Supplementary Information

A three-dimensional metal-organic framework with high performance of dual-cation sensing synthesized by single crystal transformation

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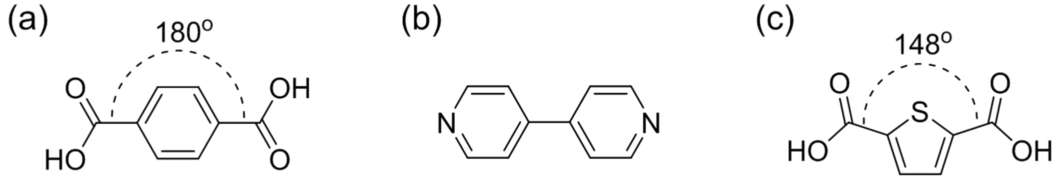

Figure S1. (a, b) Previously used linear pillars, and (b) the bent pillar H_2TDC used in this work

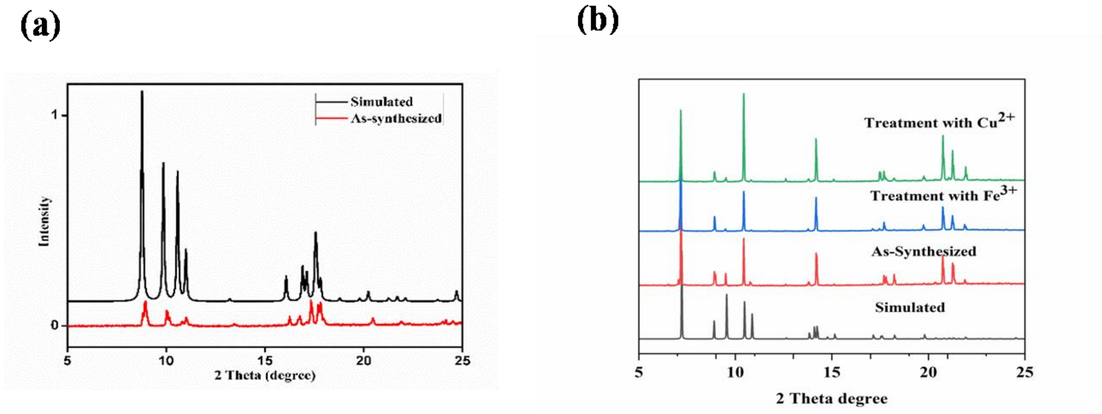

Figure S2. PXRD patterns (a) **BUT-25** (b) **BUT-26** .

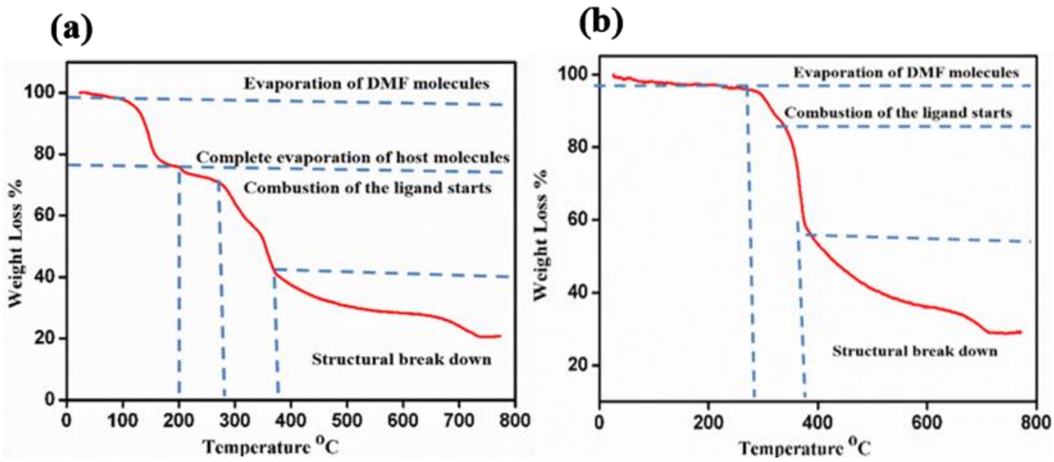

Figure S3. TGA curves of (a) **BUT-25** and (b) **BUT-26**.

Thermal stability of a MOF samples was measured on thermal analyzer from a temperature range of 25 °C to 800 °C with a heating range of 10 °C m^{-1} under nitrogen atmosphere. Different temperature ranges have observed.

(a) At above 50 °C organic solvent evaporation starts

1) At 310 °C ligand decomposition starts
2) At 400 °C structural break down.

(b) At above 50 °C organic solvent evaporation starts

1) At 160 °C total evapoaration of host mplecules
2) At 310 °C ligand decomposition starts
3) At 380 °C structural break down

