Supporting Information

Eight new complexes based on flexible multicarboxylate ligands: synthesis, structures and properties

Chang-Chun Ji,[a] Jing Li,[a] Yi-Zhi Li,[a] Zi-Jian Guo[a] and He-Gen Zheng*,[a, b]

[a]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China.* E-mail: zhenghg@nju.edu.cn. Fax: 86-25-83314502.

[b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China*

Table S1 Selected Bond Distances (Å) and Angles (deg) for complexes

Complex **1**			
Zn1 – O2	1.988(2)	Zn1 – O5a	1.953(2)
Zn1 – O7	2.077(2)	Zn1 – O1b	1.978(2)
Zn1 – O8	2.132(3)		
O5a – Zn1 – O1b	109.57(11)	O2 – Zn1 – O7	89.96(10)
O5a – Zn1 – O2	119.41(10)	O5a – Zn1 – O8	90.59(11)
O1b – Zn1 – O2	131.01(11)	O1b – Zn1 – O8	86.41(11)
O5a – Zn1 – O7	96.72(10)	O2 – Zn1 – O8	92.69(11)
O1b – Zn1 – O7	84.39(11)	O7 – Zn1 – O8	169.76(9)
Complex **2**			
Cd1 – O2a	2.265(3)	Cd1 – O6	2.358(3)
Cd1 – O7	2.300(3)	Cd1 – O5b	2.483(3)
Cd1 – O8	2.308(3)	Cd1 – O1	2.507(3)
Cd1 – O6b	2.317(3)		
O2a – Cd1 – O7	136.81(12)	O7 – Cd1 – O5b	133.43(12)
O2a – Cd1 – O8	87.04(12)	O8 – Cd1 – O5b	85.87(12)
O7 – Cd1 – O8	80.52(13)	O6b – Cd1 – O5b	54.40(10)
O2a – Cd1 – O6b	137.60(11)	O6 – Cd1 – O5b	105.97(11)

O7 – Cd1 – O6b	85.59(12)	O2a – Cd1 – O1	54.36(10)
O8 – Cd1 – O6b	102.76(12)	O7 – Cd1 – O1	83.96(12)
O2a – Cd1 – O6	103.08(11)	O8 – Cd1 – O1	88.65(11)
O7 – Cd1 – O6	84.31(12)	O6b – Cd1 – O1	163.04(11)
O8 – Cd1 – O6	164.75(11)	O6 – Cd1 – O1	88.12(10)
O6b – Cd1 – O6	77.57(11)	O5b – Cd1 – O1	140.25(10)
O2a – Cd1 – O5b	86.02(10)		
	Complex **3**		
Co1 – O2a	2.048(2)	Co2 – O8	2.096(2)
Co1 – O9	2.105(2)	Co2 – O7	2.059(2)
Co1 – O1	2.162(2)	Co2 – O6	2.108(2)
O1 – Co1 – O1	180.0	O6 – Co2 – O6b	180.00(8)
O1 – Co1 – O9	94.46(8)	O8 – Co2 – O6b	90.59(9)
O2a – Co1 – O1	92.49(9)	O7 – Co2 – O6b	90.05(8)
O2c – Co1 – O1	87.51(9)	O8 – Co2 – O6	89.41(9)
O1d – Co1 – O9	85.54(8)	O7 – Co2 – O6	89.95(8)
O9 – Co1 – O9d	180.00(12)	O8b – Co2 – O8	180.00(10)
O2a – Co1 – O9	91.24(8)	O7 – Co2 – O8	87.01(9)
O2c – Co1 – O9	88.76(8)	O7 – Co2 – O8b	92.99(9)
O2c – Co1 – O2a	180.0	O7b – Co2 – O7	180.00(13)
	Complex **4**		
Eu1 – O5a	2.335(5)	Eu1 – O3	2.502(5)
Eu1 – O7	2.416(5)	Eu1 – O9d	2.502(5)
Eu1 – O8	2.442(4)	Eu1 – O9e	2.505(5)
Eu1 – O4b	2.444(5)	Eu1 – O4	2.609(5)
Eu1 – O6c	2.485(5)		
O9e – Eu1 – O4	125.53(14)	O7 – Eu1 – O9d	126.32(18)
O9d – Eu1 – O4	65.86(15)	O5a – Eu1 – O9d	68.20(16)
O3 – Eu1 – O4	50.79(14)	O6c – Eu1 – O3	68.39(15)
O6c – Eu1 – O4	74.29(15)	O4b – Eu1 – O3	133.88(15)
O4b – Eu1 – O4	141.40(6)	O8 – Eu1 – O3	122.01(15)
O8 – Eu1 – O4	145.26(15)	O7 – Eu1 – O3	68.44(17)
O7 – Eu1 – O4	77.69(16)	O5a – Eu1 – O3	126.46(17)
O5a – Eu1 – O4	86.92(15)	O4b – Eu1 – O6c	75.47(15)
O9d – Eu1 – O9e	138.55(10)	O8 – Eu1 – O6c	139.01(15)
O3 – Eu1 – O9e	75.96(15)	O7 – Eu1 – O6c	136.81(17)
O6c – Eu1 – O9e	76.45(15)	O5a – Eu1 – O6c	137.11(16)
O4b – Eu1 – O9e	68.34(15)	O8 – Eu1 – O4b	71.22(15)
O8 – Eu1 – O9e	69.55(15)	O7 – Eu1 – O4b	140.57(17)
O7 – Eu1 – O9e	94.54(17)	O5a – Eu1 – O4b	99.50(16)
O5a – Eu1 – O9e	142.17(16)	O7 – Eu1 – O8	69.50(16)
O3 – Eu1 – O9d	110.04(14)	O5a – Eu1 – O8	72.62(16)
O6c – Eu1 – O9d	68.94(15)	O5a – Eu1 – O7	71.96(19)
O4b – Eu1 – O9d	81.21(15)	Eu1g – O9 – Eu1e	111.35(17)

