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Supporting Information For

A water stable Europium−MOF as multifunctional luminescent sensor for Trivalent metal ions (Fe^{3+},Cr^{3+},Al^{3+}), PO_4^{3-} ions, and nitroaromatic explosives

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Table S1 The crystallographic data for compound **1**

Formula		$C_{38}H_{22}N_2O_{16}Eu_2$	
Formula Weight	1066.50	V(Å^3)	1946.2(3)
Crystal System	Triclinic	*Density*（Mg/m^3）	1.820
Space Group	*P* **Error!**	μ（mm^{-1}）	3.269
T（K）	213(2)	F(000)	1036
a (Å)	7.2685(5)	*Rint*	0.0312
b (Å)	14.6954(11)	GOOF	1.084
c (Å)	19.3575(17)	R_1[a] [$I>2\sigma(I)$]	0.0244
α (°)	78.962(6)	ωR_2[b][$I>2\sigma(I)$]	0.0780
β (°)	79.280(5)	R_1 (all data)	0.0277
γ (°)	75.788(5)	ωR_2(all data)	0.0795

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Table S2. Selected bond lengths [Å] and angles [°] for **1**

Compound **1**			
Eu(1)-O(15)	2.374(3)	Eu(2)-O(16)	2.378(3)
Eu(1)-O(8)#1	2.378(2)	Eu(2)-O(2)#2	2.382(2)
Eu(1)-O(7)#1	2.390(2)	Eu(2)-O(3)#2	2.392(2)
Eu(1)-O(14)	2.397(2)	Eu(2)-O(12)#2	2.393(2)
Eu(1)-O(11)	2.419(2)	Eu(2)-O(13)	2.420(2)
Eu(1)-O(1)	2.495(3)	Eu(2)-O(9)#1	2.497(3)
Eu(1)-O(3)#2	2.543(3)	Eu(2)-O(7)	2.511(2)
Eu(1)-O(4)#2	2.544(4)	Eu(2)-O(6)	2.545(3)
Eu(1)-O(2)	2.570(2)	Eu(2)-O(8)#1	2.573(2)
Eu(1)-Eu(2)	3.9500(3)	O(16)-Eu(2)-O(2)#2	129.14(9)
O(15)-Eu(1)-O(8)#1	129.13(9)	O(16)-Eu(2)-O(3)#2	78.84(9)
O(15)-Eu(1)-O(7)#1	78.69(10)	O(2)#2-Eu(2)-O(3)#2	72.02(8)
O(8)#1-Eu(1)-O(7)#1	72.11(8)	O(16)-Eu(2)-O(12)#2	70.88(9)
O(15)-Eu(1)-O(14)	70.91(9)	O(2)#2-Eu(2)-O(12)#2	71.94(9)
O(8)#1-Eu(1)-O(14)	71.69(9)	O(3)#2-Eu(2)-O(12)#2	96.22(8)
O(7)#1-Eu(1)-O(14)	95.77(8)	O(16)-Eu(2)-O(13)	142.08(8)
O(15)-Eu(1)-O(11)	142.10(8)	O(2)#2-Eu(2)-O(13)	69.33(8)
O(7)#1-Eu(1)-O(14)	95.79(13)	O(3)#2-Eu(2)-O(13)	77.47(8)
O(15)-Eu(1)-O(11)	142.09(14)	O(12)#2-Eu(2)-O(13)	140.81(9)
O(8)#1-Eu(1)-O(11)	69.54(8)	O(16)-Eu(2)-O(9)#1	91.02(10)
O(7)#1-Eu(1)-O(11)	77.85(8)	O(2)#2-Eu(2)-O(9)#1	139.61(9)
O(7)#1-Eu(1)-Eu(2)	140.79(9)	O(16)-Eu(2)-Eu(1)	77.50(7)
O(15)-Eu(1)-O(1)	90.72(10)	O(2)#2-Eu(2)-Eu(1)	100.67(6)
O(8)#1-Eu(1)-O(1)	139.93(9)	O(3)#2-Eu(2)-Eu(1)	37.35(5)
O(7)#1-Eu(1)-O(1)	119.47(8)	O(12)#2-Eu(2)-Eu(1)	128.58(6)
O(14)-Eu(1)-O(1)	136.55(10)	O(13)-Eu(2)-Eu(1)	65.71(6)
O(11)-Eu(1)-O(1)	75.69(10)	Eu(2)#1-O(2)-Eu(1)	105.91(9)
O(15)-Eu(1)-O(3)#2	139.03(9)	Eu(1)#2-O(7)-Eu(2)	107.52(9)

Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z #2 x+1,y,z
#3 -x,-y+1,-z+1 #4 -x+1,-y+2,-z

Table S3. Hydrogen bonds with H··A < r (A) + 2.000 Angstroms and <DHA > 110 deg.

