

Electronic Supplementary Information

Synthesis, structure, and fluorescence properties of coordination polymers of 3,5-bis(1',2',4'-triazol-1'-yl) pyridine

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1. Material and methods

The ligand 3,5-bis(1',2',4'-triazol-1'-yl) pyridine (btap) was prepared according to the literature method [1, 2]. The structure was determined by single crystal X-ray diffraction, ^1H and $^{13}\text{C}\{^1\text{H}\}$ nuclear magnetic resonance (NMR) spectroscopy and mass spectroscopy (MS), and the molecular structure was depicted in Fig. S1.

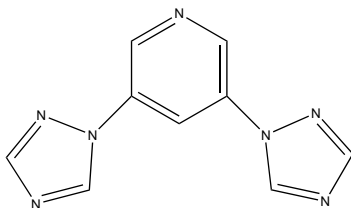


Figure S1: The chemical structure of 3,5-bis(1',2',4'-triazol-1'-yl) pyridine (btap) ligand.

2. Structure determination of single crystals

Suitable single crystals of the coordination polymers **1**, **2**, **3** and **4** were selected for single crystal X-ray diffraction analyses. Crystallographic data were collected on a Bruker AXS D8 ADVANCE single crystal X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The APEX 3 program was used to collect frames of data, index the reflections and determine the lattice parameters; SAINT [3] was used for the integration of the intensity of the reflections and scaling; SADABS [4] was used for absorption correction; and SHELXTL [5, 6] was used for space-group determinations. The structure was solved by direct methods with SHELXT program [7] and refined by full matrix least-square methods on the basis of F^2 using SHELXL-2014 program [8, 9] contained in OLEX2 suite graphical user interface [10]. The contribution of the disordered solvent molecules to the diffraction pattern could not be rigorously included in the model and were consequently removed with the SQUEEZE routine [11] of PLATON [12] or with the mask tool implemented in OLEX2. All non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. The crystallographic information files (CIFs) were compiled with OLEX2. The program

PLATON enabled checking for additional symmetry elements. The overall structures of the coordination polymers were analyzed by TOPOS software [13]. The formula for **1**, **2**, **3** and **4** were determined by single crystal structure. Crystallographic figures were generated with the Diamond 3.1e software [14]. The detailed bond lengths and bond angles for these compounds were tabulated in Tables S1–S8.

2.1. The crystal structure of compound **1**

Table S1: Selected bond lengths (Å) for compound **1**

bond	length (Å)	bond	length (Å)
Co1–N1#1 ¹	2.1780(16)	C3–C7	1.382(2)
Co1–N1	2.1779(16)	C3–C4	1.393(3)
Co1–N7#2 ¹	2.1589(15)	C6–C7	1.384(3)
Co1–N7#3 ¹	2.1589(15)	C6–C5	1.391(3)
Co1–O1	2.0595(14)	N4–C5	1.335(3)
Co1–O1#1 ¹	2.0596(14)	N4–C4	1.331(3)
N5–C6	1.419(2)	N2–C1	1.308(3)
N5–C9	1.339(2)	C9–N7	1.320(2)
N5–N6	1.365(2)	N7–Co1#4 ¹	2.1588(15)
N3–C3	1.421(2)	N7–C8	1.355(3)
N3–C2	1.337(2)	N6–C8	1.316(3)
N3–N2	1.361(2)	O1–C10	1.240(3)
N1–C2	1.316(2)	O2–C10	1.217(3)
N1–C1	1.352(3)		

¹ #1: $-x, 1-y, -z$; #2: $-1/2-x, 1/2+y, -1/2-z$;

#3: $1/2+x, 1/2-y, 1/2+z$; #4: $-1/2-x, -1/2+y, -1/2-z$.

Table S2: Selected angles (°) for compound **1**

angle	(°)	angle	(°)
N1–Co1–N1#1 ¹	180.0	C1–N1–Co1	124.78(14)
N7#2–Co1–N1#1 ¹	89.46(6)	C7–C3–N3	120.51(16)
N7#3–Co1–N1#1 ¹	90.54(6)	C7–C3–C4	120.34(17)
N7#2–Co1–N1 ¹	90.54(6)	C4–C3–N3	119.15(16)
N7#3–Co1–N1 ¹	89.46(6)	N1–C2–N3	110.22(16)
N7#2–Co1–N7#3 ¹	180.0	C7–C6–N5	120.17(16)

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Table S2 – continued from previous page

angle	(°)	angle	(°)
O1–Co1–N1#1 ¹	92.48(6)	C7–C6–C5	120.53(17)
O1#1–Co1–N1 ¹	92.48(6)	C5–C6–N5	119.30(17)
O1–Co1–N1	87.52(6)	C4–N4–C5	118.64(17)
O1#1–Co1–N1#1 ¹	87.52(6)	C3–C7–C6	116.63(17)
O1#1–Co1–N7#3 ¹	94.10(6)	N4–C5–C6	121.79(18)
O1–Co1–N7#3 ¹	85.90(6)	N4–C4–C3	122.06(18)
O1–Co1–N7#2 ¹	94.10(6)	C1–N2–N3	102.21(18)
O1#1–Co1–N7#2 ¹	85.90(6)	N2–C1–N1	115.3(2)
O1–Co1–O1#1 ¹	180.0	N7–C9–N5	110.04(17)
C9–N5–C6	129.56(16)	C9–N7–Co1#4 ¹	127.17(14)
C9–N5–N6	109.70(15)	C9–N7–C8	103.10(16)
N6–N5–C6	120.72(15)	C8–N7–Co1#4 ¹	128.55(13)
C2–N3–C3	131.13(16)	C8–N6–N5	102.22(17)
C2–N3–N2	109.52(16)	N6–C8–N7	114.92(18)
N2–N3–C3	119.34(16)	C10–O1–Co1	130.38(15)
C2–N1–Co1	132.24(13)	O2–C10–O1	129.1(2)
C2–N1–C1	102.71(17)		

¹ #1: $-x, 1-y, -z$; #2: $1/2+x, 1/2-y, 1/2+z$;

#3: $-1/2-x, 1/2+y, -1/2-z$; #4: $-1/2-x, -1/2+y, -1/2-z$.

