Construction of Zn^{II}/Cd^{II}-based MOFs containing a tripodal aromatic caboxylate ligand with unequal arms and their fluorescent detection for Cu^{2+} and Fe^{3+} cations

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Content

Figure. S14 PXRD patterns of compounds **1-4** before and after recyclable experiments.

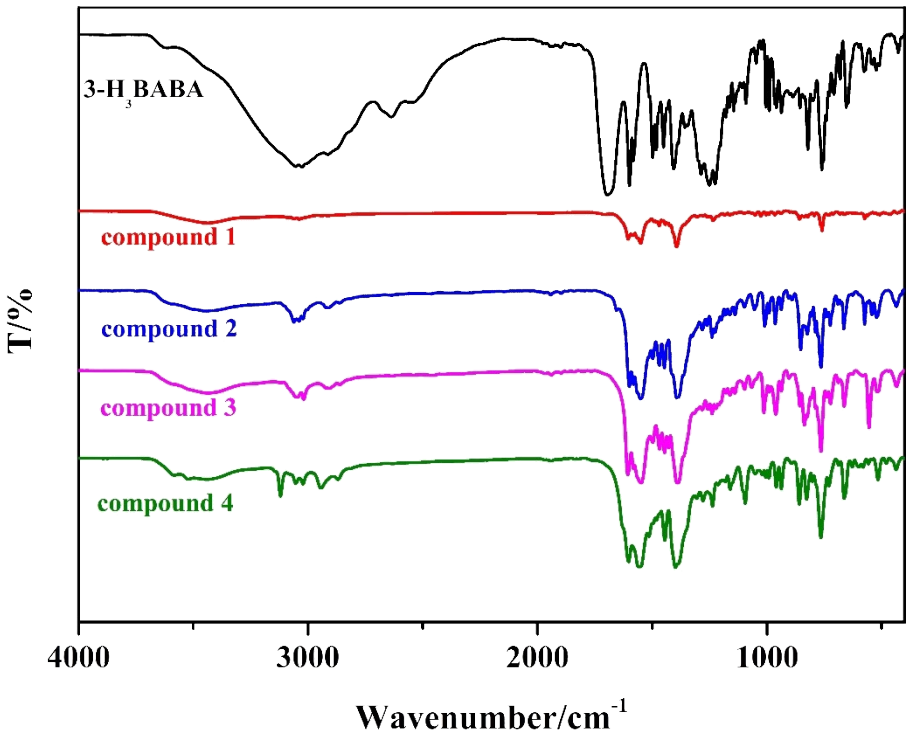

Figure. S1 Infrared spectra of 3-H_3BABA, compounds **1-4**.

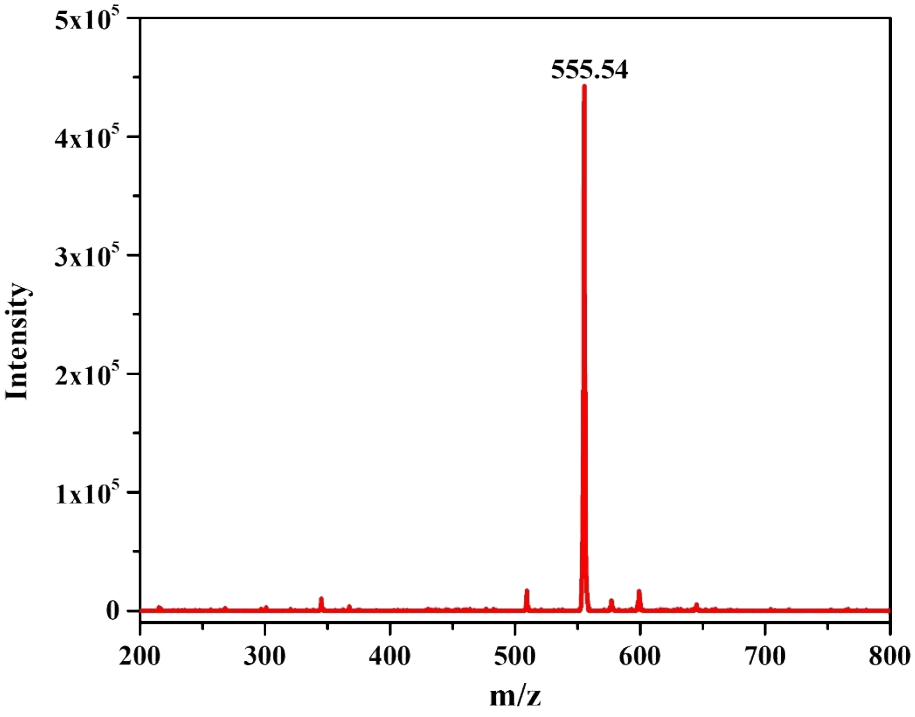

Figure. S2 EIS-MS spectra of 3-H_3BABA.

Table S1. Crystallographic data and structure refinement results for compounds **1-4**[a]

Identification code	Compound **1**	Compound **2**	Compound **3**	Compound **4**
Empirical formula	$C_{90}H_{68}N_{10}O_{14}Zn_3$	$C_{90}H_{64}Cd_3N_{10}O_{12}$	$C_{94}H_{68}Cd_3N_6O_{12}$	$C_{88}H_{82}Cd_3N_8O_{15}$
Formula weight	1709.71	1814.74	1810.74	1810.83
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*I*2/*a*	*I*2/*a*	*C*2/*c*
a/Å	16.7507(2)	26.6374(6)	27.0745(5)	38.9381(7)
b/Å	20.1161(3)	9.7433(2)	9.7503(2)	9.43740(10)
c/Å	23.6396(3)	29.7932(7)	29.6517(5)	29.5532(5)
α/°	90	90	90	90
β/°	94.5950(10)	90.922(2)	91.899(2)	132.196(3)
γ/°	90	90	90	90
Volume/Å^3	7939.97(18)	7731.4(3)	7823.3(3)	8045.7(4)
Z	4	4	4	4
ρ_{calc} g/cm^3	1.430	1.545	1.537	1.495
μ/mm^{-1}	0.973	0.889	0.878	6.866
F (000)	3520.0	3592.0	3656.0	3680.0
Independent reflections	9369 [R_{int}=0.0307, R_{sigma}=0.0375]	9072 [R_{int}=0.0358, R_{sigma}=0.0412]	8820 [R_{int}=0.0268, R_{sigma}=0.0426]	8386 [R_{int}=0.0280, R_{sigma}=0.0261]
Goodness-of-fit on F^2	1.063	1.056	1.049	1.064
Final *R* indexes [I>=2σ (I)]	R_1=0.0445, wR_2=0.1064	R_1=0.0363, wR_2=0.0761	R_1=0.0354, wR_2=0.0658	R_1=0.0262, wR_2=0.0705
Final *R* indexes [all data]	R_1=0.0647, wR_2=0.1165	R_1=0.0545, wR_2=0.0874	R_1=0.0514, wR_2=0.0739	R_1=0.0279, wR_2=0.0718
Largest diff. peak/hole/eÅ^{-3}	0.71/-0.38	0.83/-0.79	0.66/-0.55	0.44/-0.72
CCDC Number	2233885	2233886	2233887	2233888

