Supplementary Material (ESI)

Bis-pyridyl-bis-amide-modulated a series of metal-organic frameworks: Formation, transformation and selectivity for the efficient detection of multiple analytes

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Table S1. Crystallographic data for complexes **1**–**4**.

Complex	**1**	**2**	**3**	**4**	**4a**	**4b**
Empirical formula	$C_{26}H_{20}N_4O_7Zn$	$C_{26}H_{22}N_4O_8Zn$	$C_{26}H_{18}CdN_4O_6$	$C_{65}H_{49}Cd_2N_{11}O_{15}$	$C_{55}H_{43}Cd_2N_9O_{13}$	$C_{55}H_{43}Cu_2N_9O_{13}$
Formula weight	565.83	583.85	594.84	1448.95	1262.78	1165.06
Crystal system	Triclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P –1*	*C c c a*	*P –1*	*P –1*	*P 21/c*	*P 21/c*
a (Å)	7.9323(17)	17.6671(6)	4.9600(5)	10.7737(9)	10.7456(5)	10.7796(7)
b (Å)	11.895(3)	19.4948(6)	10.1397(11)	14.7826(11)	36.5825(16)	36.563(2)
c (Å)	12.694(3)	15.5450(5)	11.8715(12)	20.3526(16)	15.7867(7)	15.8187(10)
α (°)	97.585(4)	90	67.798(2)	90.830(2)	90	90
β (°)	101.921(4)	90	81.007(2)	91.007(2)	98.1640(10)	97.9780(10)
γ (°)	94.309(4)	90	86.591(2)	109.013(2)	90	90
V (Å ^{3})	1155.1(5)	5354.0(3)	545.99(10)	3063.4(4)	6142.9(5)	6174.3(7)
Z	2	8	1	2	4	4
D_c (g cm^{-3})	1.627	1.449	1.809	1.571	1.365	1.253
R_{int}	0.0518	0.0197	0.0135	0.0372	0.0295	0.0438
GOF	1.010	1.059	1.028	1.074	1.047	1.043
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0568	0.0289	0.0231	0.0849	0.0580	0.0900
$wR_2{}^b$ (all data)	0.1367	0.0842	0.0564	0.2209	0.1550	0.2844

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, [b] $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (°) for complex **1**.

Zn(1)–O(1)	1.979(3)	Zn(1)–O(3)	2.123(3)
Zn(1)–N(1)	2.080(4)	Zn(1)–O(4)	2.163(3)
Zn(1)–N(2)	2.120(5)	Zn(1)–C(23)	2.471(5)
O(1)–Zn(1)–N(1)	92.13(14)	N(2)–Zn(1)–O(4)	94.07(16)
O(1)–Zn(1)–N(2)	96.71(15)	O(3)–Zn(1)–O(4)	61.33(13)
N(1)–Zn(1)–N(2)	106.92(16)	O(1)–Zn(1)–C(23)	138.33(17)
O(1)–Zn(1)–O(3)	108.23(14)	N(1)–Zn(1)–C(23)	118.44(16)
N(1)–Zn(1)–O(3)	141.64(15)	N(2)–Zn(1)–C(23)	100.03(16)
N(2)–Zn(1)–O(3)	102.65(15)	O(3)–Zn(1)–C(23)	30.73(15)
O(1)–Zn(1)–O(4)	166.55(16)	O(4)–Zn(1)–C(23)	30.60(15)
N(1)–Zn(1)–O(4)	92.40(14)		

Table S3. Selected bond distances (Å) and angles (°) for complex **2**.

Zn(1)–O(1)#1	1.9601(11)	Zn(1)–N(1)#1	2.0747(12)
Zn(1)–O(1)	1.9601(11)	Zn(1)–N(1)	2.0748(12)
O(1)#1–Zn(1)–O(1)	133.29(8)	O(1)#1–Zn(1)–N(1)	106.26(5)
O(1)#1–Zn(1)–N(1)#1	106.31(6)	O(1)–Zn(1)–N(1)	106.32(6)
O(1)–Zn(1)–N(1)#1	106.26(5)	N(1)#1–Zn(1)–N(1)	89.95(7)

Symmetry code: #1 $-x + 3/2, -y, z$.

Table S4. Selected bond distances (Å) and angles (°) for complex **3**.

