Electronic Supplementary Information

Alkali-metal-regulated construction of suprahydrophilic Zn^{II} and Cd^{II} coordination polymers with perhalogenated terephthalate ligands

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Table S1. The selected bond distances (Å) and angles (deg) for complexes **1**–**6** [a]

		Complex **1**			
Cd1–O1	2.278(4)	Cd1–O3#1	2.476(5)	Cd1–O4#1	2.466(4)
Cd1–O4#2	2.446(4)	Cd1–O5	2.372(4)	Cd1–O7	2.238(4)
Cd1–O8	2.295(4)	Cd2–O6	2.272(4)	Cd2–O9	2.286(5)
Cd2–O10	2.317(5)				
O1–Cd1–O3#1	160.8(2)	O1–Cd1–O4#1	147.3(2)	O1–Cd1–O4#2	83.3(1)
O1–Cd1–O5	86.9(2)	O1–Cd1–O7	89.8(1)	O1–Cd1–O8	88.8(1)
O3#1–Cd1–O4#1	51.6(2)	O3#1–Cd1–O4#2	115.8(2)	O3#1–Cd1–O5	74.1(2)
O3#1–Cd1–O7	89.0(2)	O3#1–Cd1–O8	89.6(2)	O4#1–Cd1–O4#2	64.6(1)
O4#1–Cd1–O5	123.8(1)	O4#1–Cd1–O7	98.0(2)	O4#1–Cd1–O8	87.2(1)
O4#2–Cd1–O5	166.8(2)	O4#2–Cd1–O7	94.4(2)	O4#2–Cd1–O8	93.6 (1)
O5–Cd1–O7	94.3(1)	O5–Cd1–O8	77.5(1)	O7–Cd1–O8	171.6(2)
O6–Cd2–O6#3	180.0(3)	O6–Cd2–O9	89.8(2)	O6–Cd2–O9#3	90.2(1)
O6–Cd2–O10	90.4(2)	O6–Cd2–O10#3	89.6(2)	O9–Cd2–O9#3	180.0(3)
O9–Cd2–O10	88.1(2)	O9–Cd2–O10#3	91.9(2)	O10–Cd2–O10#3	180.0(2)
		Complex **2**			
Cd1–O1	2.263(2)	Cd1–O3	2.315(2)	Cd1–O4	2.314(2)
O1–Cd1–O1#4	180.0(1)	O1–Cd1–O3	93.78(9)	O1–Cd1–O3#4	86.22(9)
O1–Cd1–O4	88.45(8)	O1–Cd1–O4#4	91.55(8)	O3–Cd1–O3#4	180.0(1)
O3–Cd1–O4	91.70(9)	O3–Cd1–O4#4	88.30(9)	O4–Cd1–O4#4	180.0(2)
		Complex **3**			
Zn1–O1	1.958(4)	Zn1–O3#5	1.985(5)	Zn1–O6	1.932(4)
Zn1–O7	2.010(4)	Na1–O2	2.311(5)	Na1–O3#5	2.489(6)
Na1–O5	2.361(4)	Na1–O5#6	2.410(5)	Na1–O8	2.320(5)
Na1–O9	2.416(6)				
O1–Zn1–O3#5	107.9(2)	O1–Zn1–O6	116.9(2)	O1–Zn1–O7	93.9(2)
O3#5–Zn1–O6	107.3(2)	O3#5–Zn1–O7	134.6(2)	O6–Zn1–O7	96.5(2)
O2–Na1–O3#5	81.5(2)	O2–Na1–O5	98.2(2)	O2–Na1–O5#6	98.8(2)

O2–Na1–O8	94.1(2)	O2–Na1–O9	176.2(2)	O3#5–Na1–O5	82.3(2)
O3#5–Na1–O5#6	165.7(2)	O3#5–Na1–O8	93.9(2)	O3#5–Na1–O9	100.7(2)
O5–Na1–O5#6	83.5(2)	O5–Na1–O8	166.4(2)	O5–Na1–O9	79.2(2)
O5#6–Na1–O8	100.3(2)	O5#6–Na1–O9	78.2(2)	O8–Na1–O9	88.8(2)

