Electronic Supplementary Information

Selective Sensing and Visualization of Pesticides by ABW-Type Metal-Organic Framework Based Luminescent Sensors

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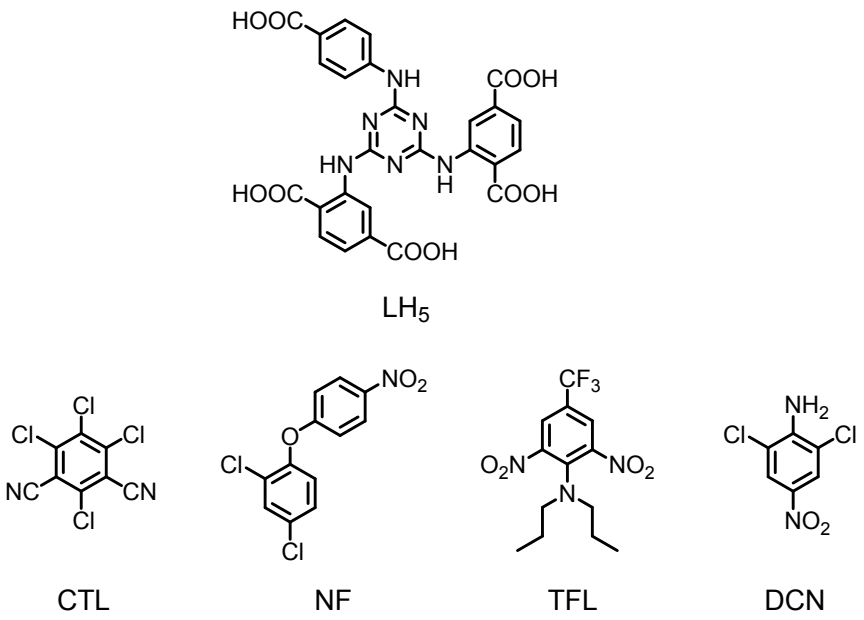

Fig. S1 Chemical structures of intraligand LH_5 and pesticides

X-ray crystallography. Intensity data were obtained by a Mar CCD 165 mm detector on the beamline 3W1A of Beijing Synchrotron Radiation Facility at 153(2) K. The wavelength is 0.80000 Å. The spherical harmonics technique was applied for the absorption effect correction of data. The structure was solved and refined by the SHELXTL.[1] Hydrogen atoms were generated in idealized positions. Because $(H_3O)^+$ and the disordered H_2O could not be modeled explicitly, the PLATON/SQUEEZE[2] program was applied for the calculation of the solvent disorder area and the contribution to the overall intensity data was removed. The residual electron densities of 233 e per formula, which roughly correspond to 1 $(H_3O)^+$, 3 NMP and 6 H_2O molecules for **1**. CCDC 1554378 contains the supplementary crystallographic data for this paper.

Table S1. Selected bond lengths (Å) and angles (°) of **1**.

Zn(1)-O(4)#1	1.971(4)	Zn(2)-O(5)	1.933(4)
Zn(1)-O(10)#2	2.044(4)	Zn(2)-O(2)	1.940(4)
Zn(1)-O(8)#3	2.044(4)	O(4)-Zn(1)#4	1.971(4)
Zn(1)-O(1)	2.046(4)	O(7)-Zn(2)#5	1.924(4)
Zn(1)-O(11)	2.057(5)	O(8)-Zn(1)#5	2.044(4)
Zn(2)-O(9)#2	1.880(4)	O(9)-Zn(2)#6	1.880(4)
Zn(2)-O(7)#3	1.924(4)	O(10)-Zn(1)#6	2.044(4)
O(4)#1-Zn(1)-O(10)#2	129.11(18)	O(7)#3-Zn(2)-O(5)	108.3(2)
O(4)#1-Zn(1)-O(8)#3	98.35(17)	O(9)#2-Zn(2)-O(2)	112.1(2)
O(10)#2-Zn(1)-O(8)#3	132.30(16)	O(7)#3-Zn(2)-O(2)	110.3(2)
O(4)#1-Zn(1)-O(1)	89.37(16)	O(5)-Zn(2)-O(2)	94.78(16)
O(10)#2-Zn(1)-O(1)	91.16(17)	C(5)-O(1)-Zn(1)	123.8(3)
O(8)#3-Zn(1)-O(1)	94.18(18)	C(5)-O(2)-Zn(2)	144.2(4)
O(4)#1-Zn(1)-O(11)	91.2(2)	C(11)-O(4)-Zn(1)#4	125.7(4)
O(10)#2-Zn(1)-O(11)	83.37(18)	C(19)-O(5)-Zn(2)	119.3(3)
O(8)#3-Zn(1)-O(11)	92.3(2)	C(18)-O(7)-Zn(2)#5	123.9(4)
O(1)-Zn(1)-O(11)	173.4(2)	C(18)-O(8)-Zn(1)#5	121.9(3)
O(9)#2-Zn(2)-O(7)#3	110.70(19)	C(26)-O(9)-Zn(2)#6	121.8(4)
O(9)#2-Zn(2)-O(5)	119.51(19)	C(26)-O(10)-Zn(1)#6	144.1(4)