Cd(1)–N(1)#1	2.2597(15)	Cd(1)–O(1)#1	2.3196(14)
Cd(1)–N(1)	2.2597(15)	Cd(1)–O(2)#2	2.4154(13)
Cd(1)–O(1)	2.3196(14)	Cd(1)–O(2)#3	2.4154(13)
N(1)#1–Cd(1)–N(1)	180	O(1)–Cd(1)–O(2)#2	84.19(6)
N(1)#1–Cd(1)–O(1)	92.05(6)	O(1)#1–Cd(1)–O(2)#2	95.81(6)
N(1)–Cd(1)–O(1)	87.95(6)	N(1)#1–Cd(1)–O(2)#3	87.25(5)
N(1)#1–Cd(1)–O(1)#1	87.95(6)	N(1)–Cd(1)–O(2)#3	92.75(5)
N(1)–Cd(1)–O(1)#1	92.05(6)	O(1)–Cd(1)–O(2)#3	95.81(6)
O(1)–Cd(1)–O(1)#1	180	O(1)#1–Cd(1)–O(2)#3	84.19(6)
N(1)#1–Cd(1)–O(2)#2	92.75(5)	O(2)#2–Cd(1)–O(2)#3	180
N(1)–Cd(1)–O(2)#2	87.25(5)		

Symmetry codes: #1 $-x, -y, -z$; #2 $x - 1, y, z$; #3 $-x + 1, -y, -z$.

Table S5. Selected bond distances (Å) and angles (°) for complex **4**.

Cd(1)–N(2)	2.297(8)	Cd(2)–O(6)#1	2.303(5)
Cd(1)–O(8)	2.324(5)	Cd(2)–N(3)	2.314(6)
Cd(1)–N(1)	2.325(7)	Cd(2)–N(4)	2.328(6)
Cd(1)–O(5)	2.368(5)	Cd(2)–O(3)	2.365(5)
Cd(1)–O(1)	2.396(5)	Cd(2)–O(7)#1	2.371(5)
Cd(1)–O(2)	2.433(5)	Cd(2)–O(4)	2.424(5)
Cd(1)–O(7)	2.645(5)	Cd(2)–C(44)	2.742(6)
N(2)–Cd(1)–O(8)	90.6(3)	O(6)#1–Cd(2)–N(3)	89.9(2)
N(2)–Cd(1)–N(1)	178.5(3)	O(6)#1–Cd(2)–N(4)	89.7(2)
O(8)–Cd(1)–N(1)	89.0(2)	N(3)–Cd(2)–N(4)	176.8(2)
N(2)–Cd(1)–O(5)	92.8(2)	O(6)#1–Cd(2)–O(3)	88.18(18)
O(8)–Cd(1)–O(5)	135.8(2)	N(3)–Cd(2)–O(3)	90.7(2)
N(1)–Cd(1)–O(5)	86.4(2)	N(4)–Cd(2)–O(3)	92.5(2)
N(2)–Cd(1)–O(1)	91.1(2)	O(6)#1–Cd(2)–O(7)#1	134.81(19)
O(8)–Cd(1)–O(1)	86.71(19)	N(3)–Cd(2)–O(7)#1	92.3(2)
N(1)–Cd(1)–O(1)	90.3(2)	N(4)–Cd(2)–O(7)#1	85.7(2)
O(5)–Cd(1)–O(1)	137.18(19)	O(3)–Cd(2)–O(7)#1	136.88(17)
N(2)–Cd(1)–O(2)	92.3(3)	O(6)#1–Cd(2)–O(4)	142.34(19)
O(8)–Cd(1)–O(2)	140.28(19)	N(3)–Cd(2)–O(4)	92.4(2)
N(1)–Cd(1)–O(2)	88.9(2)	N(4)–Cd(2)–O(4)	89.8(2)
O(5)–Cd(1)–O(2)	83.6(2)	O(3)–Cd(2)–O(4)	54.24(17)
O(1)–Cd(1)–O(2)	53.65(18)	O(7)#1–Cd(2)–O(4)	82.65(18)
N(2)–Cd(1)–O(7)	84.4(2)	O(6)#1–Cd(2)–C(44)	115.4(2)
O(8)–Cd(1)–O(7)	51.57(18)	N(3)–Cd(2)–C(44)	92.0(2)
N(1)–Cd(1)–O(7)	94.2(2)	N(4)–Cd(2)–C(44)	91.1(2)
O(5)–Cd(1)–O(7)	84.96(18)	O(3)–Cd(2)–C(44)	27.31(18)
O(1)–Cd(1)–O(7)	137.85(17)	O(7)#1–Cd(2)–C(44)	109.6(2)
O(2)–Cd(1)–O(7)	167.93(18)	O(4)–Cd(2)–C(44)	26.93(19)

Symmetry code: #1 x, $y-1$, z.