Complex **4**

Zn1–O1	1.967(2)	Zn1–O3	1.951(2)	Zn1–O5	1.984(3)
Zn1–N2	2.015(3)	K1–O1	2.867(2)	K1–O4	2.784(3)
K1–O4#7	3.044(4)	K1–O6	2.696(3)	K1–O6#7	2.709(3)
K1–O7	2.625(4)	K1–Cl1	3.608(2)	K1–Cl4#8	3.622(1)
O1–Zn1–O3	111.3(1)	O1–Zn1–O5	110.2(1)	O1–Zn1–N2	118.0 (1)
O3–Zn1–O5	118.9(1)	O3–Zn1–N2	97.3(1)	O5–Zn1–N2	100.6(1)
O1–K1–O4	74.7(1)	O1–K1–O4#7	138.1(1)	O1–K1–O6	75.8(1)
O1–K1–O6#7	144.0(1)	O1–K1–O7	87.2(1)	O1–K1–Cl1	58.4(1)
O1–K1–Cl4#8	125.4(1)	O4–K1–O4#7	104.6(1)	O4–K1–O6	65.6(1)
O4–K1–O6#7	70.4(1)	O4–K1–O7	113.7(1)	O4–K1–Cl1	129.2(1)
O4–K1–Cl4#8	159.6(1)	O4#7–K1–O6	66.7(1)	O4#7–K1–O6#7	61.9(1)
O4#7–K1–O7	127.7(1)	O4#7–K1–Cl1	98.3(1)	O4#7–K1–Cl4#8	63.1(1)
O6–K1–O6#7	97.3(1)	O6–K1–O7	162.6(1)	O6–K1–Cl1	83.7(1)
O6–K1–Cl4#8	118.0(1)	O6#7–K1–O7	98.6(2)	O6#7–K1–Cl1	157.1(1)
O6#7–K1–Cl4#8	89.2(1)	O7–K1–Cl1	84.2(1)	O7–K1–Cl4#8	69.0(1)
Cl1–K1–Cl4#8	70.4(1)				

Complex **5**

Cd1–O1	2.345(4)	Cd1–O2	2.287(4)	Cd1–O2W	2.171(4)
Cd1–O4W	2.431(4)	Cd1–O5W	2.357(4)	Cd1–O6W	2.363(4)
Cd1–O7W	2.395(8)	Cd2–O1W	2.176(5)	Cd2–O4W	2.296(4)
Cd2–O5	2.409(4)	Cd2–O5W	2.442(4)	Cd3–O3W	2.287(5)
Cd3–O6W	2.385(4)	Cd3–O7	2.399(4)	Cd3–O7W	2.417(9)
O1–Cd1–O2	55.3(1)	O1–Cd1–O2W	151.7(1)	O1–Cd1–O4W	74.2(2)
O1–Cd1–O5W	87.2(2)	O1–Cd1–O6W	105.6(1)	O1–Cd1–O7W	126.9(2)
O2–Cd1–O2W	152.9(2)	O2–Cd1–O4W	128.2(1)	O2–Cd1–O5W	106.9(1)
O2–Cd1–O6W	86.7(1)	O2–Cd1–O7W	72.5(2)	O2W–Cd1–O4W	77.9(2)
O2W–Cd1–O5W	82.7(1)	O2W–Cd1–O6W	82.6(2)	O2W–Cd1–O7W	81.1(2)

O4W–Cd1–O5W	79.1(1)	O4W–Cd1–O6W	97.1(1)	O4W–Cd1–O7W	158.9(2)
O5W–Cd1–O6W	165.3(1)	O5W–Cd1–O7W	100.0(2)	O6W–Cd1–O7W	78.4(2)
O1W–Cd2–O4W	85.1(1)	O1W–Cd2–O5	152.2(1)	O1W–Cd2–O5W	80.4(1)
O4W–Cd2–O4W#9	170.2(2)	O4W–Cd2–O5	86.7(1)	O4W–Cd2–O5#9	102.1(1)
O4W–Cd2–O5W	80.1(1)	O4W–Cd2–O5W#9	98.3(1)	O5–Cd2–O5#9	55.5(2)
O5–Cd2–O5W	72.0(1)	O5–Cd2–O5W#9	127.1(1)	O5W–Cd2–O5W#9	160.9(2)
O3W–Cd3–O6W	77.9(2)	O3W–Cd3–O7	153.0(1)	O3W–Cd3–O7W	79.8(2)
O6W–Cd3–O6W#6	155.9(2)	O6W–Cd3–O7	120.3(1)	O6W–Cd3–O7#6	82.3(1)
O6W–Cd3–O7W	77.6(2)	O6W–Cd3–O7W#6	98.1(2)	O7–Cd3–O7#6	54.0(2)
O7–Cd3–O7W	121.5(2)	O7–Cd3–O7W#6	78.1(2)	O7W–Cd3–O7W#6	159.6(4)