Symmetry transformations used to generate equivalent atoms. #1 = -x+1/2, y-1/2, -z; #2 = -x+1, y, -z+1; #3 = x, y, z-1; #4 = -x, y, -z; #5= x, y, z+1; #6 = -x+1/2, y+1/2, -z.

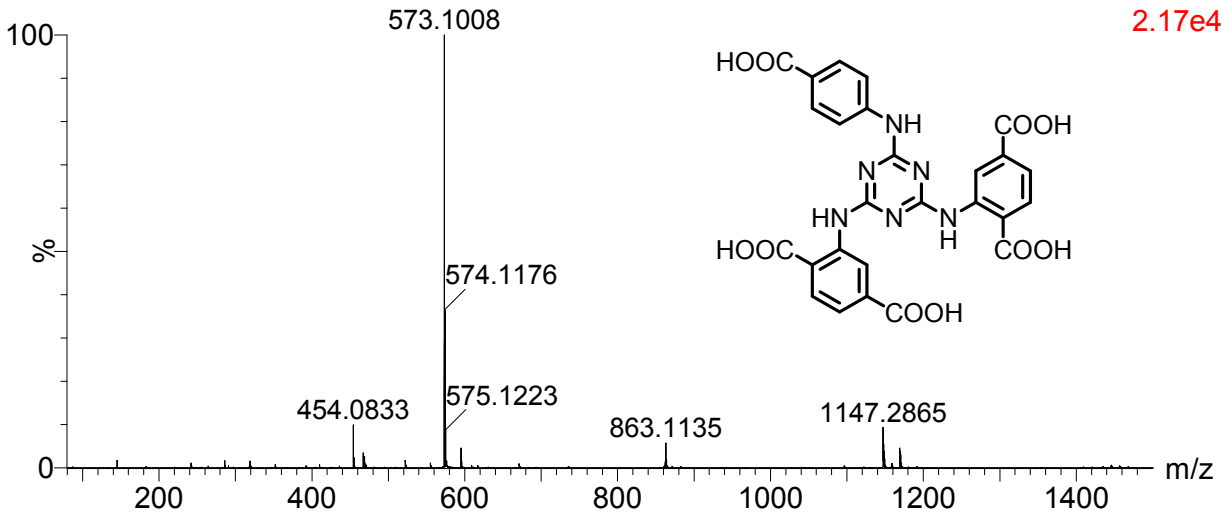

Fig. S2 HRMS spectrum of intraligand LH_5.