2.2. The crystal structure of compound 2

Table S3: Selected bond lengths (Å) for compound 2

bond	length (Å)	bond	length (Å)
Zn1–O1#1 ¹	1.9698(18)	N9–C19	1.343(4)
Zn1–O2#1 ¹	2.609(2)	N4–C13	1.331(4)
Zn1–O4	1.9968(18)	N4–C14	1.332(4)
Zn1–N6#2 ¹	2.009(2)	N7–C18	1.304(4)
Zn1–N1	2.014(2)	N8–C20	1.353(4)
		N8–C19	1.321(4)
Zn2–O7	2.1408(18)	N10–C20	1.307(4)
Zn2–O7#3 ¹	2.1408(18)	C25–C21	1.386(4)
Zn2–O5#3 ¹	2.0339(17)	C21–C22	1.380(4)
Zn2–O5	2.0340(17)	C23–C24	1.382(4)
Zn2–N8	2.239(2)	C23–C22	1.382(4)
Zn2–N8#3 ¹	2.239(2)	C23–N12A	1.39(2)

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Table S3 – continued from previous page

bond	length (Å)	bond	length (Å)
O3–C2	1.237(3)	C23–N12B	1.463(16)
O1–Zn1#4 ¹	1.9698(18)	C2–C6	1.500(3)
O1–C1	1.276(3)		
O2–Zn1#4 ¹	2.609(2)	C1–C4	1.505(3)
O2–C1	1.229(3)	C16–C15	1.380(4)
O4–C2	1.281(3)	C16–C12	1.374(4)
O5–C3	1.259(3)	C6–C7	1.396(3)
O6–C3	1.245(3)	C6–C5	1.394(3)
C3–C8	1.502(3)	C7–C8	1.381(4)
N6–Zn1#5 ¹	2.009(2)	C9–C4	1.395(3)
N6–C17	1.313(3)	C9–C8	1.395(3)
N6–C18	1.360(3)	C4–C5	1.382(4)
N11–C25	1.341(4)	C15–C14	1.375(4)
N11–C24	1.326(4)	C12–C13	1.386(4)
N1–C10	1.355(3)	C26A–N12A	1.36(2)
N1–C11	1.313(3)	C26A–N13A	1.353(13)
N3–N2	1.367(3)	N14B–C27B	1.322(9)
N3–C11	1.328(3)	N14B–N12B	1.346(14)
N3–C12	1.418(3)	N14A–N12A	1.344(18)
N2–C10	1.296(3)	N14A–C27A	1.336(12)
N5–N7	1.363(3)	N13B–C27B	1.278(11)
N5–C17	1.327(3)	N13B–C26B	1.303(10)
N5–C15	1.426(3)	C26B–N12B	1.342(15)
N9–N10	1.371(3)	N13A–C27A	1.300(13)
N9–C21	1.418(4)		

¹ #1: $-1 + x, + y, + z$; #2: $+ x, -1 + y, + z$;

#3: $1 - x, 1 - y, - z$; #4: $1 + x, + y, + z$;

#5: $+ x, 1 + y, + z$.

Table S4: Selected angles (°) for compound **2**

angle	(°)	angle	(°)
O1#1–Zn1–O2#1 ¹	55.32(7)	N7–C18–N6	113.9(2)
O1#1–Zn1–O4 ¹	99.36(7)	N11–C25–C21	122.2(3)
O1#1–Zn1–N6#2 ¹	110.62(8)	C25–C21–N9	120.5(3)
O1#1–Zn1–N1 ¹	116.82(9)	C22–C21–N9	119.7(3)
		C22–C21–C25	119.7(3)

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Table S4 – continued from previous page

angle	(°)	angle	(°)
O4–Zn1–O2#1 ¹	154.60(6)	C24–C23–N12A	116.0(7)
O4–Zn1–N6#2 ¹	107.71(8)	C24–C23–N12B	123.4(6)
O4–Zn1–N1	103.70(8)	C22–C23–C24	120.0(3)
		C22–C23–N12A	122.9(8)
		C22–C23–N12B	116.2(6)
N6#2–Zn1–O2#1 ¹	85.77(8)	N11–C24–C23	122.5(3)
N6#2–Zn1–N1 ¹	116.44(9)	C21–C22–C23	117.4(3)
		O3–C2–O4	122.7(2)
		O3–C2–C6	120.1(2)
N1–Zn1–O2#1 ¹	88.41(8)	O4–C2–C6	117.2(2)
O7#3–Zn2–O7 ¹	180.00(6)	O1–C1–C4	116.8(2)
O7–Zn2–N8	92.70(8)		
O7#3–Zn2–N8 ¹	87.30(8)	O2–C1–O1	122.9(2)
O7–Zn2–N8#3 ¹	87.30(8)	O2–C1–C4	120.3(2)
O7#3–Zn2–N8#3 ¹	92.70(8)		
O5–Zn2–O7	86.85(7)		
O5–Zn2–O7#3 ¹	93.15(7)	C12–C16–C15	116.6(2)
O5#3–Zn2–O7 ¹	93.15(7)	C7–C6–C2	121.7(2)
O5#3–Zn2–O7#3 ¹	86.85(7)	C5–C6–C2	119.8(2)
O5#3–Zn2–O5 ¹	180.0	C5–C6–C7	118.5(2)
O5#3–Zn2–N8#3 ¹	90.40(8)	C8–C7–C6	120.9(2)
O5–Zn2–N8#3 ¹	89.60(8)	C8–C9–C4	119.6(2)
O5#3–Zn2–N8 ¹	89.60(8)	C9–C4–C1	121.5(2)
O5–Zn2–N8	90.40(8)	C5–C4–C1	118.6(2)
N8–Zn2–N8#3 ¹	180.0	C5–C4–C9	119.8(2)
C1–O1–Zn1#4 ¹	105.18(15)	N2–C10–N1	114.6(2)
C1–O2–Zn1#4 ¹	76.53(15)	C4–C5–C6	121.1(2)
C2–O4–Zn1	111.28(16)	C16–C15–N5	120.1(2)
C3–O5–Zn2	130.56(17)	C14–C15–N5	119.3(2)
O5–C3–C8	116.1(2)	C14–C15–C16	120.5(3)
O6–C3–O5	124.7(2)	N1–C11–N3	109.5(2)
O6–C3–C8	119.2(2)	C16–C12–N3	120.4(2)
C17–N6–Zn1#5 ¹	128.06(18)	C16–C12–C13	120.4(2)
C17–N6–C18	103.8(2)	C13–C12–N3	119.2(2)
C18–N6–Zn1#5 ¹	128.19(18)	C7–C8–C3	119.9(2)
C24–N11–C25	118.2(3)	C7–C8–C9	120.0(2)
C10–N1–Zn1	130.70(18)	C9–C8–C3	120.0(2)

