Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A zinc(II)-organic framework as multi-responsive photoluminescence sensor for efficient and recyclable detection of pesticide 2,6-dichloro-4-nitroaniline, Fe(III) and Cr(VI)

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Table S1. Crystallographic data and structure refinements for Zn-MOF-**1**

Zn-MOF-1	
Formula	$C_{26}H_{18}ZnN_7O_3$
Mr	541.86
Crystal system	Triclinic
space group	$P\bar{1}$
a, Å	9.1505(10)
b, Å	10.4512(11)
c, Å	13.869(2)
α, deg	108.994(13)
β, deg	101.343(12)
γ , deg	97.790(9)
V, Å^3	1200.8(3)
Z	2
D_c, g cm^{-3}	1.499
μ, mm^{-1}	1.793
Unique.reflns	4297
R_1 [I>2σ(I)]	0.0922
wR_2(All data)	0.2778
GOF	1.118

Table S2. The selected bond lengths (Å) and angles (◦) for Zn-MOF-**1**.

Zn1-O2	1.935(6)
Zn1-N7A	2.027(8)
Zn1-N1	2.032(7)
Zn1-N3B	2.056(7)
O2-Zn1-N7A	115.0(3)
O2-Zn1-N1	114.7(3)
N7A-Zn1-N1	102.9(3)
O2-Zn1-N3B	114.0(3)
N7A-Zn1-N3B	94.6(3)
N1-Zn1-N3B	113.5(3)

Symmetry transformations used to generate equivalent atoms: A: x+1,y+1,z+1; B x+1,y+1,z.

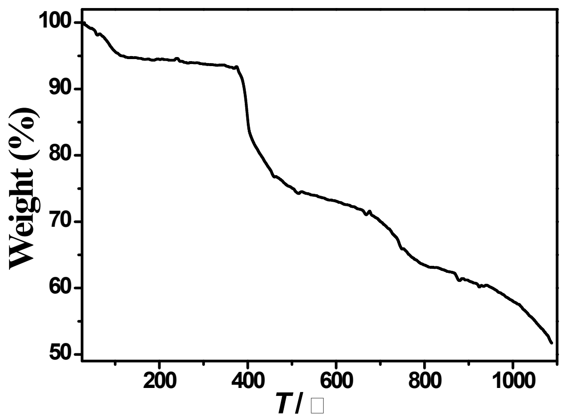

Fig. S1 The TGA curve for Zn-MOF-**1.**

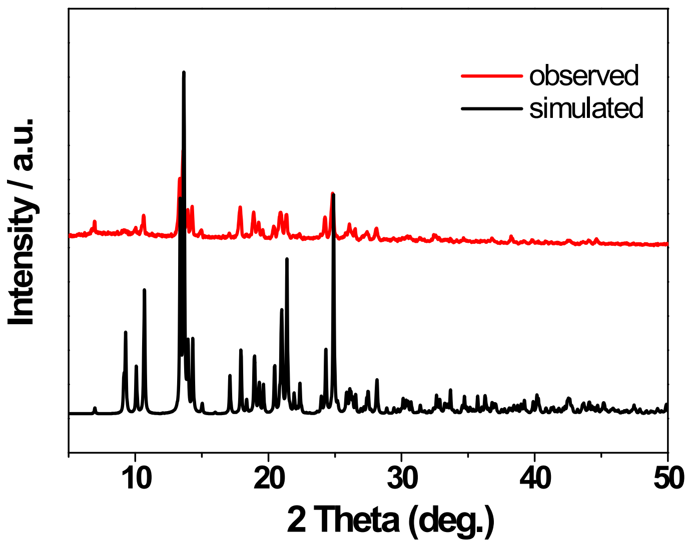

Fig. S2. PXRD patterns for Zn-MOF-**1**.

