Electronic Supplementary Information (ESI)

Exceptional Water Stable Terbium–Based Metal–Organic Framework for Selective Detection of Pesticides

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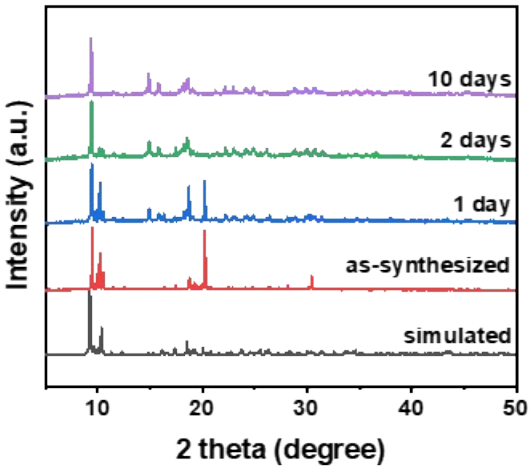

Fig. S1 PXRD patterns of compound 1 before and after storage in deionized water for several days.

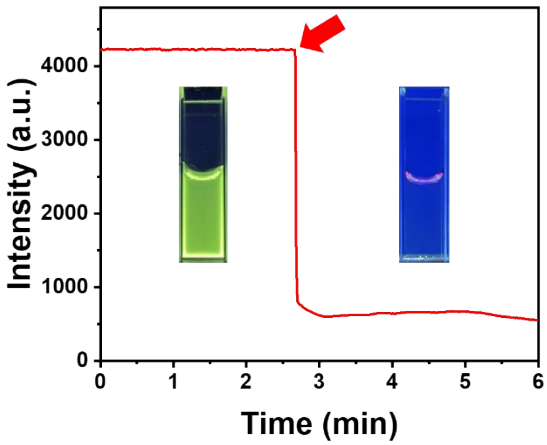

Fig. S2 The time course of the emission decay centered at 545 nm from compound **1** in aqueous solution was obtained before and after the addition of TMX (the red arrow).

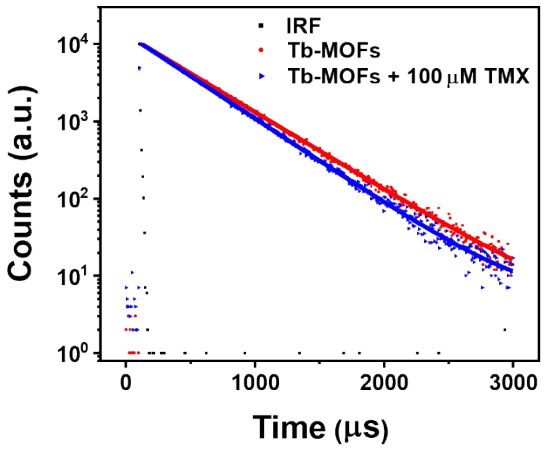

Fig. S3 Emission decay profiles of compound **1** before and after the addition of TMX. The red and blue lines represent the fitting results.

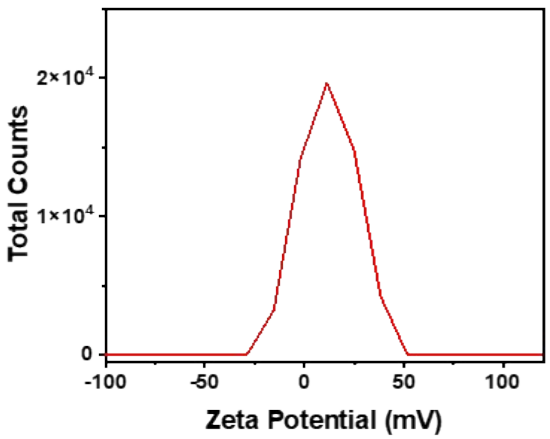

Fig. S4 The zeta potential of compound **1** in deionized water (at 25 °C).

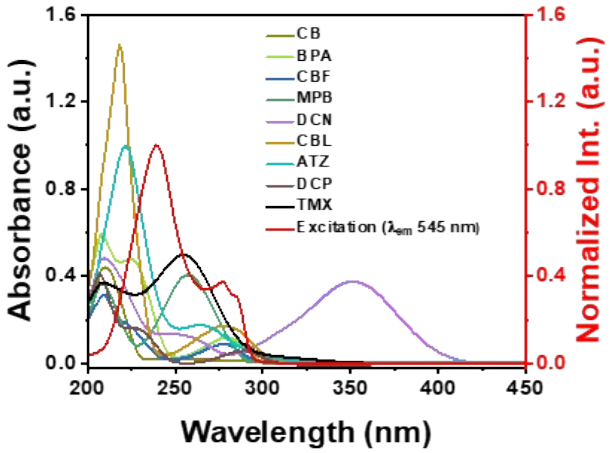

Fig. S5 Absorption spectra of various pesticides with equivalent concentrations of 30 μM compared with the excitation spectrum of compound **1**.

