Electronic Supplementary Information

Tuning the luminescence of two 3d-4f metal-organic frameworks for fast response and highly selective detection of aniline

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1. Structures

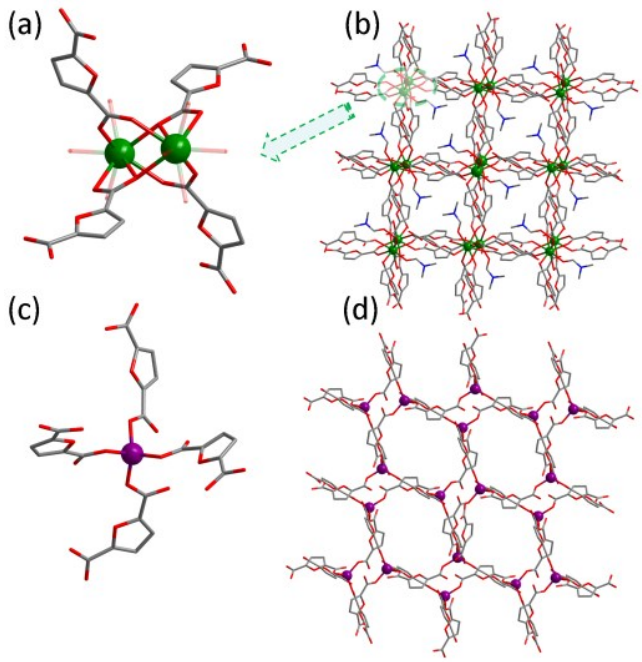

Fig. S1 (a) $Ln_2(COO)_4$ secondary building blocks in **Zn-Eu** MOFs; (b) 2D Eu layers in **Zn-Eu** MOFs; (c) $Zn(FDA)_4$ secondary building blocks in **Zn-Eu** MOFs; (d) 2D Zn layers in **Zn-Eu** MOFs.

2. Power X-Ray Diffraction

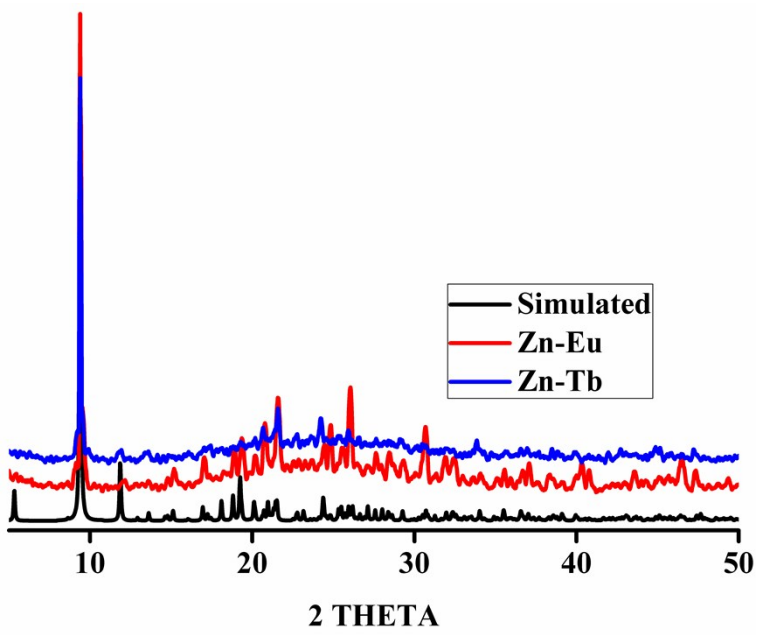

Fig. S2 Comparison of the experimental PXRD patterns of as-synthesized **Zn-Eu** and **Zn-Tb** with that simulated from its single crystal data.