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Table S4 – continued from previous page

angle	(°)	angle	(°)
C11–N1–Zn1	123.35(17)	N4–C13–C12	122.1(3)
C11–N1–C10	103.6(2)	N10–C20–N8	115.5(3)
N2–N3–C12	121.3(2)	N4–C14–C15	122.4(3)
C11–N3–N2	109.9(2)	N8–C19–N9	110.1(2)
C11–N3–C12	128.7(2)	N13A–C26A–N12A	105.8(11)
C10–N2–N3	102.4(2)	C27B–N14B–N12B	102.4(9)
N7–N5–C15	121.4(2)	C27A–N14A–N12A	100.5(11)
C17–N5–N7	109.8(2)	C27B–N13B–C26B	101.9(7)
C17–N5–C15	128.8(2)	N13B–C27B–N14B	116.8(7)
N10–N9–C21	120.8(2)	C26A–N12A–C23	126.7(13)
C19–N9–N10	109.2(2)	N14A–N12A–C23	121.2(14)
C19–N9–C21	129.3(2)	N14A–N12A–C26A	112.1(15)
C13–N4–C14	118.0(3)	N13B–C26B–N12B	112.4(9)
C18–N7–N5	102.9(2)	N14B–N12B–C23	123.2(10)
N6–C17–N5	109.7(2)	C26B–N12B–C23	130.1(9)
C20–N8–Zn2	126.8(2)	C26B–N12B–N14B	106.1(12)
C19–N8–Zn2	126.93(19)	C27A–N13A–C26A	105.0(9)
C19–N8–C20	102.9(2)	N13A–C27A–N14A	116.4(9)
C20–N10–N9	102.3(2)		

¹ #1: $-1 + x, + y, + z$; #2: $+ x, -1 + y, + z$;
#3: $1 - x, 1 - y, - z$; #4: $1 + x, + y, + z$;
#5: $+ x, 1 + y, + z$.

2.3. The crystal structure of compound **3**

Table S5: Selected bond lengths (Å) for compound **3**

bond	length (Å)	bond	length (Å)
Cd1–O2	2.3598(17)	N2–C12	1.424(2)
Cd1–O2#1 ¹	2.3599(17)	N2–C10	1.339(3)
Cd1–N4#2 ¹	2.424(2)	N1–C10	1.317(3)
Cd1–O1	2.4760(16)	N1–C11	1.359(3)
Cd1–O1#1 ¹	2.4761(16)	O3–C2	1.241(3)
Cd1–O7	2.2924(17)	O1–C1	1.259(3)
Cd1–O7#1 ¹	2.2924(17)	O5–Cd2#4 ¹	2.2893(17)
Cd2–O6#3 ¹	2.5329(19)	O5–C3	1.257(3)
Cd2–O4	2.2537(17)	N3–C11	1.300(3)

Continued on next page

Table S5 – continued from previous page

bond	length (Å)	bond	length (Å)
Cd2–N1	2.3671(18)	C1–C4	1.503(3)
Cd2–O3	2.6147(19)	C12–C13	1.384(3)
Cd2–O5#3 ¹	2.2893(17)	C12–C14	1.385(3)
Cd2–O9	2.417(2)	C13–C12#1 ¹	1.384(3)
Cd2–O8	2.327(2)	C5–C4	1.393(3)
O2–C1	1.253(3)	C5–C6	1.398(3)
O6–Cd2#4 ¹	2.5329(19)	C4–C9	1.394(3)
O6–C3	1.237(3)	C3–Cd2#4 ¹	2.755(2)
O4–C2	1.257(3)	C3–C8	1.505(3)
N4–Cd1#5 ¹	2.424(2)	C9–C8	1.393(3)
N4–C14	1.339(2)	C8–C7	1.385(3)
N4–C14#1 ¹	1.339(2)	C2–C6	1.500(3)
N2–N3	1.362(2)	C6–C7	1.396(3)

¹ #1: 1 – x, + y, 1/2 – z; #2: + x, 1 + y, + z;

#3: 1/2 – x, –1/2 + y, 3/2 – z; #4: 1/2 – x, 1/2 + y, 3/2 – z;

#5: + x, –1 + y, + z.

