Supplemental Material

Four calcium(II) coordination polymers based on 2,5-dibromoterephthalic acid and different N-donor organic species: syntheses, structures, topologies, and luminescence properties

Yuexin Sun, Yayong Sun, Hao Zheng, Hongli Wang, Yi Han, Lei Wang*

Key Laboratory of Eco-chemical Engineering, Ministry of Education, Inorganic Synthesis and Applied Chemistry, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China. E-mail: inorchemwl@126.com, Fax: (+86) 532-840-22681

(1) Table: S1 Selected bond lengths (Å) and angles (deg) for complexes **1-4**

Complex1

Ca1-O1^{ii}	2.353(3)	Ca1-O1	2.436(3)	Ca1-O2^{i}	2.419(3)
Ca1-O1^{iii}	2.436(3)	Ca1-O1^{iv}	2.353(3)	Ca1-O2^{v}	2.419(3)
Ca1-O3	2.368(5)				
O1^{i}-Ca1-O1^{iv}	82.93(10)	O1^{i}-Ca1-O1	84.52(11)	O1^{i}-Ca1-O2^{ii}	104.61(11)
O1^{iii}-Ca1-O1^{iv}	84.52(11)	O1^{iv}-Ca1-O1	73.92(14)	O1^{iii}-Ca1-O2^{ii}	81.04(10)
O1^{i}-Ca1-O1^{iii}	164.28(16)	O1^{iii}-Ca1-O1	82.93(10)	O1^{i}-Ca1-O2^{v}	81.04(10)
O1^{iii}-Ca1-O2^{v}	104.61(11)	O2^{ii}-Ca1-O1	145.88(11)	O2^{v}-Ca1-O1^{iv}	145.88(11)
O1^{iii}-Ca1-O3	97.86(8)	O2^{v}-Ca1-O1	74.72(10)	O2^{v}-Ca1-O2^{ii}	138.64(16)
O1^{i}-Ca1-O3	97.86(8)	O2^{ii}-Ca1-O1^{iv}	74.72(10)	O3-Ca1-O1^{iv}	143.04(7)
O3-Ca1-O1	143.04(7)	O3-Ca1-O2^{ii}	69.32(8)	O3-Ca1-O2^{v}	69.32(8)

Symmetry code: (i) 1-x, 2-y, 1-z; (ii) 1-x, 2-y, 2-z; (iii) x, 2-y, 1/2+z; (iv) 1-x, y, 3/2-z; (v) x, 2-y, -1/2+z; (vi) 3/2-x, 3/2-y, 1-z.

Complex2

Ca1-O1	2.375(2)	Ca1-O1^{iii}	2.375(2)	Ca1-N1^{iii}	2.703(3)
Ca1-O1^{i}	2.375(2)	Ca1-N1	2.703(3)	Ca1-N1^{ii}	2.703(3)
Ca1-O1^{ii}	2.375(2)	Ca1-N1^{i}	2.703(3)		
O1-Ca1-O1^{i}	102.17(11)	O1^{i}-Ca1-O1^{iii}	80.05(12)	O1^{ii}-Ca1-N1	73.48(9)
O1-Ca1-O1^{ii}	80.05(12)	O1^{ii}-Ca1-O1^{iii}	102.17(11)	O1^{i}-Ca1-N1	92.56(8)
O1^{i}-Ca1-O1^{ii}	164.13(12)	O1^{iii}-Ca1-N1	72.38(8)	O1-Ca1-N1^{i}	92.56(8)
O1-Ca1-O1^{iii}	164.13(12)	O1^{i}-Ca1-N1^{i}	122.83(8)	O1^{ii}-Ca1-N1^{i}	72.39(8)
O1^{iii}-Ca1-N1^{i}	73.48(9)	O1^{ii}-Ca1-N1^{iii}	92.56(8)	O1^{ii}-Ca1-N1^{ii}	122.83(8)
O1-Ca1-N1	122.83(8)	O1^{iii}-Ca1-N1^{iii}	122.83(8)	O1^{iii}-Ca1-N1^{ii}	92.56(8)
O1-Ca1-N1^{iii}	72.38(8)	O1-Ca1-N1^{ii}	73.48(9)	N1-Ca1-N1^{i}	124.30(11)
O1^{i}-Ca1-N1^{iii}	73.48(9)	O1^{i}-Ca1-N1^{ii}	72.39(8)	N1-Ca1-N1^{iii}	59.55(11)
N1^{i}-Ca1-N1^{iii}	160.61(12)	N1^{i}-Ca1-N1^{ii}	59.55(11)	N1-Ca1-N1^{ii}	160.61(12)
N1^{iii}-Ca1-N1^{ii}	124.30(11)				