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $_wR_2 = [\Sigma_w(F_o^2 - F_c^2)^2]/[\Sigma_w(F_o^2)^2]^{1/2}$

Table. S2 Selected bond lengths (Å) and angles (deg) for compound **1**

Zn1—O3[1]	1.9775(19)	O3[1]—Zn1—O4[1]	59.23(7)
Zn1—O5	1.9595(19)	O3[1]—Zn1—O7	103.09(9)
Zn1—O4[1]	2.3805(19)	O3[1]—Zn1—N5	117.69(8)
Zn1—O7	2.021(2)	O5—Zn1—O3[1]	128.25(8)
Zn1—N5	2.043(2)	O5—Zn1—O4[1]	95.29(8)
Zn2—O1	1.975(2)	O5—Zn1—O7	100.55(9)
Zn2—O1[2]	1.975(2)	O5—Zn1—N5	104.35(9)
Zn2—N2	2.071(2)	O7—Zn1—O4[1]	161.59(9)
Zn2—N2[2]	2.071(2)	O7—Zn1—N5	96.45(9)
N5—Zn1—O4[1]	88.58(8)	O1—Zn2—N2[2]	99.67(9)
O1—Zn2—O1[2]	147.69(14)	O1[2]—Zn2—N2	99.67(9)
O1[2]—Zn2—N2[2]	100.82(9)	N2[2]—Zn2—N2	100.54(13)
O1—Zn2—N2	100.82(9)		

Symmetry codes: [1]1-*x*, 1-*y*, 1-*z*; [2]-*x*, +*y*, 1/2-*z*

Table. S3 Selected bond lengths (Å) and angles (deg) for compound **2**.

Cd1—O1	2.288(2)	O1—Cd1—O1[1]	92.96(11)
Cd1—O1[1]	2.288(2)	O1[1]—Cd1—O5[2]	104.36(8)
Cd1—O5[2]	2.319(2)	O1—Cd1—O5[2]	84.44(8)
Cd1—O5[3]	2.319(2)	O1[1]—Cd1—O5[3]	84.44(8)
Cd1—N5[4]	2.367(3)	O1—Cd1—O5[3]	104.36(8)
Cd1—N5[5]	2.367(3)	O1[1]—Cd1—N5[4]	87.81(9)
Cd2—O1	2.375(2)	O1—Cd1—N5[4]	167.28(9)
Cd2—O2	2.325(2)	O1—Cd1—N5[5]	87.81(9)
Cd2—N2	2.358(3)	O1[1]—Cd1—N5[5]	167.28(9)
Cd2—O4[6]	2.440(2)	O5[3]—Cd1—O5[2]	167.39(12)
Cd2—O3[6]	2.265(2)	O5[2]—Cd1—N5[5]	88.35(10)

Cd2—O6[2]	2.185(2)	O5[2]—Cd1—N5[4]	83.07(10)
O5[3]—Cd1—N5[4]	88.35(10)	O2—Cd2—N2	87.49(9)
O5[3]—Cd1—N5[5]	83.07(10)	O2—Cd2—O4[6]	103.44(9)
N5[4]—Cd1—N5[5]	94.24(15)	N2—Cd2—O1	111.59(8)
O1—Cd2—O4[6]	99.20(8)	N2—Cd2—O4[6]	147.92(8)
O2—Cd2—O1	55.47(7)	O3[6]—Cd2—O1	138.14(8)
O3[6]—Cd2—O2	95.33(8)	O6[2]—Cd2—N2	86.92(9)
O3[6]—Cd2—N2	94.17(8)	O6[2]—Cd2—O4[6]	93.94(9)
O3[6]—Cd2—O4[6]	55.28(7)	O6[2]—Cd2—O3[6]	109.11(9)
O6[2]—Cd2—O1	104.84(8)	Cd1—O1—Cd2	118.02(9)
O6[2]—Cd2—O2	155.26(9)		

Symmetry codes：[1]1/2-*x*, +*y*, -*z*; [2]1/2-*x*, 3/2-*y*, -1/2-*z*; [3]+*x*, 3/2-*y*, 1/2+*z*; [4]-1/2+*x*, -*y*, +*z*; [5]1-*x*, -*y*, -*z*; [6]1-*x*, 1-*y*, -*z*

Table. S4 Selected bond lengths (Å) and angles (deg) for compound **3**.

Cd1—O1[1]	2.2881(18)	O3—Cd2—N2[6]	82.9(3)
Cd1—O1	2.2881(18)	O3—Cd2—N2A[6]	90.9(3)
Cd1—O4[2]	2.3255(19)	N2[6]—Cd2—O1[4]	115.6(4)
Cd1—O4[3]	2.3255(19)	N2[6]—Cd2—O6[5]	144.2(4)
Cd1—N1	2.327(17)	Cd1—O1—Cd2[2]	116.41(7)
Cd1—N1[1]	2.327(17)	O5[5]—Cd2—N2[6]	95.5(4)
Cd1—N1A[1]	2.36(2)	O3—Cd2—O1[4]	104.77(7)
Cd1—N1A	2.36(2)	O3—Cd2—O2[4]	153.59(7)
Cd2—O1[4]	2.3811(18)	O3—Cd2—O5[5]	115.99(7)
Cd2—O2[4]	2.3226(17)	O3—Cd2—O6[5]	91.97(7)
Cd2—O5[5]	2.308(2)	O2[4]—Cd2—O6[5]	107.65(8)
Cd2—O3	2.1792(18)	O2[4]—Cd2—N2[6]	90.5(3)
Cd2—O6[5]	2.406(2)	O5[5]—Cd2—O1[4]	131.30(7)

Cd2—N2^{6}	2.362(16)	O5^{5}—Cd2—O2^{4}	90.05(7)
Cd2—N2A^{6}	2.31(2)	O5^{5}—Cd2—O6^{5}	55.15(7)
O1^{1}—Cd1—O1	91.47(10)	N1^{1}—Cd1—N1A^{1}	8.4(6)
O1—Cd1—O4^{2}	85.83(7)	N1—Cd1—N1A^{1}	94.4(2)
O1^{1}—Cd1—O4^{2}	103.16(7)	N1A—Cd1—N1A^{1}	100.8(9)
O1—Cd1—O4^{3}	103.16(7)	O1^{4}—Cd2—O6^{5}	99.99(7)
O1^{1}—Cd1—O4^{3}	85.83(7)	O2^{4}—Cd2—O1^{4}	55.38(6)
O1—Cd1—N1	171.0(3)	O4^{3}—Cd1—N1A^{1}	79.7(4)
O1^{1}—Cd1—N1^{1}	171.0(3)	O4^{3}—Cd1—N1A	92.2(4)
O1—Cd1—N1^{1}	90.7(4)	O4^{2}—Cd1—N1A	79.7(4)
O1^{1}—Cd1—N1	90.7(4)	O4^{2}—Cd1—N1A^{1}	92.2(4)
O1^{1}—Cd1—N1A	85.8(5)	N1—Cd1—N1^{1}	88.5(8)
O1—Cd1—N1A	164.2(4)	O4^{2}—Cd1—N1^{1}	85.7(3)
O1—Cd1—N1A^{1}	85.8(5)	O4^{2}—Cd1—N1	85.2(3)
O1^{1}—Cd1—N1A^{1}	164.2(4)	O4^{3}—Cd1—N1^{1}	85.2(3)
O4^{3}—Cd1—O4^{2}	167.25(10)	O4^{3}—Cd1—N1	85.7(3)