Table S6: Selected angles (°) for compound **3**

angle	(°)	angle	(°)
O2–Cd1–O2#1 ¹	78.10(8)	C14–N4–Cd1#5 ¹	120.84(13)
O2–Cd1–N4#2 ¹	140.95(4)	C14#1–N4–Cd1#5 ¹	120.84(13)
O2#1–Cd1–N4#2 ¹	140.95(4)	C14#1–N4–C14 ¹	118.3(3)
O2#1–Cd1–O1#1 ¹	53.48(5)	N3–N2–C12	119.49(17)
O2–Cd1–O1	53.48(5)	C10–N2–N3	108.90(17)
O2#1–Cd1–O1 ¹	128.72(5)	C10–N2–C12	131.52(18)
O2–Cd1–O1#1 ¹	128.72(5)	C10–N1–Cd2	140.52(15)
N4#2–Cd1–O1#1 ¹	88.88(3)	C10–N1–C11	102.91(18)
N4#2–Cd1–O1 ¹	88.88(3)	C11–N1–Cd2	116.56(14)
O1–Cd1–O1#1 ¹	177.75(7)	C2–O3–Cd2	84.66(14)
O7–Cd1–O2	105.25(7)	C1–O1–Cd1	90.34(13)
O7#1–Cd1–O2 ¹	86.25(7)	C3–O5–Cd2#4 ¹	97.67(14)
O7#1–Cd1–O2#1 ¹	105.25(7)	C11–N3–N2	103.22(18)
O7–Cd1–O2#1 ¹	86.25(7)	O2–C1–O1	120.2(2)
O7#1–Cd1–N4#2 ¹	82.69(4)	O2–C1–C4	118.81(19)
O7–Cd1–N4#2 ¹	82.69(4)	O1–C1–C4	120.97(19)

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Table S6 – continued from previous page

angle	(°)	angle	(°)
O7#1–Cd1–O1 ¹	88.95(6)	C13–C12–N2	120.8(2)
O7#1–Cd1–O1#1 ¹	90.77(6)	C13–C12–C14	120.46(19)
O7–Cd1–O1#1 ¹	88.95(6)	C14–C12–N2	118.70(18)
O7–Cd1–O1	90.77(6)	C12–C13–C12#1 ¹	116.6(3)
O7#1–Cd1–O7 ¹	165.37(8)	C4–C5–C6	120.71(19)
O6#3–Cd2–O3 ¹	129.00(6)	C5–C4–C1	120.33(18)
O4–Cd2–O6#3 ¹	77.30(6)	C5–C4–C9	119.17(18)
O4–Cd2–N1	146.42(7)	C9–C4–C1	120.45(19)
O4–Cd2–O3	52.52(6)	O6–C3–Cd2#4 ¹	66.64(13)
O4–Cd2–O5#3 ¹	126.23(7)	O6–C3–O5	121.9(2)
O4–Cd2–O9	83.79(8)	O6–C3–C8	120.0(2)
O4–Cd2–O8	104.25(8)	O5–C3–Cd2#4 ¹	55.45(11)
N1–Cd2–O6#3 ¹	135.26(6)	O5–C3–C8	118.1(2)
N1–Cd2–O3	95.74(6)	C8–C3–Cd2#4 ¹	172.33(16)
N1–Cd2–O9	82.37(7)	C8–C9–C4	120.6(2)
O5#3–Cd2–O6#3 ¹	53.47(6)	C9–C8–C3	120.22(19)
O5#3–Cd2–N1 ¹	82.66(6)	C7–C8–C3	120.04(18)
O5#3–Cd2–O3 ¹	169.43(8)	C7–C8–C9	119.71(19)
O5#3–Cd2–O9 ¹	84.68(7)	O4–C2–C6	117.1(2)
O5#3–Cd2–O8 ¹	101.81(7)	O3–C2–O4	121.4(2)
O9–Cd2–O6#3 ¹	99.84(7)	O3–C2–C6	121.5(2)
O9–Cd2–O3	84.75(7)	C5–C6–C2	121.77(19)
O8–Cd2–O6#3 ¹	96.67(8)	C7–C6–C5	119.2(2)
O8–Cd2–N1	82.80(7)	C7–C6–C2	119.06(19)
O8–Cd2–O3	88.32(7)	C8–C7–C6	120.63(19)
O8–Cd2–O9	162.91(7)	N1–C10–N2	110.33(19)
C1–O2–Cd1	95.96(14)	N4–C14–C12	121.92(19)
C3–O6–Cd2#4 ¹	86.72(14)	N3–C11–N1	114.6(2)
C2–O4–Cd2	101.34(16)		

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

2.4. The crystal structure of compound 4

Table S7: Selected bond lengths (Å) for compound 4

bond	length (Å)	bond	length (Å)
Cd1–O3	2.3360(18)	N7–Cd1#4 ¹	2.307(2)
Cd1–O1	2.2757(18)	N7–C8	1.355(3)
Cd1–O4#1 ¹	2.2787(17)	N7–C9	1.326(3)
Cd1–O2#2 ¹	2.2746(18)	N3–N2	1.365(3)
Cd1–N7#3 ¹	2.307(2)	N3–C2	1.339(3)
Cd1–N1	2.312(2)	N3–C3	1.428(3)
O3–C11	1.248(3)	N1–C2	1.321(3)
O1–C10	1.254(3)	N1–C1	1.351(3)
O4–Cd1#1 ¹	2.2787(17)	N2–C1	1.317(4)
O4–C11	1.258(3)	N6–C8	1.302(3)
O2–Cd1#2 ¹	2.2746(18)	C6–C7	1.382(3)
O2–C10	1.251(3)	C6–C5	1.390(3)
N4–C4	1.337(3)	C11–C11#1 ¹	1.556(5)
N4–C5	1.327(3)	C10–C10#2 ¹	1.569(5)
N5–N6	1.368(3)	C7–C3	1.376(3)
N5–C6	1.416(3)	C3–C4	1.384(4)
N5–C9	1.335(3)		

¹ #1: 1 – x, – y, 1 – z; #2: 2 – x, – y, 1 – z;

#3: 1 + x, 1/2 – y, 1/2 + z; #4: –1 + x, 1/2 – y, –1/2 + z.