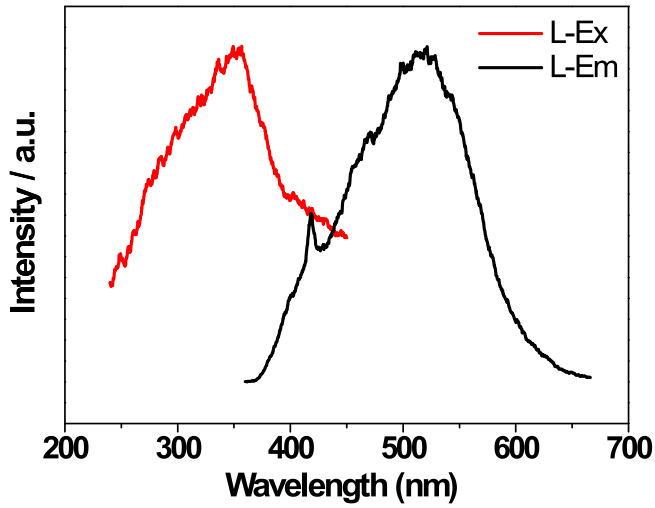

Fig. S3 The solid-state excitation (λ_{em} = 517 nm) and emission spectra (λ_{ex} = 351 nm) of free L ligands at room temperature.

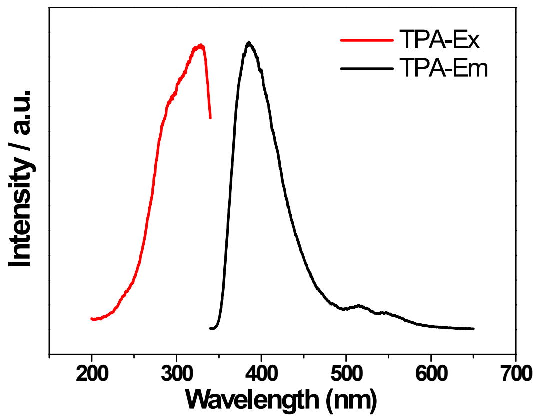

Fig. S4 The solid-state excitation (λ_{em} =385 nm) and emission spectra (λ_{ex} = 326 nm) of free TPA ligands at room temperature.

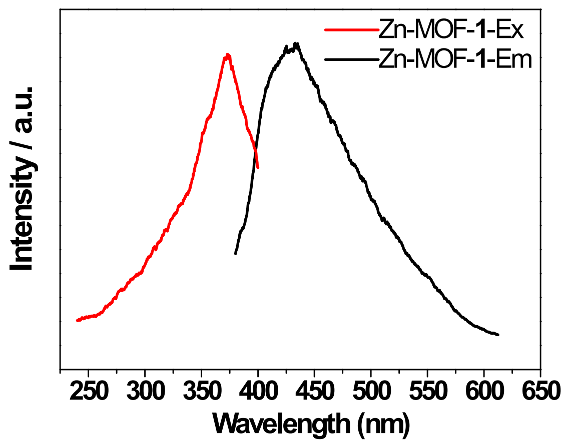

Fig. S5 The solid-state excitation (λ_{em} = 432 nm) and emission spectra (λ_{ex} = 373 nm) of Zn-MOF-**1** at room temperature.

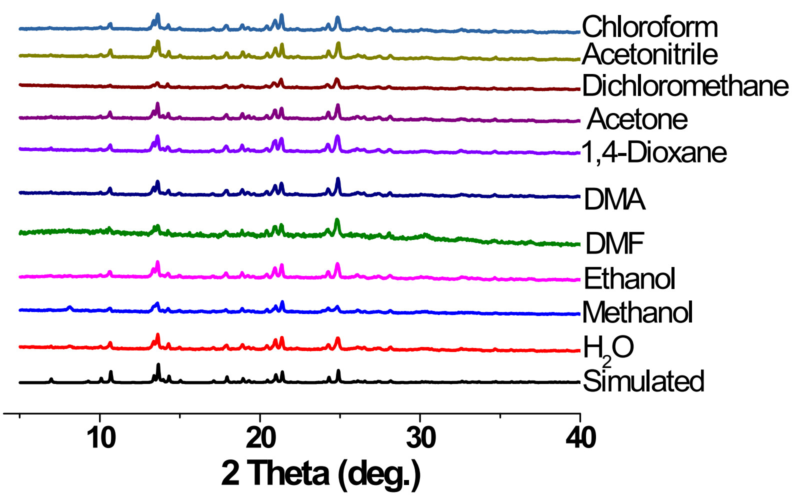

Fig. S6. The PXRD patterns of Zn-MOF-**1** in different solvents, with the simulated Zn-MOF-**1** single crystal data result as reference.