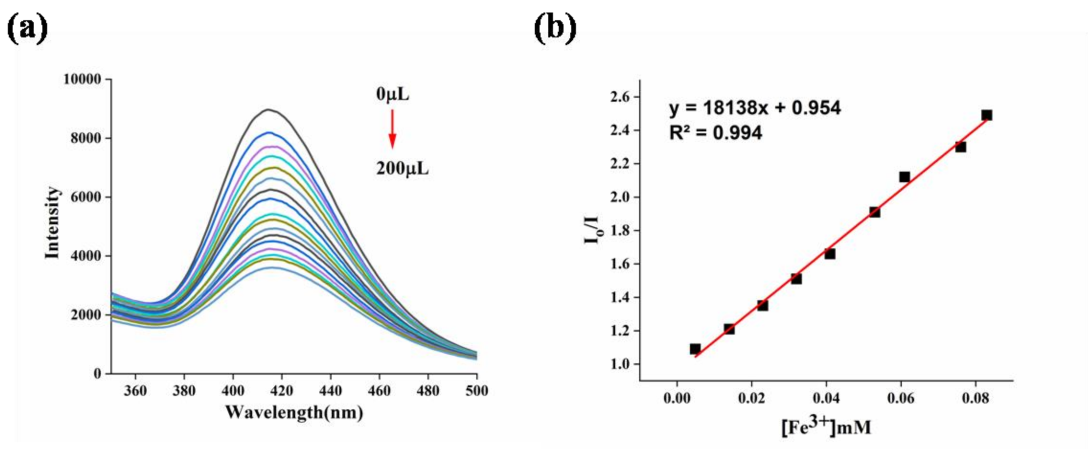

Figure S4. (a) Fluorescence spectra of **BUT-25** suspensions after incremental addition of 0.5 mM aqueous solution of Fe^{3+}. (b) Fitting of Sterrn-Volmer plot for the fluorescence quenching of **BUT-25** by Fe^{3+} ions.

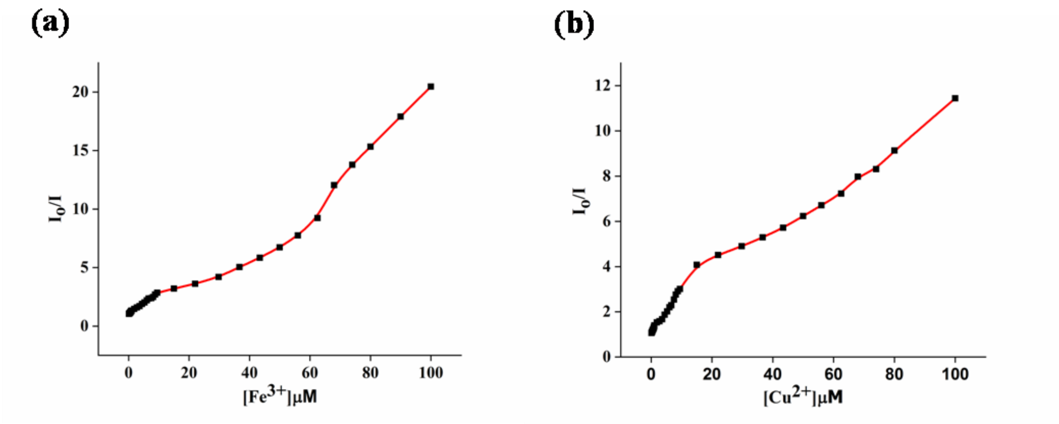

Figure S5. Stern-Volmer plot of **BUT-26** suspension quenched by (a) Fe^{3+} (b) Cu^{2+} with different concentrations.

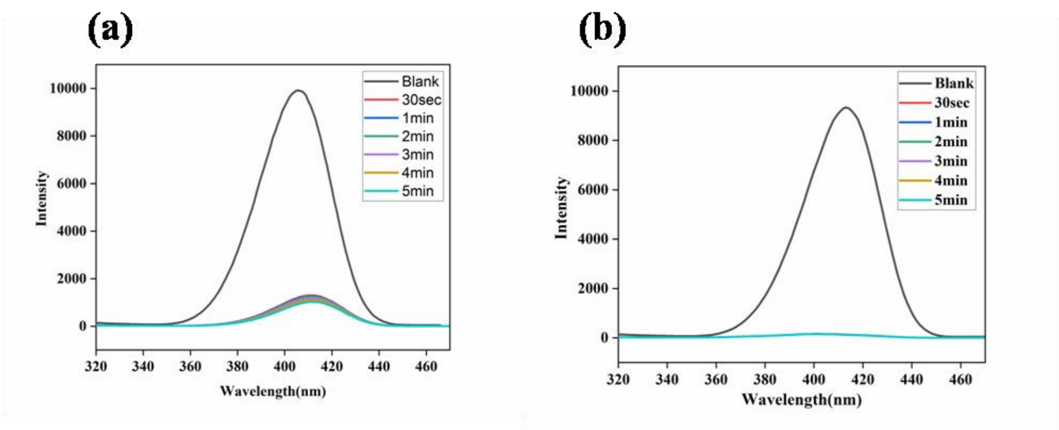

Figure S6. Fluorescence spectra of **BUT-26** obtained after insertion of 500 μM aqueous solutions of (a) Cu^{2+} and (b) Fe^{3+} for different time.

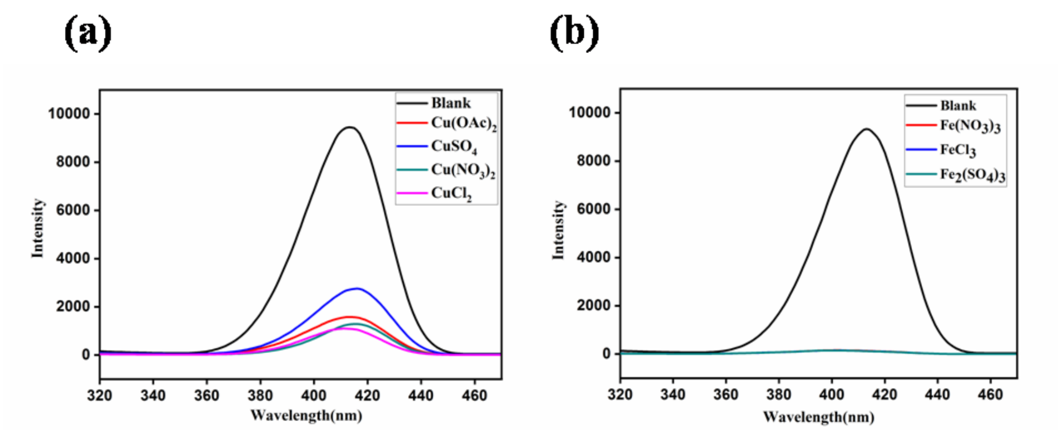

Figure S7. Luminescence quenching of **BUT-26** by anions along with (a) Cu^{2+} and (b) Fe^{3+}.