Symmetry code: (i) 1/2-x, y, 1/2-z; (ii) x, 1/2-y, 1/2-z; (iii) 1/2-x, 1/2-y, z; (iv) 1-x, -y, 1-z.

Complex3

Ca1-O1	2.5895(2)	Ca1-O2	2.4622(2)	Ca1-O3	2.4480(1)
Ca1-O4	2.6632(1)	Ca1-O5	2.4160(1)	Ca1-O6	2.3855(2)
Ca1-O1^{iv}	2.3626(1)	Ca1-O4^{v}	2.3705(1)		
O1-Ca1- O2	51.4(2)	O1-Ca1-O3	77.13(1)	O1-Ca1-O4	104.5(2)
O1-Ca1-O5	80.2(3)	O1-Ca1-O6	152.1(3)	O1-Ca1-O1^{iv}	73.6(2)
O1-Ca1-O4^{v}	128.5(3)	O2-Ca1-O3	93.6(3)	O2-Ca1-O4	78.5(3)
O2-Ca1-O5	85.6(3)	O2-Ca1-O6	151.1(4)	O2-Ca1-O1^{iv}	124.2(3)
O2-Ca1-O4^{v}	78.9(3)	O3 Ca1-O4	50.9(2)	O3-Ca1-O5	151.4(4)
O3-Ca1-O6	83.5(3)	O3-Ca1-O1^{iv}	83.5(3)	O3-Ca1-O4^{v}	124.2(4)
O4-Ca1-O5	154.4(3)	O4-Ca1-O6	77.4(3)	O4 Ca1-O1^{iv}	130.1(3)
O4-Ca1-O4^{v}	73.6(3)	O5-Ca1-O6	110.4(3)	O5-Ca1-O1^{iv}	75.5(3)

O5-Ca1-O4^{v}	83.8(3)	O6-Ca1-O1^{iv}	83.9(3)	O6-Ca1-O4^{v}	79.2(3)
O1^{iv}-Ca1-O4^{v}	83.9(3)				

Symmetry code: (i) -x, 1-y, -z; (ii) 1-x, -y, 1-z; (iii) 1-x, -y, -z; (iv) -x, 1-y, 1-z; (v) 1-x, 1-y, 1-z.

