Supplementary Material (ESI) for CrystEngComm

Four cluster-containing highly connected coordination networks: syntheses, structures, and photoluminescence

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Table S1. Selected bond distances (Å) and angles (°) for **1**.

Zn(1)-O(1)	2.426(5)	Zn(1)-O(2)	1.982(5)
Zn(1)-O(4)$^{\#2}$	2.002(5)	Zn(1)-O(6)$^{\#1}$	1.955(5)
Zn(1)-O(15)	1.965(4)	Zn(2)-O(8)	1.894(5)
Zn(2)-O(11)$^{\#3}$	1.986(5)	Zn(2)-O(15)	1.896(4)
Zn(2)-N(4)$^{\#4}$	2.070(7)	Zn(3)-O(3)$^{\#2}$	2.014(5)
Zn(3)-O(5)$^{\#1}$	2.095(5)	Zn(3)-O(13)$^{\#4}$	2.290(6)
Zn(3)-N(1)	2.022(6)	Zn(3)-O(15)	1.984(4)
Zn(4)-O(10)$^{\#3}$	1.946(5)	Zn(4)-O(15)	1.943(4)
Zn(4)-O(12)$^{\#4}$	2.016(5)	Zn(4)-N(7)	1.985(6)
O(6)$^{\#1}$-Zn(1)-O(15)	106.9(2)	O(6)$^{\#1}$-Zn(1)-O(2)	104.8(2)
O(15)-Zn(1)-O(2)	132.2(2)	O(6)$^{\#1}$-Zn(1)-O(4)$^{\#2}$	102.0(2)
O(15)-Zn(1)-O(4)$^{\#2}$	104.95(18)	O(2)-Zn(1)-O(4)$^{\#2}$	102.3(2)
O(6)$^{\#1}$-Zn(1)-O(1)	95.0(2)	O(15)-Zn(1)-O(1)	84.62(18)
O(2)-Zn(1)-O(1)	57.7(2)	O(4)$^{\#2}$-Zn(1)-O(1)	156.81(19)
O(8)-Zn(2)-O(15)	125.1(2)	O(8)-Zn(2)-O(11)$^{\#3}$	109.9(2)
O(15)-Zn(2)-O(11)$^{\#3}$	112.94(19)	O(8)-Zn(2)-N(4)$^{\#4}$	98.8(3)
O(15)-Zn(2)-N(4)$^{\#4}$	111.5(2)	O(11)$^{\#3}$-Zn(2)-N(4)$^{\#4}$	93.0(2)

O(15)-Zn(3)-O(3)$^{\#2}$	95.98(19)	O(15)-Zn(3)-N(1)	161.0(2)
O(3)$^{\#2}$-Zn(3)-N(1)	93.4(2)	O(15)-Zn(3)-O(5)$^{\#1}$	104.48(17)
O(3)$^{\#2}$-Zn(3)-O(5)$^{\#1}$	92.6(2)	N(1)-Zn(3)-O(5)$^{\#1}$	91.5(2)
O(15)-Zn(3)-O(13)$^{\#4}$	90.25(18)	O(3)$^{\#2}$-Zn(3)-O(13)$^{\#4}$	169.3(2)
N(1)-Zn(3)-O(13)$^{\#4}$	78.2(2)	O(5)$^{\#1}$-Zn(3)-O(13)$^{\#4}$	94.3(2)
O(15)-Zn(4)-O(10)$^{\#3}$	113.81(19)	O(15)-Zn(4)-N(7)	122.0(2)
O(10)$^{\#3}$-Zn(4)-N(7)	109.1(2)	O(15)-Zn(4)-O(12)$^{\#4}$	115.2(2)
O(10)$^{\#3}$-Zn(4)-O(12)$^{\#4}$	94.4(2)	N(7)-Zn(4)-O(12)$^{\#4}$	97.9(2)

Symmetry codes for **1**: $^{\#1}$ x,-y-0.5,z+0.5; $^{\#2}$ x,y+1,z; $^{\#3}$ x,y-1,z; $^{\#4}$ -x+1,y-0.5,-z+1.5.

