	25.8251(5)
α/°	90
β/°	109.529(2)
γ/°	90
Volume/Å^3	9653.9(3)
Z	4
ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	1.786
F(000)	3976.0
Radiation	$CuK\alpha$ (λ=1.54184)
2θ range for data collection/°	5.088 to 125.986
Index ranges	-21≤h≤19, -24≤k≤24, -29≤l≤ 29
Reflections collected	52056
Independent reflections	15168 [R_{int}=0.0803, R_{sigma}=0.0583]
Data/restraints/parameters	15168/88/735
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1=0.0968, wR_2=0.2632
Final R indexes [all data]	R_1=0.1135, wR_2=0.2798
CCDC	2191738

[a]$R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b]$wR_2 = [\sum w(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

Table S4. Selected bond lengths (Å) and angles (°) of the **2**.

Bond	**Length(Å)**	**Bond**	**Length(Å)**
Zn2-O3	1.924(4)	Zn4-O4^{4}	2.047(5)
Zn2-O9	1.930(4)	Zn4-O7	1.964(5)
Zn2-O8^{1}	1.908(4)	Zn4-O13^{8}	1.993(6)
Zn2-O14^{2}	1.932(6)	Zn4-O20	1.947(7)
Zn3-O2^{3}	1.936(4)	Zn4-O21	2.108(8)
Zn3-O12	1.942(4)	O2-Zn3^{9}	1.936(4)
Zn3-O5^{4}	1.902(4)	O8-Zn2^{4}	1.908(4)
Zn3-O15^{5}	1.898(6)	O16-Zn1^{6}	2.032(5)
Zn1-O1	2.064(4)	O5-Zn3^{1}	1.902(4)
Zn1-O16^{6}	2.032(5)	O4-Zn4^{1}	2.047(5)
Zn1-O6^{7}	2.023(5)	O6-Zn1^{10}	2.023(5)
Zn1-O17	2.092(7)	O15-Zn3^{5}	1.898(6)
Zn1-O19	2.085(6)	O13-Zn4^{11}	1.993(6)
Zn1-O18	2.162(6)	O14-Zn2^{2}	1.932(6)
Angles	**(Å)**	**Angles**	**(Å)**
O3-Zn2-O9	114.70(19)	O6^{7}-Zn1-O1	101.2(2)
O3-Zn2-O14^{1}	107.8(3)	O6^{7}-Zn1-O16^{6}	96.5(2)
O9-Zn2-O14^{1}	94.9(2)	O6^{7}-Zn1-O17	84.9(3)
O8^{2}-Zn2-O3	112.8(2)	O6^{7}-Zn1-O19	170.6(3)
O8^{2}-Zn2-O9	104.7(2)	O6^{7}-Zn1-O18	83.0(3)
O8^{2}-Zn2-O14^{1}	120.9(3)	O17-Zn1-O19	87.5(3)
O2^{3}-Zn3-O12	110.7(2)	O19-Zn1-O17	90.7(3)
O5^{4}-Zn3-O2^{3}	119.5(2)	O19-Zn1-O18	88.5(3)
O5^{4}-Zn3-O12	102.3(2)	O4^{4}-Zn4-O21	177.5(3)
O15^{5}-Zn3-O2^{3}	109.0(2)	O7-Zn4-O4^{4}	98.0(2)
O15^{5}-Zn3-O12	94.8(2)	O7-Zn4-O13^{8}	128.2(3)
O15^{5}-Zn3-O5^{4}	117.2(3)	O7-Zn4-O21	84.2(3)
O1-Zn1-O17	87.7(2)	O13^{8}-Zn4-O4^{4}	94.4(3)
O1-Zn1-O19	86.9(2)	O13^{8}-Zn4-O21	83.2(3)
O1-Zn1-O18	173.3(2)	O20-Zn4-O4^{4}	90.9(3)
O16^{6}-Zn1-O1	98.29(19)	O20-Zn4-O7	108.2(4)
O16^{6}-Zn1-O17	173.4(3)	O20-Zn4-O13^{8}	121.7(4)
O16^{6}-Zn1-O19	87.0(3)	O20-Zn4-O21	89.6(4)
O16^{6}-Zn1-O18	86.4(2)		

Table S5. Determination of PGA in real samples.