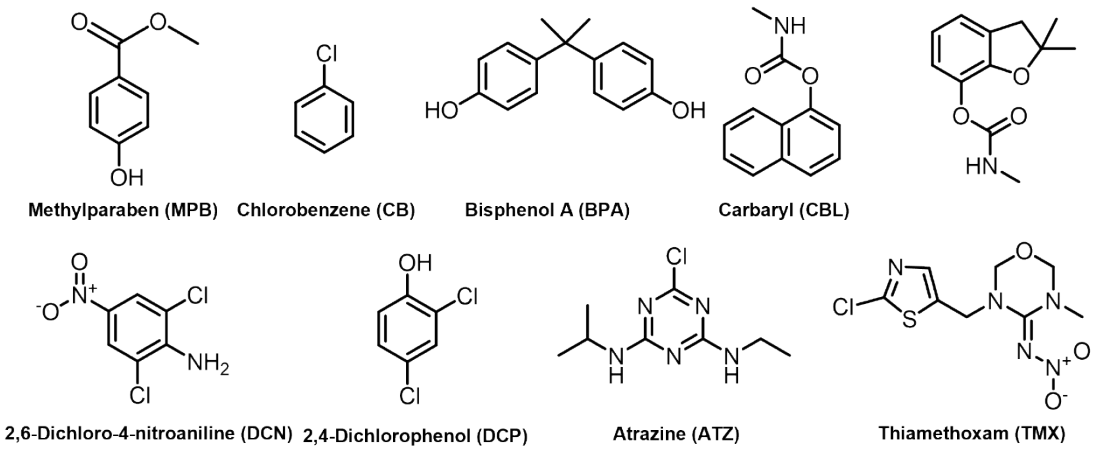

Fig. S6 Chemical structures of various pesticides shown in Fig. 4c of the main text.

Table S1. A summary of MOF-based platform for detection of various pesticides.

MOF-based platform	Sensing target	LOD (nM)	Ref.
[Eu(EDTA)(DBM)]	glyphosate	360	21
[Cd(NH_2-bdc)(azp)]·DMF	glyphosate	25	22
(UiO-67/Ce-PC)	glyphosate	37	23
N-CDs@PCN-222	glyphosate	54	24
Cd-MOF-1	DCN	360	25
Cd-MOF-2		120	
Zn-MOF	DCN	3840	26
{[$(CH_3)_2NH_2$]$_2$[Pb(TCBPE)(H_2O)$_2$]}$_n$	DCN	260	27
Cd-TM	DCN	7.6	28
mMIP@MOF-76	OPP	9	29
NH_2-CuBDC	OPP	7	30
Tb-MOF	OPP	11	31
Z1200 MOF	OPP	0.009	32
RhB@LMOF	parathion-methyl	12000	33
ZnPO-MOF	parathion-methyl	0.456	34
Zr-LMOF	parathion-methyl	19	35
[Cd(1,4-ndc)(DMA)]	parathion-methyl	3	36

$[Tb(PMBB)_{1.5}(H_2O)_2]$	nitenpyram	710	37
$[Eu(PMBB)_{1.5}(H_2O)_2]$		770	
UCNPs–PMOF	nitenpyram	220	38
Zn-CPTA	nitenpyram	625	39
$[In_3Tb_3O_3(TATAB)_4(H_2O)_6]$ ·12DMF·12H_2O	nitenpyram	628	40

DCN: 2,6-dichloro-4-nitroaniline

OPP: organophosphate pesticides

Table S2. Comparison of other compounds or nanomaterials using the fluorometric method for the detection of TMX with that for compound **1**.

Materials	Linear range (μM)	LOD (nM)	Ref.
Tb-MOFs	45-155	7300	41
Tb^{3+}	0.34-17.14	100	64
QDs	0.04-2	12.3	65
B-CDs@MIPs/R-CDs	0.05-25	13.5	66
NH_2-SiO_2@$CsPbBr_3$	0.0144-0.0624	4.11	67
Tb-MOFs (compound **1**)	0 − 40	30	This work

