Electronic Supplementary Material (ESI) for CrystEngComm.

Metal/N-donor-induced versatile structures and properties of seven 0D→3D complexes based on dpq/dppz and O-bridged tricarboxylate: fluorescent and electrochemical behaviors

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Supporting Information

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

1			
Cu(1)–N(1)	2.0221(17)	Cu(1)–N(2)	2.0148(16)
Cu(1)–O(1W)	1.9922(14)	Cu(1)–O(2W)	2.1572(15)
Cu(1)–O(1)	1.9460(14)		
O(1)–Cu(1)–O(1W)	94.79(6)	N(2)–Cu(1)–N(1)	81.39(7)
O(1)–Cu(1)–N(2)	168.34(6)	O(1)–Cu(1)–O(2W)	92.59(6)
O(1W)–Cu(1)–N(2)	90.47(6)	O(1W)–Cu(1)–O(2W)	93.72(6)
O(1)–Cu(1)–N(1)	89.82(6)	N(2)–Cu(1)–O(2W)	97.45(6)
O(1W)–Cu(1)–N(1)	156.95(7)	N(1)–Cu(1)–O(2W)	108.64(6)

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

2			
Co(1)–N(1)	2.1748(15)	Co(1)–N(2)	2.1346(15)
Co(1)–O(1)	2.0753(13)	Co(1)–O(2)	2.3672(13)
Co(1)–O(3)A	2.0749(12)	Co(1)–O(1W)	2.0390(13)
O(1W)–Co(1)–O(1)	102.66(6)	O(3)A–Co(1)–N(1)	87.93(5)
O(1W)–Co(1)–O(3)A	92.19(5)	N(2)–Co(1)–N(1)	75.93(6)
O(1)–Co(1)–O(3)A	111.29(5)	O(1W)–Co(1)–O(2)	84.66(5)
O(1W)–Co(1)–N(2)	95.82(6)	O(1)–Co(1)–O(2)	58.71(5)
O(1)–Co(1)–N(2)	140.99(5)	O(3)A–Co(1)–O(2)	168.24(5)
O(3)A–Co(1)–N(2)	101.87(5)	N(2)–Co(1)–O(2)	89.74(5)
O(1W)–Co(1)–N(1)	171.58(6)	N(1)–Co(1)–O(2)	96.84(5)
O(1)–Co(1)–N(1)	85.10(6)	Symmetry code: A: $x + 1, y, z$	

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

3			
Ni(1)–N(1)	2.068(3)	Ni(1)–N(2)	2.042(3)
Ni(1)–O(5)A	2.026(2)	Ni(1)–O(6)B	2.188(2)
Ni(1)–O(1)	2.104(2)	Ni(1)–O(1W)	2.060(2)
Ni(2)–N(5)	2.102(3)	Ni(2)–N(5)C	2.102(3)
Ni(2)–O(3)	2.015(3)	Ni(2)–O(3)C	2.015(3)
Ni(2)–O(2W)	2.103(3)	Ni(2)–O(2W)C	2.103(3)
O(5)A–Ni(1)–N(2)	169.80(11)	O(1W)–Ni(1)–N(1)	170.60(11)
O(5)A–Ni(1)–O(1W)	94.68(10)	O(5)A–Ni(1)–O(1)	91.62(10)
N(2)–Ni(1)–O(1W)	95.40(12)	N(2)–Ni(1)–O(1)	86.34(11)
O(5)A–Ni(1)–N(1)	89.94(11)	O(1W)–Ni(1)–O(1)	93.15(10)
N(2)–Ni(1)–N(1)	80.30(12)	N(1)–Ni(1)–O(1)	94.90(10)
O(5)A–Ni(1)–O(6)B	93.39(9)	N(1)–Ni(1)–O(6)B	85.55(10)
N(2)–Ni(1)–O(6)B	88.80(10)	O(1)–Ni(1)–O(6)B	174.97(9)
O(1W)–Ni(1)–O(6)B	86.01(9)		
O(3)C–Ni(2)–O(3)	94.60(17)	N(5)C–Ni(2)–N(5)	78.81(18)
O(3)C–Ni(2)–N(5)C	168.51(12)	O(3)C–Ni(2)–O(2W)	85.79(11)
O(3)–Ni(2)–N(5)C	93.91(12)	O(3)–Ni(2)–O(2W)	91.86(11)
O(3)C–Ni(2)–N(5)	93.90(12)	N(5)C–Ni(2)–O(2W)	86.23(12)
O(3)–Ni(2)–N(5)	168.51(12)	N(5)–Ni(2)–O(2W)	96.47(12)
O(3)C–Ni(2)–O(2W)C	91.86(10)	N(5)–Ni(2)–O(2W)C	86.23(12)
O(3)–Ni(2)–O(2W)C	85.78(11)	O(2W)–Ni(2)–O(2W)C	176.53(16)
N(5)C–Ni(2)–O(2W)C	96.46(12)		