Symmetry codes：^{1}1/2-*x*, +*y*, 1-*z*; ^{2}+*x*, 3/2-*y*, 1/2+*z*; ^{3}1/2-*x*, 3/2-*y*, 1/2-*z*; ^{4}+*x*, 3/2-*y*, -1/2+*z*; ^{5}1-*x*, 1/2+*y*, 1/2-*z*; ^{6}1/2+*x*, 3/2+*y*, -1/2+*z*

Table. S5 Selected bond lengths (Å) and angles (deg) for compound **4**.

Cd2—O7^{1}	2.3509(14)	O1—Cd1—N1	87.19(8)
Cd2—O7^{2}	2.3509(14)	N1—Cd1—O6^{1}	86.08(7)
Cd2—O2^{3}	2.2311(17)	N1—Cd1—O4^{4}	92.61(7)
Cd2—O2	2.2310(17)	N1—Cd1—O7^{1}	110.08(7)
Cd2—O3	2.234(3)	N1—Cd1—O5^{4}	146.97(7)
Cd2—O3^{3}	2.234(3)	O5^{4}—Cd1—O6^{1}	93.15(6)
Cd2—O2A	2.258(6)	O5^{4}—Cd1—O7^{1}	95.93(6)
Cd2—O2A^{3}	2.258(6)	O1—Cd1—O6^{1}	159.78(7)

Cd1—O6^{2}	2.3960(16)	O1—Cd1—O4^{4}	97.54(7)
Cd1—O4^{4}	2.3496(16)	O1—Cd1—O7^{1}	110.53(6)
Cd1—O7^{2}	2.3733(16)	O1—Cd1—O5^{4}	102.79(7)
Cd1—O5^{4}	2.3655(16)	O3^{3}—Cd2—O2A^{3}	23.3(2)
Cd1—O1	2.1965(17)	O2A^{3}—Cd2—O2A	125.3(5)
Cd1—N1	2.2718(19)	O4^{4}—Cd1—O6^{1}	101.80(6)
O7^{1}—Cd2—O7^{2}	178.99(8)	O4^{4}—Cd1—O7^{1}	144.16(5)
O2^{3}—Cd2—O7^{2}	88.60(7)	O4^{4}—Cd1—O5^{4}	55.19(5)
O2^{3}—Cd2—O7^{1}	92.16(7)	O7^{1}—Cd1—O6^{1}	54.69(5)
O2—Cd2—O7^{2}	92.16(7)	O3^{3}—Cd2—O7^{2}	98.74(11)
O2—Cd2—O7^{1}	88.60(7)	O3^{3}—Cd2—O7^{1}	80.49(11)
O2—Cd2—O2^{3}	83.13(11)	O3—Cd2—O7^{2}	80.49(11)
O2—Cd2—O3	172.58(11)	O3—Cd2—O7^{1}	98.74(11)
O2—Cd2—O3^{3}	97.57(15)	O3^{3}—Cd2—O3	82.7(3)
O2^{3}—Cd2—O3^{3}	172.58(11)	O3—Cd2—O2A^{3}	103.2(3)
O2^{3}—Cd2—O3	97.57(15)	O2^{3}—Cd2—O2A^{3}	158.9(3)
O2—Cd2—O2A	158.9(3)	O2^{3}—Cd2—O2A	75.8(3)
O2—Cd2—O2A^{3}	75.8(3)		

Symmetry codes：^{1}-1/2+*x*, 3/2-*y*, -1/2+*z*; ^{2}3/2-*x*, 3/2-*y*, 1-*z*; ^{3}1-*x*, +*y*, 1/2-*z*; ^{4}1-*x*, 1-*y*, 1-*z*

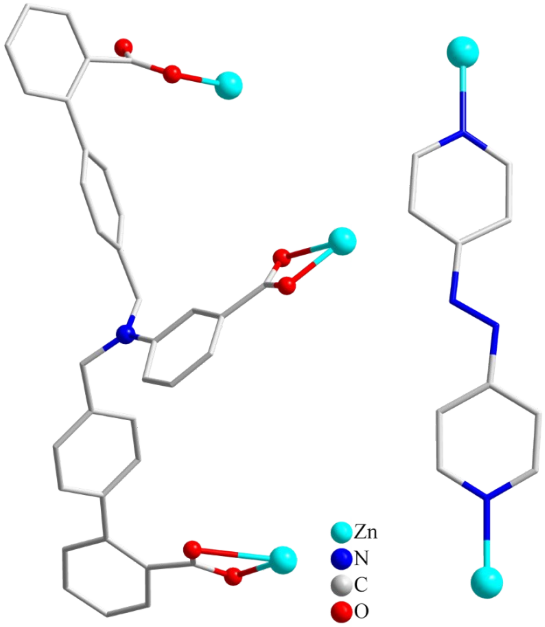

Figure. S3 Coordination modes of the 3-BAB^{3-} ligand and the *bpa* ligand in compound **1**.

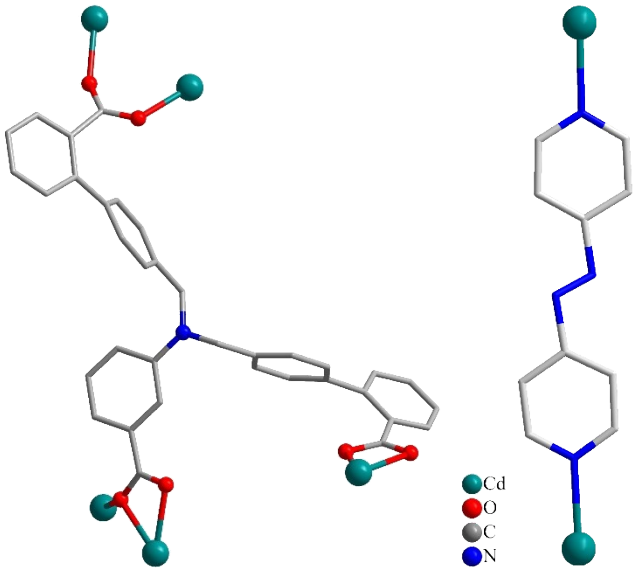

Figure. S4 Coordination modes of the 3-BAB^{3-} ligand and the *bpa* ligand in compound **2**.