Complex4

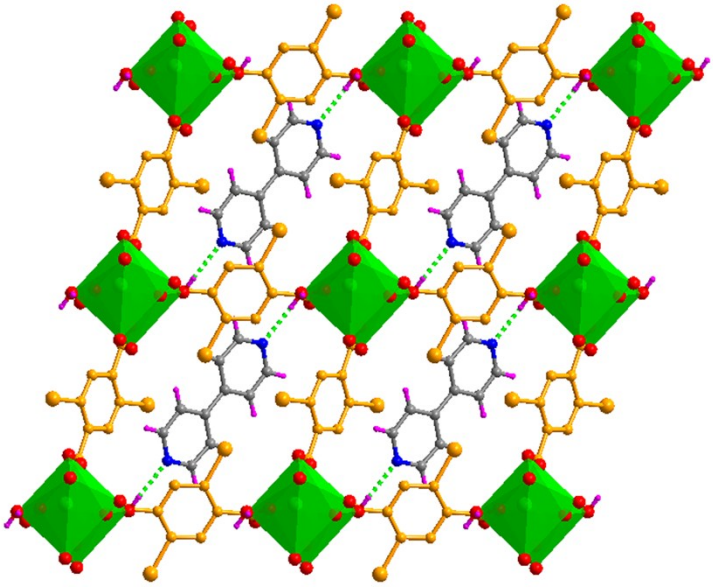
Ca1-O8^{i}	2.551(3)	Ca1-O4	2.572(2)	Ca1-O9	2.407(3)
Ca1-O1	2.350(3)	Ca1-O5	2.325(3)	Ca1-O3	2.555(3)
Ca1-O2^{ii}	2.490(3)	Ca2-O6^{i}	2.367(3)	Ca2-O10^{i}	2.332(3)
Ca2-O7^{i}	2.307(3)	Ca2-O6	2.367(3)	Ca2-O10	2.332(3)
Ca2-O7	2.307(3)				
O1-Ca1-O5	159.51(11)	O1-Ca1-O4	77.88(9)	O1-Ca1-O9	73.46(11)
O1-Ca1-O8^{i}	95.72(10)	O1-Ca1-O2^{ii}	112.93(11)	O1-Ca1-O3	76.20(12)
O5-Ca1-O4	83.52(10)	O5-Ca1-O9	127.02(11)	O5-Ca1-O8^{i}	87.61(10)
O5-Ca1-O2^{ii}	73.60(10)	O5-Ca1-O3	85.51(11)	O9-Ca1-O8^{i}	82.52(11)
O9-Ca1-O4	142.66(11)	O9-Ca1-O2^{ii}	84.27(11)	O9-Ca1-O3	138.65(11)
O2^{ii}-Ca1-O4	85.37(9)	O2^{ii}-Ca1-O3	133.98(10)	O2^{ii}-Ca1-O8^{i}	143.35(9)
O8^{i}-Ca1-O4	124.19(9)	O8^{i}-Ca1-O3	73.22(8)	O3-Ca1-O4	51.24(8)
O7^{i}-Ca2-O7	180.0(3)	O7-Ca2-O6^{i}	90.34(10)	O7-Ca2-O10	89.62(12)
O7^{i}-Ca2-O6^{i}	89.66(10)	O7^{i}-Ca2-O6	90.34(10)	O7^{i}-Ca2-O10^{i}	89.62(12)
O7-Ca2-O6	89.66(10)	O7-Ca2-O10^{i}	90.38(12)	O7^{i}-Ca2-O10	90.38(12)
O10-Ca2-O6	99.69(13)	O10-Ca2-O6^{i}	80.31(13)	O10^{i}-Ca2-O10	180.0
O10^{i}-Ca2-O6	80.31(13)	O10^{i}-Ca2-O6^{i}	99.69(13)	O6^{i}-Ca2-O6	180.00(16)

Symmetry code: (i) 2-x, -y, 1-z; (ii) 2-x, -y, 2-z; (iii) 1-x, -y, 1-z; (iv) 3-x, -y, 2-z; (v) 1-x, 1-y, 2-z; (vi) 2-x, 1-y, 1-z; (vii) 2-x, 1-y, 2-z.