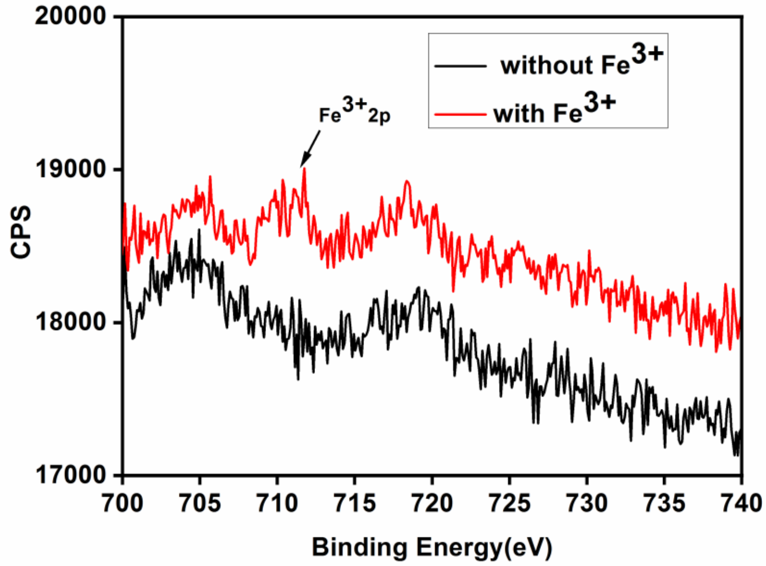

Figure S8. XPS measurements of **BUT-26** with and without Fe^{3+}.

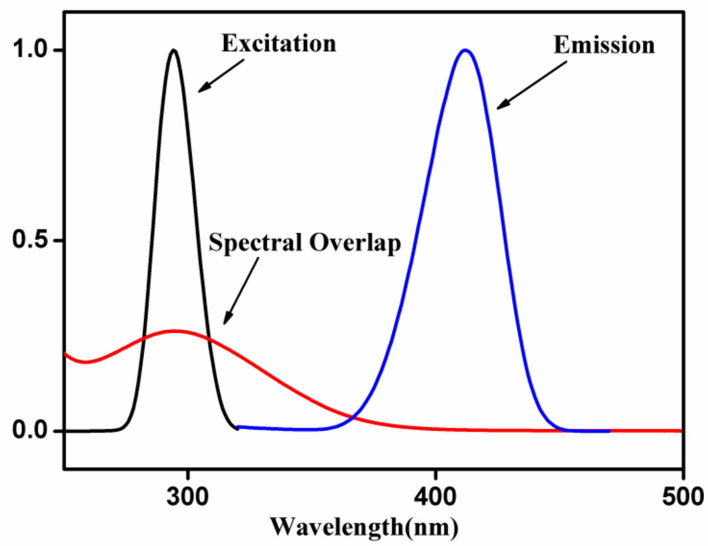

Figure S9. Spectral overlap between excitations spectra of **BUT-26** and absorption spectra of Fe^{3+}.

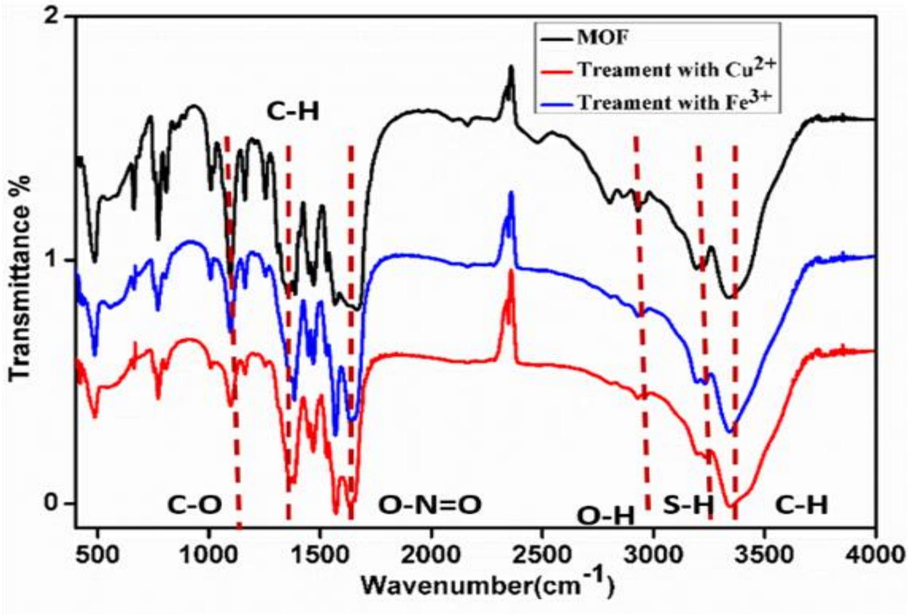

Figure S10. FT-IR of **BUT-26** before and after treatment with Cu^{2+}/Fe^{3+}.