Table S6. Selected bond distances (Å) and angles (°) for complex **4a**.

Cd(1)–O(2)#1	2.275(4)	Cd(2)–O(13)	2.352(4)
Cd(1)–O(1)	2.329(4)	Cd(2)–N(4)#2	2.355(3)
Cd(1)–N(1)	2.344(4)	Cd(2)–O(3)	2.371(3)
Cd(1)–N(2)#2	2.350(4)	Cd(2)–O(6)	2.382(4)
Cd(1)–O(8)#3	2.379(3)	Cd(2)–O(5)	2.416(4)
Cd(1)–O(7)#3	2.412(3)	Cd(2)–O(4)	2.455(3)
Cd(1)–C(52)#3	2.733(4)	Cd(2)–C(45)	2.736(4)
Cd(2)–N(3)	2.322(4)	Cd(2)–C(44)	2.747(4)
O(2)#1–Cd(1)–O(1)	121.11(13)	N(4)#2–Cd(2)–O(6)	92.66(14)
O(2)#1–Cd(1)–N(1)	93.96(15)	O(3)–Cd(2)–O(6)	79.22(12)
O(1)–Cd(1)–N(1)	87.77(15)	N(3)–Cd(2)–O(5)	91.25(14)
O(2)#1–Cd(1)–N(2)#2	94.88(15)	O(13)–Cd(2)–O(5)	87.77(15)
O(1)–Cd(1)–N(2)#2	87.92(15)	N(4)#2–Cd(2)–O(5)	89.76(13)
N(1)–Cd(1)–N(2)#2	171.15(15)	O(3)–Cd(2)–O(5)	133.31(13)
O(2)#1–Cd(1)–O(8)#3	139.65(13)	O(6)–Cd(2)–O(5)	54.47(13)
O(1)–Cd(1)–O(8)#3	99.25(12)	N(3)–Cd(2)–O(4)	85.86(13)
N(1)–Cd(1)–O(8)#3	86.91(13)	O(13)–Cd(2)–O(4)	84.83(14)
N(2)#2–Cd(1)–O(8)#3	86.16(13)	N(4)#2–Cd(2)–O(4)	91.94(12)
O(2)#1–Cd(1)–O(7)#3	85.19(12)	O(3)–Cd(2)–O(4)	53.91(11)
O(1)–Cd(1)–O(7)#3	153.58(12)	O(6)–Cd(2)–O(4)	133.04(12)
N(1)–Cd(1)–O(7)#3	87.82(14)	O(5)–Cd(2)–O(4)	172.15(12)
N(2)#2–Cd(1)–O(7)#3	92.62(14)	N(3)–Cd(2)–C(45)	93.33(14)
O(8)#3–Cd(1)–O(7)#3	54.50(12)	O(13)–Cd(2)–C(45)	115.28(17)
O(2)#1–Cd(1)–C(52)#3	112.52(14)	N(4)#2–Cd(2)–C(45)	91.80(13)
O(1)–Cd(1)–C(52)#3	126.37(14)	O(3)–Cd(2)–C(45)	105.94(14)
N(1)–Cd(1)–C(52)#3	87.89(14)	O(6)–Cd(2)–C(45)	26.93(15)
N(2)#2–Cd(1)–C(52)#3	88.45(14)	O(5)–Cd(2)–C(45)	27.55(15)
O(8)#3–Cd(1)–C(52)#3	27.13(13)	O(4)–Cd(2)–C(45)	159.84(14)
O(7)#3–Cd(1)–C(52)#3	27.39(13)	N(3)–Cd(2)–C(44)	84.52(14)
N(3)–Cd(2)–O(13)	87.77(15)	O(13)–Cd(2)–C(44)	111.55(15)
N(3)–Cd(2)–N(4)#2	170.79(14)	N(4)#2–Cd(2)–C(44)	97.54(13)
O(13)–Cd(2)–N(4)#2	83.12(15)	O(3)–Cd(2)–C(44)	27.13(12)
N(3)–Cd(2)–O(3)	87.15(14)	O(6)–Cd(2)–C(44)	106.35(13)
O(13)–Cd(2)–O(3)	138.68(14)	O(5)–Cd(2)–C(44)	159.97(14)
N(4)#2–Cd(2)–O(3)	98.79(14)	O(4)–Cd(2)–C(44)	26.86(12)
N(3)–Cd(2)–O(6)	95.37(14)	C(45)–Cd(2)–C(44)	133.00(15)
O(13)–Cd(2)–O(6)	142.10(15)		