Samples	Added (mM)	Found (mM)	Recovery (%)	RSD (%, n=3)
MOF 1	0.11	0.12	109	3.28
	0.25	0.29	116	2.80
	0.39	0.43	110	2.23
MOF 2	0.11	0.13	118	5.01
	0.25	0.30	120	2.16
	0.39	0.49	126	2.09

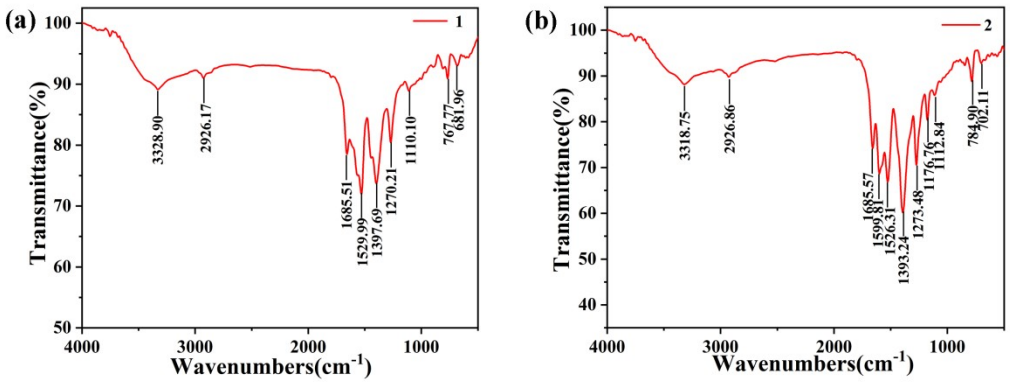

Figure S1 FT-IR spectra of **1** and **2**.

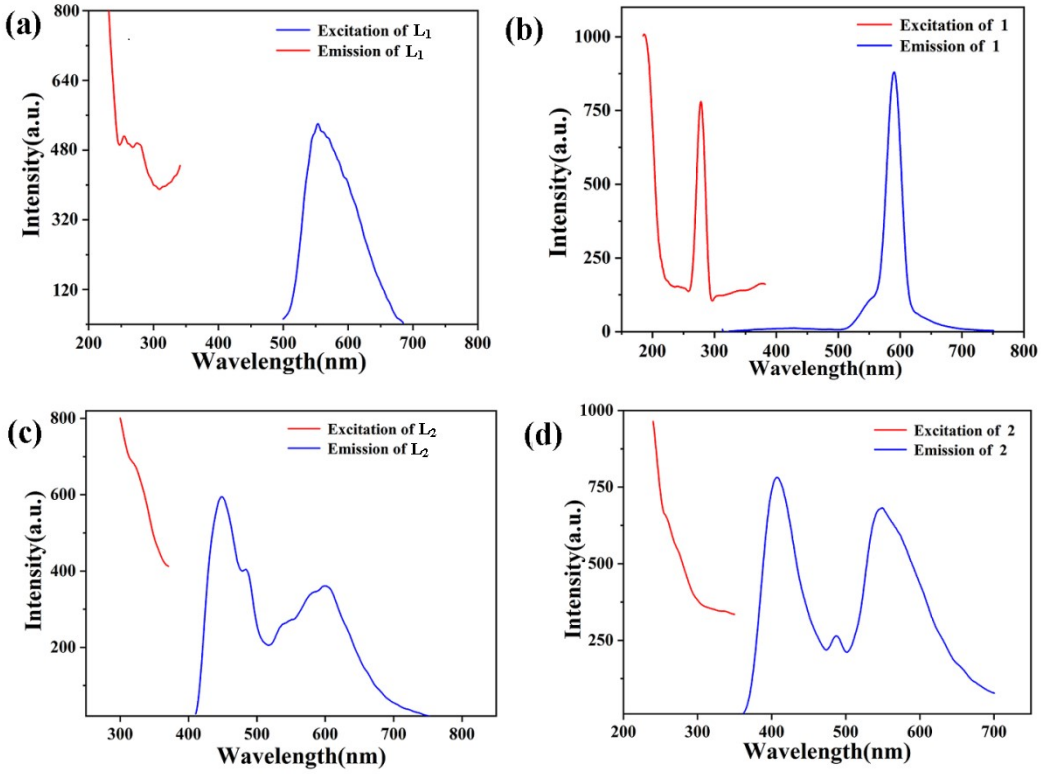

Fig. S2 Solid state fluorescence spectra of (a) L_1; (b)**1**; (c) L_2; (d)**2**.