O8 – Eu1 – O9d	126.81(14)	Eu1f – O4 – Eu1	109.81(17)
	Complex **5**		
Sm1 – O1a	2.351(4)	Sm1 – O5	2.515(4)
Sm1 – O2c	2.497(4)	Sm1 – O6	2.613(4)
Sm1 – O6b	2.460(4)	Sm1 – O7	2.452(4)
Sm1 – O9d	2.503(4)	Sm1 – O8	2.425(4)
Sm1 – O9e	2.517(4)		
O9e – Sm1 – O6	125.40(13)	O8 – Sm1 – O5	68.79(14)
O5 – Sm1 – O6	50.37(12)	O1a – Sm1 – O5	126.33(14)
O9d – Sm1 – O6	66.05(13)	O2c – Sm1 – O9d	68.82(13)
O2c – Sm1 – O6	74.14(12)	O6b – Sm1 – O9d	81.01(13)
O6b – Sm1 – O6	141.27(6)	O7 – Sm1 – O9d	126.11(13)
O7 – Sm1 – O6	145.49(12)	O8 – Sm1 – O9d	126.22(13)
O8 – Sm1 – O6	77.51(14)	O1a – Sm1 – O9d	68.02(13)
O1a – Sm1 – O6	86.75(13)	O6b – Sm1 – O2c	75.37(13)
O5 – Sm1 – O9e	76.23(13)	O7 – Sm1 – O2c	139.15(12)
O9d – Sm1 – O9e	138.15(8)	O8 – Sm1 – O2c	136.78(15)
O2c – Sm1 – O9e	76.29(12)	O1a – Sm1 – O2c	136.79(13)
O6b – Sm1 – O9e	68.16(12)	O7 – Sm1 – O6b	71.02(13)
O7 – Sm1 – O9e	70.15(12)	O8 – Sm1 – O6b	140.88(14)
O8 – Sm1 – O9e	95.03(14)	O1a – Sm1 – O6b	99.73(14)
O1a – Sm1 – O9e	142.65(13)	O8 – Sm1 – O7	70.03(14)
O9d – Sm1 – O5	109.67(13)	O1a – Sm1 – O7	72.51(14)
O2c – Sm1 – O5	68.03(14)	O1a – Sm1 – O8	71.89(16)
O6b – Sm1 – O5	133.69(13)	Sm1g – O9 – Sm1e	111.48(14)
O7 – Sm1 – O5	123.11(13)	Sm1f – O6 – Sm1	109.72(15)
	Complex **6**		
Cd1 – O3	2.150(4)	Cd1 – O6b	2.268(3)
Cd1 – O7	2.195(4)	Cd1 – O6	2.325(4)
Cd1 – O5a	2.258(4)	Cd1 – O2	2.534(4)
O3 – Cd1 – O7	164.92(14)	O5a – Cd1 – O6	150.45(14)
O3 – Cd1 – O5a	81.30(15)	O6b – Cd1 – O6	72.88(16)
O7 – Cd1 – O5a	83.68(14)	O3 – Cd1 – O2	89.80(16)
O3 – Cd1 – O6b	103.26(15)	O7 – Cd1 – O2	88.00(14)
O7 – Cd1 – O6b	88.16(14)	O5a – Cd1 – O2	86.55(13)
O5a – Cd1 – O6b	134.10(15)	O6b – Cd1 – O2	138.33(13)
O3 – Cd1 – O6	106.66(17)	O6 – Cd1 – O2	65.46(11)
O7 – Cd1 – O6	85.94(15)		
	Complex **7**		
Co1 – O1	2.105(2)	Co1 – O3	2.084(2)
Co1 – O2	2.063(2)		
O2a – Co1 – O2	180.0	O2 – Co1 – O1	89.61(9)
O2 – Co1 – O3a	88.14(9)	O3a – Co1 – O1	91.69(9)
O2 – Co1 – O3	91.86(9)	O3 – Co1 – O1	88.31(9)