Symmetry codes: #1 $-x, -y + 1, -z$; #2 $x - 1, y, z + 1$; #3 $x + 1, -y + 1/2, z + 1/2$.

Table S7. Selected bond distances (Å) and angles (°) for complex **4b**.

Cu(1)–O(1)	2.275(7)	Cu(2)–N(2)#1	2.328(8)
Cu(1)–N(6)#1	2.328(8)	Cu(2)–O(13)	2.356(8)
Cu(1)–N(5)	2.333(7)	Cu(2)–O(4)#4	2.375(7)
Cu(1)–O(2)#2	2.341(8)	Cu(2)–O(6)	2.379(7)
Cu(1)–O(7)	2.386(6)	Cu(2)–O(5)	2.426(7)
Cu(1)–O(8)	2.409(7)	O(2)–Cu(1)#2	2.341(7)
N(1)–Cu(2)	2.355(7)	O(4)–Cu(2)#5	2.375(7)
N(2)–Cu(2)#3	2.329(8)	N(6)–Cu(1)#3	2.328(8)
O(1)–Cu(1)–N(6)#1	93.6(3)	N(2)#1–Cu(2)–N(1)	170.1(3)
O(1)–Cu(1)–N(5)	94.8(3)	N(2)#1–Cu(2)–O(13)	87.2(3)
N(6)#1–Cu(1)–N(5)	171.6(3)	N(1)–Cu(2)–O(13)	83.3(3)
O(1)–Cu(1)–O(2)#2	121.3(2)	N(2)#1–Cu(2)–O(4)#4	87.5(3)
N(6)#1–Cu(1)–O(2)#2	88.5(3)	N(1)–Cu(2)–O(4)#4	97.9(3)
N(5)–Cu(1)–O(2)#2	87.7(3)	O(13)–Cu(2)–O(4)#4	138.3(3)
O(1)–Cu(1)–O(7)	139.4(3)	N(2)#1–Cu(2)–O(6)	96.1(3)
N(6)#1–Cu(1)–O(7)	86.9(3)	N(1)–Cu(2)–O(6)	93.2(3)
N(5)–Cu(1)–O(7)	86.3(3)	O(13)–Cu(2)–O(6)	143.0(3)
O(2)#2–Cu(1)–O(7)	99.3(2)	O(4)#4–Cu(2)–O(6)	78.7(2)
O(1)–Cu(1)–O(8)	84.3(2)	N(2)#1–Cu(2)–O(5)	92.1(3)
N(6)#1–Cu(1)–O(8)	87.9(3)	N(1)–Cu(2)–O(5)	90.2(3)
N(5)–Cu(1)–O(8)	92.2(3)	O(13)–Cu(2)–O(5)	87.8(3)
O(2)#2–Cu(1)–O(8)	154.3(2)	O(4)#4–Cu(2)–O(5)	133.7(3)
O(7)–Cu(1)–O(8)	55.1(2)	O(6)–Cu(2)–O(5)	55.3(2)

Symmetry codes: #1 $x + 1, y, z – 1$; #2 $–x, –y + 1, –z + 1$; #3 $x – 1, y, z + 1$; #4 $–x + 1, y – 1/2, –z + 3/2$; #5 $–x + 1, y + 1/2, –z + 3/2$.

Table S8 K_{sv} values and LOD of complexes **1**–**4** for different analytes.