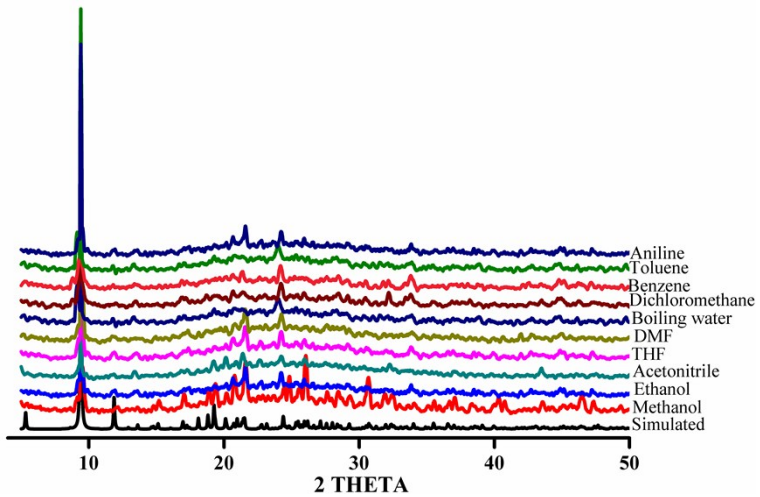

Fig. S3 Comparison of the PXRD patterns of **Zn-Eu** after soaking in different solvents with that simulated from its single crystal data.

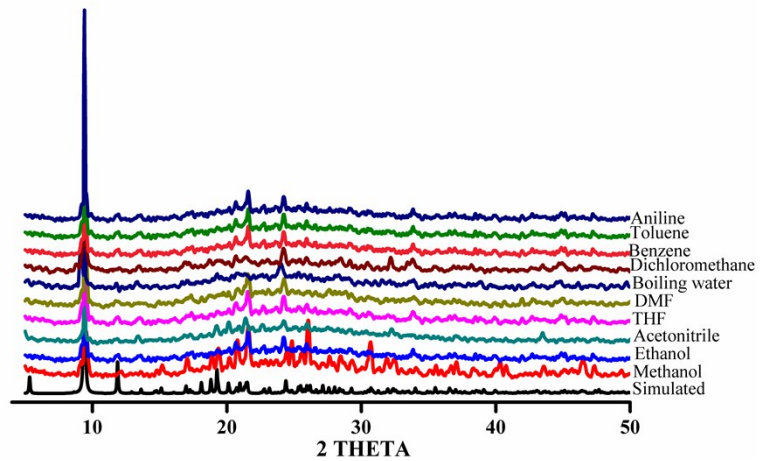

Fig. S4 Comparison of the PXRD patterns of **Zn-Tb** after soaking in different solvents with that simulated from its single crystal data.