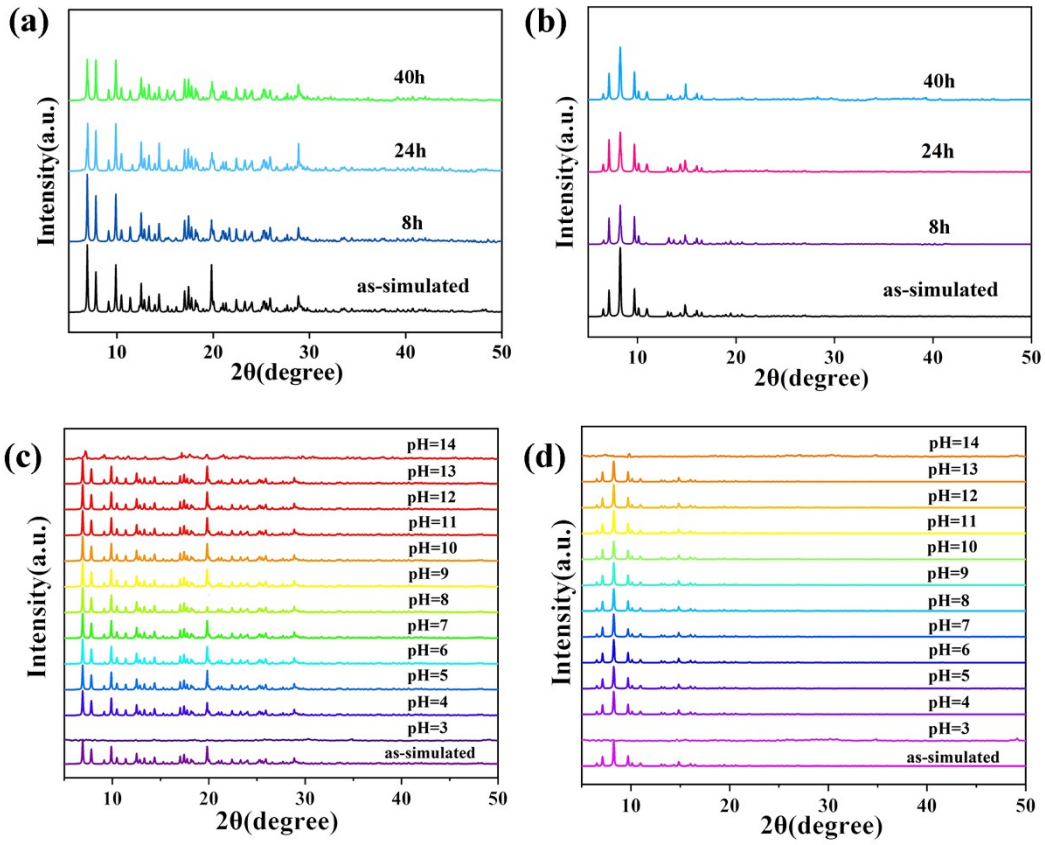

Fig. S3 PXRD patterns of the (a) **1** (b) **2** after immersion in water for different hours; PXRD patterns of the (c) **1** (d) **2** after treated by aqueous solutions with various pH values from 3-14.