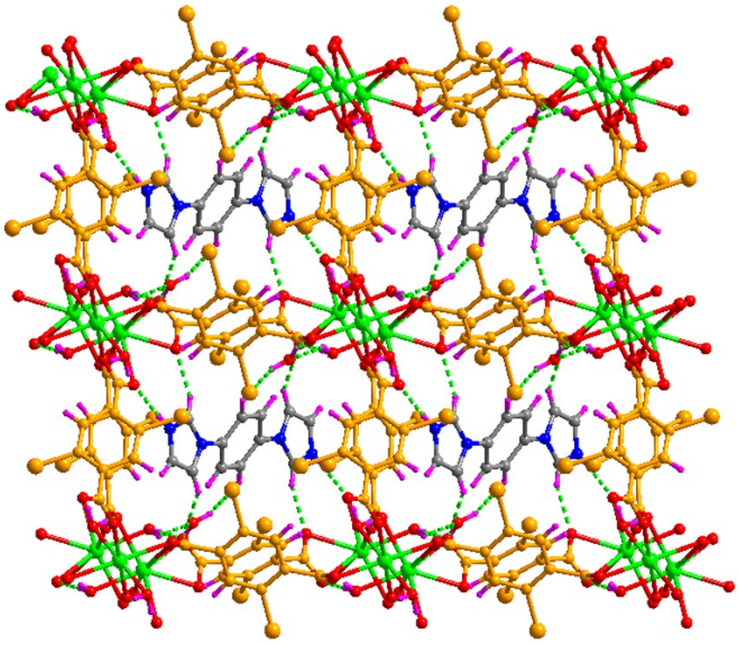
(2) Table: S2 Selected H-bond lengths and angles of complexes **3** and **4**

D-H…A(Å)(symmetry mode)	H…A(Å)	D…A(Å)	D-H...A(deg)
Complex 1			
O6-H3A···Br1 (x, 2-y, 1/2+z)	2.644(2)	3.438(2)	155.9(3)
O6-H3B···Br1 (x, 2-y, 1/2+z)	2.644(2)	3.438(2)	155.9(3)
Complex 3			
O6-H6A···N1 (x, y, z)	2.085(1)	2.863(1)	162.6(9)
Complex 4			
N1-H1…O8 (1-x, -y, 2-z)	1.858(1)	2.710(1)	172.1(8)
C17-H17…O3 (2-x, -y, 2-z)	2.216(1)	2.996(2)	141.0(8)
C19-H19…O4 (x, -1+y, z)	2.428(1)	3.209(2)	141.6(7)

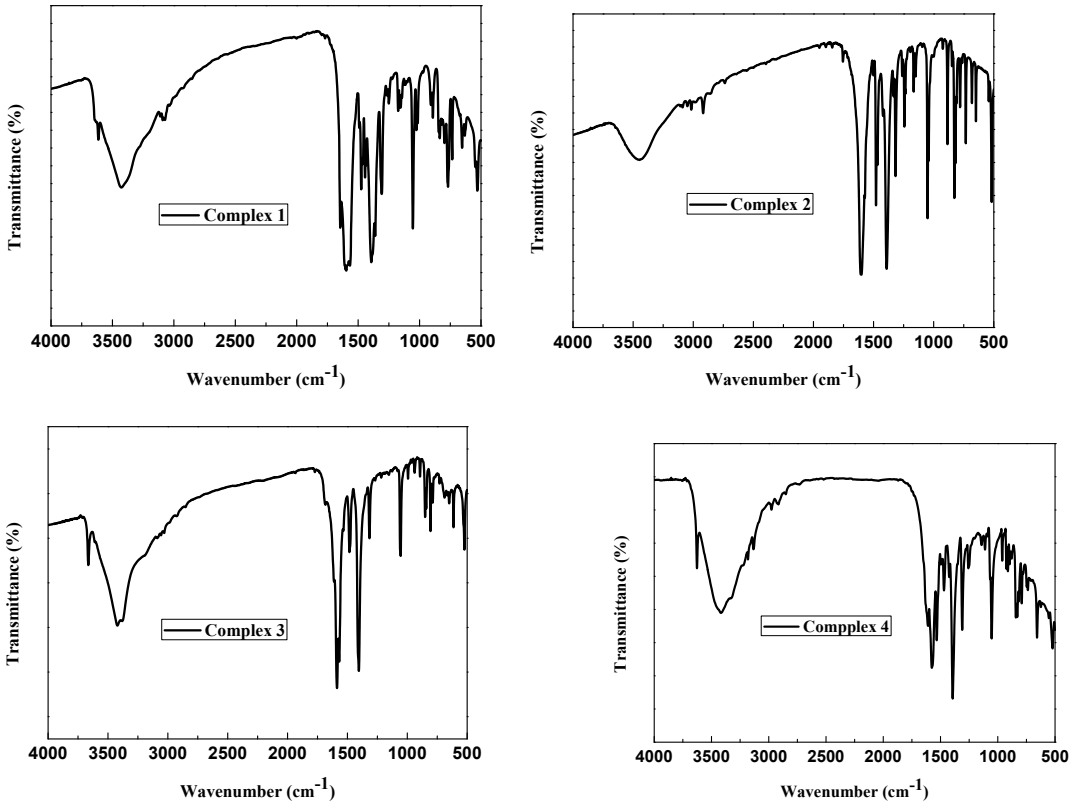
(3) Fig. S1: The view of hydrogen bonds interaction between 4,4'-bpy ligands and the neutral framework of complex **3**