Symmetry code: A: x, $-y + 1$, $z - 1/2$; B: $-x + 1/2$, $y - 1/2$, $-z + 3/2$; C: $-x$, y, $-z + 3/2$

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

4			
Zn(1)–N(1)	2.1498(19)	Zn(1)–N(2)	2.1946(19)
Zn(1)–O(1)	2.0228(16)	Zn(1)–O(3)A	2.0281(15)
Zn(1)–O(1W)	2.0542(17)	Zn(1)–O(2)	2.5912(17)
O(1)–Zn(1)–O(3)A	116.59(6)	O(1W)–Zn(1)–N(2)	168.89(7)
O(1)–Zn(1)–O(1W)	98.91(7)	N(1)–Zn(1)–N(2)	75.73(7)
O(3)A–Zn(1)–O(1W)	92.58(7)	O(1)–Zn(1)–O(2)	55.39(6)
O(1)–Zn(1)–N(1)	136.63(7)	O(3)A–Zn(1)–O(2)	169.08(6)
O(3)A–Zn(1)–N(1)	104.09(7)	O(1W)–Zn(1)–O(2)	82.13(6)
O(1W)–Zn(1)–N(1)	93.41(7)	N(1)–Zn(1)–O(2)	85.83(6)
O(1)–Zn(1)–N(2)	87.73(7)	N(2)–Zn(1)–O(2)	94.54(6)
O(3)A–Zn(1)–N(2)	92.38(7)	Symmetry code: A: $x - 1, y, z$	

Table S5 Selected bond distances (Å) and angles (deg) for complex **5**.

5			
Cu(1)–O(1)	1.9222(19)	Cu(2)–N(1)	2.024(2)
Cu(1)–O(8)	1.932(2)	Cu(2)–N(2)	1.989(3)
Cu(1)–O(5)	1.945(2)	Cu(2)–O(8)A	2.239(2)
Cu(1)–O(8)A	1.9806(18)	Cu(2)–O(6)	1.945(2)
Cu(1)–O(4)B	2.394(2)	Cu(2)–O(4)B	1.985(2)
Cu(1)–O(8)	1.932(2)		
O(1)–Cu(1)–O(8)	98.37(9)	O(6)–Cu(2)–N(1)	91.07(10)
O(1)–Cu(1)–O(5)	88.14(9)	O(4)B–Cu(2)–N(1)	162.26(11)
O(8)–Cu(1)–O(5)	167.64(10)	O(6)–Cu(2)–O(8)A	87.09(8)
O(1)–Cu(1)–O(8)A	166.99(9)	O(4)B–Cu(2)–O(8)A	89.32(8)
O(8)–Cu(1)–O(8)A	79.30(9)	N(2)–Cu(2)–O(8)A	96.39(9)
O(5)–Cu(1)–O(8)A	91.99(8)	N(1)–Cu(2)–O(8)A	108.07(9)
O(1)–Cu(1)–O(4)B	107.87(9)	N(2)–Cu(2)–N(1)	81.82(10)
O(8)–Cu(1)–O(4)B	101.17(8)	O(6)–Cu(2)–O(4)B	93.34(9)
O(5)–Cu(1)–O(4)B	86.65(9)	O(6)–Cu(2)–N(2)	172.76(9)
O(8)A–Cu(1)–O(4)B	85.12(8)	O(4)B–Cu(2)–N(2)	93.04(10)
Symmetry code: A: $-x + 3/2, -y + 1/2, -z + 1$; B: $-x + 5/2, -y + 1/2, -z + 1$			