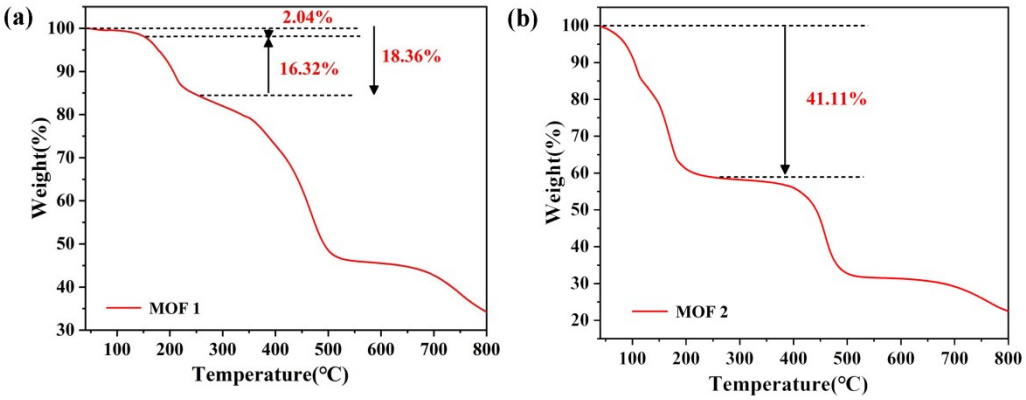

Fig. S4 Thermal gravimetric analyses (TGA) curve of **1** and **2**.

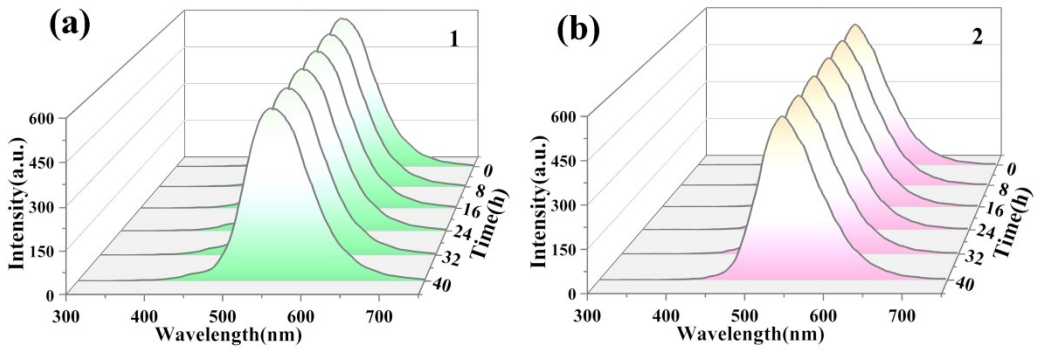

Fig. S5 The fluorescence intensities measured after (c)**1**, (d)**2** powder were soaked in real samples for different time.

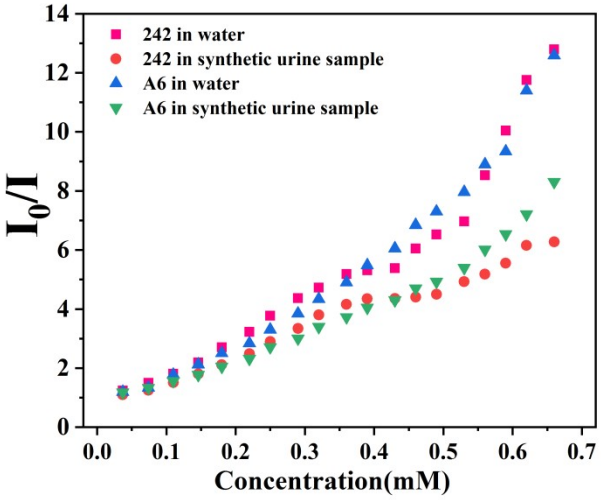

Fig. S6 Concentration gradient experiment of PGA.