Compound **1**					
D-H	d (D-H)	d (H··A)	<DHA	d (D··A)	A
O15-H15A	0.850	2.264	114.11	2.724	O2
O15-H15A	0.850	2.274	129.78	2.892	O13
O15-H15C	0.850	2.031	130.62	2.664	N1_b
O15-H15C	0.850	2.075	136.14	2.752	N1_a
O16-H16A	0.850	1.934	146.80	2.686	N2'_b
O16-H16A	0.850	1.964	154.68	2.756	N2_a

Table S4 Fluorescent quantum yield data of compound **1**

Compound **1**			
ν_{00} (cm^{-1})	16892	A_{00}	48.286
ν_{01} (cm^{-1})	16313	A_{01}	50
ν_{02} (cm^{-1})	16155	A_{02}	212.710
ν_{03} (cm^{-1})	14598	A_{03}	195.448
ν_{04} (cm^{-1})	14327	A_{04}	19.243
I_{01} (a.u)	15030	**Ar**	**525.687**
I_{02} (a.u)	63320	**τ(ms)**	**0.513**
I_{02}/I_{01}	4.213	**$1/\tau$**	**1.949**
η%		**26.97**	

The luminescence quantum yield η of the $^5D_0$ emission lever in the ternary Eu(III) complex could be calculated based on the measurements: Eq. (1) is a means to determine the η values from experimental spectroscopic data,

η = Ar /(Ar +Anr) Eq. (1)

where Ar and Anr are radiative and non-radiative transition rates, respectively. The denominator in Eq. (1) is calculated from the lifetime of the emitting level ($1/\tau$ = Ar +Anr, where τ stands for fluorescence lifetime).

In the case of europium luminescence, value of Ar could be obtained from the Eq. (2),

$Ar = \Sigma A_{0J} = A_{00}+A_{01}+A_{02}+A_{03}+A_{04}$ Eq. (2)

where J represents the final $^7F_{0\text{-}4}$ levers. The values of A_{0J} could be calculated by the Eq. (3) and Eq. (4) ,

$A_{0J} = A_{01}(I_{0J}/I_{01})(\nu_{01}/\nu_{0J})$ Eq. (3)

$\nu_{0J} = 1/\lambda_J$ Eq. (4)

Where λ stands for wavelength correspondingly, A_{01} is the Einstein coefficient of spontaneous emission between the $^5D_0$ and the $^7F_1$ Stark levels, which may be used as a reference for the whole spectrum in vacuum, A_{01} = 50 s^{-1}. The needed calculated responding data are shown in Table S3.

Table S5 The EDS analyses for **1**

Sample	El	AN	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]
1@Al^{3+}	C	6	45.25	51.17	65.99
	O	8	29.11	32.92	31.87
	Eu	63	13.10	14.81	1.51
	Al	13	0.97	1.10	0.63
	Total:		88.43	100.00	100.00
1@Cr^{3+}	C	6	53.30	52.09	65.50
	O	8	35.98	35.16	33.19
	Eu	63	12.81	12.52	1.24
	Cr	24	0.24	0.23	0.07
	Total:		102.33	100.00	100.00
1@Fe^{3+}	C	6	30.69	44.85	69.18
	O	8	21.55	31.50	3.84
	Eu	63	15.85	23.16	26.82
	Fe	26	0.33	0.48	0.16
	Total:		68.42	100.00	100.00