O3a – Co1 – O3	180.00(7)	O1 – Co1 – O1	180.0
O2a – Co1 – O1	90.39(9)		
	Complex **8**		
Ni1 – O1	2.050(2)	Ni1 – O5	2.027(2)
Ni1 – O4	2.079(3)		
O5a – Ni1 – O5	180.00(12)	O1 – Ni1 – O4	91.73(11)
O5 – Ni1 – O1	92.73(10)	O5 – Ni1 – O4a	88.70(11)
O5 – Ni1 – O1a	87.27(10)	O1 – Ni1 – O4a	88.27(11)
O1 – Ni1 – O1a	180.00(8)	O4 – Ni1 – O4a	180.00(17)
O5 – Ni1 – O4	91.30(11)		

Symmetry transformations used to generate equivalent atoms:

complex **1**: a = *x*, *y* - 1, *z* - 1; b = - *x*+ 1, -*y* + 1, - *z*.

complex **2**: a = -*x*, -*y* + 1, -*z* + 1; b = -*x*, -*y*, -*z* + 2.

complex **3**: a = *x* + 1, *y*, *z*; b = - *x* + 2, -*y* + 2 , - *z*; c = - *x*, -*y*, - *z* + 1; d = - *x* + 1, - *y*, - *z* +1.

complex **4**: a = *x* – 1, *y*, *z*; b = - *x*, *y* – 1/2, - *z* + 1/2; c = - *x* + 1, *y* – 1/2, - *z* + 1/2; d = *x*, - *y* + 1/2, *z* + 1/2; e = - *x*, - *y*, - *z*; f = - *x*, *y* + 1/2, - *z* + 1/2. g = *x*, - *y* + 1/2, *z* – 1/2.

complex **5**: a = *x* + 1, *y*, *z*; b = - *x* + 2, *y* + 1/2, - *z* + 1/2; c = - *x* + 1, *y* + 1/2, - *z* + 1/2; d = *x*, - *y* + 1/2, *z* - 1/2; e = - *x* + 2, - *y* + 1, - *z* + 1; f = - *x* + 2, *y* - 1/2, - *z* + 1/2; g = *x*, - *y* + 1/2, *z* + 1/2.

complex **6**: a = *x* - 1, *y*, *z*; b = - *x* + 1, - *y* + 2, - *z*.

complex **7**: a = - *x*, - *y* + 1, - *z*.

complex **8**: a = - *x*, - *y*, - *z*.