Table S6 Selected bond distances (Å) and angles (deg) for complex **6**.

6			
Co(1)–O(1)A	1.984(3)	Co(1)–N(2)	2.146(3)
Co(1)–O(3)B	1.995(3)	Co(1)–N(1)	2.126(3)
Co(1)–O(4)	2.001(3)	O(1)A–Co(1)–N(1)	90.26(12)
O(1)–Co(1)–O(3)B	97.05(11)	O(3)B–Co(1)–N(1)	139.10(10)
O(1)A–Co(1)–O(4)	102.24(11)	O(4)–Co(1)–N(1)	114.43(11)
O(3)B–Co(1)–O(4)	103.24(12)	N(2)–Co(1)–N(1)	76.02(12)
O(1)A–Co(1)–N(2)	161.30(12)	O(4)–Co(1)–N(2)	95.07(11)
O(3)B–Co(1)–N(2)	85.69(11)		
Symmetry code: A: $x-1, y, z$; B: $-x, -y, -z$			

Table S7 Selected bond distances (Å) and angles (deg) for complex **7**.

7			
Ni(1)–O(1)	2.012(3)	Ni(2)–O(7)	2.005(3)
Ni(1)–N(2)	2.075(4)	Ni(2)–N(5)	2.083(4)
Ni(1)–N(1)	2.080(4)	Ni(2)–O(14)#1	2.086(3)
Ni(1)–O(1W)	2.086(3)	Ni(2)–N(6)	2.087(4)
Ni(1)–O(8)	2.108(3)	Ni(2)–O(4)#2	2.087(3)
Ni(1)–O(9)	2.115(3)	Ni(2)–O(3)#2	2.180(3)
Ni(3)–O(10)	2.080(3)	Ni(3)–O(13)#2	2.032(3)
Ni(3)–O(3W)	2.083(3)	Ni(3)–N(9)	2.076(4)
Ni(3)–N(10)	2.094(4)	Ni(3)–O(2W)	2.077(3)
O(1)–Ni(1)–N(2)	90.19(14)	O(7)–Ni(2)–N(5)	90.18(14)
O(1)–Ni(1)–N(1)	169.42(15)	O(7)–Ni(2)–O(14)#1	92.88(14)
N(2)–Ni(1)–N(1)	79.30(15)	N(5)–Ni(2)–O(14)#1	103.57(14)
O(1)–Ni(1)–O(1W)	90.16(13)	O(7)–Ni(2)–N(6)	169.46(15)
N(2)–Ni(1)–O(1W)	97.68(14)	N(5)–Ni(2)–N(6)	79.30(14)
N(1)–Ni(1)–O(1W)	89.99(14)	O(14)#1–Ni(2)–N(6)	90.24(14)
O(1)–Ni(1)–O(8)	95.69(12)	O(7)–Ni(2)–O(4)#2	91.78(13)
N(2)–Ni(1)–O(8)	164.23(14)	N(5)–Ni(2)–O(4)#2	98.40(14)
N(1)–Ni(1)–O(8)	94.80(13)	O(14)#1–Ni(2)–O(4)#2	157.51(12)
O(1W)–Ni(1)–O(8)	96.93(13)	N(6)–Ni(2)–O(4)#2	89.16(14)
O(1)–Ni(1)–O(9)	90.95(13)	O(7)–Ni(2)–O(3)#2	103.31(12)
N(2)–Ni(1)–O(9)	102.69(15)	N(5)–Ni(2)–O(3)#2	155.86(15)
N(1)–Ni(1)–O(9)	92.58(13)	O(14)#1–Ni(2)–O(3)#2	95.74(13)
O(1W)–Ni(1)–O(9)	159.60(13)	N(6)–Ni(2)–O(3)#2	86.37(13)
O(8)–Ni(1)–O(9)	62.69(13)	O(4)#2–Ni(2)–O(3)#2	61.78(13)
O(13)#2–Ni(3)–N(9)	88.84(14)	O(2W)–Ni(3)–O(3W)	85.11(13)
O(13)#2–Ni(3)–O(2W)	94.59(13)	O(10)–Ni(3)–O(3W)	92.43(13)
N(9)–Ni(3)–O(2W)	86.29(15)	O(13)#2–Ni(3)–N(10)	166.70(17)
O(13)#2–Ni(3)–O(10)	90.44(13)	N(9)–Ni(3)–N(10)	78.70(17)
N(9)–Ni(3)–O(10)	96.02(15)	O(2W)–Ni(3)–N(10)	89.28(15)
O(2W)–Ni(3)–O(10)	174.52(12)	O(10)–Ni(3)–N(10)	86.30(15)
O(13)#2–Ni(3)–O(3W)	93.29(13)	O(3W)–Ni(3)–N(10)	99.73(16)
N(9)–Ni(3)–O(3W)	171.27(14)	Symmetry code: A: $x + 1, y, z$; B: $x, -y + 1/2, z - 1/2$	