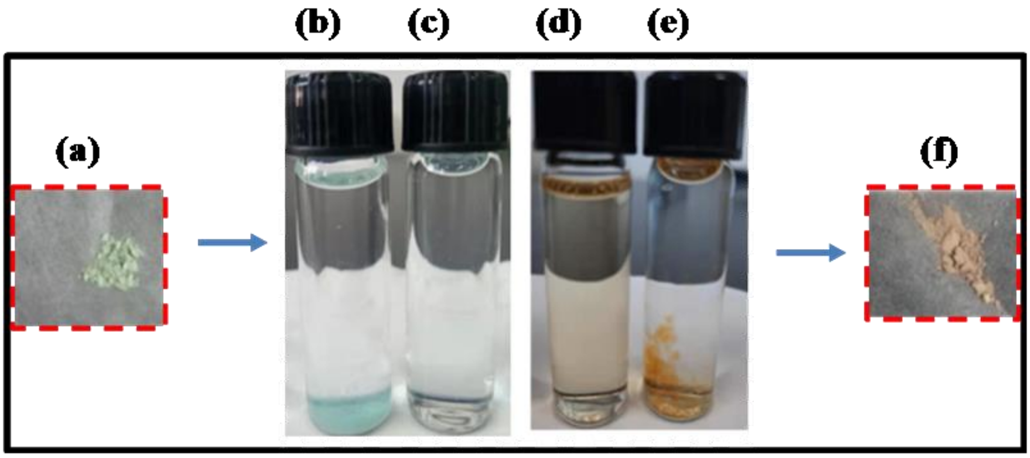

Figure S11. (a) BUT-26 dried after quenching with Cu^{2+} ion. (b) Cu^{2+} ion solution with BUT-26 after 24 hrs. (c) Cu^{2+} ion solution before addition of BUT-26 (d) Fe^{3+} ion solution before addition of BUT-26. (e) Fe^{3+} ion solution with BUT-26 after 24hrs. (f) BUT-26 dried after quenching with Fe^{3+} ion.

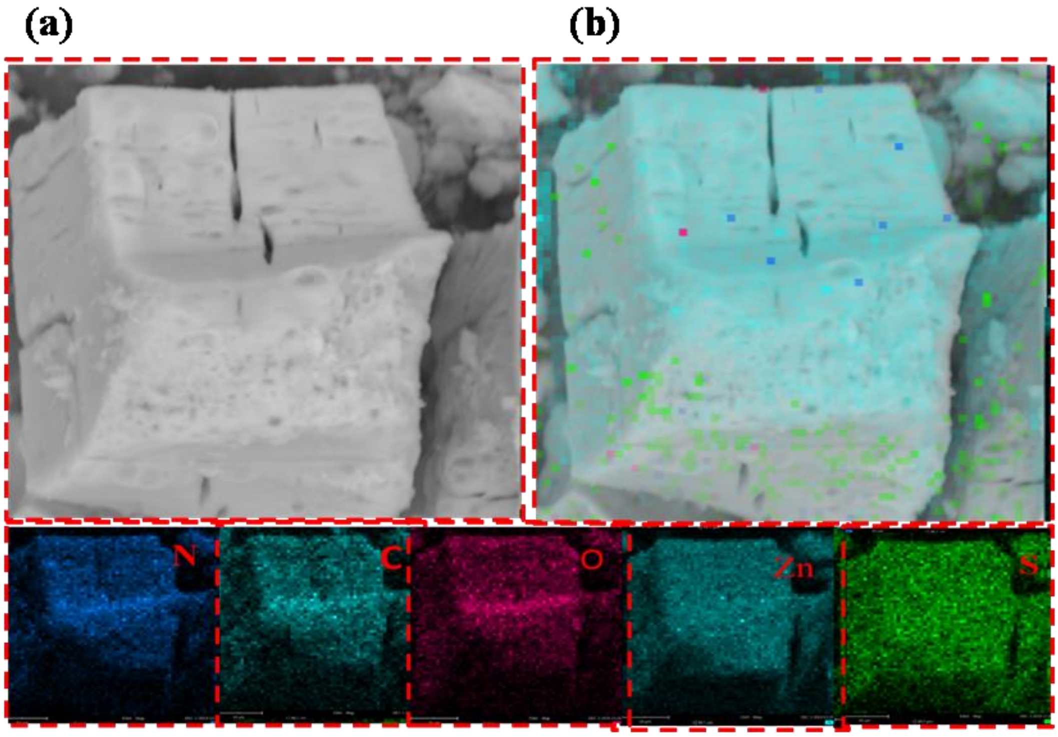

Figure S12. (a) SEM images (b) Elemental mapping of **BUT-26** before quenching.