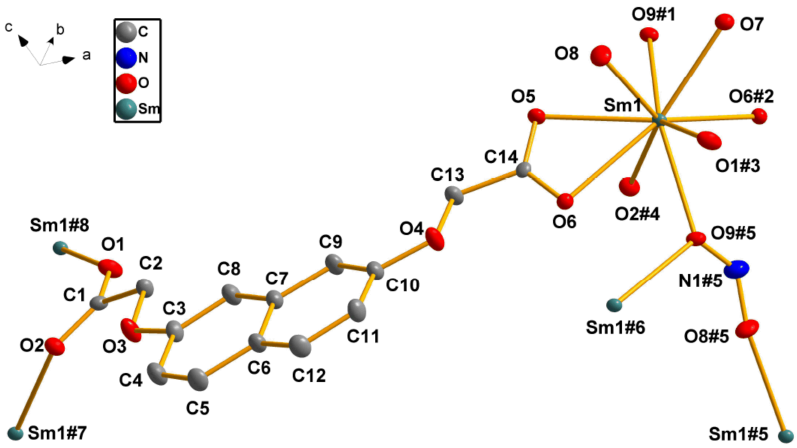

Fig. S1 An ORTEP drawing of **5** showing 30% ellipsoid probability (hydrogen atoms are omitted for clarity). Symmetry codes: #1 = 2 – *x*, 1 – *y*, 1 – *z*; #2 = 2 – *x*, 0.5 + *y*, 0.5 – z; #3 = 1 + *x*, *y*, *z*; #4 = 1 – *x*, 0.5 + *y*, 0.5 – *z*; #5 = *x*, 0.5 – *y*, - 0.5 + *z*; #6 = 2 – *x*, - 0.5 + *y*, 0.5 – *z*; #7 = 1 – *x*, - 0.5 + *y*, 0.5 – *z*; #8 = - 1 + *x*, *y*, *z*.

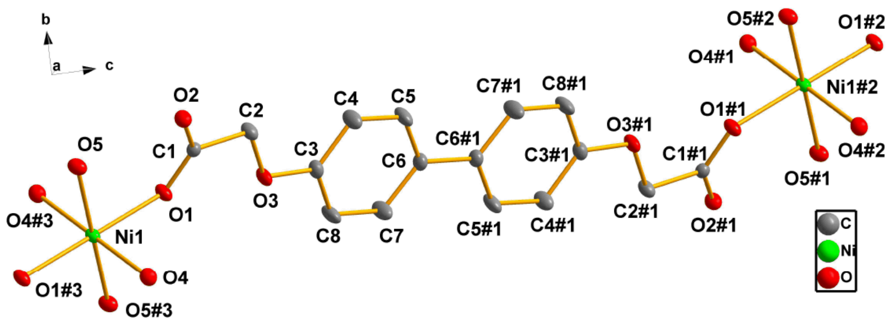

Fig. S2 An ORTEP drawing of **8** showing 30% ellipsoid probability (hydrogen atoms are omitted for clarity). Symmetry codes: #1 = 2 – *x*, - *y*, 1 – *z* ; #2 = 2 + *x*, *y*, 1 + *z*; #3 = - *x*, - *y*, - *z*.

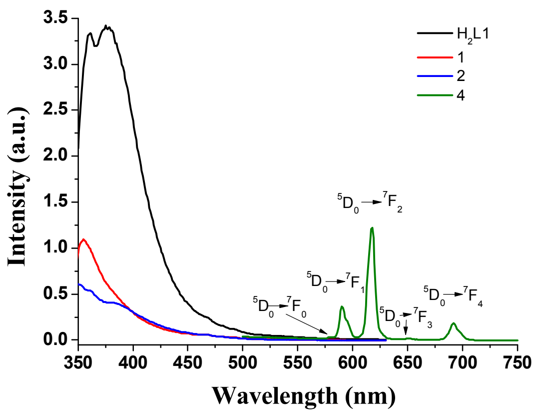

Fig. S3 Emission spectra of free H_2L1, complex **1**, **2**, and **4** in the solid state at room temperature.