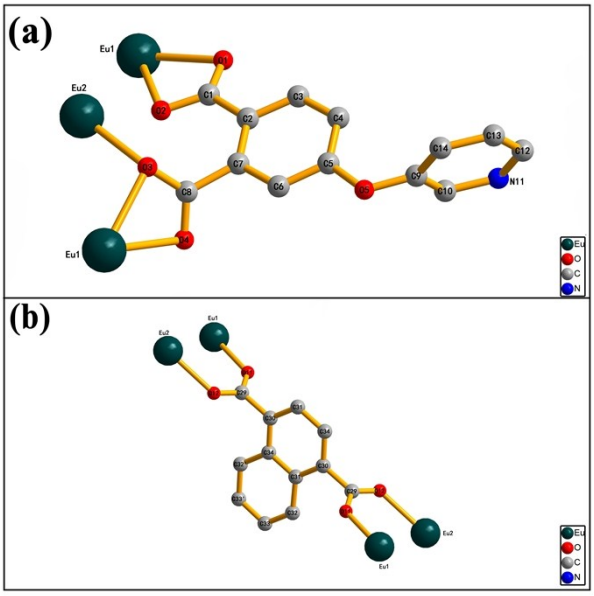

Fig. S1 The coordination mode of ligands (a) H_2ppda and (b) H_2npdc.

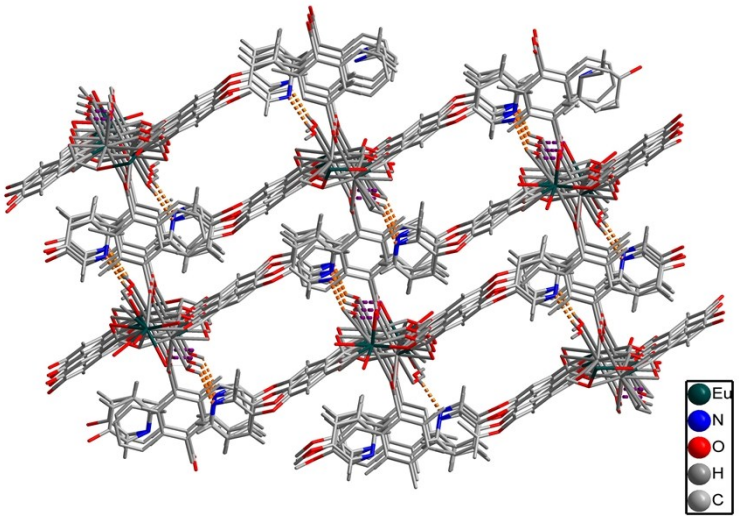

Fig. S2 3D supramolecular framework of **1** and the hydrogen bonds in it, the yellow dotted lines represent N···H-O, and the pink dotted lines represent O···H-O.

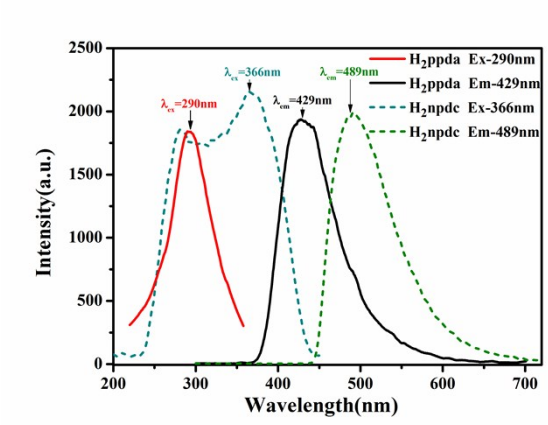

Fig. S3 The PL spectra of H_2ppda (solid line) and H_2npdc ligand (dotted line).

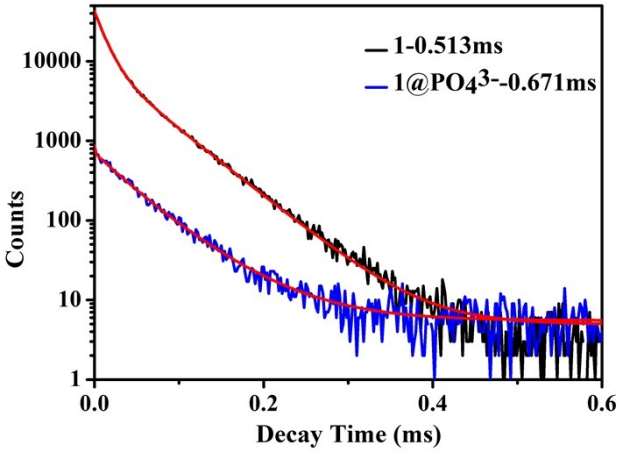

Fig. S4 The decay curves and fit curves for compound **1** and **1** after adding PO_4^{3-} (10^{-2}M).