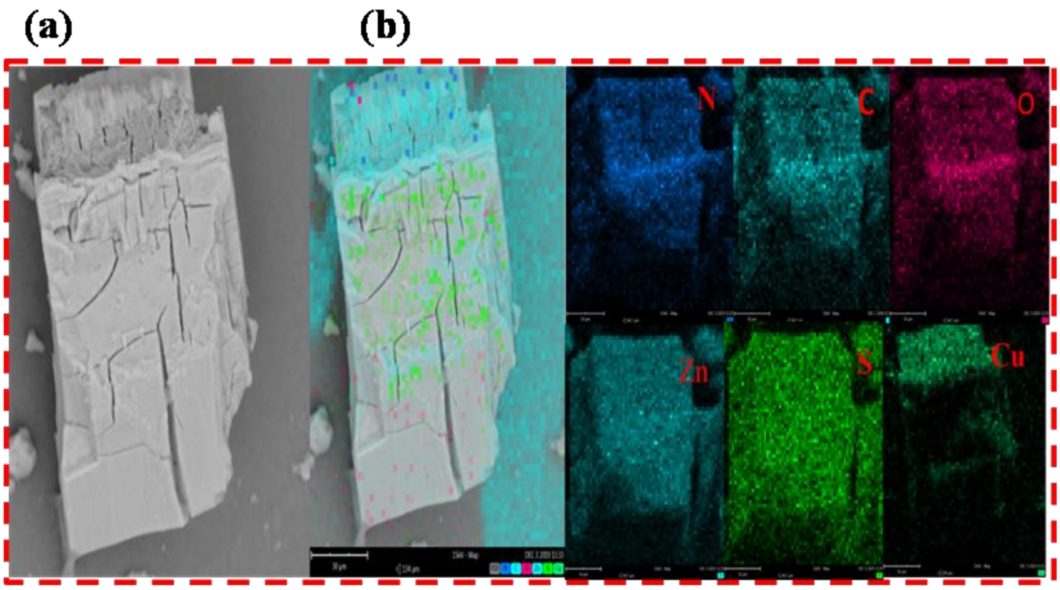

Figure S13. SEM images and Elemental mapping of **BUT-26** after quenching with Cu^{2+}.

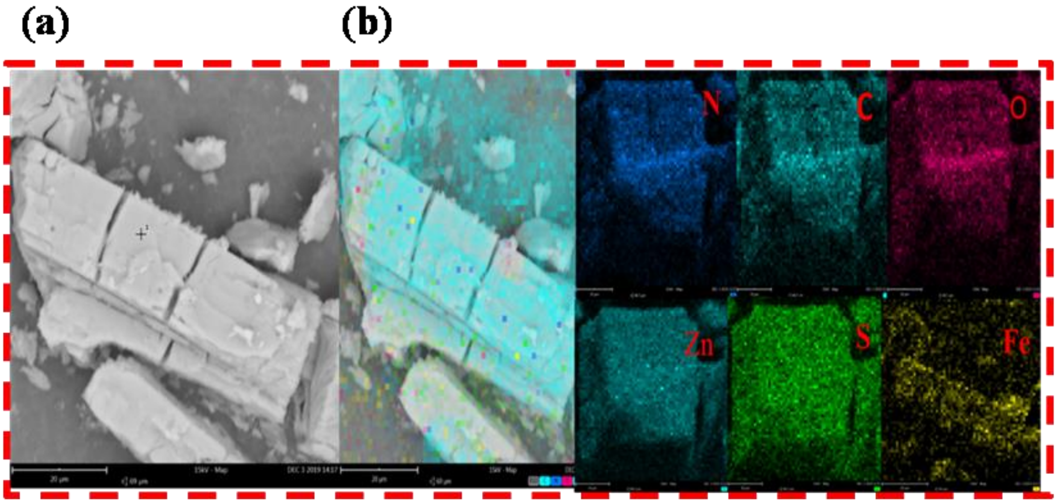

Figure S14. SEM images and Elemental mapping of **BUT-26** after quenching with Fe^{3+}.

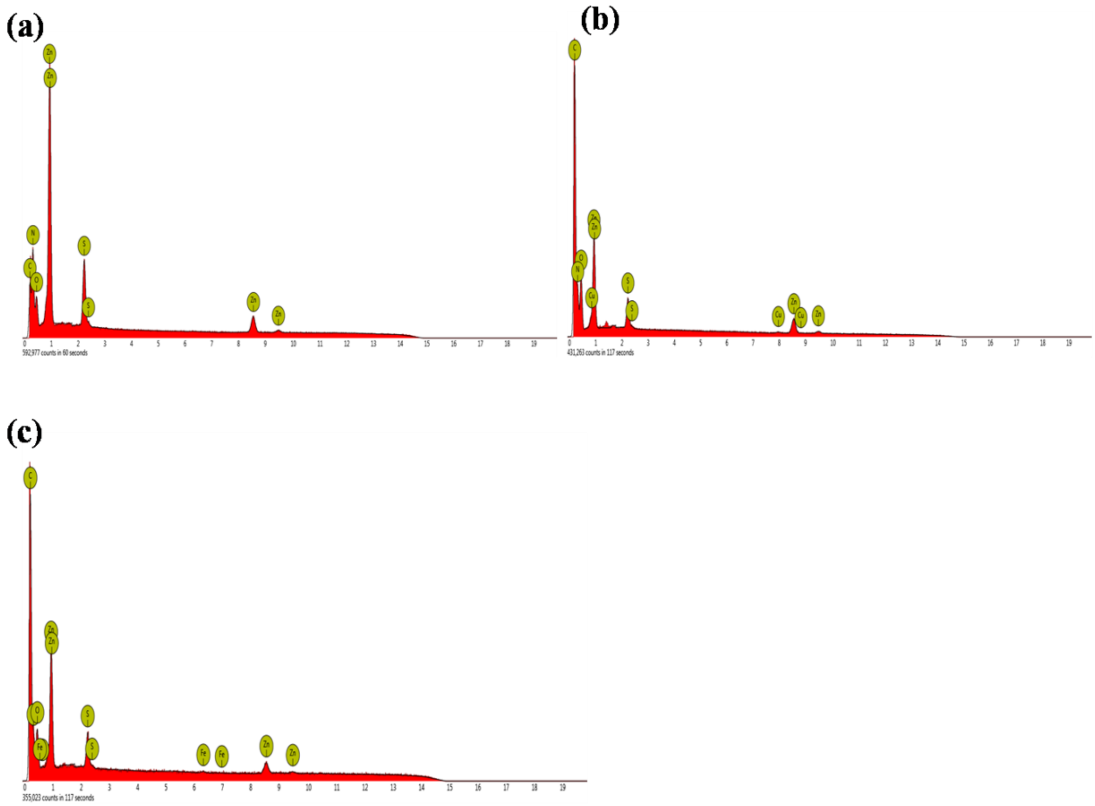

Figure S15. EDX of **BUT-26** (a) before quenching after quenching with (b) Cu^{2+} (c) Fe^{3+}.