Analyte	Complex **1**		Complex **2**		Complex **3**		Complex **4**	
	K_{sv} (M^{-1})	LOD (M)	K_{sv} (M^{-1})	LOD (M)	K_{sv} (M^{-1})	LOD (M)	K_{sv} (M^{-1})	LOD (M)
Fe^{3+}	1.38×10^{4}	1.41×10^{-4}	1.10×10^{4}	1.62×10^{-4}	1.27×10^{4}	5.63×10^{-5}	2.89×10^{3}	2.03×10^{-4}
CrO_4^{2-}	6.69×10^{3}	7.80×10^{-4}	4.63×10^{3}	1.26×10^{-4}	6.87×10^{4}	2.20×10^{-2}	4.52×10^{2}	2.63×10^{-5}
$Cr_2O_7^{2-}$	5.43×10^{3}	3.63×10^{-5}	6.80×10^{4}	1.98×10^{-4}	4.26×10^{4}	1.21×10^{-2}	2.36×10^{4}	3.11×10^{-5}
MnO_4^{-}	6.99×10^{3}	1.09×10^{-3}	3.88×10^{4}	4.03×10^{-5}	4.77×10^{4}	8.79×10^{-4}	5.73×10^{2}	3.17×10^{-4}
DMSO	3.70×10^{3}	1.21×10^{-3}	1.36×10^{3}	1.40×10^{-2}	1.06×10^{3}	8.02×10^{-3}	0.92×10^{2}	2.68×10^{-3}
NB	1.65×10^{3}	5.71×10^{-3}	1.71×10^{3}	2.25×10^{-2}	9.75×10^{2}	9.45×10^{-3}	2.38×10^{2}	1.35×10^{-2}
NM	2.82×10^{3}	4.69×10^{-3}	1.89×10^{3}	2.29×10^{-2}	9.75×10^{2}	1.22×10^{-2}	2.39×10^{2}	4.61×10^{-3}
AH	1.26×10^{3}	1.35×10^{-2}	1.11×10^{3}	4.63×10^{-2}	7.87×10^{2}	1.41×10^{-2}	1.65×10^{2}	2.26×10^{-2}

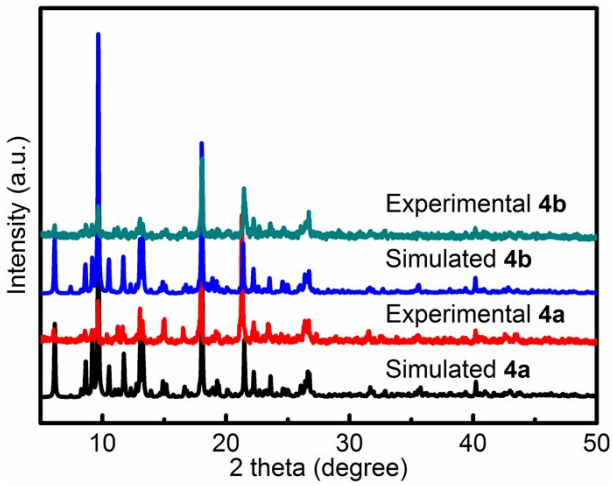

Fig. S1 The PXRD patterns for complexes **4a** and **4b**.

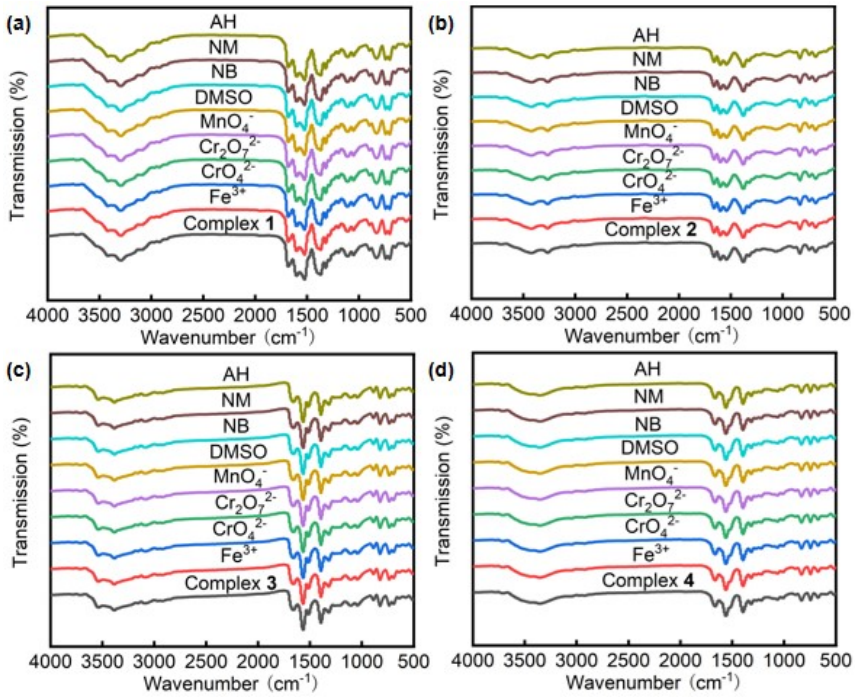

Fig. S2 The IR spectra of complexes **1**–**4** before and after being soaked in different analyzes.