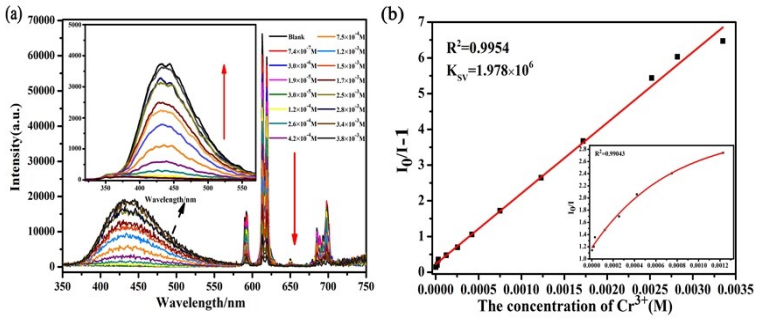

Fig. S5 (a) Emission spectra of **1** dispersed in the various concentrations of Cr^{3+} ions at the excitation of 314nm. (b) Linear Stern-Volmer curves in low concentration range of Cr^{3+} ions. (Inset: Nonlinear Stern-Volmer curves of Cr^{3+} ions)

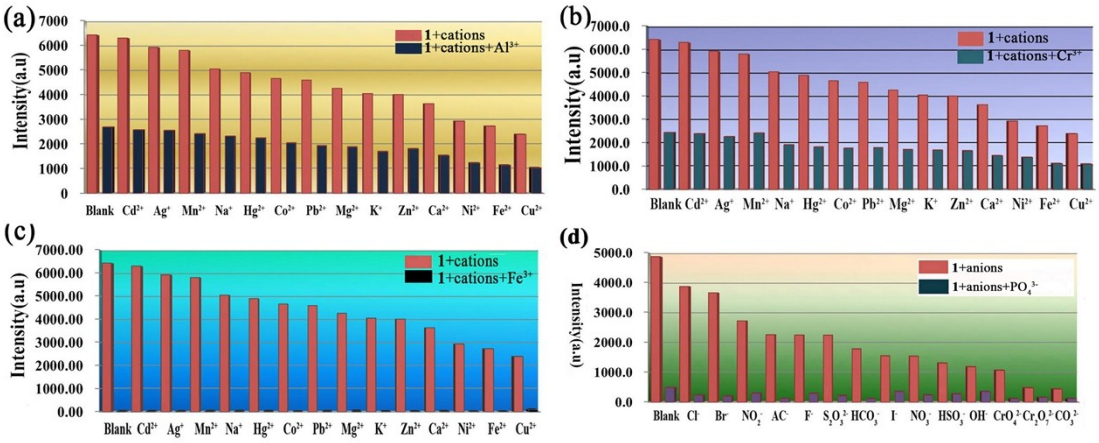

Fig. S6 Fluorescence intensity for **1** exposed to single ion (a for Al^{3+}, b for Cr^{3+}, c for Fe^{3+} and d for PO_4^{3-}) and mixed ions in aqueous solutions.