Table S2. Selected bond distances (Å) and angles (°) for **2**.

Zn(1)-O(1)	1.899(2)	Zn(1)- O(4)$^{\#1}$	1.938(2)
Zn(1)-O(13)$^{\#2}$	1.982(3)	Zn(1)-O(16)$^{\#2}$	1.984(2)
Zn(2)-O(8)	1.932(2)	Zn(2)-O(11)$^{\#1}$	1.925(2)
Zn(2)-O(15)	1.944(2)	Zn(2)-O(1W)	2.042(3)
Zn(3)-O(15)	2.064(2)	Zn(3)-O(16)$^{\#3}$	2.070(2)
Zn(3)-O(6)$^{\#3}$	2.092(2)	Zn(3)-O(2)$^{\#4}$	2.094(2)
Zn(3)-O(10)$^{\#1}$	2.143(2)	Zn(3)-O(15)$^{\#15}$	2.160(2)
Zn(4)-O(12)	1.969(2)	Zn(4)-O(16)	1.982(2)
Zn(4)-N(1)	1.991(2)	Zn(4)-O(5)	2.082(2)
Zn(4)-O(3)$^{\#6}$	2.180(2)	O(1)-Zn(1)-O(4)$^{\#1}$	128.03(9)
O(1)-Zn(1)-O(13)$^{\#2}$	102.01(11)	O(4)$^{\#1}$-Zn(1)-O(13)$^{\#2}$	97.43(11)
O(1)-Zn(1)-O(16)$^{\#2}$	112.90(10)	O(4)$^{\#1}$-Zn(1)-O(16)$^{\#2}$	105.07(9)
O(13)$^{\#2}$-Zn(1)-O(16)$^{\#2}$	109.10(10)	O(11)$^{\#1}$-Zn(2)-O(8)	126.73(9)
O(11)$^{\#1}$-Zn(2)-O(15)	113.03(9)	O(8)-Zn(2)-O(15)	114.45(9)
O(11)$^{\#1}$-Zn(2)-O(1W)	97.75(10)	O(8)-Zn(2)-O(1W)	94.33(11)
O(15)-Zn(2)-O(1W)	102.55(10)	O(15)-Zn(3)-O(16)$^{\#3}$	169.41(9)
O(15)-Zn(3)-O(6)$^{\#3}$	94.48(9)	O(16)$^{\#3}$-Zn(3)-O(6)$^{\#3}$	94.79(9)
O(15)-Zn(3)-O(2)$^{\#4}$	92.30(8)	O(16)$^{\#3}$-Zn(3)-O(2)$^{\#4}$	93.23(8)
O(6)$^{\#3}$-Zn(3)-O(2)$^{\#4}$	87.39(10)	O(15)-Zn(3)-O(10)$^{\#1}$	88.66(8)

O(16)$^{\#3}$-Zn(3)-O(10)$^{\#1}$	86.21(8)	O(6)$^{\#3}$-Zn(3)-O(10)$^{\#1}$	90.06(10)
O(2)$^{\#4}$-Zn(3)-O(10)$^{\#1}$	177.34(10)	O(15)-Zn(3)-O(15)$^{\#5}$	79.35(9)
O(16)$^{\#3}$-Zn(3)-O(15)$^{\#5}$	91.28(8)	O(6)$^{\#3}$-Zn(3)-O(15)$^{\#5}$	173.75(8)
O(2)$^{\#4}$-Zn(3)-O(15)$^{\#5}$	93.75(9)	O(10)$^{\#1}$-Zn(3)-O(15)$^{\#5}$	88.86(9)
O(12)-Zn(4)-O(16)	122.17(9)	O(12)-Zn(4)-N(1)	103.35(11)
O(16)-Zn(4)-N(1)	133.91(11)	O(12)-Zn(4)-O(5)	92.17(11)
O(16)-Zn(4)-O(5)	95.69(9)	N(1)-Zn(4)-O(5)	88.94(10)
O(12)-Zn(4)-O(3)$^{\#6}$	85.62(10)	O(16)-Zn(4)-O(3)$^{\#6}$	86.15(9)
N(1)-Zn(4)-O(3)$^{\#6}$	90.83(9)	O(5)-Zn(4)-O(3)$^{\#6}$	177.66(10)

Symmetry codes for **2**: $^{\#1}$ x-1,y,z; $^{\#2}$ -x+1,-y-1,-z+1; $^{\#3}$ -x+1,-y,-z; $^{\#4}$ x,y+1,z-1; $^{\#5}$ -x+1,-y+1,-z; $^{\#6}$ -x+2,-y-1,-z+1.