Complex **6**

Zn1–O3	2.080(5)	Zn1–O4	2.061(5)	Zn1–O5	2.117(5)
O3–Zn1–O3#10	180.0(3)	O3–Zn1–O4	92.6 (2)	O3–Zn1–O4#10	87.4(2)
O3–Zn1–O5	86.2(2)	O3–Zn1–O5#10	93.8(2)	O4–Zn1–O4#10	180.0(1)
O4–Zn1–O5	87.2(2)	O4–Zn1–O5#10	92.8(2)	O5–Zn1–O5#10	180.0(1)

[a] Symmetry transformations used to generate equivalent atoms: For **1**, #1: $-x+1, -y+1, -z+1$; #2: $x, y+1, z$; #3: $-x+2, -y, -z$; For **2**, #4: $-x, -y, -z$; For **3**, #5: $-x+1/2, y+1/2, -z+1/2$; #6: $-x, y, -z+1/2$; For **4**, #7: $-x+1, -y+2, -z+1$; #8: $x+1/2, -y+3/2, z+1/2$; For **5**, #9: $-x+1, y, -z+1/2$; For **6**, #10: $-x, -y+2, -z$.

Table S2. Possible hydrogen-bonding interactions in the crystal structures of complexes **1**–**6**

Complex	D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry code
1	O8–H8···O2	1.79	2.569(7)	159	
	O9–H9···O5	2.23	2.775(7)	125	$-x+2, -y, -z$
	O9–H9···O8	2.57	3.142(7)	128	$-x+2, -y, -z$
	C13–H13···O1	2.55	3.193(9)	127	
	C15–H15A···O7	2.33	2.74(1)	105	
	C15–H15C···O2	2.56	3.52(1)	179	$x-1, y, z$
2	O4–H4A···O2	1.93	2.687(3)	153	$-x, -y, -z$
	O4–H4B···O1	2.50	3.137(3)	136	$-x+1, -y, -z$
	O4–H4B···O3	2.47	3.131(3)	139	$x+1, y, z$
	C7–H7A···O3	2.40	2.790(6)	104	
3	C13–H13···O4	2.24	2.96(1)	135	$-x+1/2, y-1/2, -z+1/2$
	C15–H15A···O7	2.32	2.74(1)	106	
	C18–H18A···O8	2.37	2.79(1)	106	
4	N2–H2···O2	2.10	2.881(5)	152	$-x+1, -y+2, -z$
5	O1W–H1X···O1	2.00	2.783(5)	137	$-x+1, y, -z+1/2$
	O1W–H1Y···O1	2.01	2.783(5)	136	
	O2W–H2X···O7	2.10	2.708(6)	128	$-x, y, -z+1/2$
	O2W–H2Y···O5	1.91	2.744(6)	167	
	O3W–H3X···O2	2.24	2.763(5)	113	$-x, y, -z+1/2$
	O3W–H3X···O4	2.56	3.377(4)	143	$x-1/2, -y+3/2, z-1/2$
	O3W–H3Y···O2	1.84	2.763(5)	161	