3. Thermogravimetric Analysis

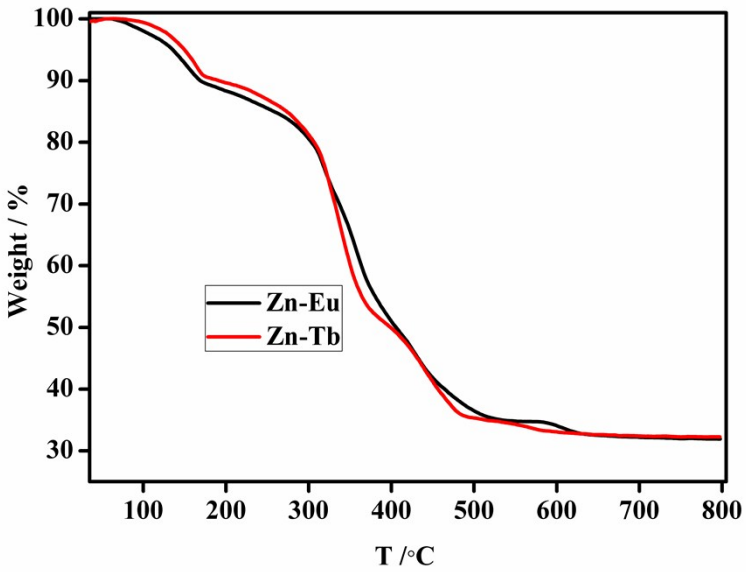

Fig. S5 The thermal gravimetric analysis (TGA) of **Zn-Eu** and **Zn-Tb.**

4. Infrared Spectrum

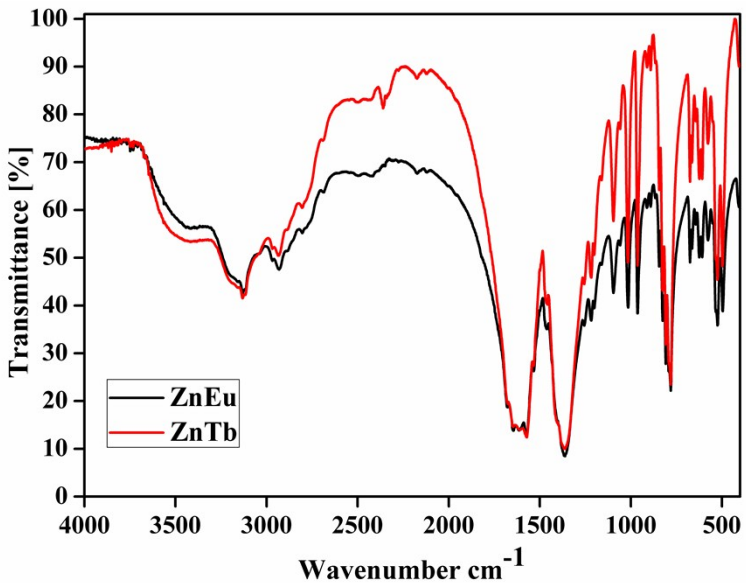

Fig. S6 Infrared spectrum of **Zn-Eu** and **Zn-Tb**.

5. Luminescence Spectrum

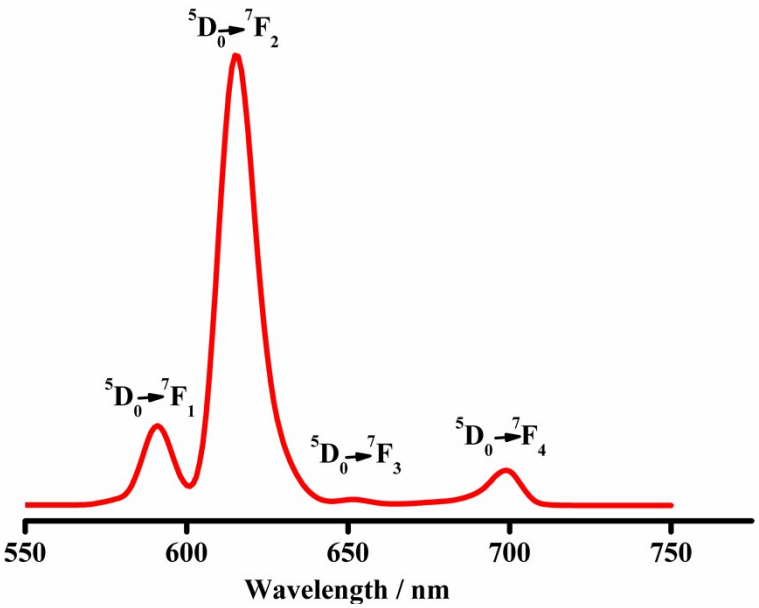

Fig. S7 Emission spectra of **Zn-Eu** crystalline samples at room temperature.