X-ray crystallography measurements

A single crystal of **1** suitable for crystallographic analysis was measured at 150K for intensity data collection on a Bruker D8 VENTURE diffractometer fitted with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Data reduction included absorption corrections by the MULTI-SCAN method, using SAINT[1] and SADABS.[2] Crystal data and experimental details are given in Table S1. The X-ray structure was determined by direct methods and difference Fourier techniques and were refined by full-matrix least squares, using SHELXT.[3,4] For **1**, all non-hydrogen atoms were refined anisotropically except for the DEF and guest water molecules. The hydrogen atoms of guest water molecules are located in a difference Fourier map. The O-bound H atoms were refined in the riding-model approximation with U_{iso}(H) = 1.5U_{eq}(O). The C-bound H atoms were placed in calculated positions and refined as riding model with U_{iso}(H) = 1.2U_{eq}(O). The coordinated DEF molecule was observed to present two-site disordered behaviour. The site-occupancy of the disordered DEF molecule was refined to be 0.55 and 0.45. For guest water molecule, only half occupancy was assigned and was refined anisotropically. Also, due to the disorderness, the H atom position of the guest water molecule was only approximately assigned based on an optimised calculated position. Crystallographic CIF data for **Tb-FJU7** have been deposited at the Cambridge Crystallographic Data Center, under the deposition number of CCDC 2378574.

Table S3. Crystal data and structure refinement for compound **1**.

Identification code	ic22483	
Empirical formula	C34 H36 N2 O15 Tb2	
Formula weight	1030.49	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 17.9401(7) Å	α = 90°
	b = 11.5274(5) Å	β = 109.0656(12)°
	c = 18.6602(7) Å	γ = 90°
Volume	3647.3(3) Å^3	
Z	4	
Density (calculated)	1.877 Mg/m^3	
Absorption coefficient	3.920 mm^{-1}	
F(000)	2016	
Crystal size	0.153 x 0.127 x 0.094 mm^3	
Theta range for data collection	2.136 to 30.000°	
Index ranges	-25<=h<=25, -16<=k<=16, -26<=l<=26	
Reflections collected	46223	
Independent reflections	5309 [R(int) = 0.0574]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6042 and 0.5451	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5309 / 83 / 264	
Goodness-of-fit on F^2	1.279	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0307, *w*R2 = 0.0711	
R indices (all data)	R1 = 0.0347, *w*R2 = 0.0738	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.370 and -2.048 e.Å^{-3}	

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S4. Bond lengths [Å] and angles [°] for compound **1** (ic22483).

Tb(1)-O(1)	2.258(2)	C(16')-C(17')	1.498(19)
Tb(1)-O(2)#1	2.302(2)	O(1)-Tb(1)-O(2)#1	83.47(8)
Tb(1)-O(3)#2	2.312(3)	O(1)-Tb(1)-O(3)#2	103.11(12)
Tb(1)-O(4)#3	2.325(3)	O(2)#1-Tb(1)-O(3)#2	73.94(11)
Tb(1)-O(5)	2.356(3)	O(1)-Tb(1)-O(4)#3	104.01(9)
Tb(1)-O(6)#4	2.365(2)	O(2)#1-Tb(1)-O(4)#3	145.51(10)
Tb(1)-O(7)	2.411(3)	O(3)#2-Tb(1)-O(4)#3	133.99(11)
Tb(1)-O(5)#4	2.846(3)	O(1)-Tb(1)-O(5)	81.82(9)
Tb(1)-C(12)#4	2.968(3)	O(2)#1-Tb(1)-O(5)	141.77(10)
O(1)-C(7)	1.282(4)	O(3)#2-Tb(1)-O(5)	75.37(12)
O(2)-C(7)	1.233(4)	O(4)#3-Tb(1)-O(5)	72.57(11)
O(3)-C(8)	1.258(5)	O(1)-Tb(1)-O(6)#4	150.57(8)
O(4)-C(8)	1.260(5)	O(2)#1-Tb(1)-O(6)#4	77.41(9)
O(5)-C(12)	1.265(4)	O(3)#2-Tb(1)-O(6)#4	92.93(12)
O(6)-C(12)	1.253(4)	O(4)#3-Tb(1)-O(6)#4	80.84(10)
O(7)-C(13)	1.212(5)	O(5)-Tb(1)-O(6)#4	126.55(9)
C(1)-C(6)	1.393(4)	O(1)-Tb(1)-O(7)	76.09(9)
C(1)-C(2)	1.397(5)	O(2)#1-Tb(1)-O(7)	78.06(9)
C(1)-C(7)	1.496(5)	O(3)#2-Tb(1)-O(7)	151.87(11)
C(2)-C(3)	1.387(5)	O(4)#3-Tb(1)-O(7)	71.47(9)
C(3)-C(4)	1.390(5)	O(5)-Tb(1)-O(7)	131.18(10)
C(4)-C(5)	1.392(5)	O(6)#4-Tb(1)-O(7)	78.18(9)
C(4)-C(8)	1.501(6)	O(1)-Tb(1)-O(5)#4	160.09(8)
C(5)-C(6)	1.385(5)	O(2)#1-Tb(1)-O(5)#4	112.56(9)
C(9)-C(11)	1.393(5)	O(3)#2-Tb(1)-O(5)#4	71.97(11)
C(9)-C(10)	1.394(5)	O(4)#3-Tb(1)-O(5)#4	69.87(9)
C(9)-C(12)	1.505(5)	O(5)-Tb(1)-O(5)#4	78.27(10)
C(10)-C(11)#5	1.387(5)	O(6)#4-Tb(1)-O(5)#4	48.94(8)
N(1)-C(13)	1.312(6)	O(7)-Tb(1)-O(5)#4	117.58(9)
N(1)-C(14')	1.432(11)	O(1)-Tb(1)-C(12)#4	174.09(9)
N(1)-C(14)	1.465(9)	O(2)#1-Tb(1)-C(12)#4	94.38(10)
N(1)-C(16)	1.475(9)	O(3)#2-Tb(1)-C(12)#4	81.50(12)
N(1)-C(16')	1.548(12)	O(4)#3-Tb(1)-C(12)#4	74.72(11)
C(14)-C(15)	1.493(15)	O(5)-Tb(1)-C(12)#4	103.09(10)
C(16)-C(17)	1.496(16)	O(6)#4-Tb(1)-C(12)#4	23.93(9)
C(14')-C(15')	1.480(17)	O(7)-Tb(1)-C(12)#4	98.08(10)