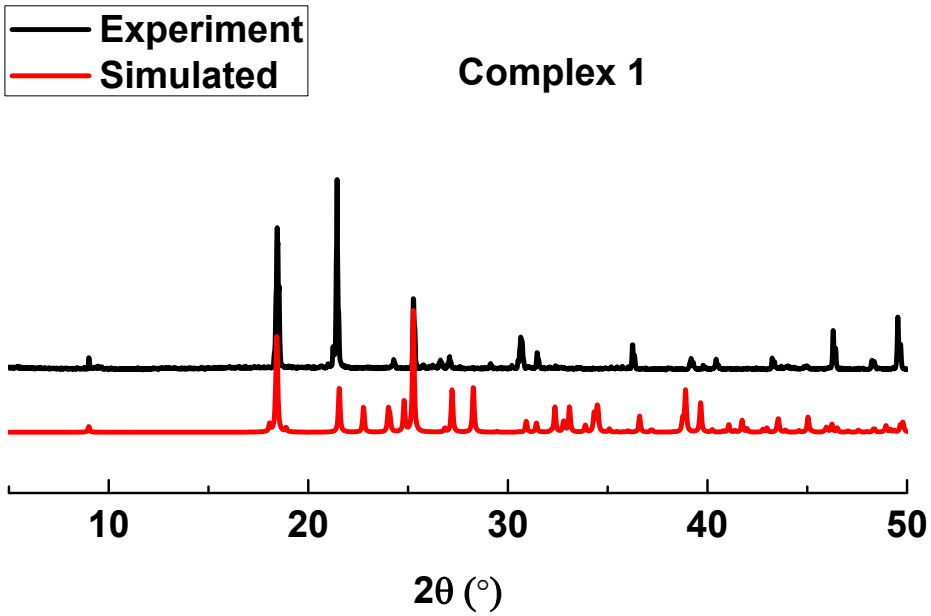
(4) Fig. S2: The view of hydrogen bonds interaction between diprotonated bib ligands and the anion ic framework of complex **4**