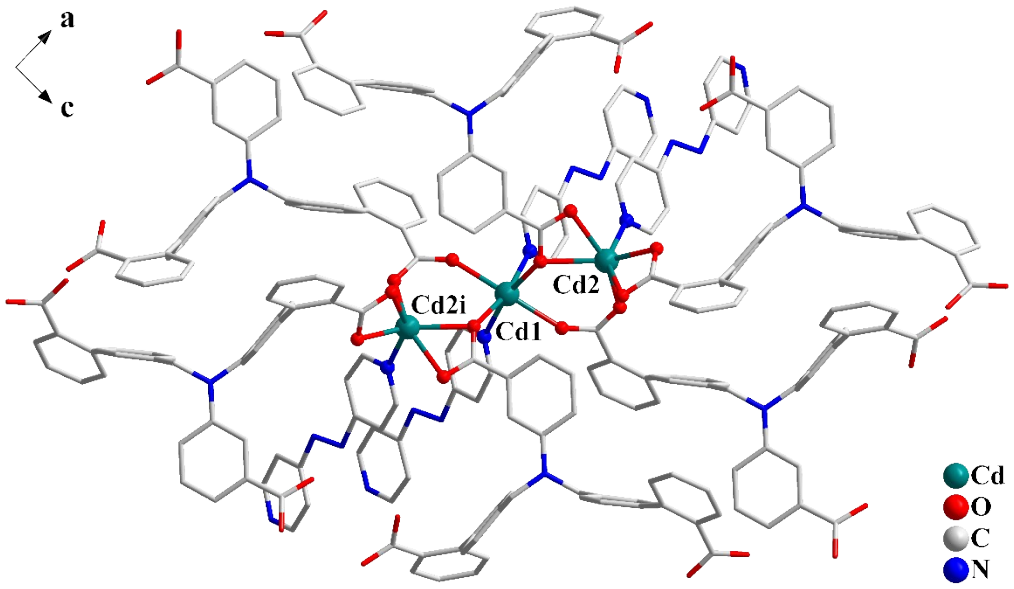

Figure. S5 The coordination environment of Cd^{2+} ions in compound **2** with hydrogen atoms omitted for clarity. Symmetry codes: (i) 1/2-*x*, +*y*, -*z*.

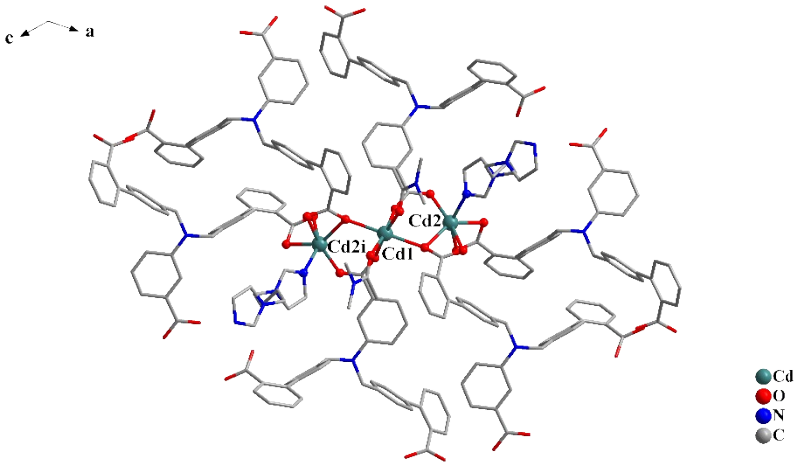

Figure. S6 The coordination environment of Cd^{2+} ions in compound **4**. Symmetry codes: (i) 1/2-*x*, +*y*, -*z*.

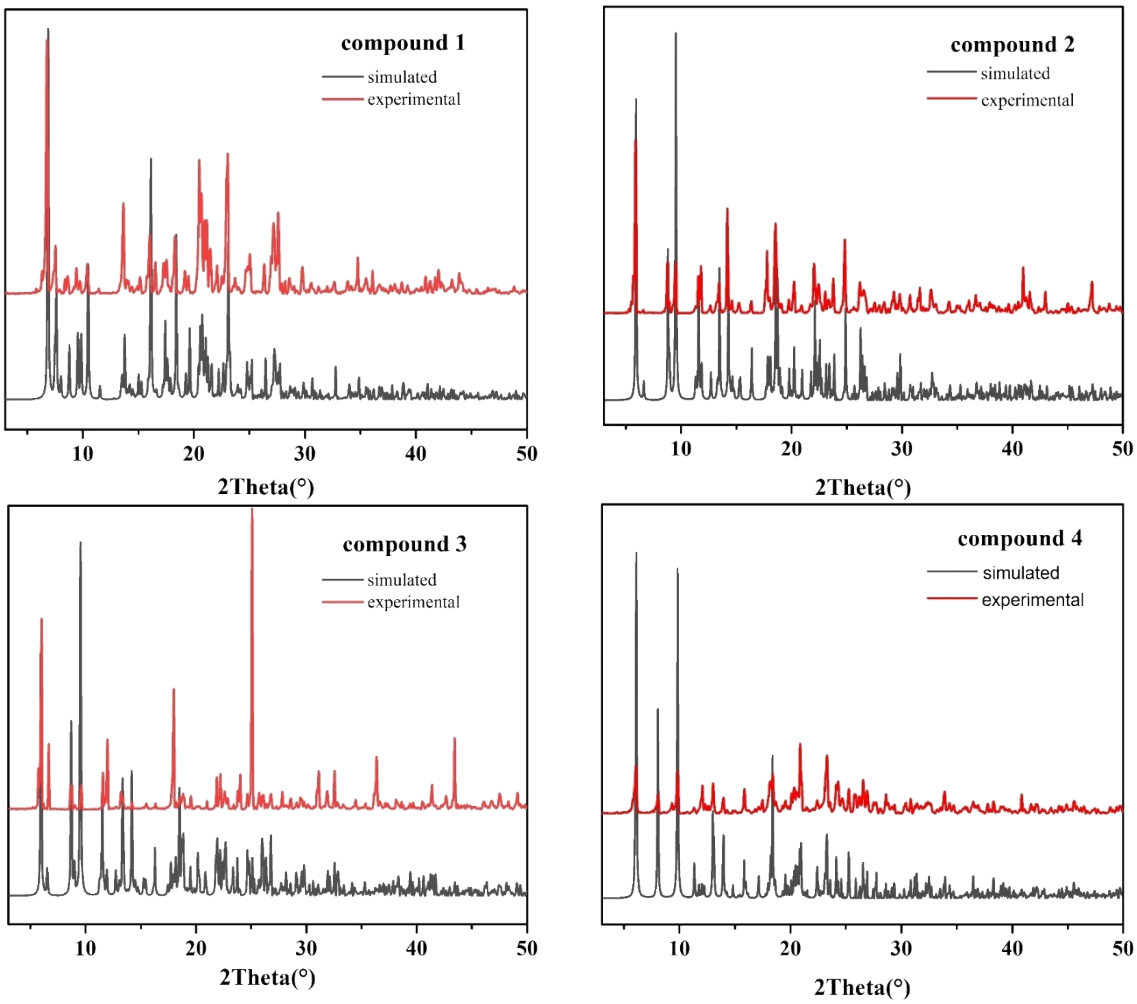

Figure.S7 PXRD patterns of compounds **1-4**.