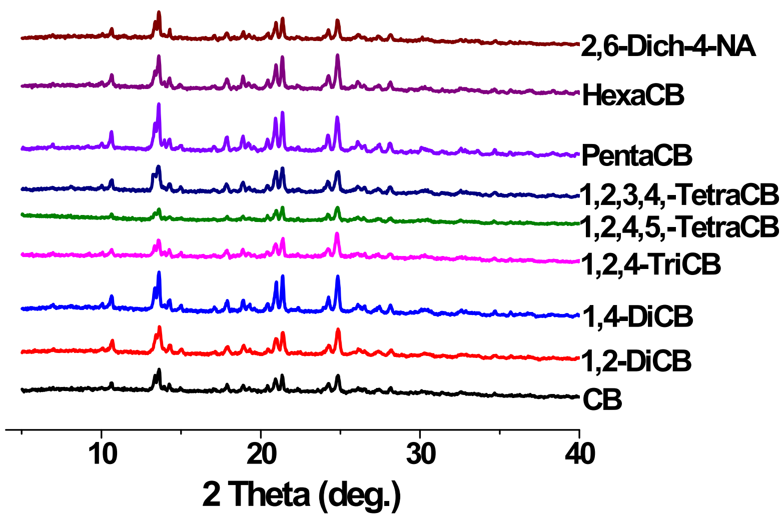

Fig. S7. PXRD patterns of Zn-MOF-**1** in different organochlorine pesticides.

Table S3. Sensing performance comparison between other MOF-based fluorescent sensors with Zn-MOF-**1** for Fe^{3+} ions.

MOF-based fluorescent materials	**analyte**	**detection limits**	**quenching constant**	**recyclability**	**solvent**	**Ref**
Zn-MOF-**1**	Fe^{3+}	3.84 μM	6.4 × 10^3	YES	Water	This work
$\{(Me_2NH_2)[Tb(OBA)_2]\cdot(Hatz)\cdot(H_2O)_{1.5}\}_n$	Fe^{3+}	1.0 μM	3.4 × 10^4	NO	Water	[1]
$[Eu(HL)_{1.5}(H_2O)(DMF)]\cdot 2H_2O$	Fe^{3+}	1.03	1 × 10^4	YES	Water	[2]
$[ZnL]\cdot 2H_2O$	Fe^{3+}	0.92 μM	4.67 × 10^4	YES	Water	[3]
$\{[Cd(5\text{-asba})(bimb)]\}_n$	Fe^{3+}		1.78 × 10^4	NO	Water	[4]
$[Eu(HL)(H_2O)_3]_n$	Fe^{3+}	1.16×10^{-3} M	5.3 × 10^3	NO	Water	[5]
CDs@UiO-66$(OH)_2$	Fe^{3+}	0.76 μM	4.58 ×10^4	NO	Water	6
FJI-C8	Fe^{3+}	0.0233 mM	8245	NO	DMF	7
Al-MIL-53-N_3	Fe^{3+}	0.03 μM	6.13× 10^3	YES	Water	8
$[Zn(L)(bpdc)]\cdot 1.6H_2O$	Fe^{3+}	152 ppb	1.73×10^4	NO	Water	9
Pb_3O_2L	Fe^{3+}	7.85 μM	7.8× 10^3	YES	Water	10