	O4W–H4X···O10 W	2.13	2.977(1)	172	
	O4W–H4Y···O6	1.80	2.640(6)	170	$-x+1, -y+2, -z+1$
	O5W–H5X···O8W	2.30	3.143(9)	173	$x, y, z-1$
	O5W–H5Y···O3	1.82	2.659(6)	169	$-x+1/2, -y+3/2, -z$
	O6W–H6X···O8W	2.21	3.058(9)	176	
	O6W–H6Y···O4	1.91	2.758(6)	176	$-x+1/2, -y+3/2, -z+1$
	O7W–H7X···O9W	1.68	2.503(9)	161	$x, y, z-1$
	O7W–H7Y···O8	1.94	2.786(9)	175	$x, -y+2, z-1/2$
	O8W–H8X···F7	2.46	3.193(9)	145	
	O8W–H8X···F6	2.01	2.541(9)	120	$-x+1, -y+2, -z+1$
	O8W–H8Y···F8	2.40	3.098(9)	140	$x, -y+2, z+1/2$
	O8W–H8Y···O8	1.97	2.603(9)	131	$x, -y+2, z+1/2$
	O9W–H9X···O4	2.01	2.685(5)	135	$-x+1/2, -y+3/2, -z+1$
	O9W–H9Y···O4	2.34	2.685(5)	104	$x-1/2, -y+3/2, z+1/2$
6	O3–H3A···O6	2.10	2.877(7)	152	$x+1/2, -y+3/2, z-1/2$
	O3–H3B···O2	1.92	2.687(7)	150	$x, y+1, z$
	O4–H4A···O1	1.99	2.768(7)	153	$-x, -y+1, -z$
	O4–H4B···O5	2.16	2.980(7)	161	$-x+1, -y+2, -z$
	O5–H5A···O6	1.96	2.757(7)	156	$-x+1/2, y+1/2, -z+1/2$
	O5–H5B···O7	1.87	2.670(7)	157	$x, y+1, z$
	O6–H6A···O2	2.12	2.966(7)	176	$x+1/2, -y+1/2, z+1/2$
	O6–H6B···O1	1.98	2.811(7)	166	$-x, -y+1, -z+1$
	O7–H7A···O1	2.29	3.060(7)	152	
	O7–H7B···O2	1.97	2.802(7)	167	$-x+1/2, y+1/2, -z+1/2$

Fig. S1. The coordination environment of Zn^{II} ion in complex **3**.

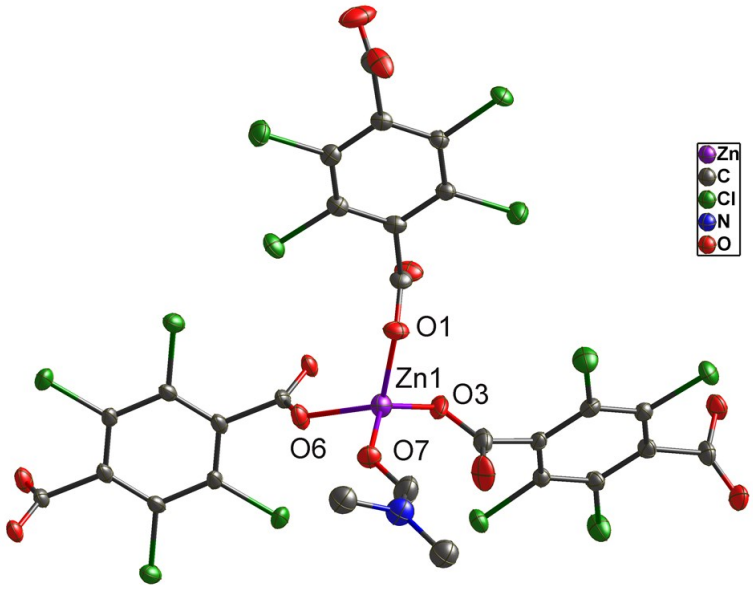

Fig. S2. The coordination environment of Na^{I} ion in complex **3**.