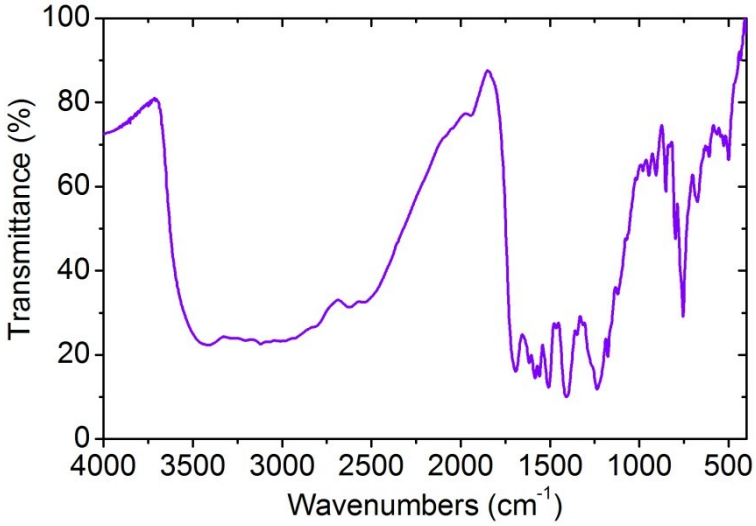

Fig. S3 IR spectrum of **1**.

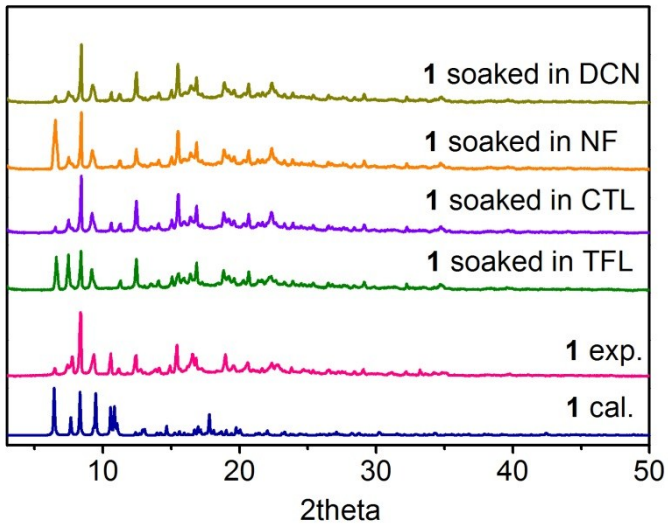

Fig. S4 PXRD patterns of **1**.

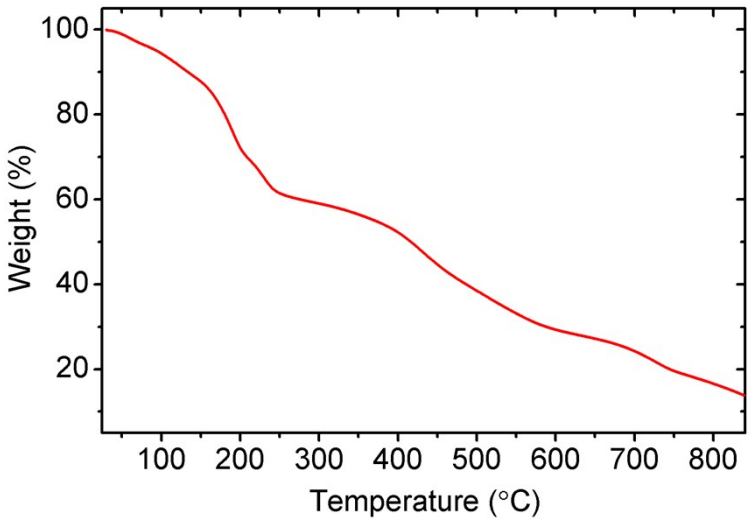

Fig. S5 TGA curves of **1**.