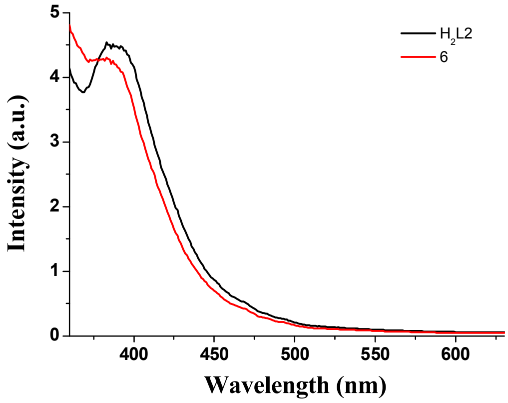

Fig. S4 Emission spectra of free H_2L2 and complex **6** in the solid state at room temperature.

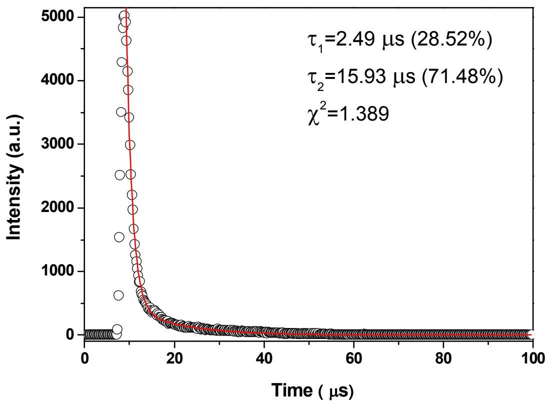

Fig. S5 The fitted decay curve monitored at 354 nm for complex **1** in the solid state at room temperature. The sample was excited at 340 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A+B_1\times\exp(-t/\tau_1)+B_2\times\exp(-t/\tau_2)$.

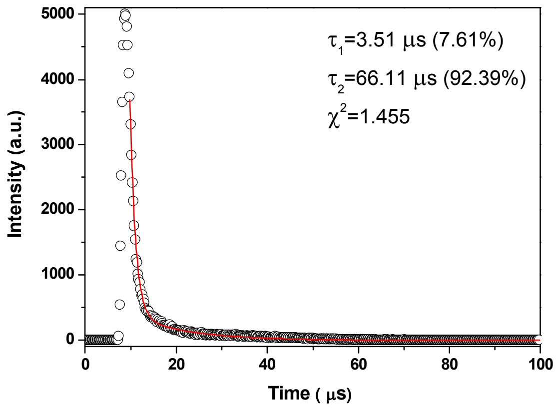

Fig. S6 The fitted decay curve monitored at 387 nm for complex **2** in the solid state at room temperature. The sample was excited at 350 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A+B_1\times\exp(-t/\tau_1)+B_2\times\exp(-t/\tau_2)$.

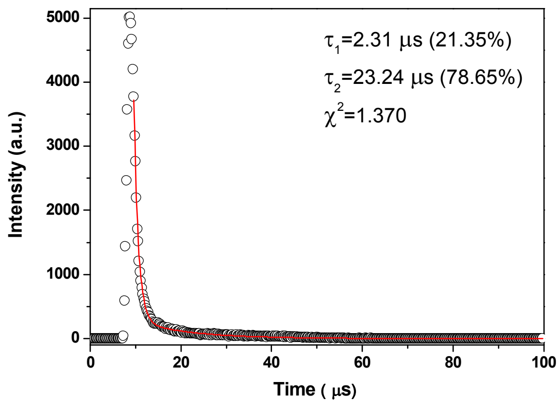

Fig. S7 The fitted decay curve monitored at 618 nm for complex **4** in the solid state at room temperature. The sample was excited at 395 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A+B_1\times\exp(-t/\tau_1)+B_2\times\exp(-t/\tau_2)$.