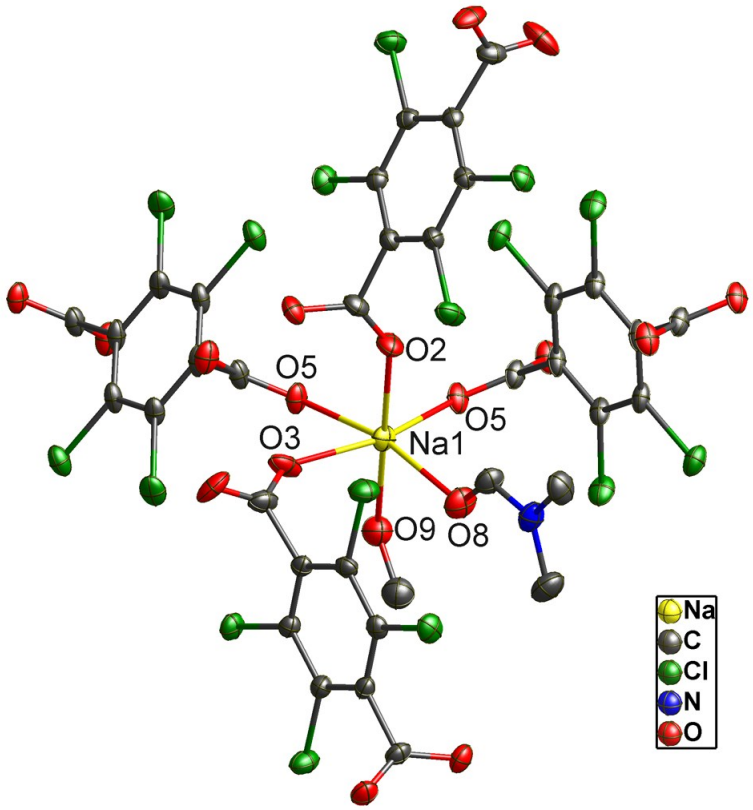

Fig. S3. The tetranuclear cluster $[Zn_2Na_2(–COO)_6(\mu_2\text{-MeOH})(DMF)_4]$ in complex **3**. Symmetric codes: (1) $–x, y, –z + 1/2$; (2) $–x + 1/2, y – 1/2, –z + 1/2$.

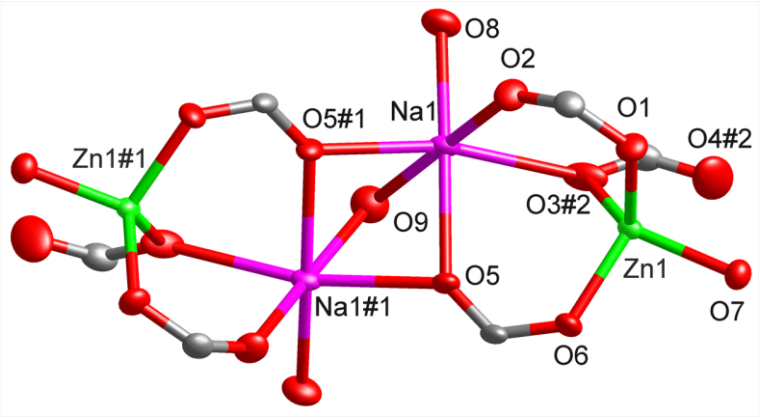

Fig. S4. The coordination environment of Zn^{II} ion in complex **4**.

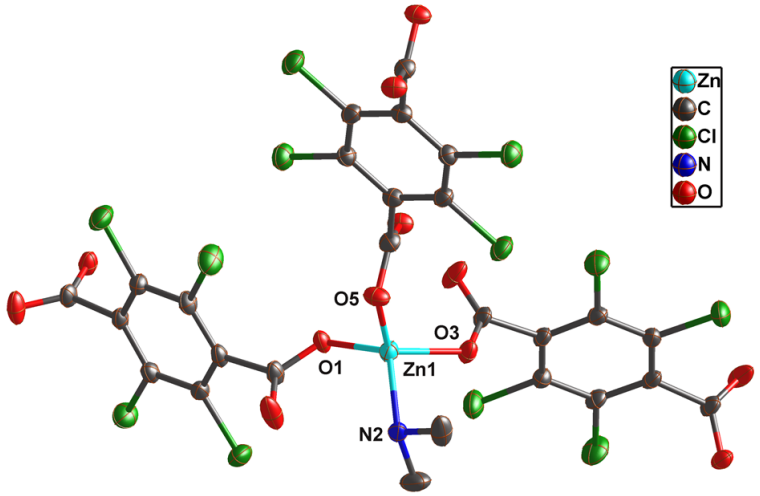

Fig. S5. The coordination environment of K^I ion in complex **4**.