Table S8: Selected angles (°) for compound 4

angle	(°)	angle	(°)
O1–Cd1–O3	83.01(7)	C2–N3–N2	110.5(2)
O1–Cd1–O4#1 ¹	154.78(7)	C2–N3–C3	129.3(2)
O1–Cd1–N7#2 ¹	104.83(8)	C2–N1–Cd1	130.41(18)
O1–Cd1–N1	86.73(7)	C2–N1–C1	104.0(2)
O4#1–Cd1–O3 ¹	72.30(6)	C1–N1–Cd1	124.06(17)
O4#1–Cd1–N7#2 ¹	100.33(7)	C1–N2–N3	101.9(2)
O4#1–Cd1–N1 ¹	89.40(7)	C8–N6–N5	102.4(2)
O2#3–Cd1–O3 ¹	88.79(7)	C7–C6–N5	121.1(2)
O2#3–Cd1–O1 ¹	73.72(6)	C7–C6–C5	119.9(2)
O2#3–Cd1–O4#1 ¹	110.01(7)	C5–C6–N5	119.0(2)
O2#3–Cd1–N7#2 ¹	86.02(7)	O3–C11–O4	124.5(2)
O2#3–Cd1–N1 ¹	160.03(7)	O3–C11–C11#1 ¹	117.4(3)
N7#2–Cd1–O3 ¹	168.93(7)	O4–C11–C11#1 ¹	118.1(3)

Continued on next page

Table S8 – continued from previous page

angle	(°)	angle	(°)
N7#2–Cd1–N1 ¹	95.30(8)	O1–C10–C10#3 ¹	117.3(3)
N1–Cd1–O3	92.92(8)	O2–C10–O1	124.8(2)
C11–O3–Cd1	115.47(15)	O2–C10–C10#3 ¹	117.9(2)
C10–O1–Cd1	115.05(16)	C3–C7–C6	116.6(2)
C11–O4–Cd1#1 ¹	116.58(15)	N1–C2–N3	109.0(2)
C10–O2–Cd1#3 ¹	114.79(16)	C7–C3–N3	120.0(2)
C5–N4–C4	118.4(2)	C7–C3–C4	121.1(2)
N6–N5–C6	120.2(2)	C4–C3–N3	118.8(2)
C9–N5–N6	109.8(2)	N4–C4–C3	121.5(2)
C9–N5–C6	129.8(2)	N6–C8–N7	115.2(2)
C8–N7–Cd1#4 ¹	132.22(17)	N7–C9–N5	109.6(2)
C9–N7–Cd1#4 ¹	124.62(17)	N4–C5–C6	122.5(2)
C9–N7–C8	103.0(2)	N2–C1–N1	114.6(2)
N2–N3–C3	120.2(2)		

¹ #1: 1 – x, – y, 1 – z; #2: 1 + x, 1/2 – y, 1/2 + z;
#3: 2 – x, – y, 1 – z; #4: –1 + x, 1/2 – y, –1/2 + z.

3. PXRD and FT-IR

The PXRD patterns of compounds **1**, **2**, **3** and **4** were shown in Fig. S2. All the reflection peaks of the compounds were in good agreement with the corresponding simulated patterns without additional peaks, indicating the high purity of these compounds. The difference in intensities could be due to the preferred orientation in the powder samples.

The FT-IR spectra of compounds **1**, **2**, **3** and **4** (Fig. S3) exhibited related features with the bands at 1700–1300 cm^{-1} ascribed to the asymmetric and symmetric carboxyl groups in carboxylic acid ligands, and the stretching vibrations of $\nu_{\text{as}}(\text{C}=\text{C})$, $\nu_{\text{as}}(\text{C}=\text{N})$ and $\nu_{\text{as}}(\text{N}=\text{N})$ in btap ligand. Vibrational absorption of C=N in btap ligand appeared near 730 cm^{-1} . The broad absorption peaks near 3400 cm^{-1} should be attributed to the vibration of $\nu(\text{OH})$ of water molecules.