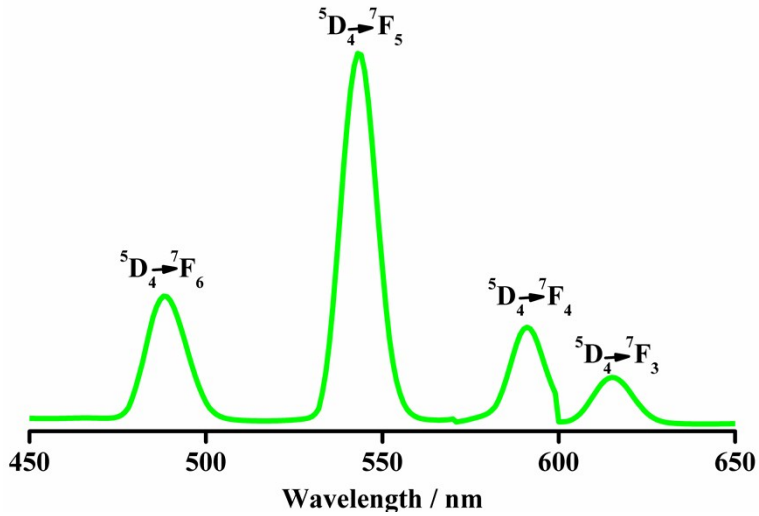

Fig. S8 Emission spectra of **Zn-Tb** crystalline samples at room temperature.

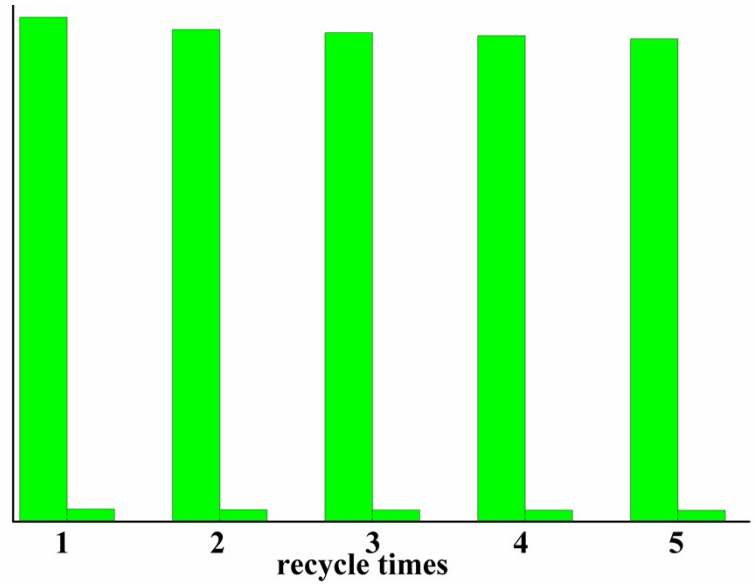

Fig. S9 The luminescence intensity ($^5D_0 \rightarrow {}^7F_2$) of five recycling times that **Zn-Eu** detects aniline in CH_3OH solution.

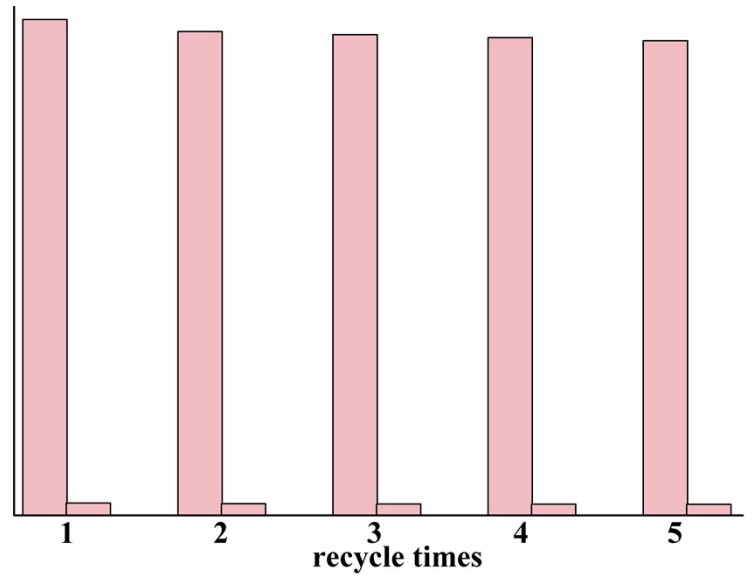

Fig. S10 The luminescence intensity ($^5D_4 \rightarrow {}^7F_5$) of five recycling times that **Zn-Tb** detects aniline in CH_3OH solution.