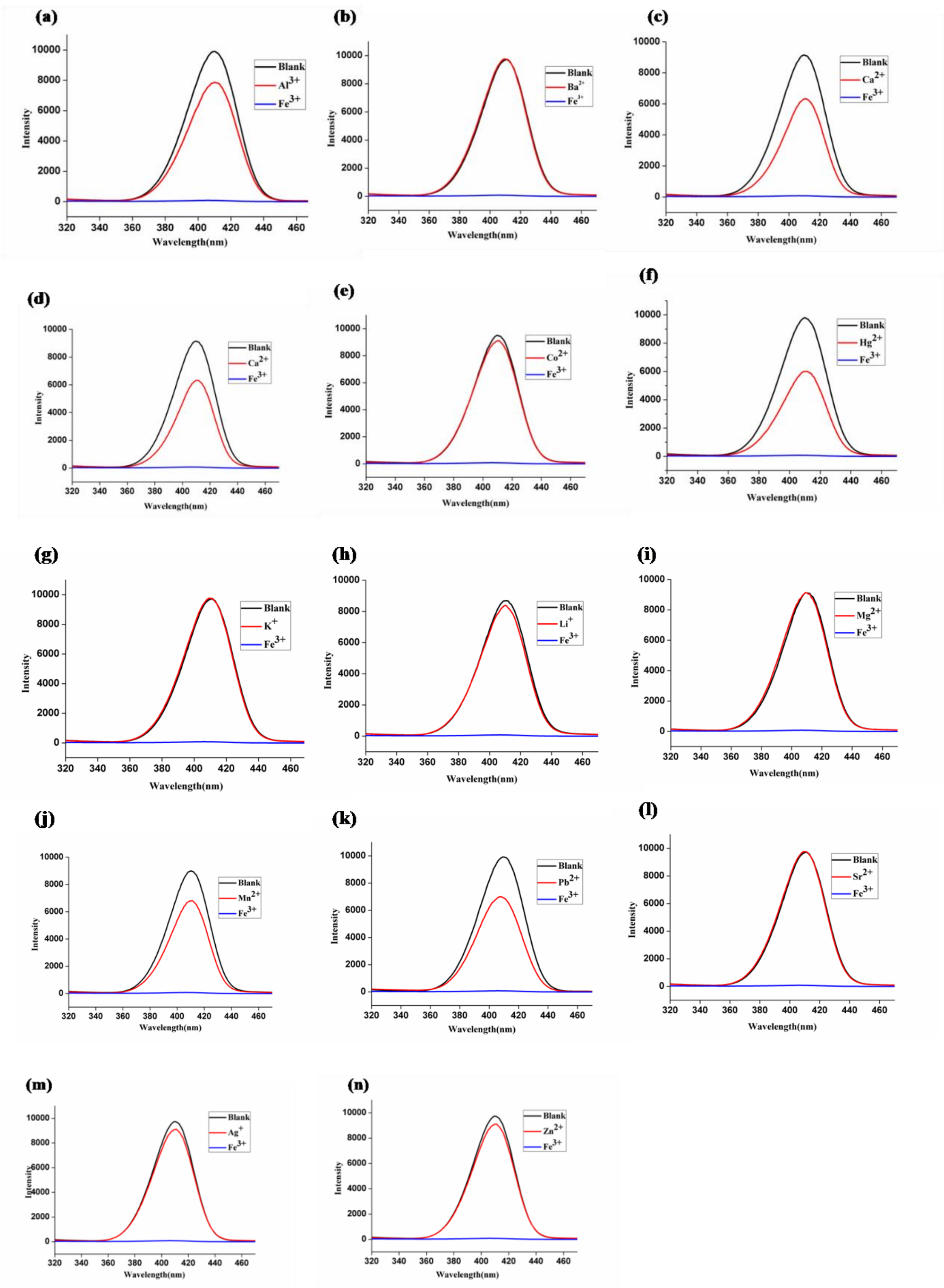

Figure S16. Quenching of luminescence by Fe^{3+} in the presence of other cations (500μM of other cations and subsequently 500 μM of Fe^{3+} were added) of **BUT-26**.