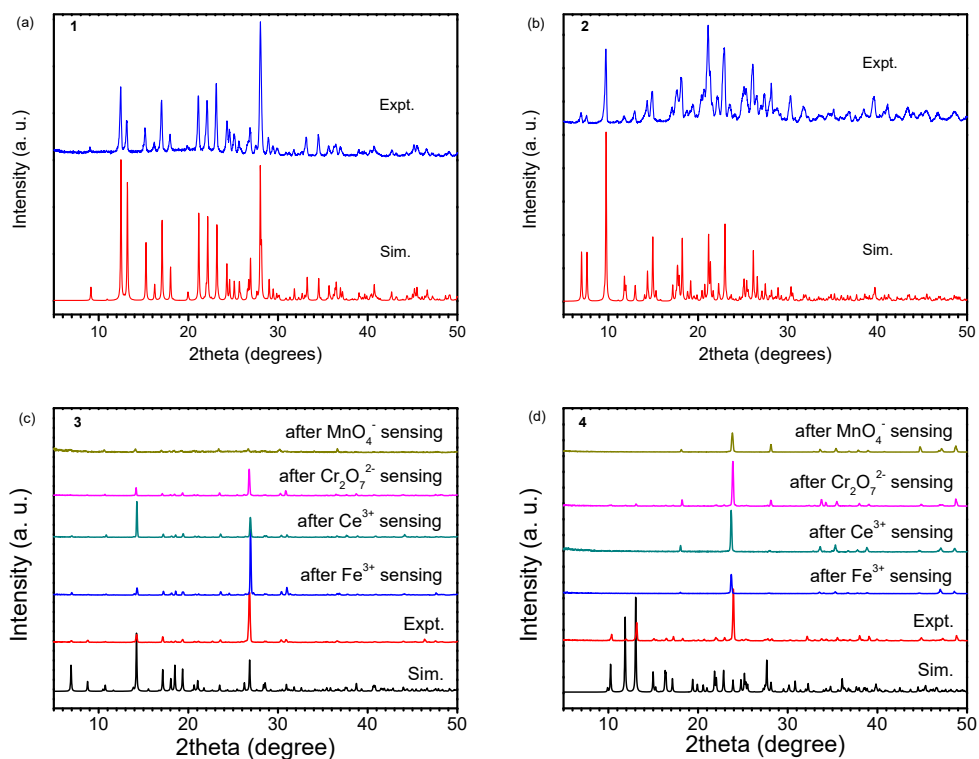


Figure S2: Experimental powder X-ray diffraction patterns versus simulated patterns for compounds (a) **1**, (b) **2**, (c) **3** and (d) **4**.

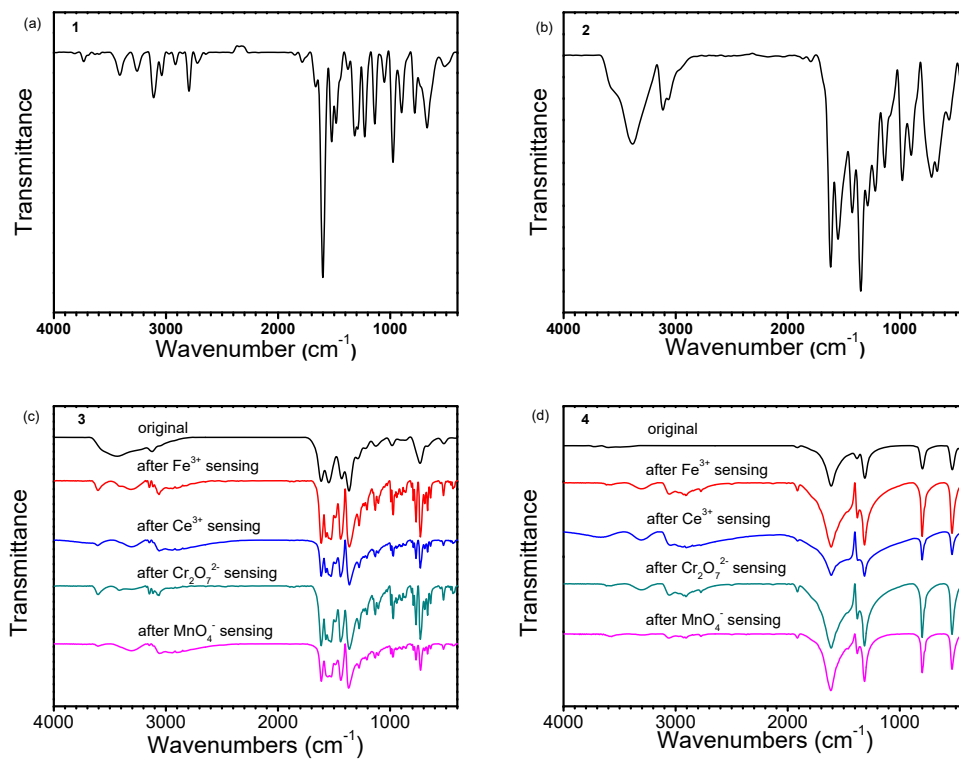


Figure S3: FT-IR spectra for compounds (a) **1**, (b) **2**, (c) **3** and (d) **4**.

4. Photoluminescence properties of compounds **3** and **4**

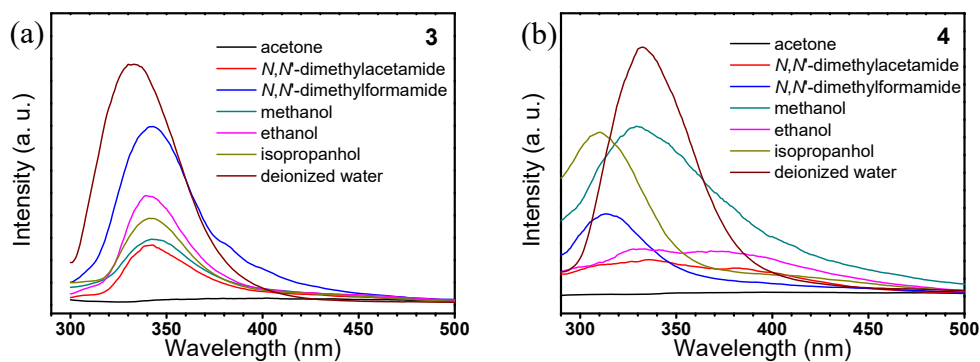


Figure S4: The emission spectra of (a) compound **3** and (b) compound **4** dispersed in different solvents ($\lambda_{\text{ex}} = 280$ nm).

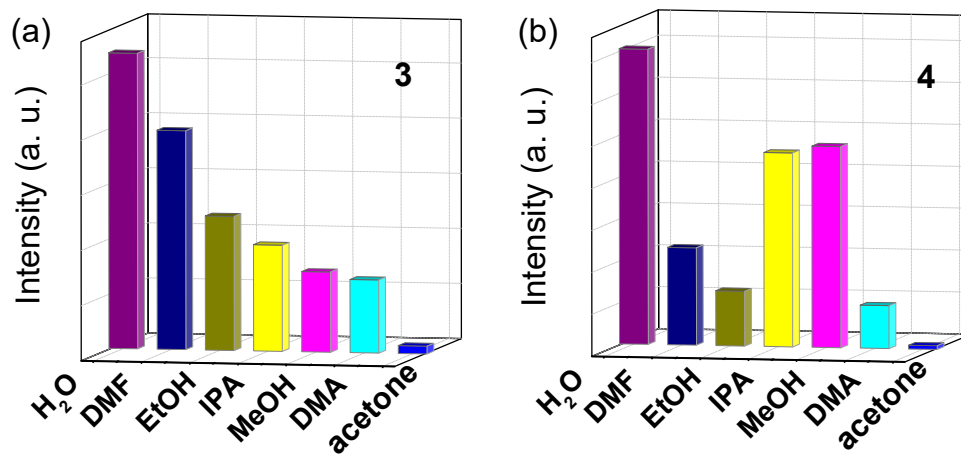


Figure S5: Emission intensities of (a) compound **3** and (b) compound **4** dispersed in different solvents ($\lambda_{\text{ex}} = 280$ nm).