H_2OBA = 4,4'-oxybis(benzoic acid) (H_2oba), Hatz = 3-amino-1,2,4-triazole[1]; HL = 5-(3',5'-dicarboxylphenyl) nicotinic acid[2]; L^{2-} = pphenylenebis(1-[3,5-dicarboxylatophenyl]methyl]pyrid-4-yl)[3]; $H_2$5-asba = 2-amino-5-sulfobenzoic acid, [bimb = 1,4-bis(1H-imidazol-1-yl)butane][4]; H_4L = 1-(3,5-dicarboxylatobenzyl)-3,5-pyrazole dicarboxylic acid[5]; CDs = carbon dots[6]; H_6TDPAT = (2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine)[7]; L = 1,4-di(1H-imidazol-4-yl)benzene, H_2bpdc = 4,4'-benzophenonedicarboxylic acid[9]; H_2L = 4-(1H-tetrazol-5-yl)phenol)[10].

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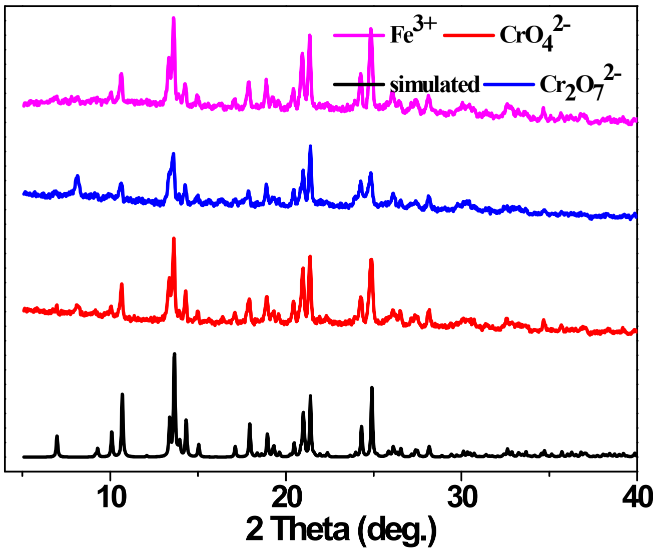

Fig. S8. PXRD patterns of Zn-MOF-**1** after Fe^{3+}, CrO_4^{2-} and $Cr_2O_7^{2-}$ sensing process, with the simulated Zn-MOF-**1** single crystal data result as reference.

Table S4. Sensing performance comparison between other MOF-based fluorescent sensors with Zn-MOF-**1** for Cr(VI) ions

MOF-based fluorescent materials	**analyte**	**detection limits**	**quenching constant**	**recyclability**	**solvent**	**Ref**
Zn-MOF-**1**	CrO_4^{2-}	2.10 μM	1.3×10^4	YES	Water	This work
	$Cr_2O_7^{2-}$	3.80 μM	6.05×10^3			
$[Zn_2(TPOM)(BDC)_2] \cdot 4H_2O$	CrO_4^{2-}	4.8 μM	4.45×10^3	YES	DMF	1
	$Cr_2O_7^{2-}$	3.9 μM	7.59×10^3			
$[Zn(L)(BBI)\cdot(H_2O)_2]$	$Cr_2O_7^{2-}$	–		YES	Water	2
Eu_4L_3	$Cr_2O_7^{2-}$	10 μM	1.526×10^3	YES	DMF	3
$[Cd(TPTZ)(H_2O)_2(HCOOH)(IPA)_2]_n$	$Cr_2O_7^{2-}$	–		NO	Water	4
$[Cd_6(L)_2(bib)_2(DMA)_4]$	CrO_4^{2-}	–		NO	Water	5
$[Zn(2\text{-}NH_2bdc)(bibp)]_n$	$Cr_2O_7^{2-}$	–		NO	Water	6
1-Eu	$Cr_2O_7^{2-}$	22 μM		NO	Ethanol	7
$[Zn_2(tpeb)_2(2,3\text{-}ndc)_2]\cdot H_2O\}_n$	CrO_4^{2-}	1.734 ppb		YES	Water	8
	$Cr_2O_7^{2-}$	2.623 ppb				
$[EuL(H_2O)_3]\cdot 3H_2O\cdot 0.75DMF$	$Cr_2O_7^{2-}$	–		YES	DMF	9
$[Eu_2(tpbpc)_4\cdot CO_3\cdot H_2O]\cdot DMF\cdot solvent$	CrO_4^{2-}	0.33 ppm	4.85×10^3	YES	Water	10
	$Cr_2O_7^{2-}$	1.07 ppm	1.04×10^4			
$[Tb(TATAB)(H_2O)_2]\cdot NMP\cdot H_2O\}_n$	$Cr_2O_7^{2-}$	1 μM	1.11×10^4	NO	Water	11
Eu^{3+}@MIL-121	$Cr_2O_7^{2-}$	0.054 μM	4.34×10^3	NO	Water	12
$[Zn(btz)]_n$	CrO_4^{2-}	10 μM	3.19×10^3	YES	Water	13
	$Cr_2O_7^{2-}$	20 μM	4.23×10^3			