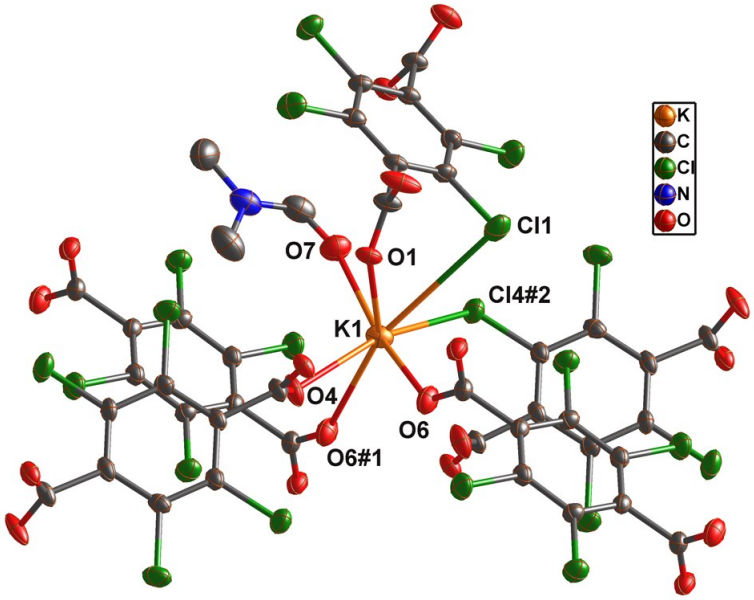

Fig. S6. The connecting mode of two centralsymmetry-related K^I ions in complex **4**. Symmetric codes: (1) $-x + 1, -y + 2, -z + 1$; (2) $x + 1/2, -y + 3/2, z + 1/2$.

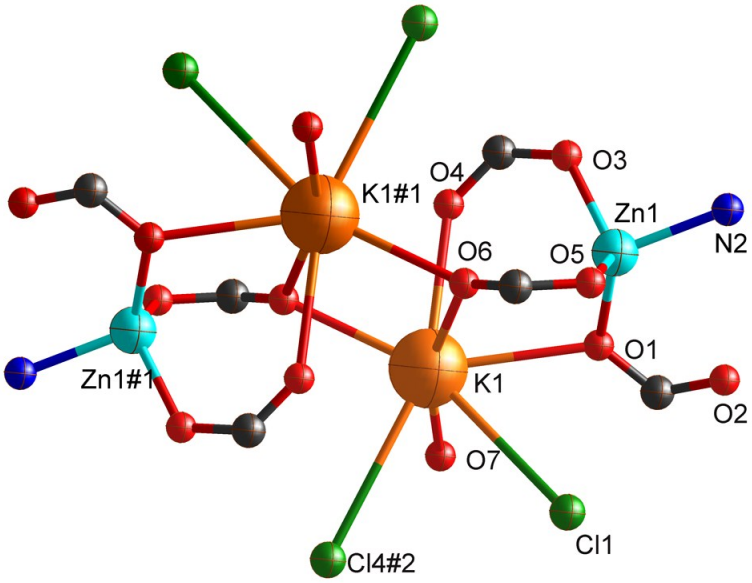

Fig. S7. The IR spectra of complexes **1**–**6**.

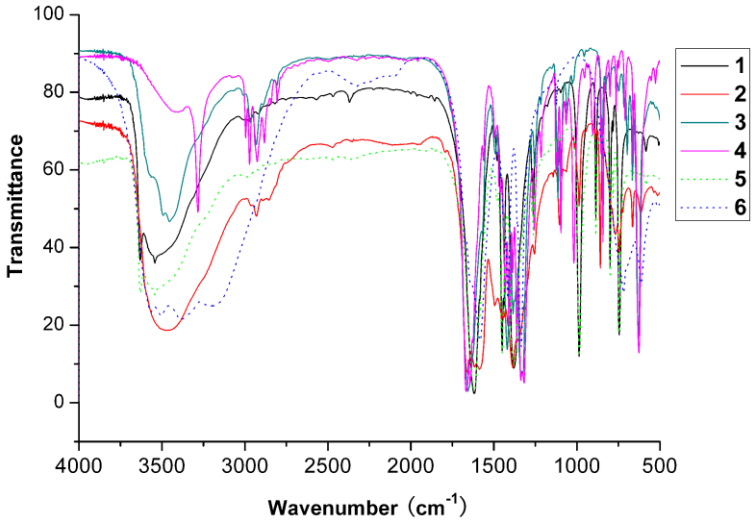

Fig. S8. Simulated (blue) and experimental (red) X-ray powder diffraction patterns of complexes **1**–**6**.