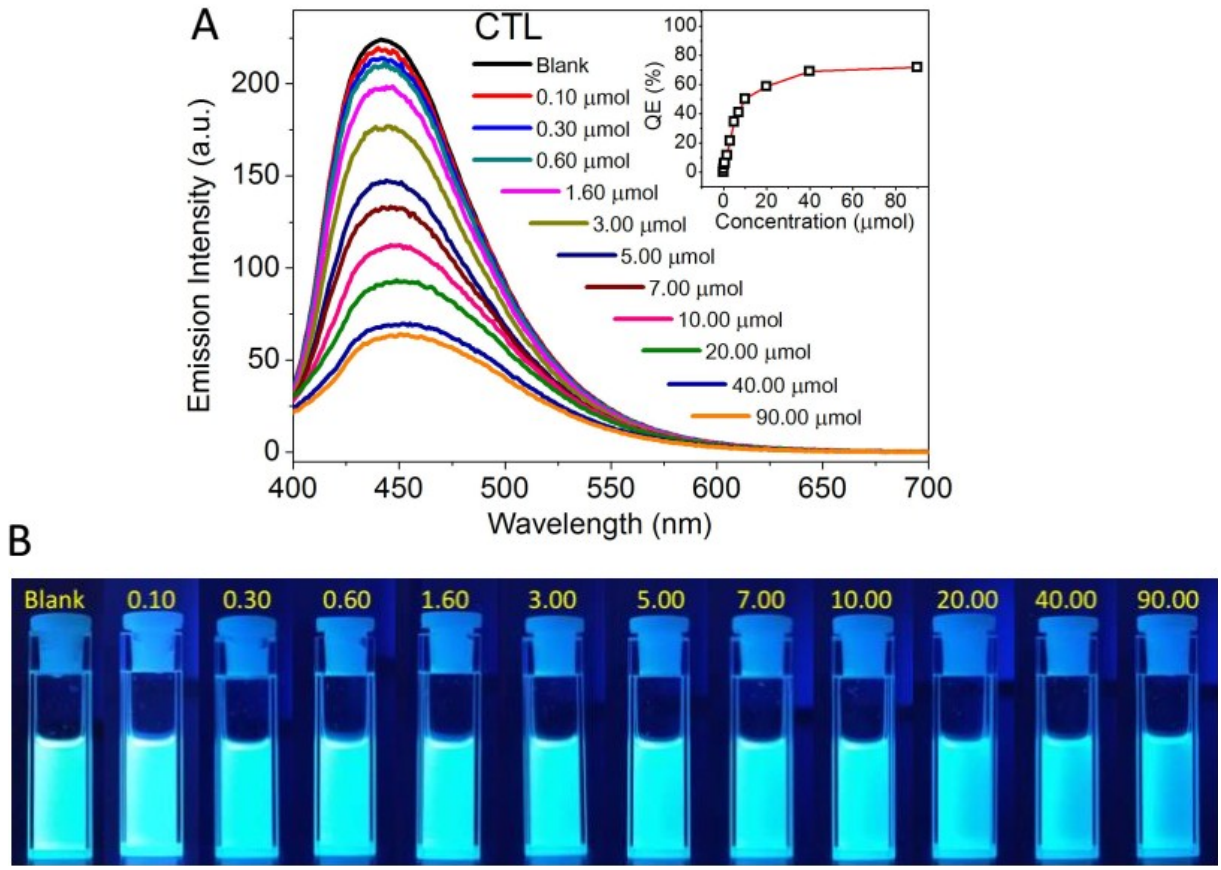

Fig. S6 (A) Concentration-dependent fluorescence responses of **1**(NMP) with different concentrations of CTL (λ_{ex} = 365 nm). Inset: luminescent quenching efficiency (QE) versus addition concentration of CTL. (B) Fluorescence variations of **1**(NMP) with step-by-step addition of CTL (μmol) under 365 nm UV light.