$[Zn_2(ttz)H_2O]_n$	CrO_4^{2-}	2 μM	2.35×10^3	YES	Water	13
	$Cr_2O_7^{2-}$	20 μM	2.19×10^3			
$[Zn_{2.5}(cpbda)(OH)_2]\cdot DMF$	CrO_4^{2-}	–		NO	Water	14
	$Cr_2O_7^{2-}$					
$\{[Cu(butylmalonate)_2(H_2O)]$	$Cr_2O_7^{2-}$	–		NO	Water	15
$(2\text{-}APH)_2\cdot H_2O$						
$[Eu_7(mtb)_5(H_2O)_{16}]\cdot NO_3$	CrO_4^{2-}	0.56 ppb	–	NO	deionized	16
$\cdot 8DMA\cdot 18H_2O$					water	

TPOM= tetrakis(4-pyridyloxymethylene)methane, BDC= 2-aminoterephthalic acid;[1] L=benzo-(1,2;4,5)-bis(thiophene-2′-carboxylic acid, BBI=1,1′-(1,4-butanediyl)bis(imidazole;[2] L= 5,5′-(carbonylbis(azanediyl))diisophthalic acid;[3] TPTZ =4-[4-(1H-1,2,4-triazol-1-yl)phenyl]phenyl}-1H-1,2,4-triazole, IPA=isophthalic acid;[4] L= 4-(carboxyphenyl)oxamethyl]-3-oxapentane acid, bib = 4,4′-di(1H-imidazol-1-yl)-1,1′-biphenyl, tib= 1,3,5-tri(1H-imidazol-1-yl)benzene;[5] bibp = 4,4′-bis(imidazol-1-ylmethyl)-biphenyl;[6] 1= 3-(1H-pyrazol-3-yl) benzoic acid;[7] tpeb = 1,3,5-tri-4-pyridyl-1,2-ethenylbenzene, 2,3-ndc = 2,3-naphthalenedicarboxylic acid;[8] L = biphenyl-3′-nitro-3,4′,5-tricarboxylic acid;[9] tpbpc =4′-[4,2′;6′,4″]-terpyridin-4′-yl-biphenyl -4-carboxylic acid;[10] TATAB = 4,4′,4″-s-triazine-1,3,5-triyltri-m-aminobenzoic acid, NMP = N-methyl-2-pyrrolidone;[11] btz =1,5-bis(5-tetrazolo)-3-oxapentane, ttz= 1,2,3-tris-[2-(5-tetrazolo)-ethoxy] propane;[13] cpbda =3,5-bis(4-carboxyphenoxy)benzoic acid;[14] 2-APH= protonated 2-aminopyridine;[15] 4mtb = 4-[tris(4-carboxyphenyl) methyl]benzoic acid.[16]