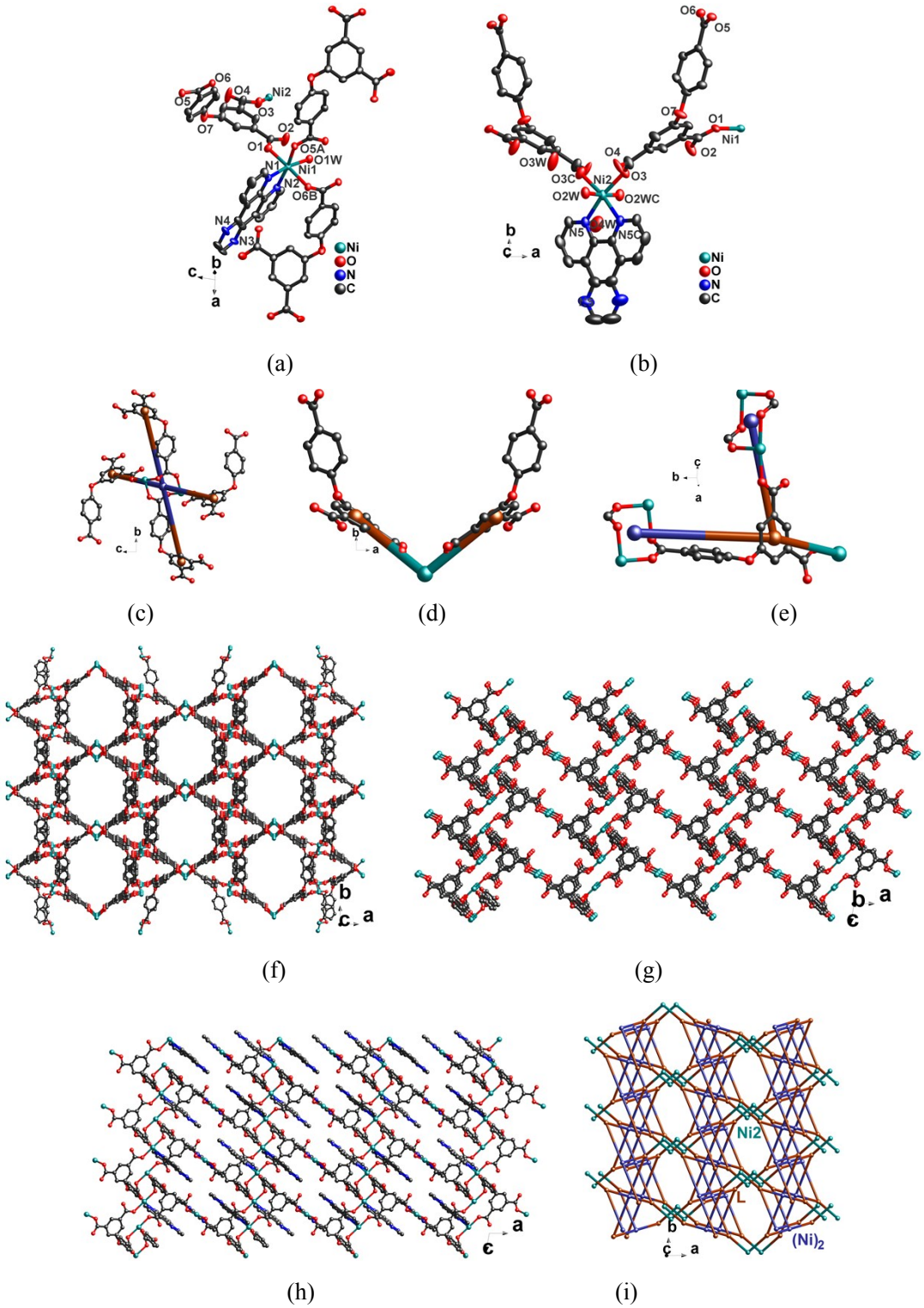


Figure S1. The coordination environments of Ni1 (a) and Ni2 (b) ions in **3**. The connected modes of bimetallic subunit $(Ni1)_2$ (c), Ni2 (d) and L anion (e). 3D framework based on Ni ions and L anions viewed along *c* (f) axis and *b* (g) axis. 3D structure and 3D topology structure viewed along *b* (h) axis and *c* (i) axis.

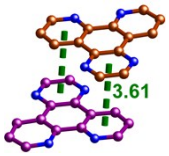
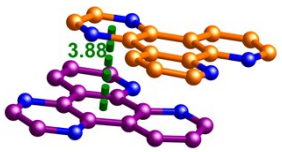
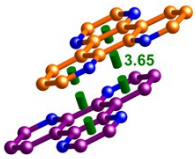
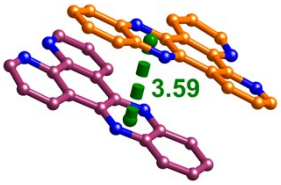
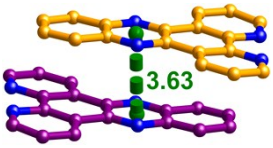
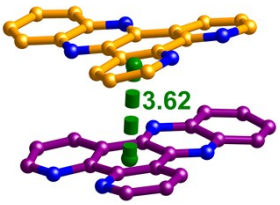
Complexes	π-π Interaction Modes
1	✕
2	
3	
4	
5	
6	
7	

Chart S1 The comparisons of π-π interactions in complexes **1**–**7**.