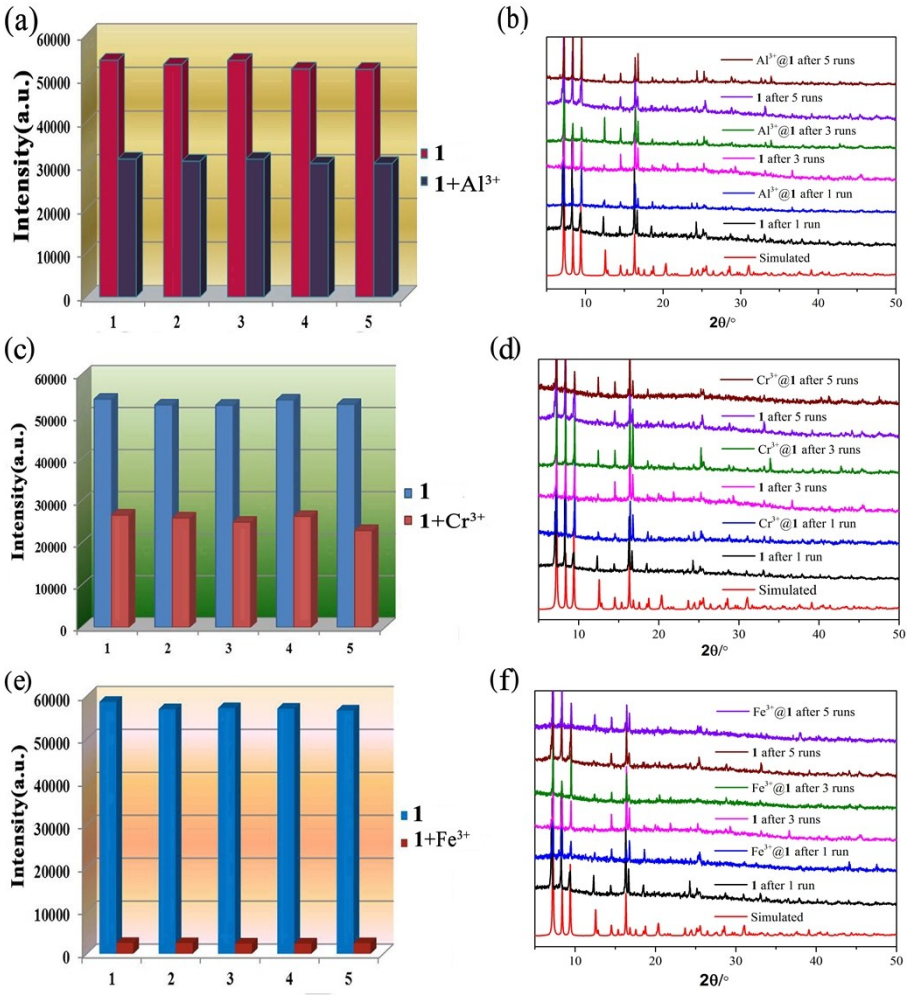

Fig. S7 (a) Recovery test of **1** in aqueous solution for (a) Al^{3+}: The red columns represent the initial relative luminescent intensity and the purple columns represent the relative intensity on addition of Al^{3+}; (c) Cr^{3+} and (e) Fe^{3+} : The blue columns represent the initial relative luminescent intensity of **1** and the red columns represent the relative intensity on addition of Cr^{3+} or Fe^{3+}; (b, d, f) PXRD patterns of **1**@Al^{3+}, **1**@ Cr^{3+} and **1**@ Fe^{3+} after 5 runs.

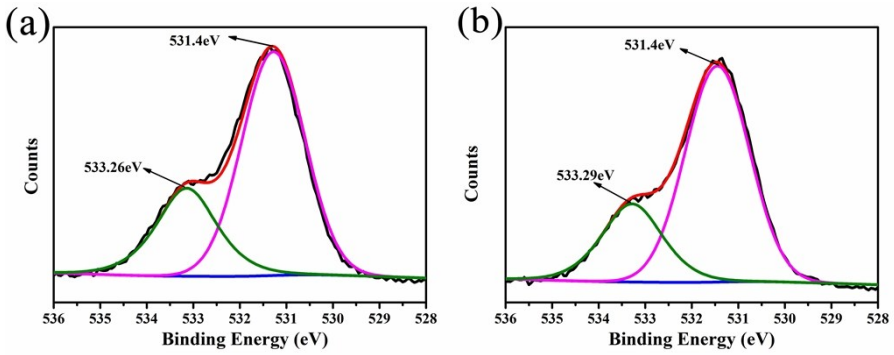

Fig. S8 (a) The XPS spectra for the O 1 s region of Cr^{3+}-incorporated@1; (b) The XPS spectra for the O 1 s region of Al^{3+}-incorporated@1.

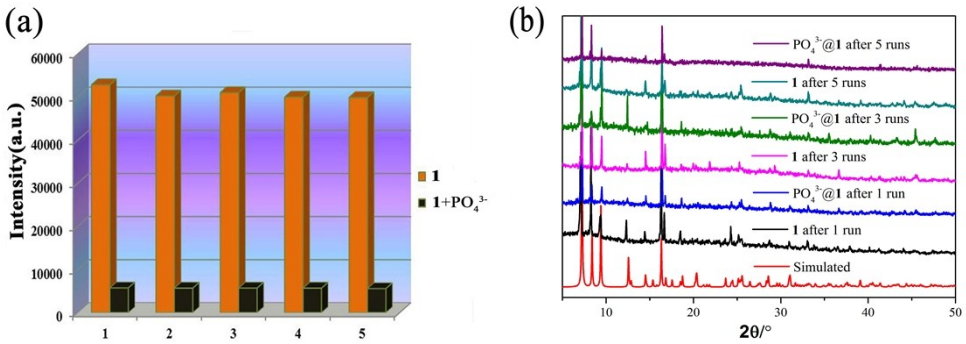

Fig. S9 (a) Recovery test of **1** in aqueous solution. The orange columns represent the initial relative luminescent intensity and the black columns represent the relative intensity on addition of PO_4^{3-}, (b) PXRD patterns of PO_4^{3-}@**1** after 5 runs.