Table S3. Selected bond distances (Å) and angles (°) for **3**.

Cd(1)-O(4)$^{\#1}$	2.208(2)	Cd(1)-O(15)	2.254(2)
Cd(1)-O(1)	2.270(2)	Cd(1)-O(13)	2.333(3)
Cd(1)-O(2)	2.390(2)	Cd(1)-O(8)$^{\#2}$	2.534(3)
Cd(2)-O(12)	2.135(2)	Cd(2)-O(15)	2.172(2)
Cd(2)-N(1)	2.201(3)	Cd(2)-O(1W)	2.315(3)
Cd(2)-O(2W)	2.435(3)	Cd(3)-O(16)$^{\#3}$	2.272(2)
Cd(3)-O(15)	2.282(2)	Cd(3)-O(10)$^{\#4}$	2.284(2)
Cd(3)-O(3)$^{\#1}$	2.286(2)	Cd(3)-O(16)	2.297(3)
Cd(3)-O(5)$^{\#5}$	2.349(3)	Cd(4)-O(11)$^{\#6}$	2.187(2)
Cd(4)-O(16)	2.221(2)	Cd(4)-O(9)$^{\#2}$	2.252(2)
Cd(4)-O(6)$^{\#7}$	2.306(3)	Cd(4)-O(4)$^{\#1}$	2.496(2)
Cd(4)-O(8)$^{\#2}$	2.533(2)	O(4)$^{\#1}$-Cd(1)-O(15)	103.86(8)
O(4)$^{\#1}$-Cd(1)-O(1)	108.10(8)	O(15)-Cd(1)-O(1)	147.35(8)
O(4)$^{\#1}$-Cd(1)-O(13)	104.98(9)	O(15)-Cd(1)-O(13)	94.41(9)
O(1)-Cd(1)-O(13)	83.81(10)	O(4)#1-Cd(1)-O(2)	158.01(9)
O(15)-Cd(1)-O(2)	91.26(8)	O(1)-Cd(1)-O(2)	56.19(8)
O(13)-Cd(1)-O(2)	89.40(9)	O(4)$^{\#1}$-Cd(1)-O(8)$^{\#2}$	83.20(8)