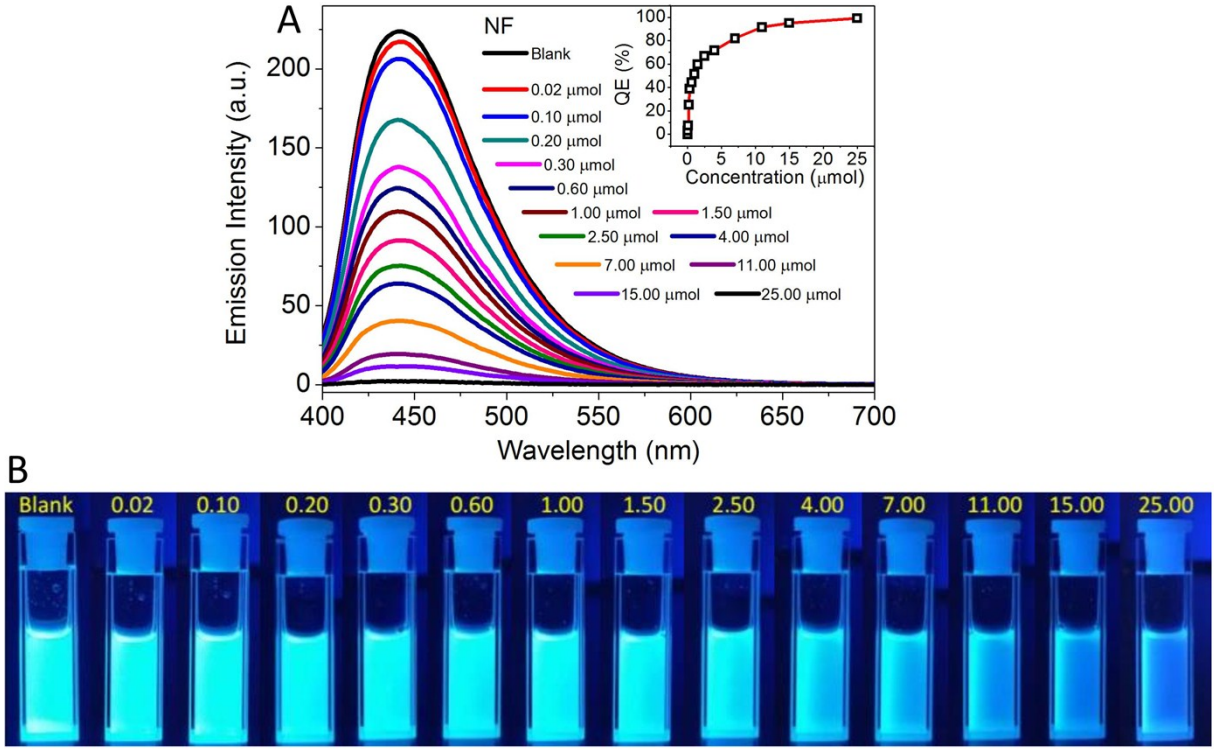

Fig. S7 (A) Concentration-dependent fluorescence responses of **1**(NMP) with different concentrations of NF (λ_{ex} = 365 nm). Inset: luminescent quenching efficiency (QE) versus addition concentration of NF. (B) Fluorescence variations of **1**(NMP) with step-by-step addition of NF (μmol) under 365 nm UV light.