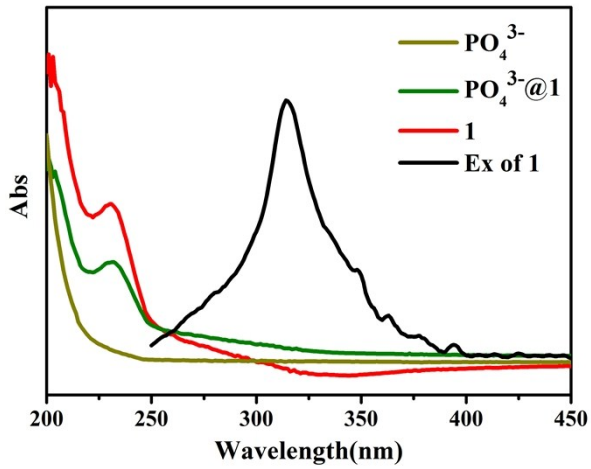

Fig. S10 The UV-Vis adsorption spectra of **1**, PO_4^{3-}, **1** soaked in Na_3PO_4 solutions and excitation spectrum of **1.**

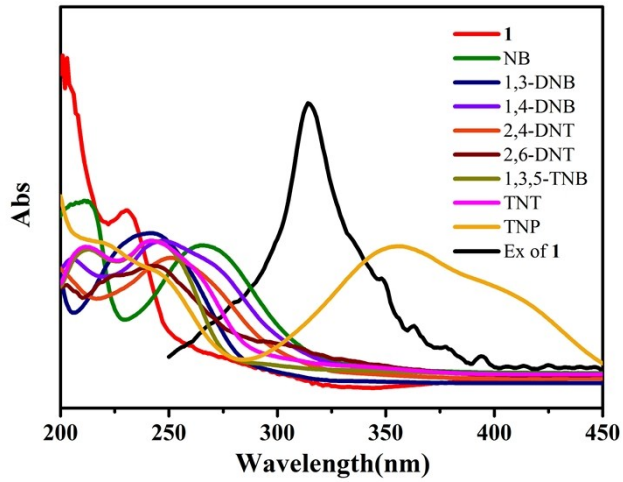

Fig. S11 The UV-Vis adsorption spectra of **1**, **1** after adding various nitro aromatics and excitation spectrum of **1.**

Table S6 Comparison of literature reports for MOFs as sensors of Cr^{3+}

MOF	K_{SV} (M^{-1})	Detection Limit	Medium	Ref.
$[Eu_2(ppda)_2(npdc)(H_2O)]\cdot H_2O$ (**1**)	1.98×10^6	6.17×10^{-5} M (61.7μM)	H_2O	**This work**
Tb-BTC films	/	10^{-4} mM (0.11ppb)	H_2O	27 (a)
{[Eu(HL)$(H_2O)_3$]·H_2O}n (**1**)	2.1×10^4	/	H_2O	27 (b)
(Tb^{3+})@Cd-MOF	1.81×10^5	7.5×10^{-8} M (0.075μM)	EtOH	15
$Tb^{3+} \subset [Y(DPA)_3]$	3.04×10^4	/	DMF	27 (c)
$[Zn(L)(H_2O)] \cdot H_2O$ (**1**)	3.64×10^4	2.44×10^{-6} M (2.44μM)	H_2O	27 (d)
{$[Zn_2(\mu_3\text{-OH})(cpta)(4,4\quad\text{-bipy})] \cdot H_2O\}_n$ (**1**)	9.47×10^3	5.55×10^{-6} M (5.55μM)	H_2O	27 (e)