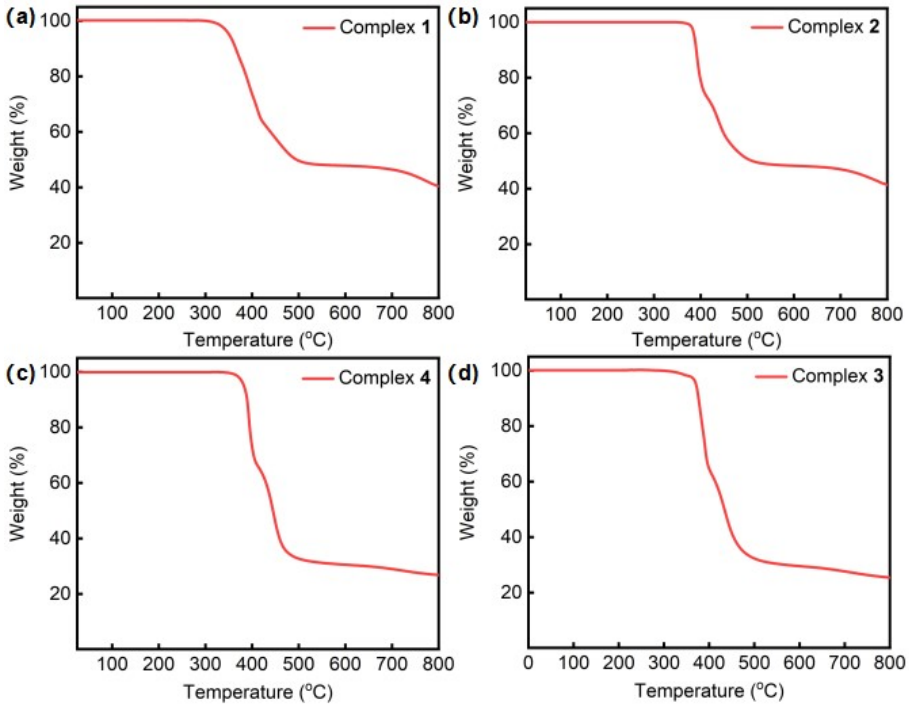

Fig. S3 The TG curves of complexes **1**–**4**.

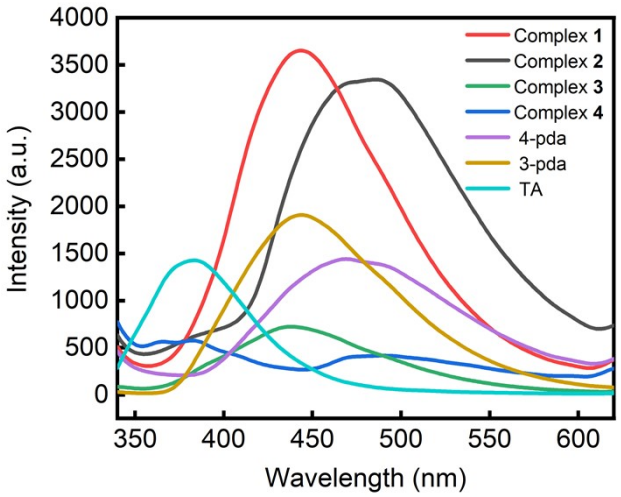

Fig. S4 The emission spectra of the ligands and complexes **1**–**4**.