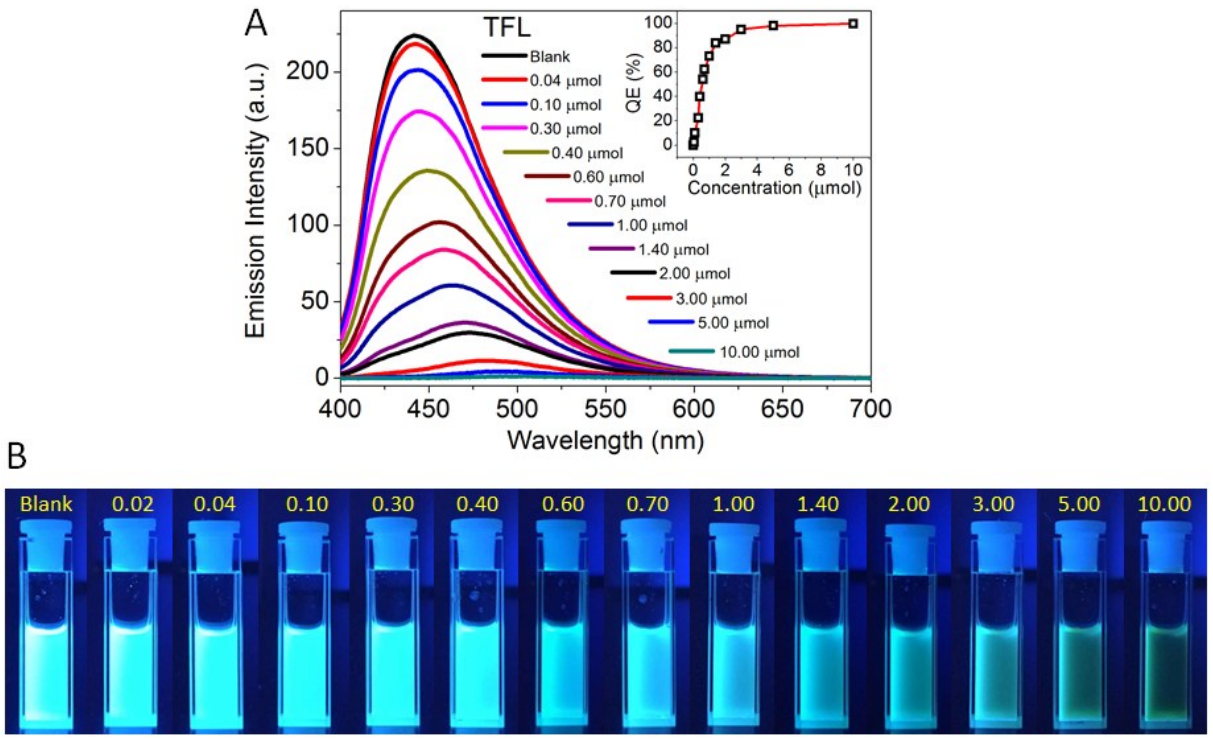

Fig. S8 (A) Concentration-dependent fluorescence responses of **1**(NMP) with different concentrations of TFL (λ_{ex} = 365 nm). Inset: luminescent quenching efficiency (QE) versus addition concentration of TFL. (B) Fluorescence variations of **1**(NMP) with step-by-step addition of TFL (μmol) under 365 nm UV light.

Fitting formula of luminescent pesticide sensing[3-4]

$$\frac{I_0}{I} = \left(\frac{f_1}{1 + K_{SV}\cdot[Q]} + f_2\right)^{-1} \quad \textbf{(Eqn. S1)}$$

where I_0 is the original luminescent intensity of **1**(NMP) in the absence of the pesticide, I is the corresponding value in the presence of the pesticide. f_1 and f_2 are the quenchable and unquenchable fractions,respectively. [Q] expresses addition concentration (μmol) of the pesticide as quencher. The quenching constant K_{SV} means the guide of luminescent detection efficiency of the MOF to the pesticides.

Table S2. Parameters of **1**(NMP) for luminescent sensing of organic pesticides (fitting of the result to the Stern-Volmer relationship).

Pesticides	λ_{ex}(nm)	λ_{em}(nm)	f_1[a]	f_2[a]	K_{SV}[b] (μmol^{-1})	*Standard* (μmol^{-1})	R^2[c]
CTL	365	440	0.78	0.22	0.163	0.017	0.991
NF	365	440	1.06	-0.06	0.574	0.014	0.999
TFL	365	440	1.02	-0.02	6.072	0.682	0.995
DCN	365	440	1.04	-0.04	11.194	0.345	0.999

[a] Ratio of the two portions of **1**(NMP). [b] Quenching constant (bar^{-1}). [c] Determination coefficients.

Limits of detection (LODs)[3]

$$LOD\ (ppm) = \frac{(S/N) \times 10^3}{K_{SV} \times V}$$

S/N: signal to noise ratio S/N = 20log(U_1/U_0)

U_1: signal amplitude U_0: noise amplitude

U_1 = 223.439, U_0 = 0.167, S/N =65.528 for **1**(NMP)

V: The volume of **1**(NMP), V = 2000 μL

The LODs of **1**(NMP) for luminescent sensing of CTL, NF, TFL, and DCN:
CTL: LOD = 201.01 ppm
NF: LOD = 57.08 ppm
TFL: LOD = 5.40 ppm
DCN: LOD = 2.93 ppm

References.

1 G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement,* University of Göttingen, Göttingen, (Germany), 1997.
2 A. L. Spek, *PLATON, Multipurpose Crystallographic Tool, Utrecht University,* Utrecht, The Netherlands, 2008.
3 X. D. Wang and O. S. Wolfbeis, *Chem. Soc. Rev.*, 2014, **43**, 3666.
4 L. Di, Y. Xing, X. Wang, D. Zheng, Y. Yang and F. Li, *RSC Adv.*, 2018, **8**, 41040.