O(15)-Cd(1)-O(8)$^{\#2}$	92.05(8)	O(1)-Cd(1)-O(8)$^{\#2}$	85.29(9)
O(13)-Cd(1)-O(8)$^{\#2}$	168.00(9)	O(2)-Cd(1)-O(8)$^{\#2}$	80.35(8)
O(12)-Cd(2)-O(15)	116.99(9)	O(12)-Cd(2)-N(1)	117.27(11)
O(15)-Cd(2)-N(1)	125.64(11)	O(12)-Cd(2)-O(1W)	91.91(10)
O(15)-Cd(2)-O(1W)	87.77(9)	N(1)-Cd(2)-O(1W)	93.31(12)
O(12)-Cd(2)-O(2W)	81.98(11)	O(15)-Cd(2)-O(2W)	94.84(11)
N(1)-Cd(2)-O(2W)	89.66(12)	O(1W)-Cd(2)-O(2W)	173.89(10)
O(16)$^{\#3}$-Cd(3)-O(10)$^{\#4}$	87.63(9)	O(16)$^{\#3}$-Cd(3)-O(15)	166.05(9)
O(10)$^{\#4}$-Cd(3)-O(15)	88.63(9)	O(16)$^{\#3}$-Cd(3)-O(3)$^{\#1}$	97.41(8)
O(10)$^{\#4}$-Cd(3)-O(3)$^{\#1}$	170.82(9)	O(15)-Cd(3)-O(3)$^{\#1}$	88.21(8)
O(16)$^{\#3}$-Cd(3)-O(16)	79.26(10)	O(10)$^{\#4}$-Cd(3)-O(16)	95.68(9)
O(15)-Cd(3)-O(16)	87.74(8)	O(3)$^{\#1}$-Cd(3)-O(16)	92.81(8)
O(16)$^{\#3}$-Cd(3)-O(5)$^{\#5}$	92.16(9)	O(10)$^{\#4}$-Cd(3)-O(5)$^{\#5}$	86.39(9)
O(15)-Cd(3)-O(5)$^{\#5}$	101.02(9)	O(3)$^{\#1}$-Cd(3)-O(5)$^{\#5}$	85.75(9)
O(16)-Cd(3)-O(5)$^{\#5}$	171.06(8)	O(11)$^{\#6}$-Cd(4)-O(16)	120.59(9)
O(11)$^{\#6}$-Cd(4)-O(9)$^{\#2}$	97.19(9)	O(16)-Cd(4)-O(9)$^{\#2}$	142.12(8)
O(11)$^{\#6}$-Cd(4)-O(6)$^{\#7}$	94.52(11)	O(16)-Cd(4)-O(6)$^{\#7}$	87.41(10)
O(9)$^{\#2}$-Cd(4)-O(6)$^{\#7}$	86.83(10)	O(11)$^{\#6}$-Cd(4)-O(4)$^{\#1}$	94.15(9)
O(16)-Cd(4)-O(4)$^{\#1}$	90.17(8)	O(9)$^{\#2}$-Cd(4)-O(4)$^{\#1}$	89.79(9)
O(6)$^{\#7}$-Cd(4)-O(4)$^{\#1}$	171.02(9)	O(11)$^{\#6}$-Cd(4)-O(8)$^{\#2}$	150.01(9)
O(16)-Cd(4)-O(8)$^{\#2}$	88.59(8)	O(9)$^{\#2}$-Cd(4)-O(8)$^{\#2}$	54.49(8)
O(6)$^{\#7}$-Cd(4)-O(8)$^{\#2}$	93.50(9)	O(4)$^{\#1}$-Cd(4)-O(8)$^{\#2}$	77.79(8)

Symmetry codes for **3**: $^{\#1}$ x+1,y,z; $^{\#2}$ x,y,z+1; $^{\#3}$ -x+3,-y+2,-z+1; $^{\#4}$ -x+2,-y+2,-z; $^{\#5}$ -x+2,-y+1,-z+1; $^{\#6}$ x+1,y,z+1.

Table S4. Selected bond distances (Å) and angles (°) for **4**.

Cd(1)-O(1)	2.274(5)	Cd(1)-O(1)$^{\#1}$	2.274(5)
Cd(1)-N(8)	2.306(6)	Cd(1)-N(8)$^{\#1}$	2.306(6)
Cd(1)-N(1)$^{\#1}$	2.424(6)	Cd(1)-N(1)	2.424(6)
Cd(2)-O(2)	2.211(5)	Cd(2)-N(12)$^{\#2}$	2.248(6)