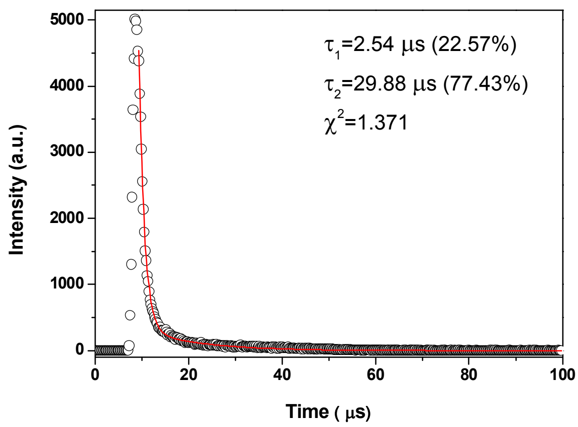

Fig. S8 The fitted decay curve monitored at 383 nm for complex **6** in the solid state at room temperature. The sample was excited at 344 nm. Blank circles: experimental data; Solid line: fitted by Fit = $A+B_1\times\exp(-t/\tau_1)+B_2\times\exp(-t/\tau_2)$.

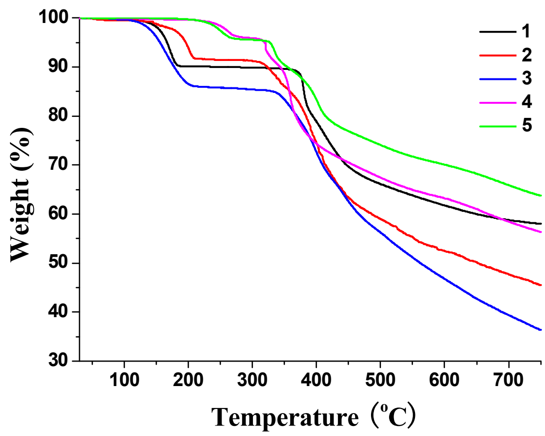

Fig. S9 TGA plot of compounds **1 – 5.**

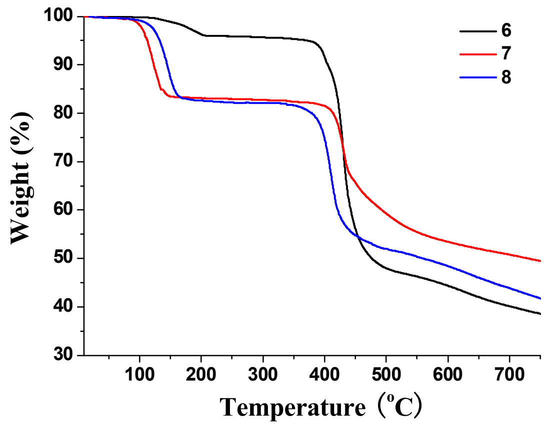

Fig. S10 TGA plot of compounds **6 – 8.**

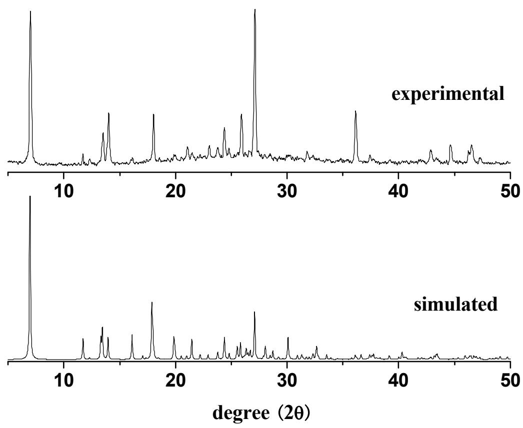

Fig. S11 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **1** at 293K.

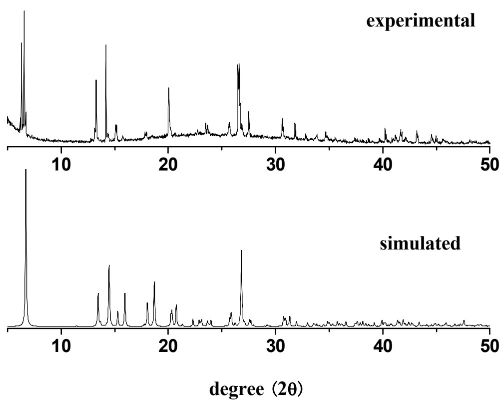

Fig. S12 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **2** at 293K.