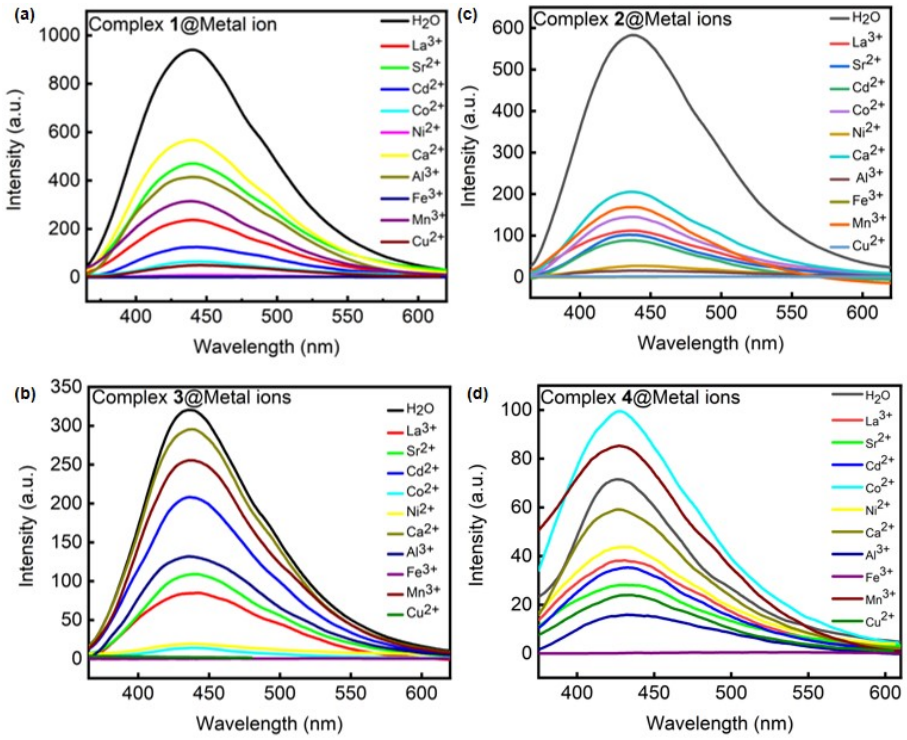

Fig. S5 Luminescence spectra of complexes **1**–**4** in different metal ion solutions.

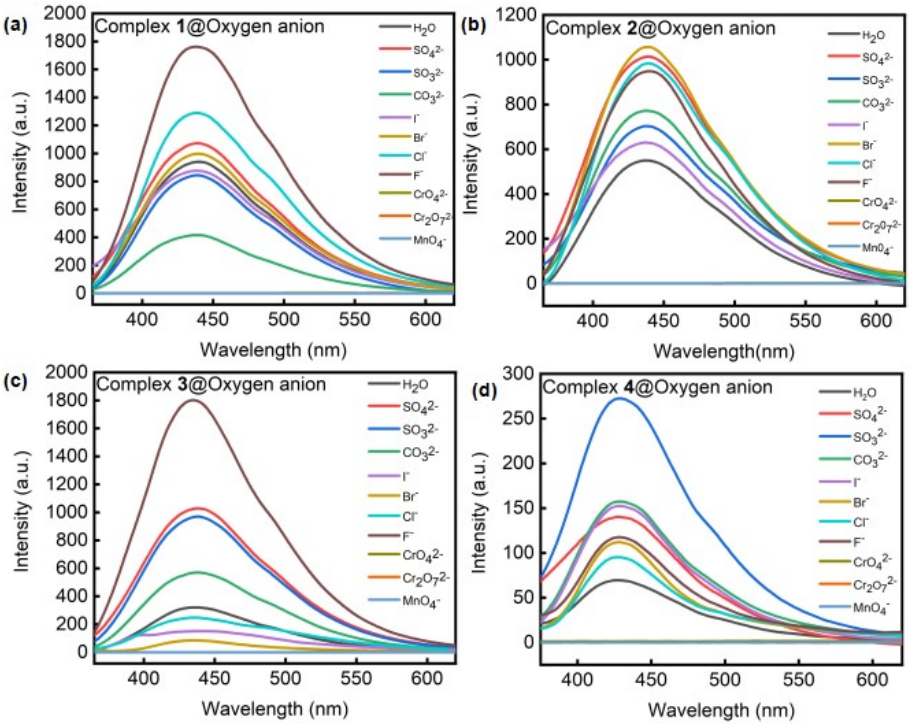

Fig. S6 Luminescence spectra of complexes **1**–**4** after the addition of various metal cations.