Cd(2)-N(2)	2.277(6)	Cd(2)-O(1W)	2.285(6)
Cd(2)-N(7)	2.410(6)	Cd(2)-O(1)	2.621(5)
Cd(3)-N(6)$^{\#3}$	2.251(7)	Cd(3)-O(4)$^{\#4}$	2.290(6)
Cd(3)-N(10)	2.313(6)	Cd(3)-O(6)$^{\#5}$	2.332(6)
Cd(3)-O(3)$^{\#4}$	2.369(5)	Cd(3)-O(5)$^{\#5}$	2.403(6)
O(1)-Cd(1)-N(8)	86.26(19)	O(1)$^{\#1}$-Cd(1)-N(8)	93.74(19)
O(1)$^{\#1}$-Cd(1)-N(8)$^{\#1}$	86.26(19)	O(1)-Cd(1)-N(1)$^{\#1}$	93.61(19)
O(1)$^{\#1}$-Cd(1)-N(1)$^{\#1}$	86.39(19)	N(8)-Cd(1)-N(1)$^{\#1}$	95.2(2)
N(8)$^{\#1}$-Cd(1)-N(1)$^{\#1}$	84.8(2)	O(1)-Cd(1)-N(1)	86.39(19)
O(1)$^{\#1}$-Cd(1)-N(1)	93.61(19)	N(8)-Cd(1)-N(1)	84.8(2)
N(8)$^{\#1}$-Cd(1)-N(1)	95.2(2)	O(2)-Cd(2)-N(12)$^{\#2}$	121.8(2)
O(2)-Cd(2)-N(2)	133.4(2)	N(12)$^{\#2}$-Cd(2)-N(2)	104.7(2)
O(2)-Cd(2)-O(1W)	88.3(2)	N(12)$^{\#2}$-Cd(2)-O(1W)	90.7(2)
N(2)-Cd(2)-O(1W)	87.7(2)	O(2)-Cd(2)-N(7)	92.0(2)
N(12)$^{\#2}$-Cd(2)-N(7)	100.5(2)	N(2)-Cd(2)-N(7)	82.4(2)
O(1W)-Cd(2)-N(7)	166.6(2)	O(2)-Cd(2)-O(1)	53.04(17)
N(12)$^{\#2}$-Cd(2)-O(1)	174.78(19)	N(2)-Cd(2)-O(1)	80.43(19)
O(1W)-Cd(2)-O(1)	88.3(2)	N(7)-Cd(2)-O(1)	81.20(18)
N(6)$^{\#3}$-Cd(3)-O(4)$^{\#4}$	143.1(2)	N(6)$^{\#3}$-Cd(3)-N(10)	99.3(2)
O(4)$^{\#4}$-Cd(3)-N(10)	96.0(2)	N(6)$^{\#3}$-Cd(3)-O(6)$^{\#5}$	93.5(2)
O(4)$^{\#4}$-Cd(3)-O(6)$^{\#5}$	92.3(2)	N(10)-Cd(3)-O(6)$^{\#5}$	145.9(2)
N(6)$^{\#3}$-Cd(3)-O(3)$^{\#4}$	87.7(2)	O(4)$^{\#4}$-Cd(3)-O(3)$^{\#4}$	55.4(2)
N(10)-Cd(3)-O(3)$^{\#4}$	116.1(2)	O(6)$^{\#5}$-Cd(3)-O(3)$^{\#4}$	95.8(2)
N(6)$^{\#3}$-Cd(3)-O(5)$^{\#5}$	81.2(2)	O(4)$^{\#4}$-Cd(3)-O(5)$^{\#5}$	130.4(2)
N(10)-Cd(3)-O(5)$^{\#5}$	95.9(2)	O(6)$^{\#5}$-Cd(3)-O(5)$^{\#5}$	54.94(19)
O(3)$^{\#4}$-Cd(3)-O(5)$^{\#5}$	147.5(2)		

Symmetry codes for **4**: $^{\#1}$ -x+1,-y,-z; $^{\#2}$ -x,-y,-z+1; $^{\#3}$ x,y,z+1; $^{\#4}$ x,y-1,z; $^{\#5}$ -x+2,-y,-z.

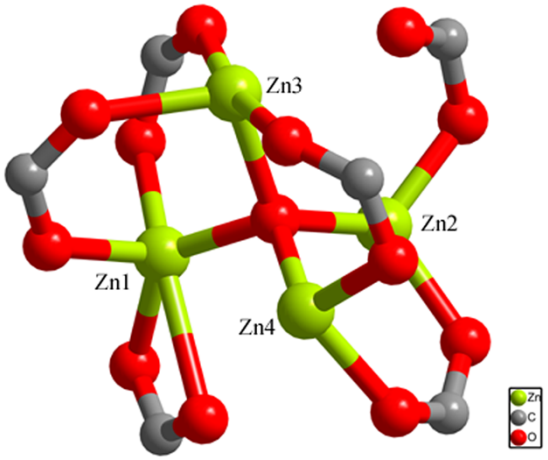

Fig. S1. The representation of tetranuclear $[Zn_4(\mu_4\text{-}O)(COO)_6]$ cluster in **1**.