Table S7 Comparison of literature reports for MOFs as sensors of Al^{3+}

MOF	K_{SV} (M^{-1})	Detection Limit	Medium	Ref.
$[Eu_2(ppda)_2(npdc)(H_2O)]\cdot H_2O$ (**1**)	8.68×10^5	1.09×10^{-4} M (109μM)	H_2O	**This work**
$[\{Cd_2(syn\text{-}dftpmcp)(1,3\text{-}BDC)_2\}\cdot 0.5DMF\cdot H_2O]_n$ (**2**)	/	183ppb	CH_3CN	28 (a)
$[Cd_2(bptc)(HCOO)]\cdot NH_2(CH_3)_2\cdot 3H_2O$ (**1**)	7.3×10^4	/	H_2O	28 (b)
Eu-MOF	3.79×10^4	/	DMF	11
$[Cd(PAM)(4\text{-}bpdb)_{1.5}]\cdot DMF$ (Cd-MOF)	2.3×10^4	5.6×10^{-7} M (0.56μM)	H_2O	28 (c)
{$(Me_2NH_2)[Tb(OBA)_2] \cdot (Hatz) \cdot (H_2O)_{1.5}\}_n$ (**1**)	3.4×10^4	/	H_2O	14
$[Zn_2(HL)_3]^+$@MOF-5	7.478×10^4	/	DMF	28 (d)

Table S8 Comparison of literature reports for MOFs as sensors of PO_4^{3-}

MOF	K_{SV} (M^{-1})	Detection Limit	Medium	Ref.
$[Eu_2(ppda)_2(npdc)(H_2O)]\cdot H_2O$ (**1**)	1.8×10^5	1.42×10^{-5} M (14.2μM)	H_2O	**This work**
$[Eu(BTB)(phen)(H_2O)_2]_n$ (**1**)	3.97×10^3	4×10^{-5} M (40μM)	H_2O	41 (a)
activated $\{Eu_2L_3(DMF)\}\cdot 2DMF$ (**1**)	4×10^4	6.62×10^{-6} M (6.62μM)	H_2O	41 (b)
$\{[Eu_{1.5}(BTB)_{1.5}(H_2O)]\cdot 3DMF\}n$ (**1**)	7.97×10^3	1×10^{-5} M (10μM)	H_2O	5
Tb@Zn-MOF	4.07×10^3	1.29×10^{-6} M (0.1ppm)	H_2O	41 (c)
$[Tb(H_2O)(BTB)]$ (**2**).	/	3.5×10^{-5} M (35μM)	DMF	41 (d)
CDs–Eu^{3+}	1.3×10^5	5.1×10^{-8} M (0.051μM)	H_2O	41 (e)

Table S9 Comparison of literature reports for MOFs as sensors of TNP

MOF	K_{SV} (M^{-1})	Detection Limit	Medium	Ref
$[Eu_2(ppda)_2(npdc)(H_2O)]\cdot H_2O$ (**1**)	3.44×10^5	2.97×10^{-6} M (2.97μM)	H_2O:MeOH	**This work**
Eu_4L_3	2.001×10^3	1×10^{-5} M (10μM)	DMF	46 (a)
$\{Cd(INA)(pytpy)(OH)\cdot 2H_2O\}_n$ (**1**)	4.3×10^4	2.41×10^{-3} mM (2.41μM)	DMF	46 (b)
$[Eu_3(bpydb)_3(HCOO)(\mu_3\text{-}OH)_2(DMF)]\cdot(DMF)_3(H_2O)_2$ (**1**)	1.5×10^4	/	DMF	46 (c)
$\{[Eu_2(TDC)_3(CH_3OH)_2]\cdot CH_3OH\}$ thin film	1.1×10^4	9.5×10^{-6} M (9.5μM)	MeOH	46 (d)
RBH@Eu(BTC)	3.15×10^5	1×10^{-5} M (10μM)	EtOH	46 (e)
$(C_2H_6NH_2)_2[Tb_2(ptptc)_2(DMF)(H_2O)]\cdot DMF\cdot 6H_2O$ (complex **1**)	3.89×10^4	/	MeOH	46 (f)
$[Zn_{24}(BDPO)_{12}(DMF)_{12}]\cdot 6DMF\cdot 52H_2O$ (**1**)	1.6×10^4	/	DMF	46 (g)
$Zn_2(H_2L)_2(Bpy)_2(H_2O)_3\cdot H_2O$ (MOF-**2**).	1.36×10^4	0.49μM (110ppb)	H_2O	46 (h)