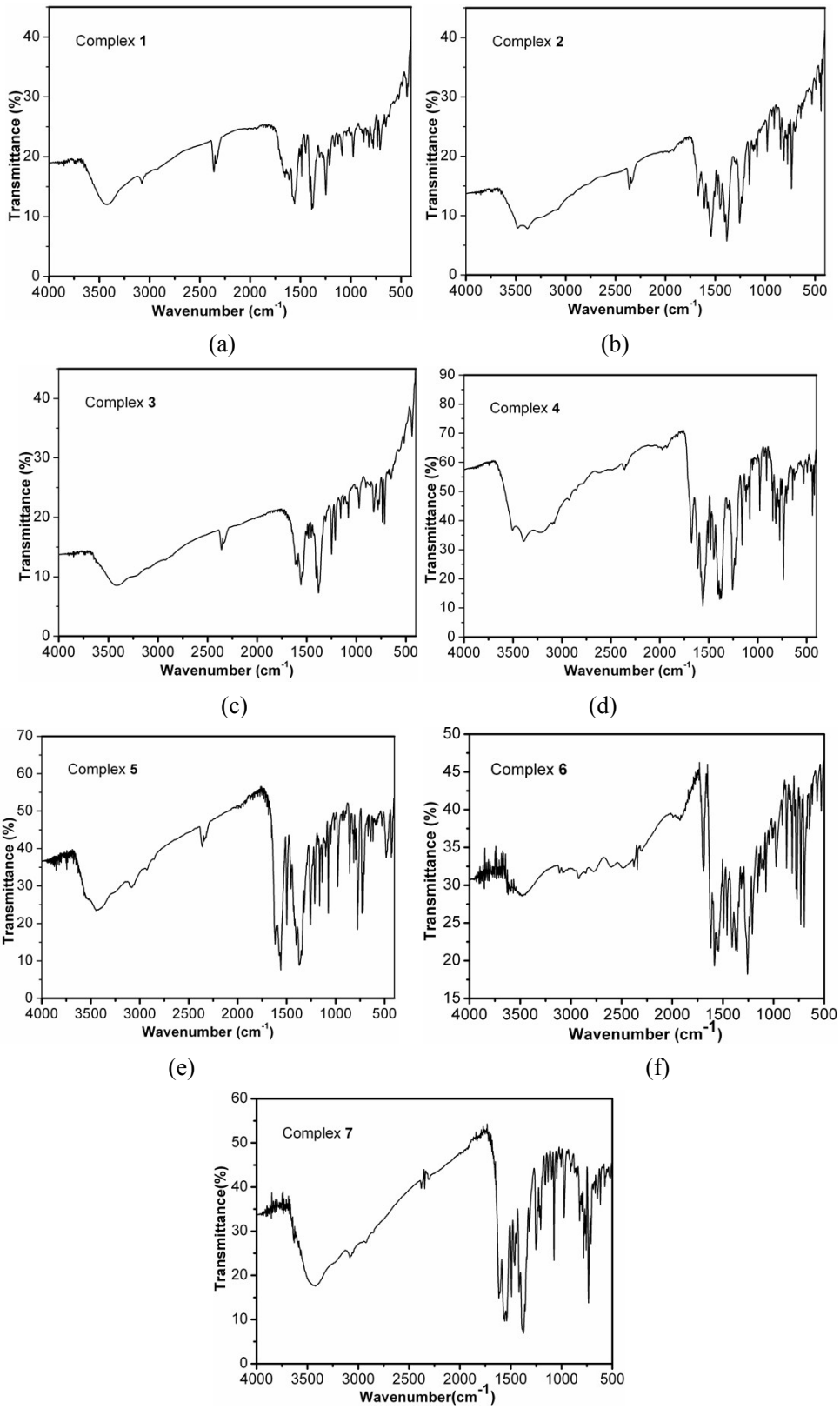


Figure S2 The IR spectra of complexes **1**–**7**.