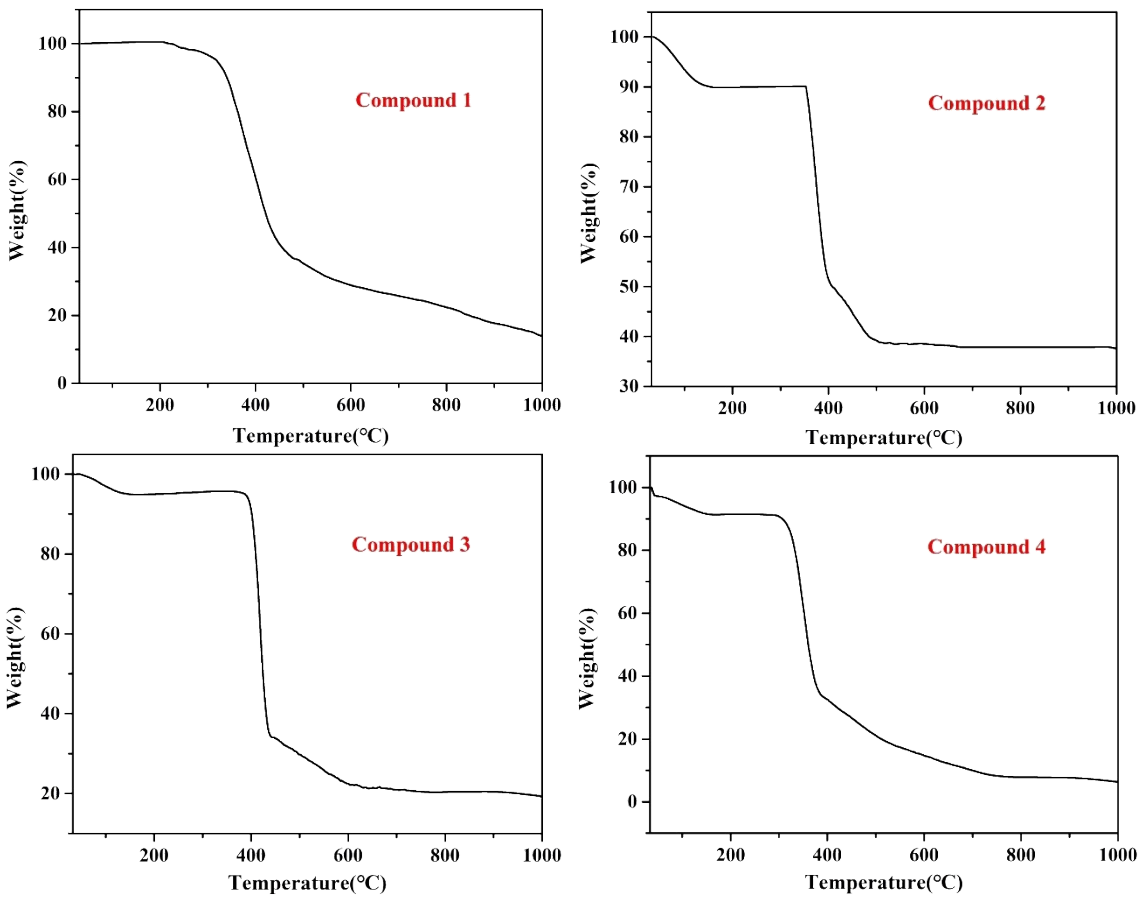

Figure. S8 TGA plot of compounds **1-4**.

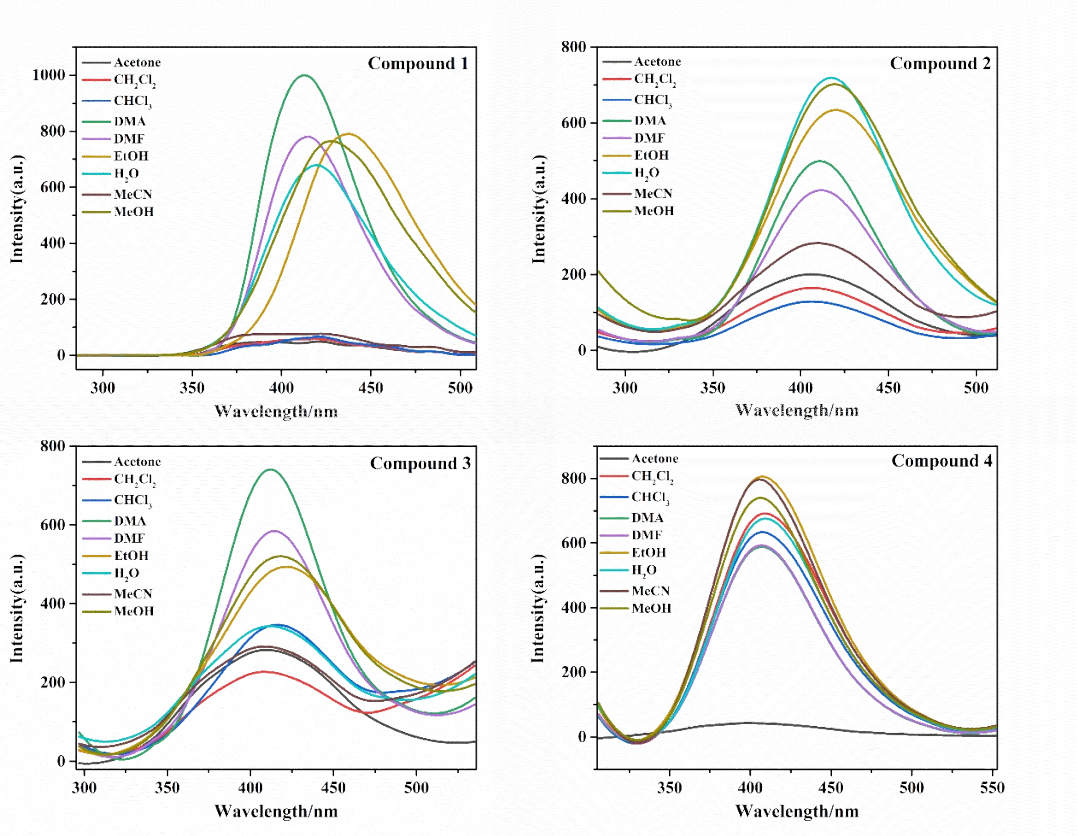

Figure.S9 Emission spectra of compounds **1-4** (1 mg/5 mL) in different solvents, e_x of compounds **1-4**: 266 nm, 265 nm, 277 nm, 286 nm, respectively.