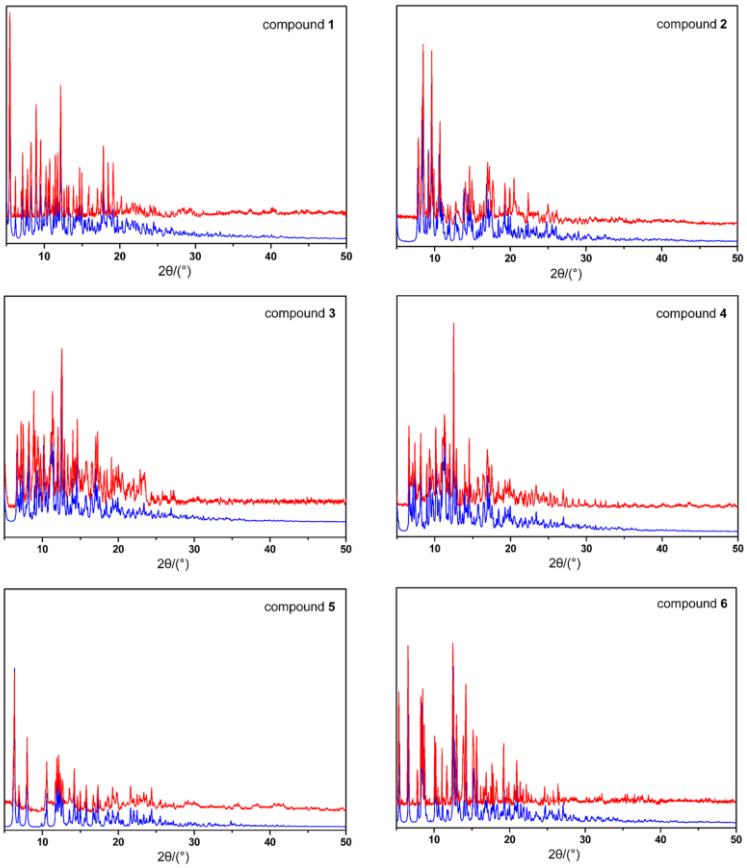

Fig. S9. TGA curves of complexes **1**–**6**.

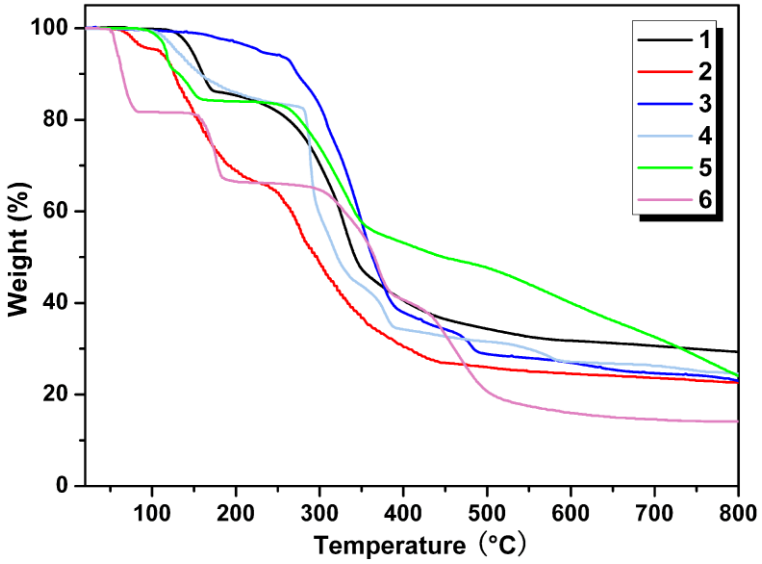

Fig. S10. Emission spectra of the free ligands $H_2BDC\text{-}F_4$ and $H_2BDC\text{-}Cl_4$ in the solid state at room temperature.