O(5)#4-Tb(1)-C(12)#4	25.03(9)	O(3)-C(8)-C(4)	117.4(4)
C(7)-O(1)-Tb(1)	138.0(2)	O(4)-C(8)-C(4)	117.4(4)
C(7)-O(2)-Tb(1)#1	162.9(2)	C(11)-C(9)-C(10)	120.3(3)
C(8)-O(3)-Tb(1)#6	136.5(3)	C(11)-C(9)-C(12)	119.3(3)
C(8)-O(4)-Tb(1)#3	141.1(3)	C(10)-C(9)-C(12)	120.4(3)
C(12)-O(5)-Tb(1)	171.3(3)	C(11)#5-C(10)-C(9)	119.3(3)
C(12)-O(5)-Tb(1)#4	82.9(2)	C(10)#5-C(11)-C(9)	120.4(3)
Tb(1)-O(5)-Tb(1)#4	101.73(10)	O(6)-C(12)-O(5)	121.9(3)
C(12)-O(6)-Tb(1)#4	106.1(2)	O(6)-C(12)-C(9)	117.8(3)
C(13)-O(7)-Tb(1)	126.7(3)	O(5)-C(12)-C(9)	120.2(3)
C(6)-C(1)-C(2)	119.6(3)	O(6)-C(12)-Tb(1)#4	49.94(17)
C(6)-C(1)-C(7)	120.8(3)	O(5)-C(12)-Tb(1)#4	72.1(2)
C(2)-C(1)-C(7)	119.5(3)	C(9)-C(12)-Tb(1)#4	167.3(2)
C(3)-C(2)-C(1)	120.0(3)	C(13)-N(1)-C(14')	119.0(5)
C(2)-C(3)-C(4)	120.2(4)	C(13)-N(1)-C(14)	119.7(5)
C(3)-C(4)-C(5)	119.8(4)	C(13)-N(1)-C(16)	116.6(5)
C(3)-C(4)-C(8)	121.0(4)	C(14)-N(1)-C(16)	116.4(6)
C(5)-C(4)-C(8)	119.0(3)	C(13)-N(1)-C(16')	124.5(6)
C(6)-C(5)-C(4)	120.2(3)	C(14')-N(1)-C(16')	102.0(7)
C(5)-C(6)-C(1)	120.2(3)	O(7)-C(13)-N(1)	127.5(4)
O(2)-C(7)-O(1)	124.3(3)	N(1)-C(14)-C(15)	115.3(9)
O(2)-C(7)-C(1)	118.9(3)	N(1)-C(16)-C(17)	107.5(8)
O(1)-C(7)-C(1)	116.8(3)	N(1)-C(14')-C(15')	114.7(10)
O(3)-C(8)-O(4)	125.2(4)	C(17')-C(16')-N(1)	107.6(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+1/2 #2 x-1/2, y-1/2, z #3 -x+3/2, -y+3/2, -z+1

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

References

[1] SAINT, Bruker (2003), Bruker AXS Inc., Madison Wisconsin, USA.

[2] SADABS, Bruker (2002), Bruker AXS Inc, Madison Wisconsin, USA.

[3] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112−122.

[4] A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7−13.