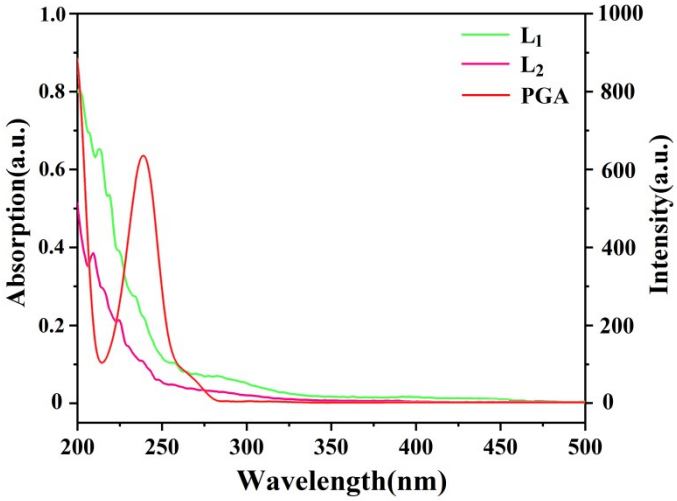

Fig. S7 Spectral overlap between the excitation spectrum of ligands and the UV-vis absorption spectrum of PGA.

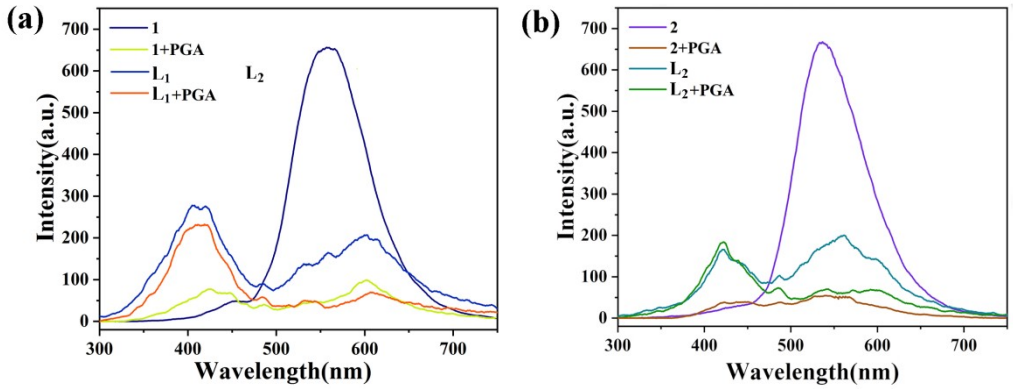

Fig. S8 Fluorescence emission of ligand and MOFs before and after PGA addition.

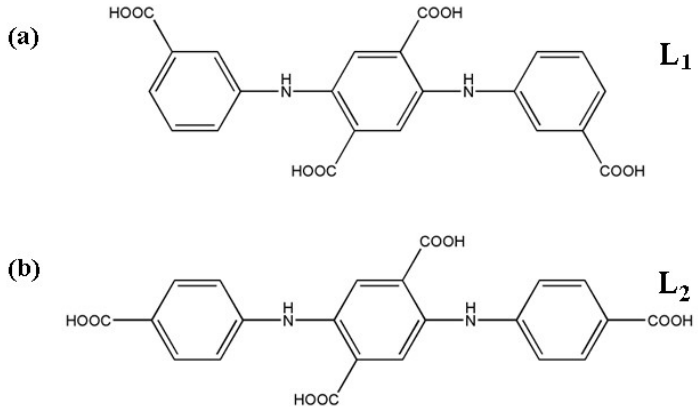

Fig. S9 Structures of L_1 and L_2.

Thermo gravimetric analysis of MOF 1

The thermogravimetric analysis (TGA) of **1** was measured in the temperature range of 40-800°C(Fig. S4a). **1** shows a weight loss of 2.04% (calcd. 2.02%) from 40°C to 145°C, which corresponds to the release of a free water molecule. Between 145°C and 248°C, the weight loss was 16.32% (calcd. 16.39%), corresponding to two free DMF molecules. Further heating induced sharp weight losses are attributed to the decomposition of the frameworks.

Thermo gravimetric analysis of MOF 2

The thermogravimetric analysis (TGA) of **2** was measured in the temperature range of 40-800°C (Fig. S4b). **2** shows a weight loss of 41.11 % (calcd. 41.02%) from 40°C to 255°C, we speculate that the reason is the loss of eight free DMF molecules, two coordinated DMF molecules, and one coordinated water molecule. Subsequently, **2** starts to decompose above 400°C.