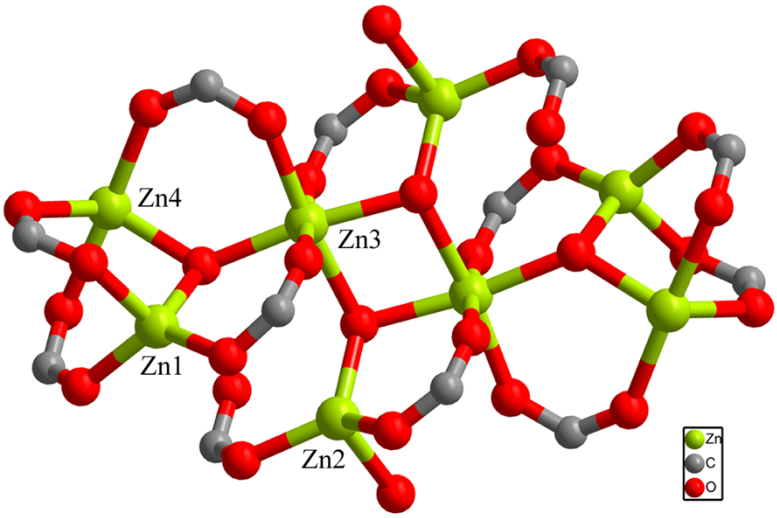

Fig. S2. The representation of octanuclear $[Zn_8(\mu_3\text{-}O)_4(COO)_{12}]$ cluster in **2**.

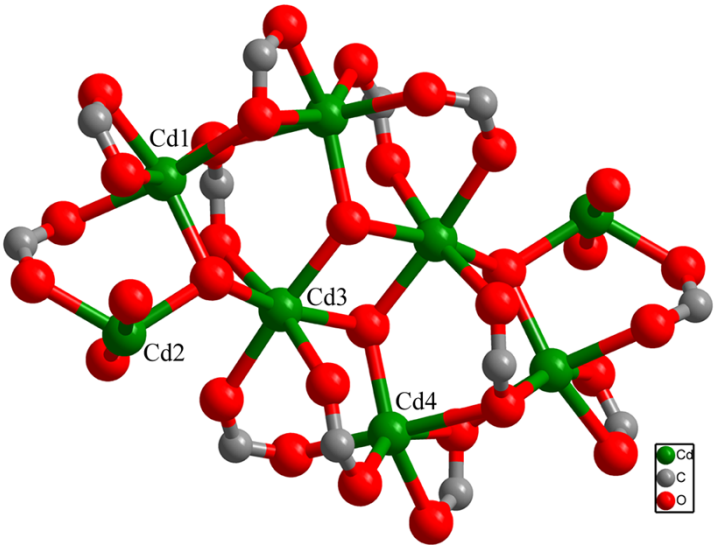

Fig. S3. The presentation of octanuclear $[Cd_8(\mu_3\text{-}O)_4(COO)_{12}(H_2O)_2]$ cluster in **3**.

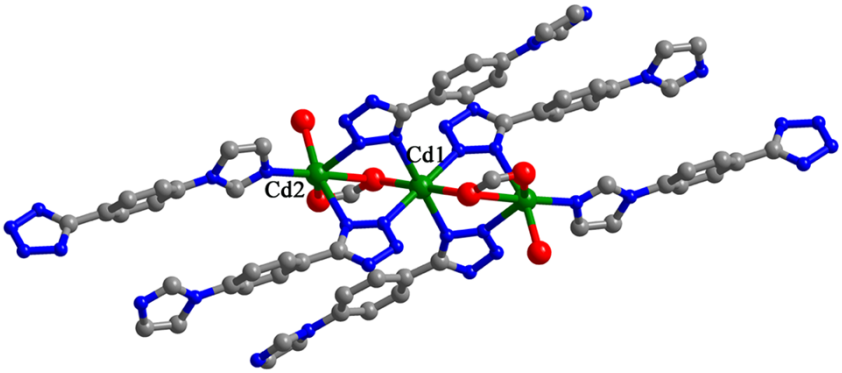

Fig. S4. The presentation of trinuclear $[Cd_3(COO)_2(H_2O)_2]$ unit in **4**.