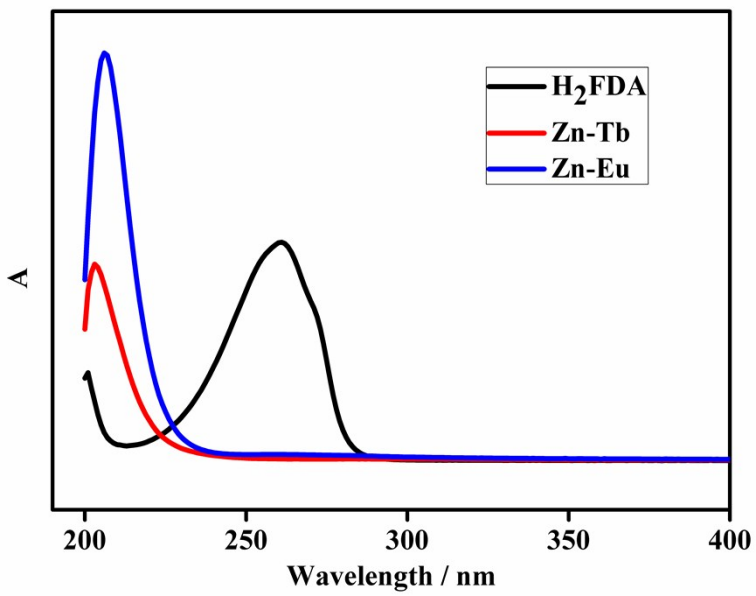

Fig. S11 The UV-vis absorption spectra of suspensions **Zn-Eu**, **Zn-Tb** and H_2FDA in methanol.

Table S1 the selected bond lengths (Å) and angles (°) for **Zn-Eu** and **Zn-Tb.**

		Zn-Eu	
Eu(1)-O(1)	2.549(2)	O1-Eu1-O9$^{\#3}$	129.57(8)
Eu(1)-O(5)$^{\#2}$	2.382(2)	O6-Eu1-O9$^{\#3}$	94.87(8)
Eu(1)-O(6)	2.495(2)	O7-Eu1-O9$^{\#3}$	69.31(7)
Eu(1)-O(7)$^{\#1}$	2.386(2)	O16-Eu1-O9$^{\#3}$	70.78(8)
Eu(1)-O(7)	2.719(2)	O1-Eu1-O10$^{\#4}$	70.81(7)
Eu(1)-O(9)$^{\#3}$	2.433(2)	O(5)$^{\#2}$-Eu1-O10$^{\#4}$	141.78(8)
Eu(1)-O(10)$^{\#4}$	2.361(2)	O6-Eu1-O10$^{\#4}$	72.41(8)
Eu(1)-O(11)	2.385(2)	O7$^{\#1}$-Eu1-O10$^{\#4}$	75.42(7)
Eu(1)-O(16)	2.455(2)	O7-Eu1-O10$^{\#4}$	68.83(7)
Zn(1)-O(2)	1.965(2)	O9$^{\#3}$-Eu1-O10$^{\#4}$	133.60(7)
Zn(1)-O(4)$^{\#2}$	1.972(2)	O11-Eu1-O10$^{\#4}$	79.85(7)
Zn(1)-O(15)$^{\#5}$	1.959(2)	O16-Eu1-O10$^{\#4}$	134.52(8)
Zn(1)-O(12)	1.950(2)	O1-Eu1-O11	72.86(7)
O1-Eu1-O7	132.16(7)	O6-Eu1-O11	75.81(7)
O1-Eu1-O5$^{\#2}$	71.10(7)	O7$^{\#1}$-Eu1-O11	142.40(7)
O6-Eu1-O5$^{\#2}$	137.75(8)	O9$^{\#3}$-Eu1-O11	141.44(7)
O7-Eu1-O5$^{\#2}$	96.07(8)	O16-Eu1-O11	71.16(8)
O(7)$^{\#1}$-Eu1-O5$^{\#2}$	145.21(7)	O1-Eu1-O11	122.59(7)
O9$^{\#3}$-Eu1-O5$^{\#2}$	75.94(8)	O7-Eu1-O16	128.59(8)
O11-Eu1-O5$^{\#2}$	86.16(8)	O6-Eu1-O16	67.06(8)
O16-Eu1-O5$^{\#2}$	71.03(8)	O7-Eu1-O16	98.26(8)
O1-Eu1-O6	134.90(7)	O2-Eu1-O4$^{\#2}$	114.51(10)
O6-Eu1-O7	49.72(7)	O2-Eu1-O12	111.73(10)
O1-Eu1-O7$^{\#1}$	72.49(7)	O4$^{\#2}$-Eu1-O12	118.59(10)
O6-Eu1-O7$^{\#1}$	121.42(7)	O15$^{\#5}$-Eu1-O12	109.53(10)
O7-Eu1-O7$^{\#1}$	73.42(8)	O2-Eu1-O15$^{\#5}$	96.86(10)
O9$^{\#3}$-Eu1-O7$^{\#1}$	74.31(7)	O4$^{\#2}$-Eu1-O15$^{\#5}$	102.70(10)
O16-Eu1-O7$^{\#1}$	144.75(8)		