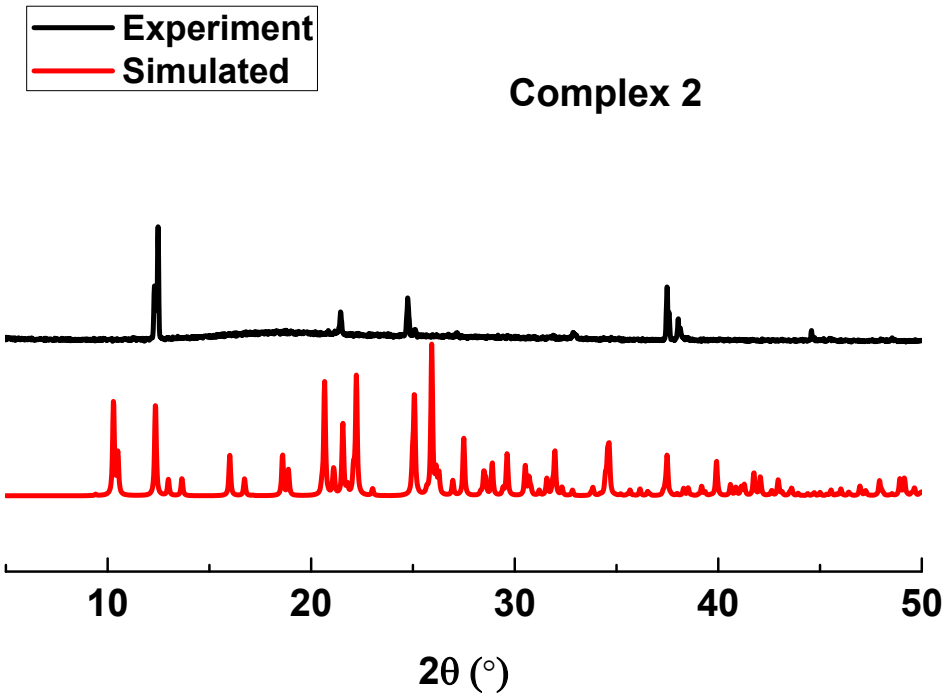


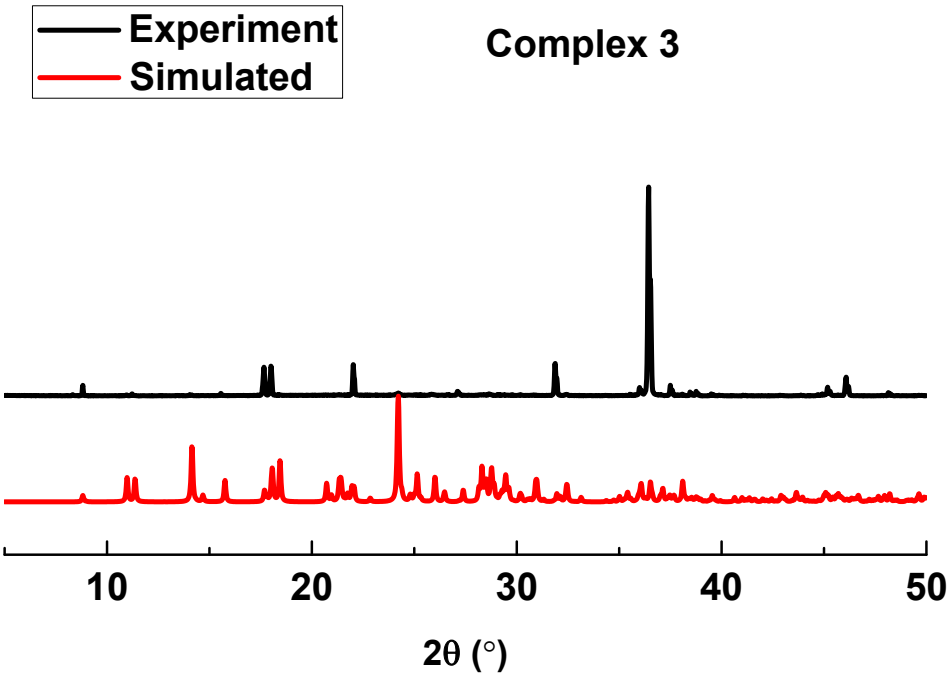
(5) Fig. S3: IR spectra of **1-4**

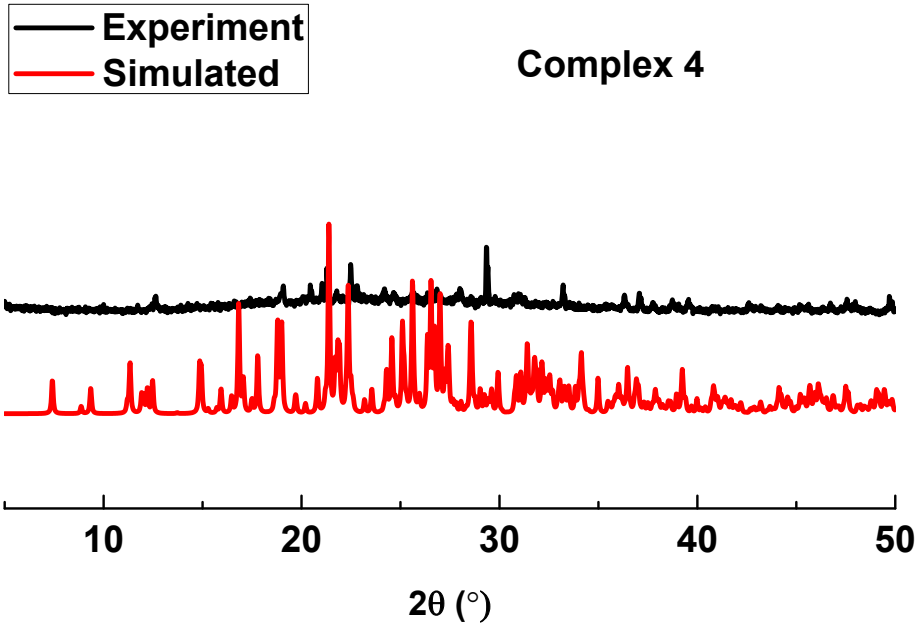


(6) Fig. S4. The PXRD of **1-4**




Experiment
Simulated
Complex 2
10
20
30
40
50
2θ (°)

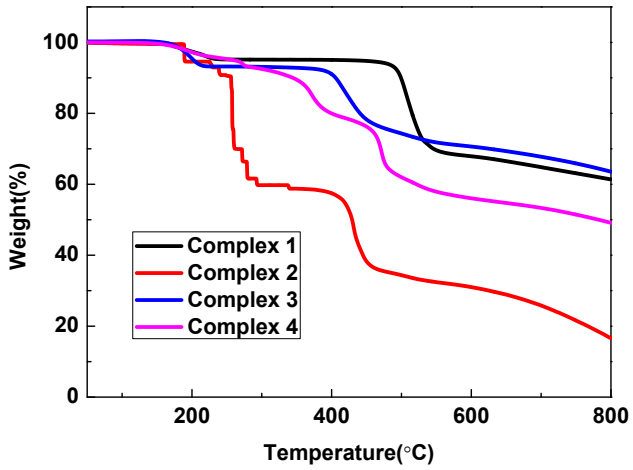

Experiment
Simulated
Complex 3
10
20
30
40
50
2θ (°)



(7) Thermogravimetric analysis

The thermogravimetric analysis (TGA) has been performed under N_2 atmosphere to study the thermal stability of complexes **1**-**4**. As shown in Fig. S5, complexes **1** and **3** have two identifitable weight loss steps. For complex **1**, the first weight loss from 50 to 270 ℃ is attributed to the loss of coordination water molecules (obsd 4.80%, calcd 4.74%), and then it starts to decompose. The TGA curve of **2** shows a weight loss from 50 to 320 ℃, corresponding to the removal of 5,5'-dmbpy ligands. Upon heating beyond 320 °C, the H-dbt ligands began to decompose, leading to the collapse of the framework. The TGA curve of **3** shows the first weight loss from 85 to 270 ℃, corresponding to the loss of coordination water molecules (obsd 7.12%, calcd 7.56%). Upon further heating, the 4,4'-bpy ligands were lost, and then the framework begins to collapse. For **4**, the weight losses corresponding to the release of lattice water molecules, coordinated water molecules, H_2-dib and dbt ligands were observed without stop until the collapse and decompose of the framework.

(8) Fig. S5: Thermogravimetric analysis (TGA) curves of complexes **1**-**4**



(9) Fig. S6: Luminescence quenching studies of complexes **3**-**4** exposing to NB.