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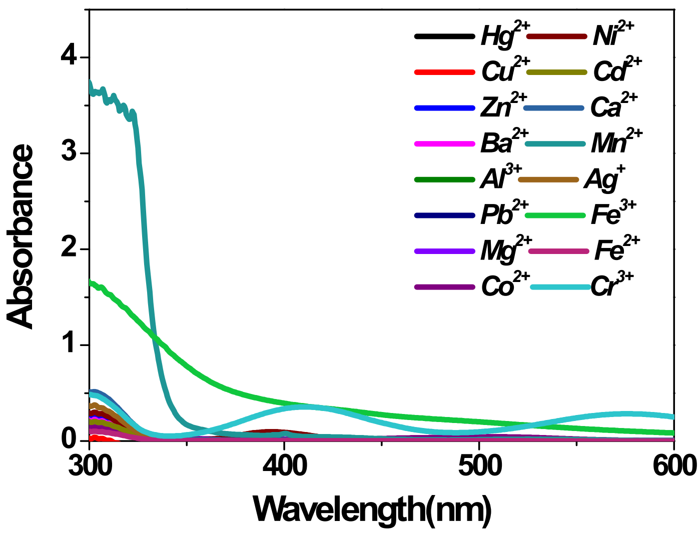

Fig. S9. The UV-Vis absorption spectrum of selected 0.001 M different M^{z+} (Hg^{2+}, Cu^{2+}, Zn^{2+}, Ba^{2+}, Al^{3+}, Pb^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+}, Mn^{2+}, Ag^{+}, Cr^{3+}, Fe^{2+} and Fe^{3+}) ions aqueous solution.

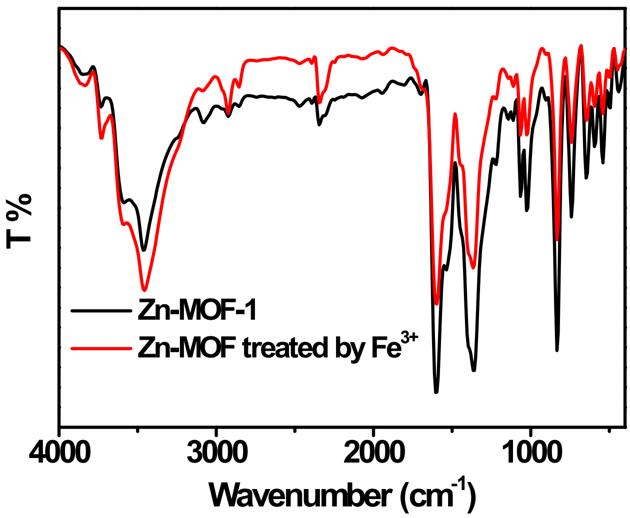

Fig. S10. IR characterization of as-synthesized Zn-MOF-**1,** Zn-MOF-**1** treated by Fe^{3+} ions.

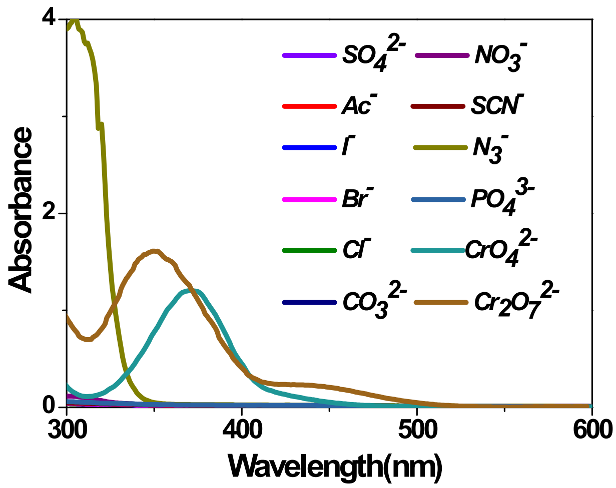

Fig. S11. The UV-Vis absorption spectrum of selected 10^{-4} M different anions (SO_4^{2-}, PO_4^{3-}, Br^-, OAc^-, SCN^-, Cl^-, NO_3^-, CO_3^{2-}, N_3^-, I^-, CrO_4^{2-} and $Cr_2O_7^{2-}$) ions aqueous solution.