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$-X,-Y,-Z; $^{\#2}$+X,-1/2-Y,-1/2+Z; $^{\#3}$+X,1/2-Y,-1/2+Z; $^{\#4}$-X,-1/2+Y,1/2-Z; $^{\#5}$1-X,-1/2+Y,1/2-Z;

		Zn-Tb	
Tb(1)-O(7) $^{\#1}$	2.330(3)	O7$^{\#1}$-Tb1-O9$^{\#3}$	72.87(9)
Tb(1)-O(10)$^{\#2}$	2.343(3)	O10$^{\#2}$-Tb1-O9$^{\#3}$	121.83(9)
Tb(1)-O(5)	2.347(3)	O5-Tb1-O9$^{\#3}$	138.69(9)
Tb(1)-O(11)	2.357(3)	O11-Tb1-O9$^{\#3}$	76.58(9)
Tb(1)-O(6)	2.408(3)	O6-Tb1-O9$^{\#3}$	92.90(9)
Tb(1)-O(16)	2.436(3)	O16-Tb1-O9$^{\#3}$	67.50(9)
Tb(1)-O(9)$^{\#3}$	2.460(3)	O7$^{\#1}$-Tb1-O1$^{\#4}$	70.46(9)
Tb(1)-O(1)$^{\#4}$	2.549(3)	O10$^{\#2}$-Tb1-O1$^{\#4}$	71.92(8)
Tb(1)-O(10)$^{\#3}$	2.753(3)	O5-Tb1-O1$^{\#4}$	71.12(9)
Zn(1)-O(12)	1.945(3)	O11-Tb1-O1$^{\#4}$	72.96(9)
Zn(1)-O(14)$^{\#5}$	1.959(3)	O6-Tb1-O1$^{\#4}$	130.69(9)
Zn(1)-O(2)$^{\#4}$	1.961(3)	O16-Tb1-O1$^{\#4}$	128.37(9)
Zn(1)-O(4)	1.966(3)	O9$^{\#3}$-Tb1-O1$^{\#4}$	135.56(9)
O10$^{\#2}$-Tb1-O7$^{\#1}$	76.13(9)	O7$^{\#1}$-Tb1-O10$^{\#3}$	68.02(8)
O5-Tb1-O7$^{\#1}$	141.53(9)	O10$^{\#2}$-Tb1-O10$^{\#3}$	73.54(9)
O11-Tb1-O7$^{\#1}$	79.68(9)	O5-Tb1-O10$^{\#3}$	145.23(9)
O10$^{\#2}$-Tb1-O5	94.01(10)	O11-Tb1-O10$^{\#3}$	122.55(8)
O11-Tb1-O10$^{\#2}$	142.31(9)	O6-Tb1-O10$^{\#3}$	68.89(8)
O11-Tb1-O5	87.26(10)	O16-Tb1-O10$^{\#3}$	99.82(8)
O6-Tb1-O7$^{\#1}$	132.92(9)	O9$^{\#3}$-Tb1-O10$^{\#3}$	49.53(8)
O6-Tb1-O10$^{\#2}$	74.37(9)	O1$^{\#4}$-Tb1-O10$^{\#3}$	130.81(8)
O6-Tb1-O5$^{\#1}$	76.54(10)	O12-Zn1-O15$^{\#5}$	109.79(12)
O6-Tb1-O11	141.57(9)	O12-Zn1-O2$^{\#4}$	111.77(12)
O16-Tb1-O7$^{\#1}$	134.91(9)	O14$^{\#5}$-Zn1-O2$^{\#4}$	96.71(12)
O16-Tb1-O10$^{\#2}$	144.38(9)	O12-Zn1-O4	118.30(12)
O16-Tb1-O5	71.33(10)	O14$^{\#5}$-Zn1-O4	102.58(12)
O16-Tb1-O11	71.11(9)	O2$^{\#4}$-Zn1-O4	114.81(12)
O16-Tb1-O6	70.72(9)		