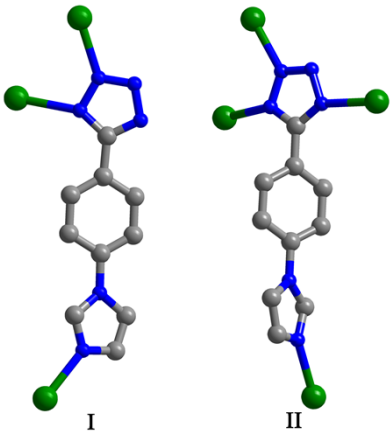

Fig. S5. The coordination modes of ipt anions in complex **4**.

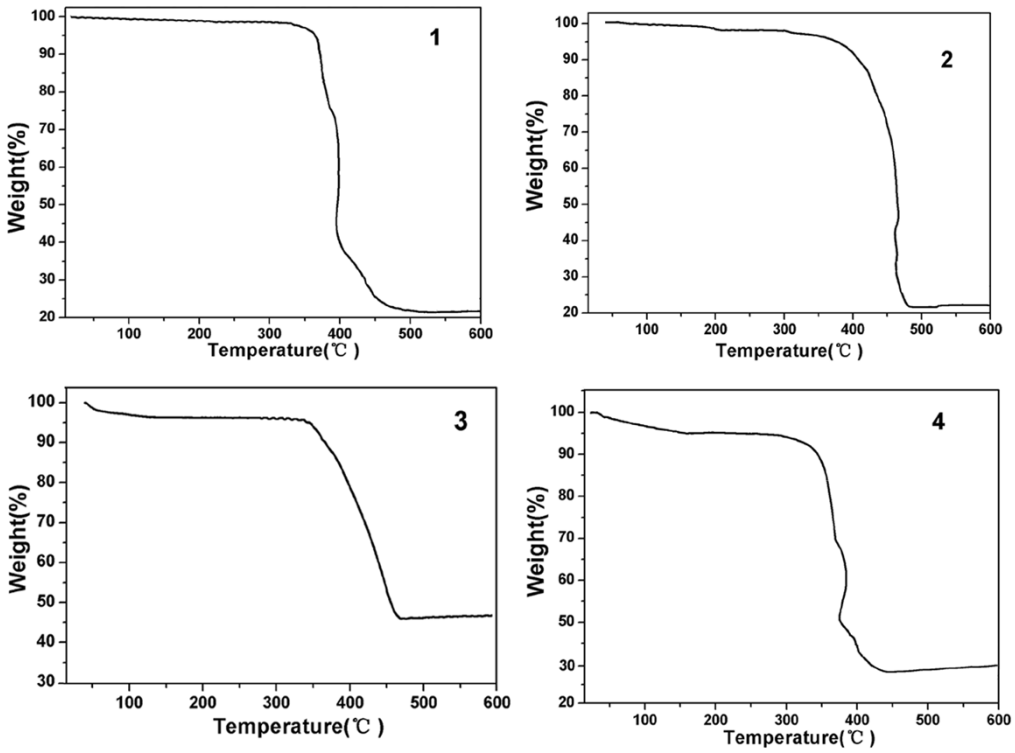

Fig. S6. The TGA curves of complexes **1**–**4**.