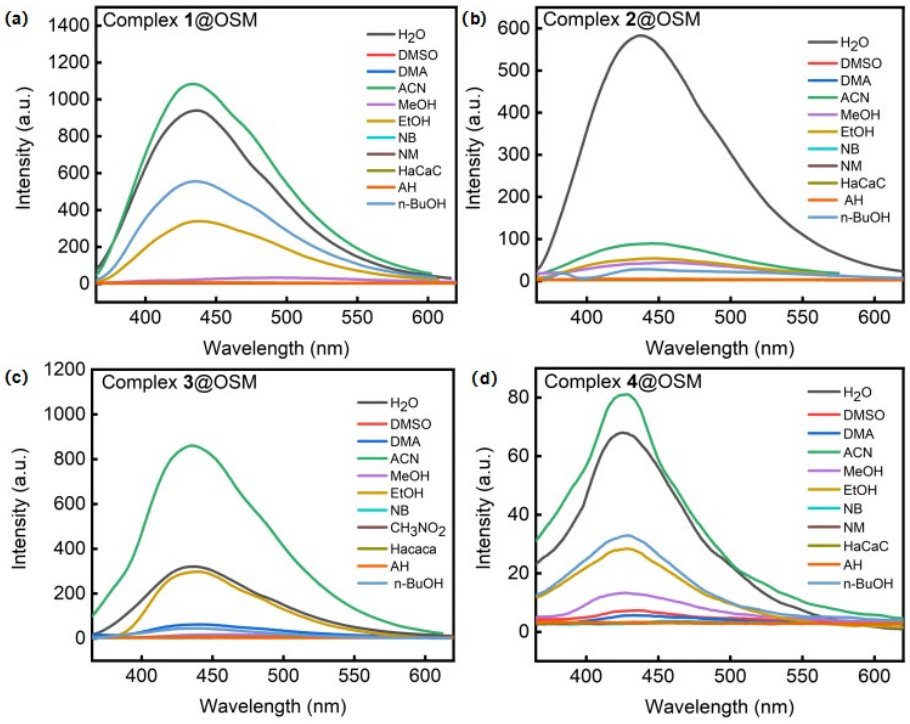

Fig. S7 Luminescence spectra of complexes **1**–**4** after the addition of various oxygen anions.

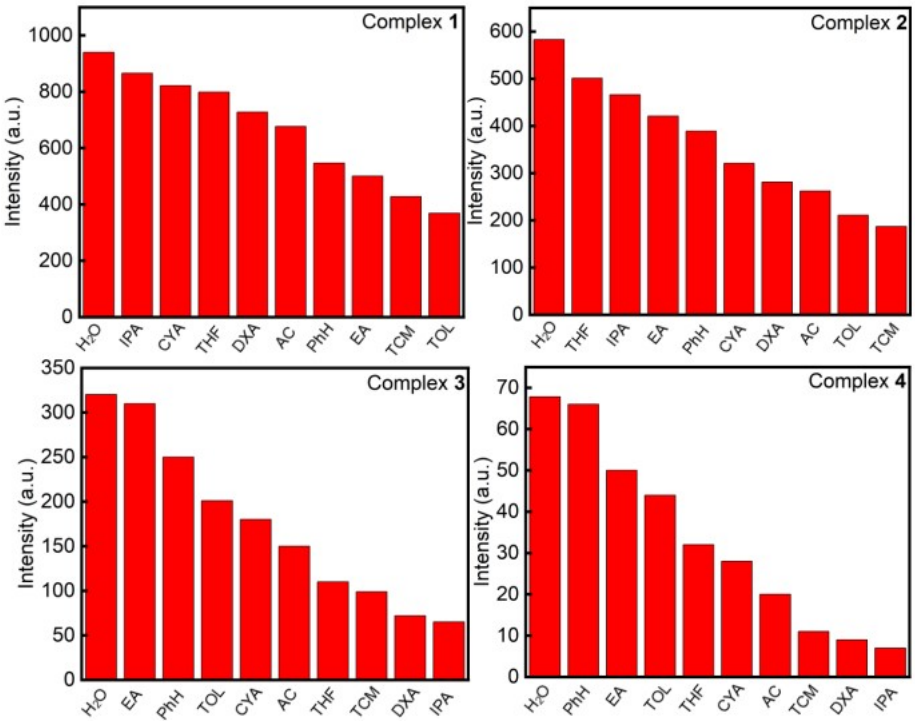

Fig. S8 Fluorescence spectra of complexes 1–4 after the addition of some other aromatic solvents.