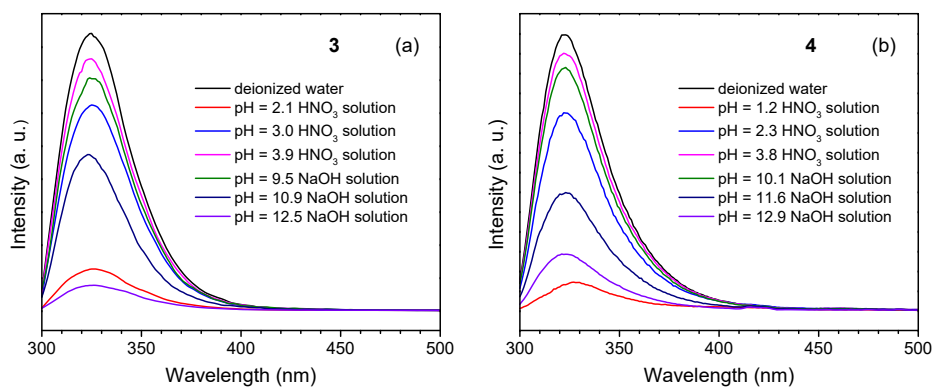


Figure S6: The effect of pH on the emission spectra of (a) compound **3** and (b) compound **4** ($\lambda_{\text{ex}} = 280 \text{ nm}$).

Table S9: ICP-AES analysis results for **3**-Fe(NO₃)₃, **3**-Ce(NO₃)₃, **4**-Fe(NO₃)₃ and **4**-Ce(NO₃)₃

Samples	Amount of Fe or Ce	Amount of Cd
3 -Fe(NO ₃) ₃	15.8 ppm (Fe)	8862 ppm
3 -Ce(NO ₃) ₃	3.6 ppm (Ce)	3560 ppm
4 -Fe(NO ₃) ₃	15.3 ppm (Fe)	2513 ppm
4 -Ce(NO ₃) ₃	9.3 ppm (Ce)	1381 ppm