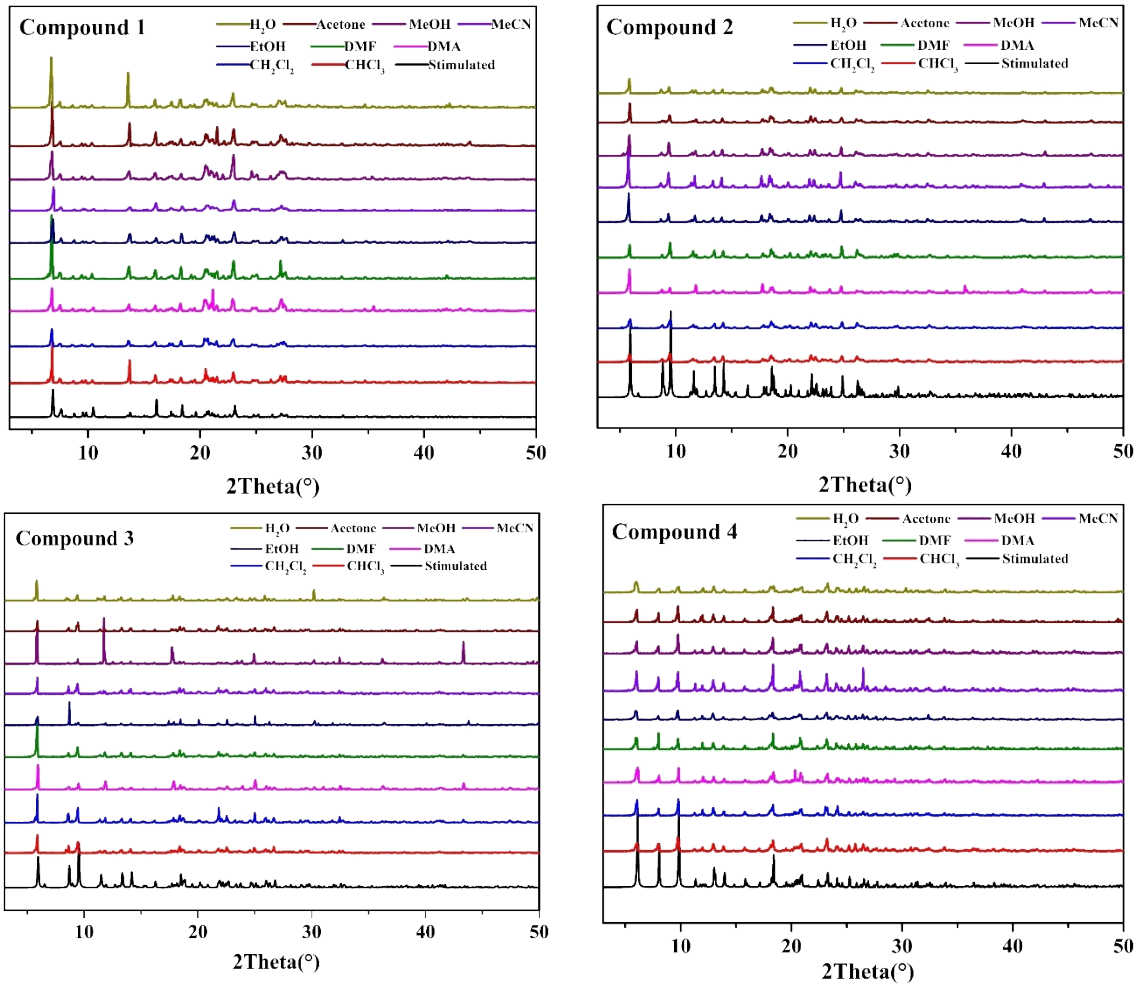

Figure. S10 PXRD patterns of compounds **1-4** immersed 60 h in different solvents.

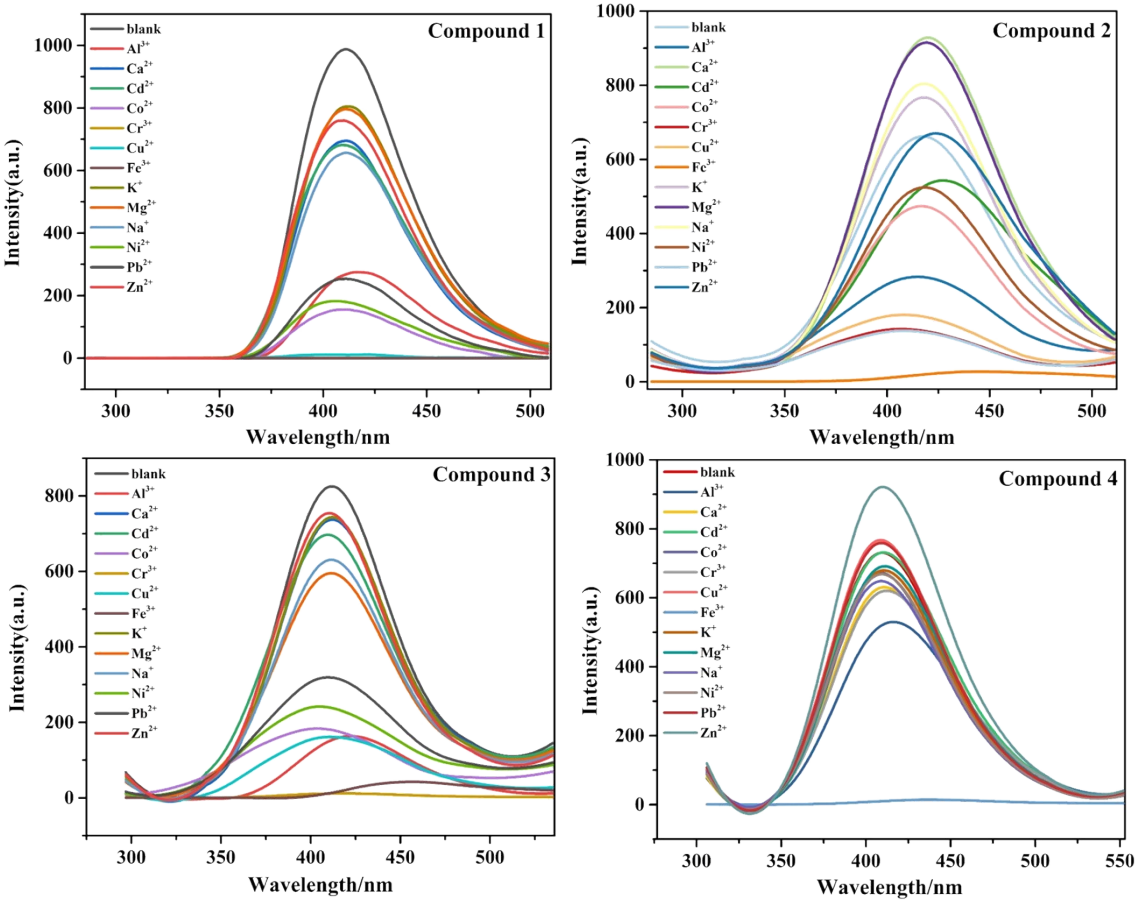

Figure. S11 Emission spectra of compounds **1-4** (1 mg/5 mL) in different metal solutions, e_x of compounds **1-4**: 266 nm, 265 nm, 277 nm, 286 nm, respectively.