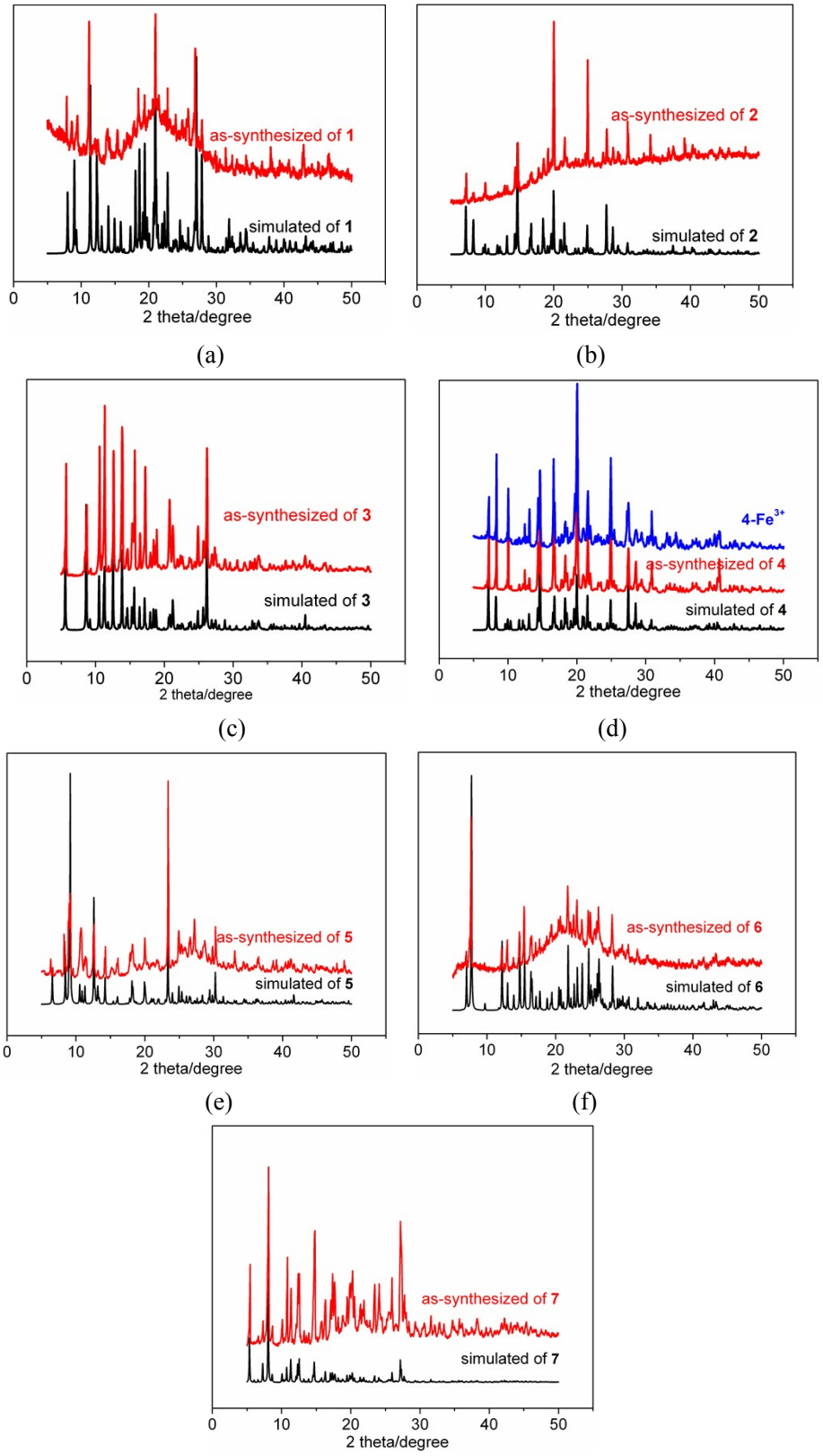


Figure S3 The PXRD patterns of complexes **1**–**7** and the **4**-Fe^{3+}.

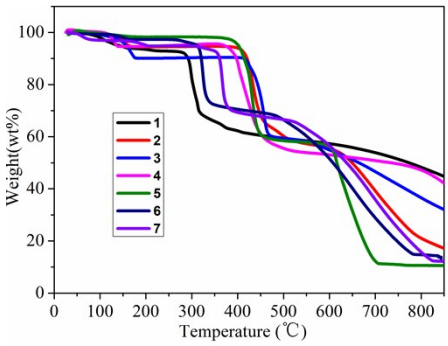


Figure S4 The TG curves of complexes **1**–**7**.