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$1-X,2-Y,1-Z; $^{\#2}$1-X,1/2+Y,3/2-Z; $^{\#3}$+X,3/2-Y,-1/2+Z; $^{\#4}$+X,5/2-Y,-1/2+Z; $^{\#5}$-X,1/2+Y,1/2-Z;

Table S2 The comparison between various luminescence sensors based on MOFs for aniline detection.

MOF-based luminescence sensing materials	Quenching constant (K_{SV} , M^{-1})	Detection limits	Solvent	Ref.
Zn-Eu	1200.2	7.5 μmol.L^{-1}	CH_3OH	**This work**

Zn-Tb	987.6	5.2 μmol.L^{-1}	CH_3OH	**This work**
Mg–NDI MOF	-	1×10^{-5} M	C_2H_5OH	11a
$[EMI]_2[Eu_2(BDC)_3(H_2BDC)Cl_2]$	-	6.8×10^{-6} mol · L^{-1}	H_2O	11b
	-	1×10^{-5} mol · L^{-1}	DMF	
$[Eu(BDC)Cl(H_2O)]$	-	9×10^{-6} mol · L^{-1}	H_2O	11b
	-	7×10^{-6} mol · L^{-1}	DMF	
$[Tb(BCB)(DMF)]\cdot(DMF)_{1.5}(H_2O)_2$	-	-	CH_3OH	11c
$(DMA)_2[Y_9(\mu_3\text{-}OH)_8(\mu2\text{-}OH)_3BTB_6]_n\cdot(solv)_x$	-	150 ppm	CH_3OH	11d
$[ZnL\cdot H_2O]_n$	-	-	CH_3CN	11e
$[CdL\cdot H_2O]n\cdot 2nH_2O$	-	-	CH_3OH	
$[CdL]\cdot[^+H_2N(CH_3)_2]$ $(DMF)(H_2O)_3$	-	-	CH_3CN	11f
$[Cu_4(tdhb)]$	-	670 mg/g	H_2O	11g
$[Ln_2(TDC)_3$ $(CH_3OH)_2\cdot(CH_3OH)]$ (Ln = Eu and Tb)	-	-	CH_3OH	11h

MI = imidazolium, H_2BDC = 1,4-benzendicarboxylic acid, H_3BCB = 4,4,4-benzenetricarbonyltribenzoic acid , BTB = 1,3,5-benzene(tris)benzoate, NDI =N,N-bis(5-isophthalic acid)naphthalenediimide , L = 5-aminoisophthalic acid, H_4L = bis(3,5-dicarboxyphenyl)terephthalamide, H_8 tdhb = 3,3',5,5'-tetra(3,5-dicarboxyphenyl)-2,2',4,4',6,6'-hexamethylbiphenyl), TDC = 2,5-thiophenedicarboxylic acid.