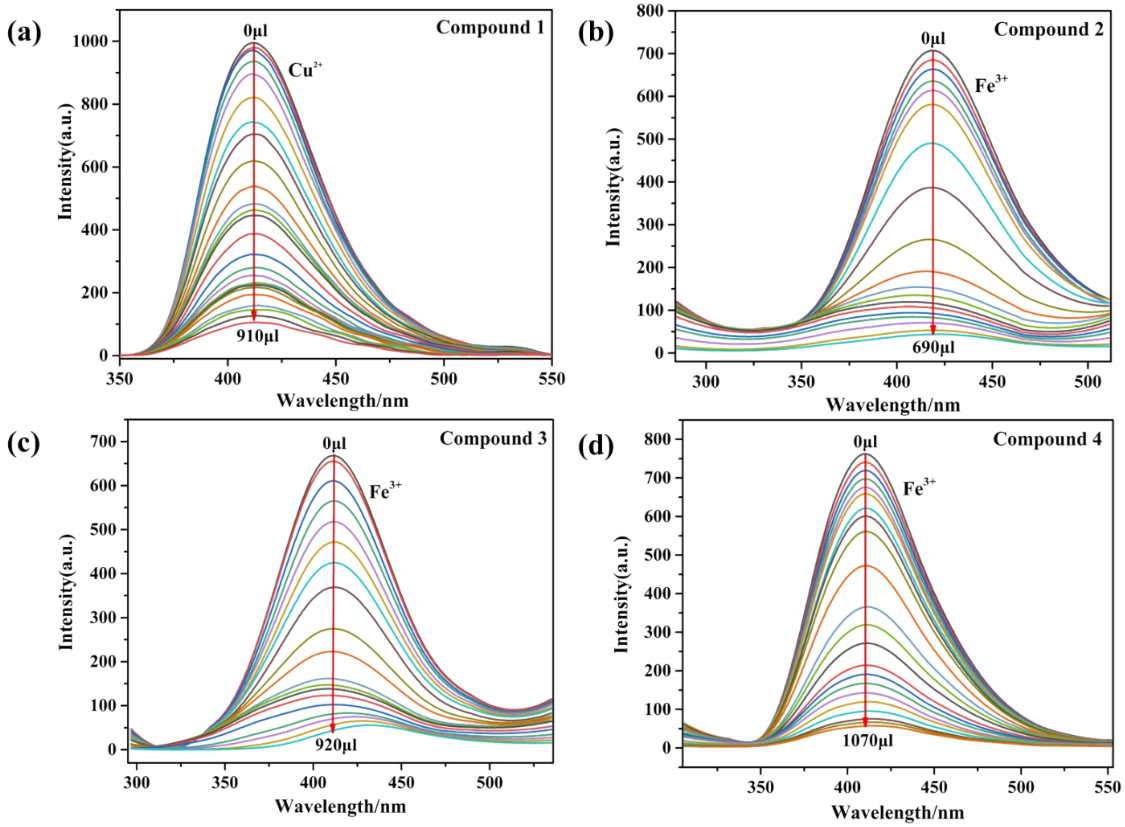

Figure. S12 (a) Luminescence spectra of compound **1**@Cu^{2+} DMA suspensions with Cu^{2+} concentrations varying from 0 to 3.07×10^{-1} mM; (b) Luminescence spectra of compound **2**@Fe^{3+} H_2O suspensions with Fe^{3+} concentrations varying from 0 to 2.43×10^{-1} mM; (c) Luminescence spectra of compound **3**@Fe^{3+} DMA suspensions with Fe^{3+} concentrations varying from 0 to 3.11×10^{-1} mM (d) Luminescence spectra of compound **4**@Fe^{3+} H_2O suspensions with Fe^{3+} concentrations varying from 0 to 3.53×10^{-1} mM.

Table S6 Performance comparison between various fluorescent material sensors for Fe^{3+} and Cu^{2+}

Compounds	Analyte	K_{SV}	LOD	References
[Zn(1,1'-bbi)(C_2O_4)] n	Fe^{3+}	6.98×10^4	0.43 μM	[1]
[Cd_3(L)$_2$(NH_2-BDC)$_6$(DMF)$_2$]	Fe^{3+}	3.23×10^4	2.23 μM	[2]
[Cd_3(3-BABA)$_2$(bpe)$_2$]$_n$ (3)	**Fe^{3+}**	**2.98×10^4**	**0.265**	**This work**
[Cd_3(L)$_2$(1,1'-bbi)(H_2O)$_4$]$_n$	Fe^{3+}	2.36×10^4	1.27 μM	[3]
{[Cd_2(SA)$_2$(L)$_2$]·H_2O}$_n$	Fe^{3+}	2.1×10^4	2.40 μM	[4]
[Cd_2(1,3-bimb)(bpta)(H_2O)]$_n$·0.5nH_2O	Fe^{3+}	1.91×10^4	/	[5]
[Zn_2(TPOM)(NDC)$_2$]·3.5H_2O	Fe^{3+}	1.9×10^4	2 μM	[6]
[Zn_3(3-BABA)$_2$(bpa)$_2$(H_2O)$_2$]$_n$ (1)	**Cu^{2+}**	**1.77×10^4**	**0.363**	**This work**
[Cd_3(3-BABA)$_2$(bpa)$_2$]$_n$ (2)	**Fe^{3+}**	**1.14×10^4**	**0.539**	**This work**
{[Cd_3(3-BABA)$_2$(bib)(DMA)$_2$]·0.9H_2O}$_n$ (4)	**Fe^{3+}**	**8050**	**0.748**	**This work**
[Cd(CDC)(L)]n	Fe^{3+}	4900	74 μM	[7]
[Zn_2(L_1)$_2$(bpe)$_2$(H_2O)$_2$]	Fe^{3+}	2395	25 μM	[8]