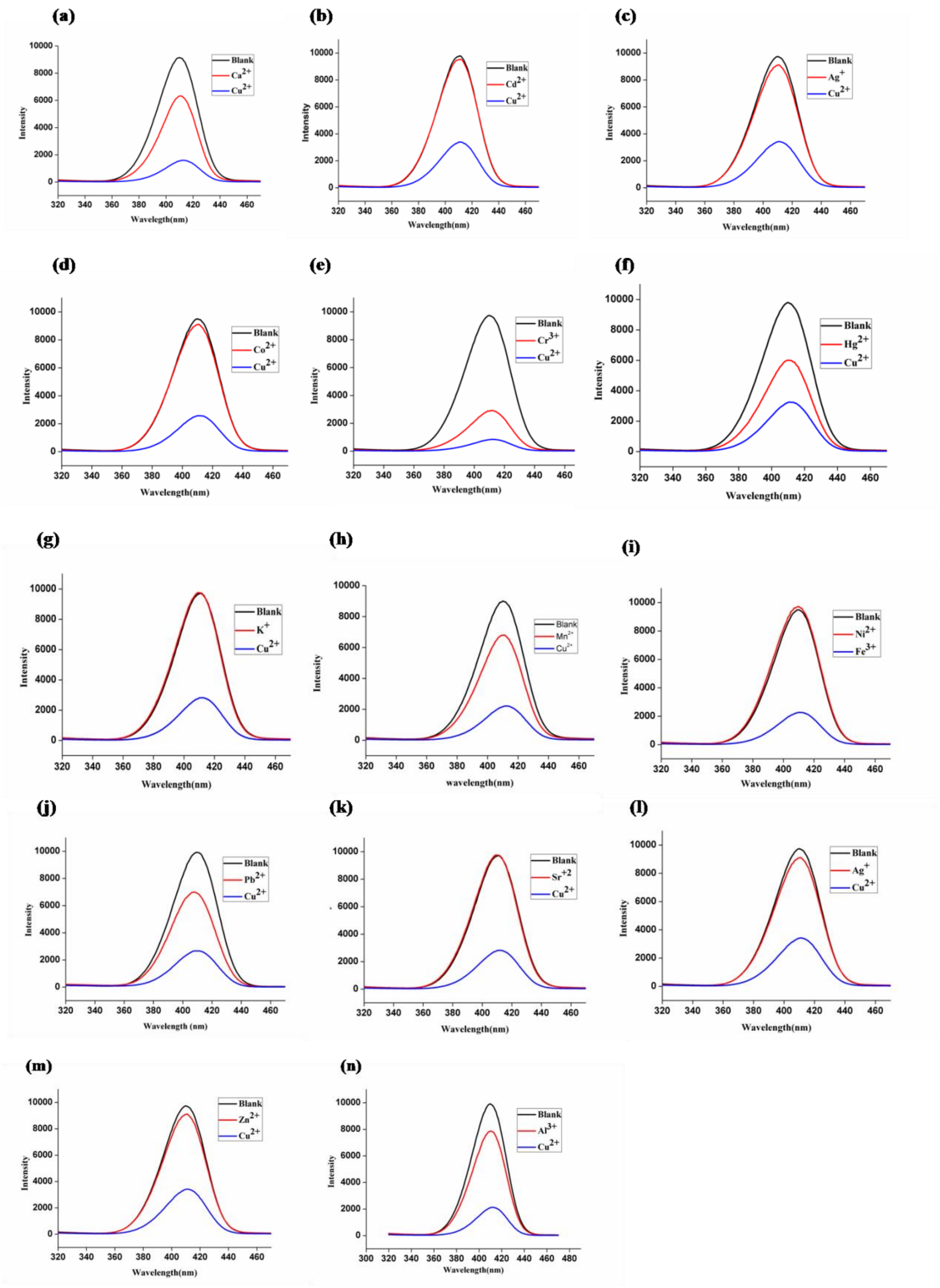

Figure S17. Quenching of luminescence by Cu^{2+} in the presence of other cations (500 μM of other cations and subsequently 500 μM of Fe^{3+} were added) of **BUT-26**.

Table S1. ICP-AES analysis results of **BUT-26** before and after treatment with Cu^{2+} and Fe^{3+} for 24 hrs.

	Amount of Zn	**Amount of Cu^{2+}/Fe^{3+}**
BUT-26	6.562mg/L	
BUT-26+ Cu^{2+}	6.146mg/L	0.503mg/L
BUT-26+ Fe^{3+}	7.247mg/L	0.110mg/L

Table S2. Crystal and Structure Refinement Data for **BUT-25** and **BUT-26**.

Parameters	**BUT-25**	**BUT-26**
Formula	$C_4H_7N_{15}O_2Zn_2$	$C_9H_2N_{15}O_4SZn_2$
Formula weight	427.99 g/mol	547.06 g/mol
Space group	*C*2/*m* (12)	*Ama*2 (40)
a	10.3743(5) Å	17.2632(7) Å
b	17.9247(7) Å	25.2792(15) Å
c	11.0539(6) Å	10.2353(4) Å
α (deg)	90	90
β (deg)	114.4820	90
γ (deg)	90	90
v	1870.73(17) $Å^3$	4466.68(40) $Å^3$
Z	4	4
D. calcd (g cm^{-3})	1.51952 g/cm^3	0.813454 g/cm^3
GOF on F^2	0.947	0.970
F(000)	848.0	1076.0
μ(mm-)	3.453	1.145
Rint	0.127	0.0444
R_1/wR_2 (all Data)	0.1474/0.3770	0.0566/0.1102