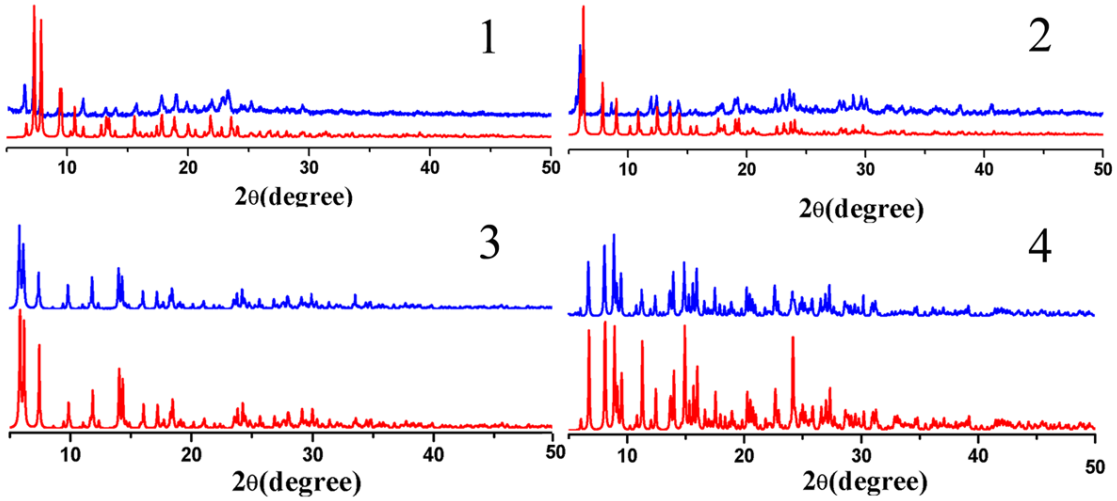

Fig. S7. Simulated (red) and experimental (blue) PXRD patterns of complexes **1**–**4**.

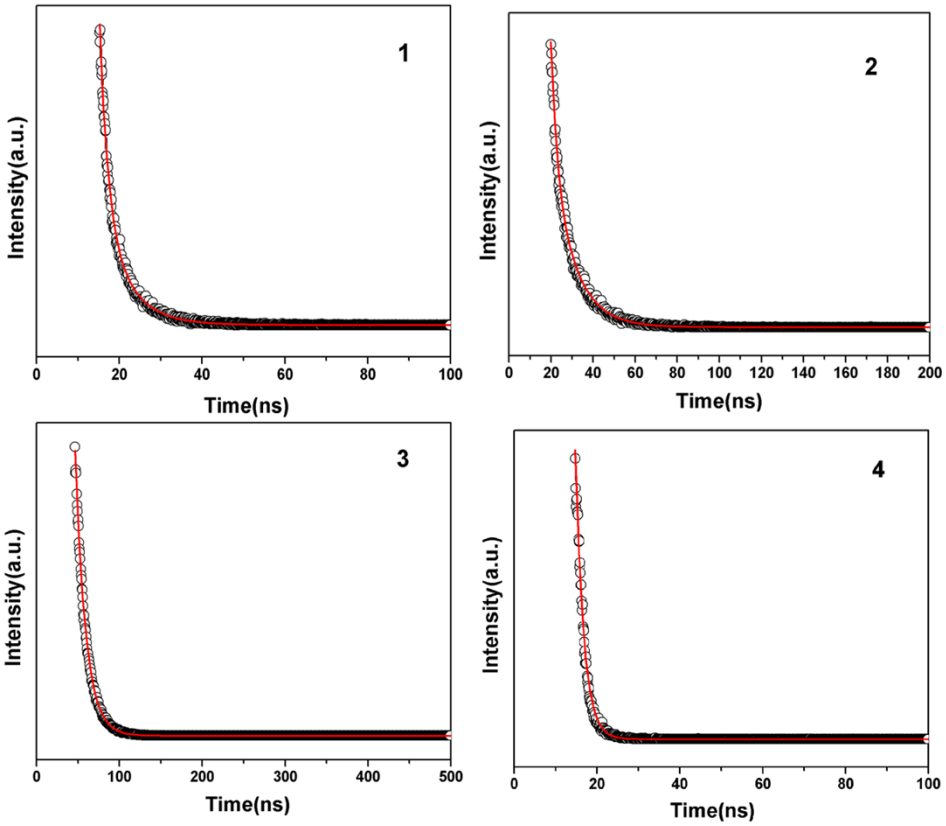

Fig. S8 Luminescence decay curves for complexes **1**–**4** (the black circles represent experimental data, and the solid red lines represent fitting results) **1** (λ_{em} = 437 nm), **2** (λ_{em} = 428 nm), **3** (λ_{em} = 481 nm), **4** (λ_{em} = 378 nm).