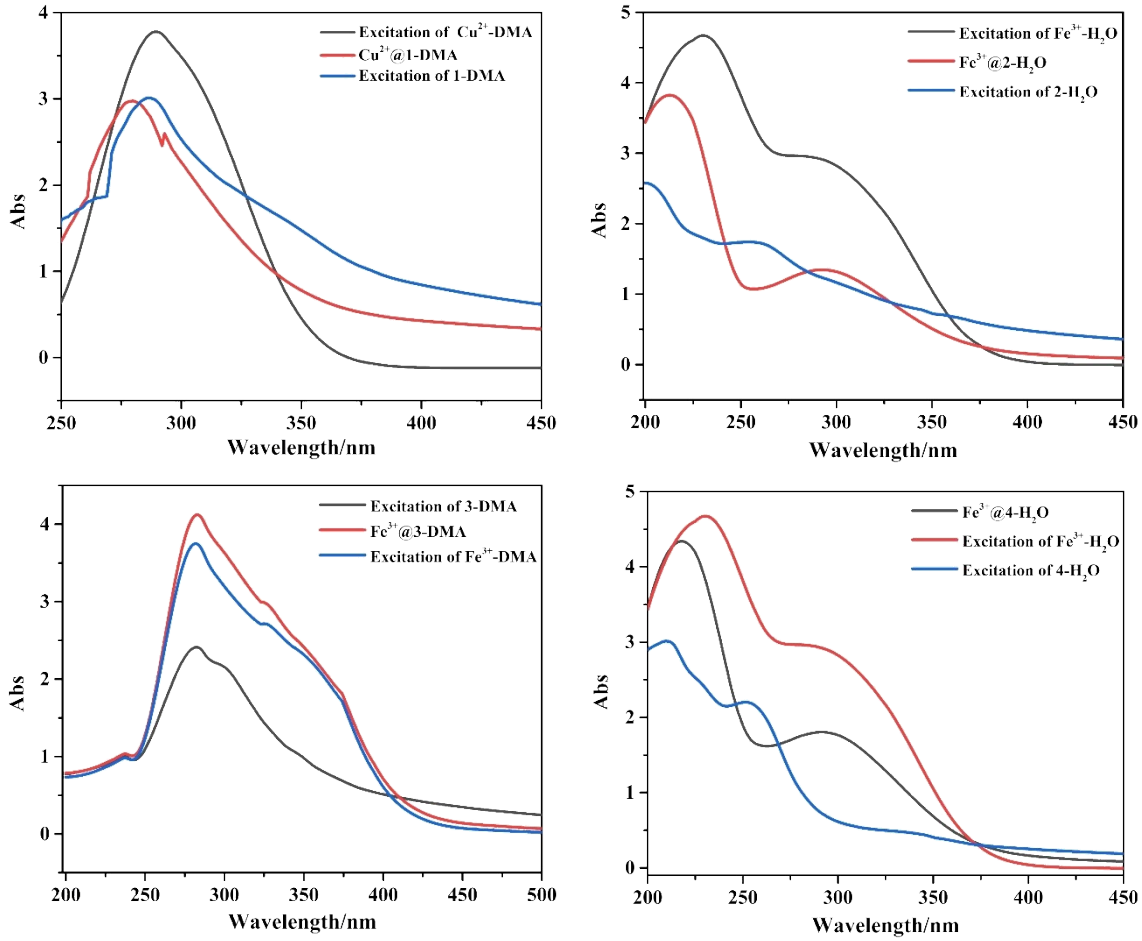

Figure. S13 UV-vis adsorption spectra of $M(NO_3)_n$ solutions and the excitation spectrum of **1-4**.

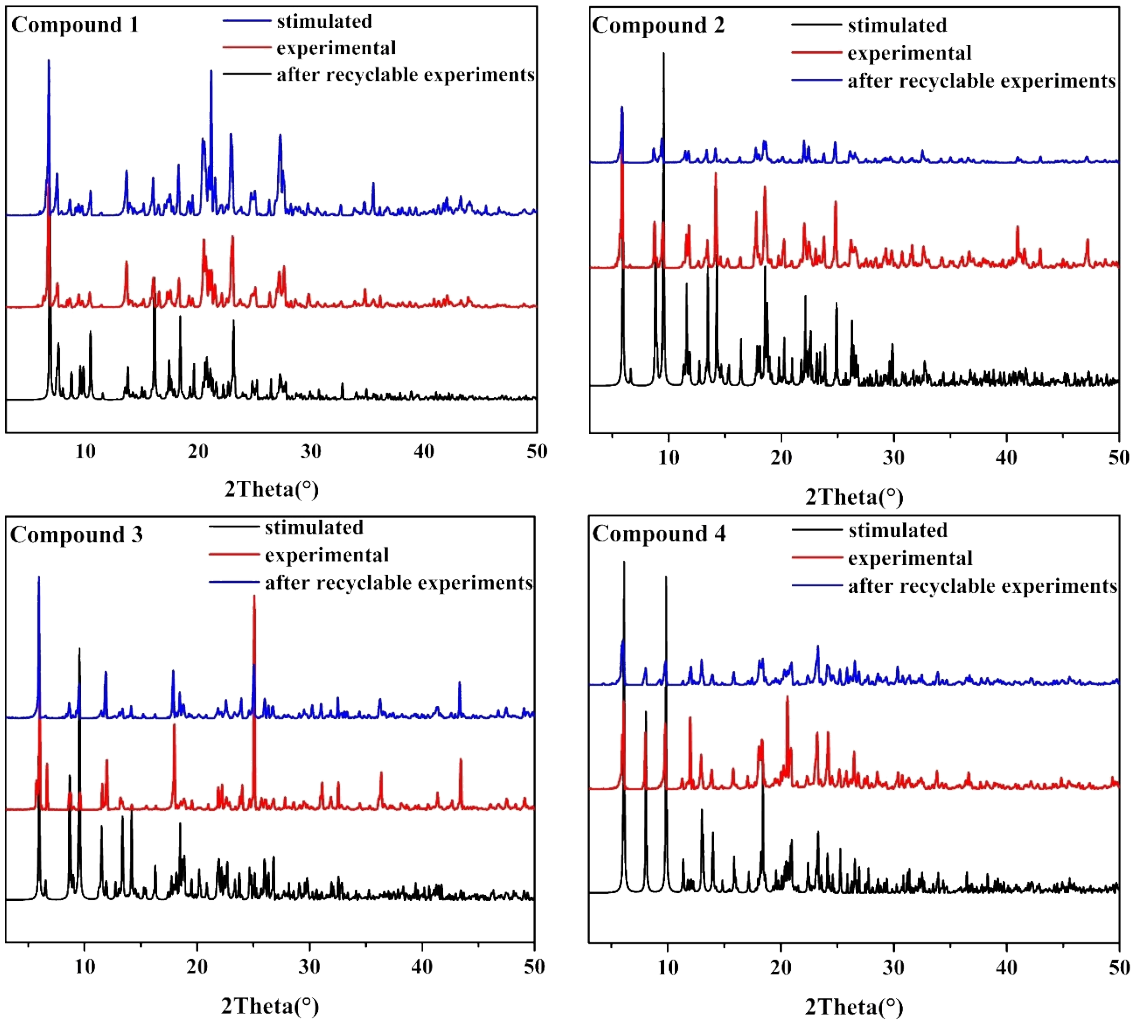

Figure. S14 PXRD patterns of compounds **1-4** before and after recyclable experiments.

References

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