Table S3. Comparison of Performance of Reported MOFs for Detecting Cu^{2+}

Sr#	MOF	Solvents	Ksv(M^{-1})	LOD (μM)	Ref
1	$[Eu_2L_2(DMF)(H_2O)_2]\cdot 2DMF\cdot H_2O$	DMF	2.84×10^3		1
2	$\{(C_3H_4N_2)[BaZn_3(C_9H_3O_6)_3(H_2O)_3]4H_2O\}_n$	H_2O	1.49×10^5	5.4	2
3	$[Eu_2(MTBC)(OH)_2(DMF)_3(H_2O)4]\cdot 2DMF\cdot 7H_2O$	DMF/H_2O	2.2×10^3		3
4	UIO-66-$(OH)_2$@MOF (PCN-224)	$EtOH/H_2O$	4.03×10^5	0.00068	4
5	$[Cd(L)_2]\cdot(DMF)_{0.92}$	DMF	4.4×10^3	16.9	5
6	$[Cd_2(pbdc)(H_2O)_3]$	H_2O	1.57×10^6	0.0389	6
7	$\{[Zn_2Na(L)(HL)_2(H_2O)_2][OAc]\cdot 2H_2O\}_n$	H_2O	7.75×10^5	0.65	7
8	$Eu@H_3[Cd_{2.5}L_2]\cdot 4DMF\cdot 3H_2O$	DMF	5.0×10^2	7100	8
9	$[Zn_3L_2(bpy)]\cdot 3DMF\cdot 6H_2O$	DMF	1.1×10^3		9
10	MOF-525	DMF	4.5×10^5	0.067	10
11	$Cd(L)\text{-}(TPOM)_{0.75}]\cdot xS$	H_2O	1.7×10^4		11
12	Cd-MOF-74	H_2O	1.8×10^3	78.7	12
13	Eu3@Bio-MOF-1	H_2O		0.14	13
14	$Tb_2(H_2O)_2(H_2L)_{0.5}(ox)_3\cdot nH_2O$ (Tb-1, n=2 and Tb-2)	H_2O	Tb1=1077.6 Tb2=868.7		14
15	MIL-53-L	H_2O	6.15×10^3	10	15
16	PCN-222-Pd(II)	CH_3CN/H_2O		0.05	16
17	$[Cd_3(L)_2(H_2O)_5]\cdot(H_2O)_4$	H_2O	3.65×10^4		17
18	$\{[Eu_2K_2(dcppa)_2(H_2O)_6]\cdot 5H_2O\}_n$	EtOH	5.2×10^4		18
19	Eu3@UiO-66-2COOH Eu3@UiO-66-COOH	H_2O	5.3×10^4 683.8		19
20	$[Tb_3(L)_2(HCOO)(H_2O)_5]\cdot DMF\cdot 4H_2O$	DMF	$2.0\text{x}10^3$		20
21	$[Zn(ATZ)_{1.5}(TDC)_{0.5}]\cdot NH_2(CH_3)_2$	**DMF/H_2O**	**1.9×10^5**	0.12	**This work**

Table S4. Comparison of Performance of Reported MOFs for Detecting Fe^{3+}

Sr#	MOF	Solvent	Ksv	LOD (μM)	Ref
1	ZSB-1	DMF		0.05	[21]
2	FJI-C8(Zn)	DMF	3.75×10^4	0.37	[22]
3	Al-MIL-53-N_3	DMF/H_2O	6.13×10^5	0.03	[23]
4	$\{[Zn(L)(bpp)]\cdot DMF\}_n$	DMF	2.56×10^4	7	[24]
5	$\{[Zn(L)(bpe)]\cdot DMF_n$	DMF	2.27×10^4	1.55	[24]
6	$[Zn_3(L)_2(bipy)(\mu_3OH)_2]\cdot 3H_2O$	DMF/H_2O	2.3×10^4		[25]
7	$[Cd(L1)(oba)]\cdot DMF$	DMF	2.69×10^4		[26]
8	$[Zr_6O_4(OH)_4(C_8H_2O_4S_2)_6]\cdot DMF\cdot 18H_2O$	H_2O	4.41×10^3	1.26	[27]
9	$[Zr_6O_4(OH)_4(C_{10}H_8O_4S_2)_6]\cdot 0.5DMF$	H_2O	8.81×10^3	0.857	[27]
10	$[Zr_6O_4(OH)_4(C_{15}H_8O_4S_2)_6]\cdot 4DMF\cdot 21H_2O$	H_2O	1.08×10^4	0.93	[27]
11	$[Zr_6O_4(OH)_4(C_{20}H_{10}O_4S_2)_6]\cdot 2.5DMF\cdot 11H_2O$	H_2O	9.10×10^3	0.34	[27]
12	$[Eu(atpt)_{1.5}(phen)(H_2O)]_n$	EtOH	7.60×10^3	45	[28]
13	Eu-BPDA	H_2O	1.25×10^4	0.9	[29]
14	CTGU-1 (Tb)	H_2O/DMF	1.88×10^6	0.001	[30]
15	HPU-1 (Zn)	H_2O	1.0×10^4	1000	[31]
16	$Cd_2(OBA)_2(BPTP)(H_2O)$	DMF		0.36	[32]
17	$\{[Zn(BBPTZ)_2(MeCN)_2]\cdot(MeCN)_2\cdot(ClO_4)_2\}_n$	MeOH	$7.49x\ 10^2$	0.015	[33]
18	$[Zn_3(HL)_2(DMF)_2(H_2O)_2]\cdot 2H_2O$	H_2O	2.05×10^5		[34]
19	SUMOF-7II	DMF/EtOH	4.3×10^3	16	[35]
20	$[Zr_6O_4(OH)_4(2,7\text{-}CDC)_6]\cdot 19H_2O\cdot 2DMF$	THF/H_2O	5.5×10^3	0.018	[36]
21	$[Zn(ATZ)_{1.5}(TDC)_{0.5}]\cdot NH_2(CH_3)_2$	DMF/H_2O	$1.7x10^5$	0.1	This work

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