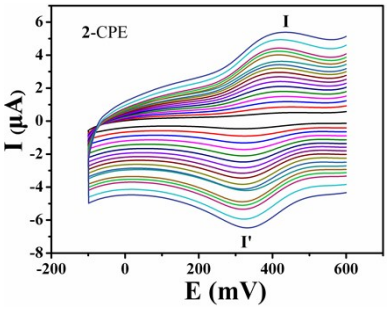
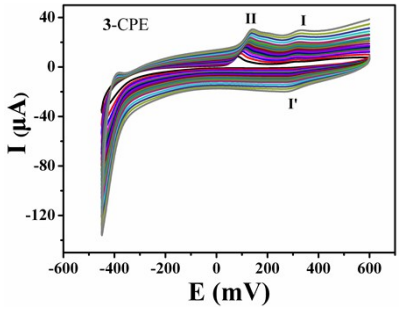
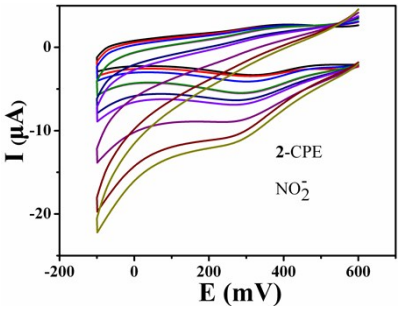
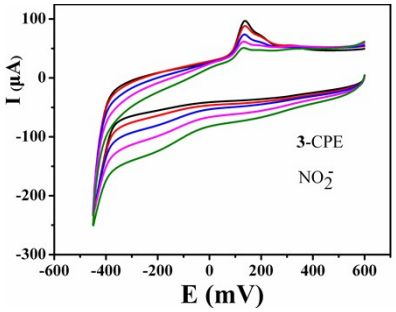
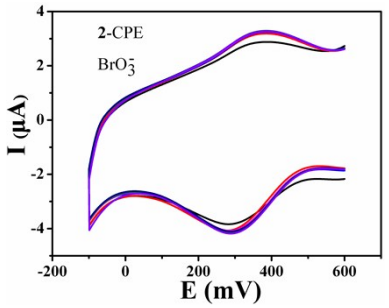
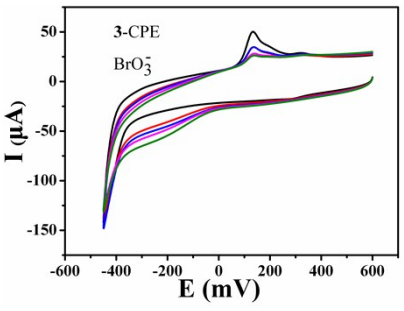
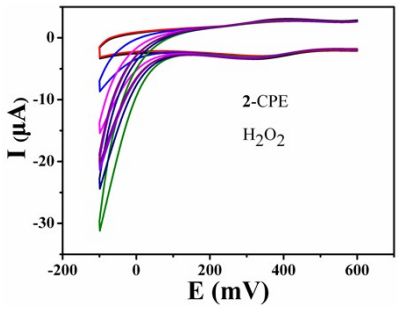
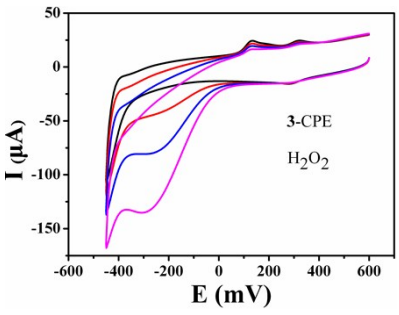
	2-CPE	**3**-CPE
Scan Rate		
NO_2^-		
BrO_3^-		
H_2O_2		

Chart S2 The comparisons of electrochemical activities of **2**-CPE and **3**-CPE.