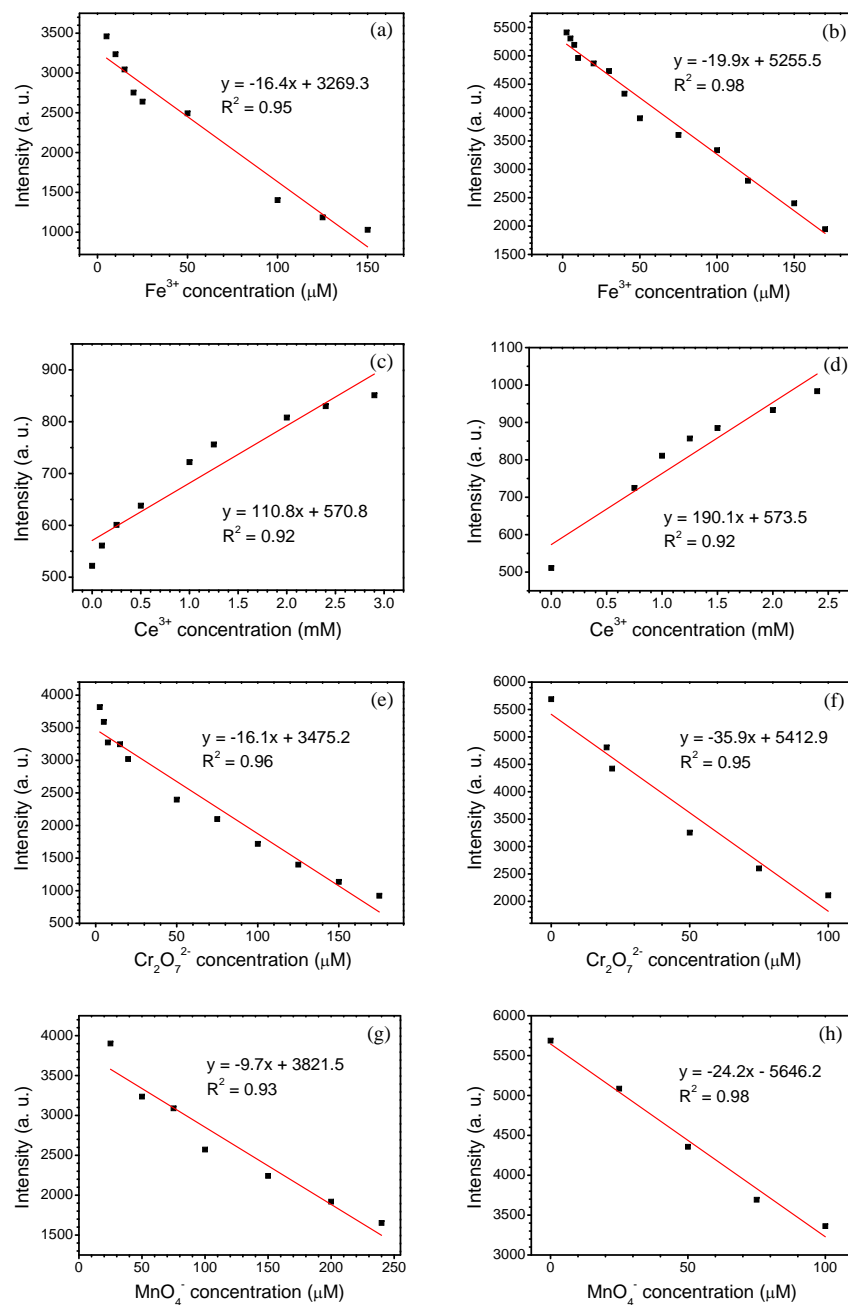


Figure S7: Linear region of fluorescence intensity of compound **3** dispersed in deionized water upon addition of (a) Fe^{3+} , (c) Ce^{3+} , (e) $\text{Cr}_2\text{O}_7^{2-}$ and (g) MnO_4^- . Linear region of fluorescence intensity of compound **4** dispersed in deionized water upon addition of (b) Fe^{3+} , (d) Ce^{3+} , (f) $\text{Cr}_2\text{O}_7^{2-}$ and (h) MnO_4^- .

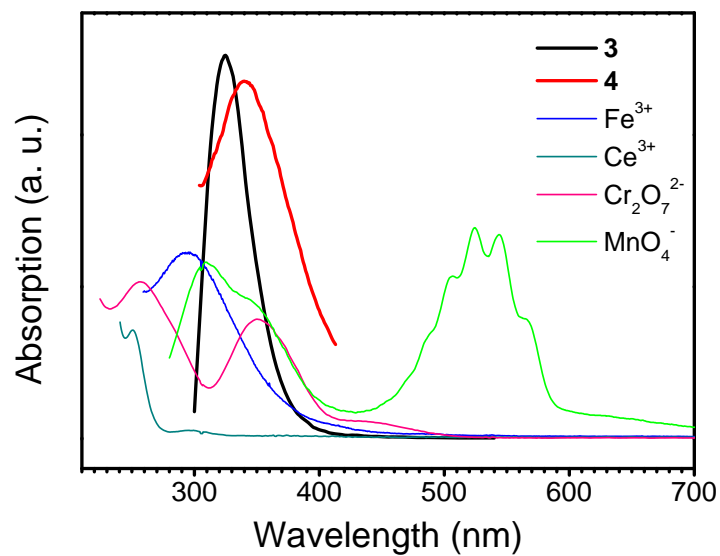


Figure S8: UV-vis adsorption spectra of $\text{Fe}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$, $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 (1×10^{-3} M) and the emission spectra of compounds **3** and **4** dispersed in deionized water (5×10^{-5} M).

1 mL 30 % H₂O₂ and 5–8 % NaClO solutions were diluted in 50 mL deionized water, respectively. The fluorescence titration experiments were performed in 2.0 mL 5 × 10⁻⁵ M aqueous emulsions of compounds **3** and **4** by successive addition of above solutions followed by sonication for 30 min.

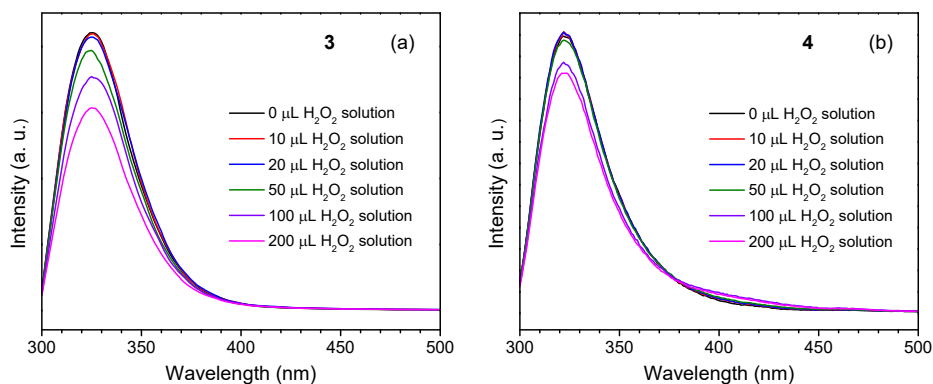


Figure S9: Luminescence responses towards different amounts of H₂O₂ in the aqueous emulsions of (a) compound **3** and (b) compound **4** ($\lambda_{\text{ex}} = 280$ nm).

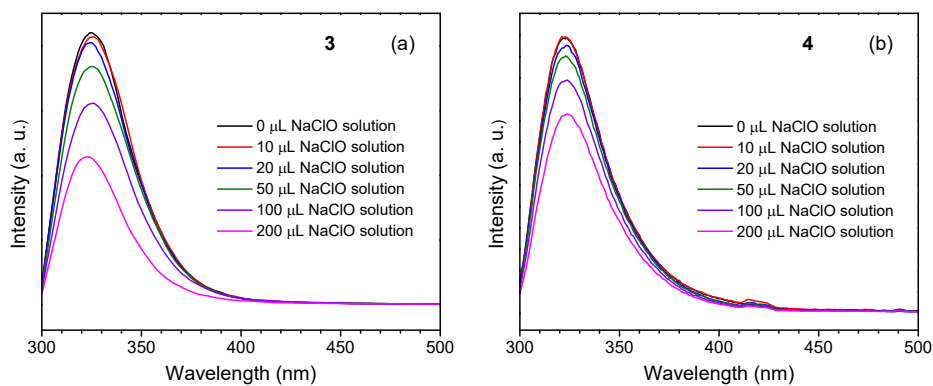


Figure S10: Luminescence responses towards different amounts of NaClO in the aqueous emulsions of (a) compound **3** and (b) compound **4** ($\lambda_{\text{ex}} = 280$ nm).

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