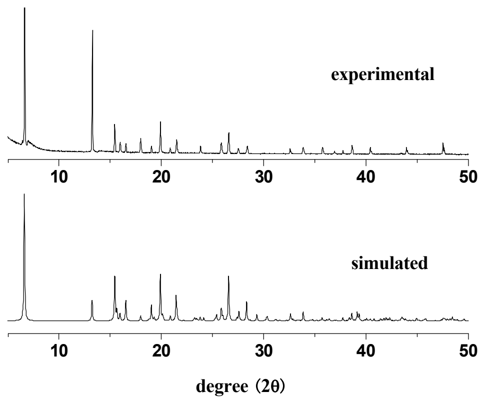

Fig. S13 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **3** at 293K.

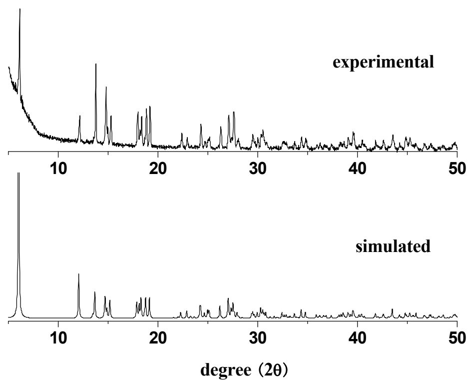

Fig. S14 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **4** at 293K.

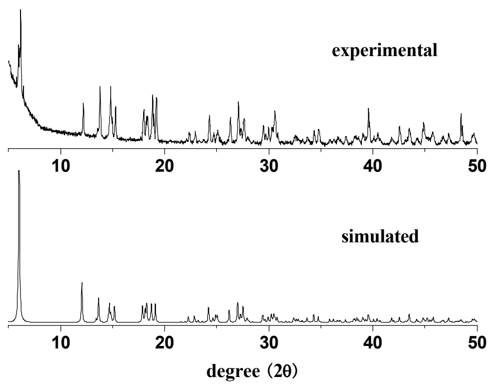

Fig. S15 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **5** at 293K.

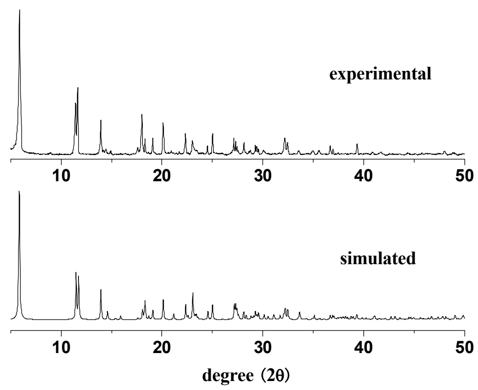

Fig. S16 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **6** at 293K.

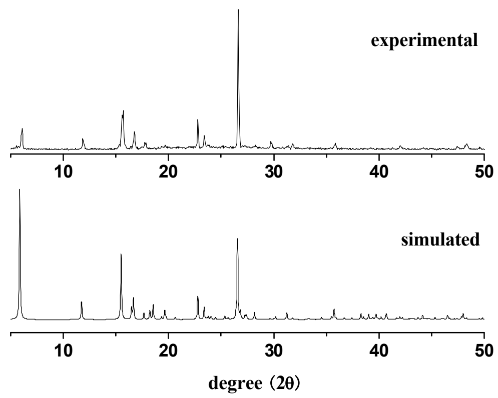

Fig. S17 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **7** at 293K.

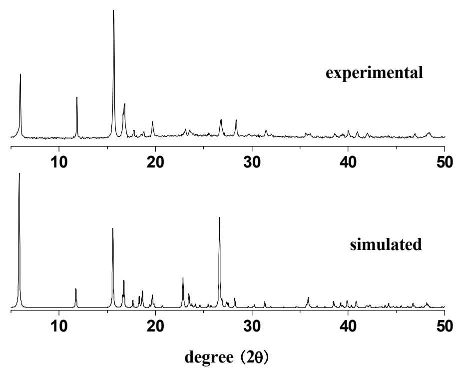

Fig. S18 Experimental (top) and simulated (bottom) powder X-ray diffraction patterns of complex **8** at 293K.