Polycarboxylate-directed semi-rigid pyridyl-amide-based various Ni^{II} complexes: electrochemical properties and enhancements of photocatalytic activities by calcination

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Table S1 Selected bond distances (Å) and angles (°) for **1**–**4**.

1 $C_{26}H_{28}N_4NiO_{10}S$			
Ni(1)–O(2W)	2.0593(16)	Ni(1)–O(2W)#1	2.0593(16)
Ni(1)–O(1W)	2.0737(15)	Ni(1)–O(1W)#1	2.0736(15)
Ni(1)–N(1)	2.1278(18)	Ni(1)–N(1)#1	2.1277(18)
O(2W)–Ni(1)–O(2W)#1	180.0	O(1W)#1–Ni(1)–N(1)#1	91.24(7)
O(2W)–Ni(1)–O(1W)#1	86.07(6)	O(1W)–Ni(1)–N(1)#1	88.76(7)
O(2W)#1–Ni(1)–O(1W)#1	93.93(6)	O(2W)–Ni(1)–N(1)	96.47(7)
O(2W)–Ni(1)–O(1W)	93.93(6)	O(2W)#1–Ni(1)–N(1)	83.53(7)
O(2W)#1–Ni(1)–O(1W)	86.07(6)	O(1W)#1–Ni(1)–N(1)	88.76(7)
O(1W)#1–Ni(1)–O(1W)	179.999(1)	O(1W)–Ni(1)–N(1)	91.24(7)
O(2W)–Ni(1)–N(1)#1	83.53(7)	N(1)#1–Ni(1)–N(1)	180.0
O(2W)#1–Ni(1)–N(1)#1	96.47(7)		
O(2W)–Ni(1)–O(2W)#1	180.0	O(1W)#1–Ni(1)–N(1)#1	91.24(7)
O(2W)–Ni(1)–O(1W)#1	86.07(6)	O(1W)–Ni(1)–N(1)#1	88.76(7)
O(2W)#1–Ni(1)–O(1W)#1	93.93(6)	O(2W)–Ni(1)–N(1)	96.47(7)
Symmetry code for 1: #1 –x, –y + 1, –z + 1			
2 $C_{56}H_{62}N_8Ni_2O_{21}$			
Ni(1)–O(7)#1	2.049(2)	Ni(2)–O(5)	2.040(2)
Ni(1)–O(1)	2.051(2)	Ni(2)–O(3)	2.046(2)
Ni(1)–O(2W)	2.072(2)	Ni(2)–O(3W)	2.065(2)
Ni(1)–O(1W)	2.086(2)	Ni(2)–O(4W)	2.111(2)
Ni(1)–N(5)	2.114(3)	Ni(2)–N(7)	2.110(3)
Ni(1)–N(1)	2.120(3)	Ni(2)–N(4)#2	2.129(3)
O(7)#1–Ni(1)–O(1)	178.71(9)	O(5)–Ni(2)–O(3)	177.47(9)
O(7)#1–Ni(1)–O(2W)	88.10(9)	O(5)–Ni(2)–O(3W)	92.80(9)
O(1)–Ni(1)–O(2W)	91.52(9)	O(3)–Ni(2)–O(3W)	88.84(9)
O(7)#1–Ni(1)–O(1W)	91.55(10)	O(5)–Ni(2)–N(7)	92.94(10)
O(1)–Ni(1)–O(1W)	88.89(10)	O(3)–Ni(2)–N(7)	89.04(9)
O(2W)–Ni(1)–O(1W)	177.04(10)	O(3W)–Ni(2)–N(7)	88.14(11)
O(7)#1–Ni(1)–N(5)	89.73(10)	O(5)–Ni(2)–O(4W)	85.55(9)
O(1)–Ni(1)–N(5)	89.08(10)	O(3)–Ni(2)–O(4W)	92.91(9)

O(2W)–Ni(1)–N(5)	95.98(10)	O(3W)–Ni(2)–O(4W)	176.65(9)
O(1W)–Ni(1)–N(5)	86.95(11)	N(7)–Ni(2)–O(4W)	89.03(10)
O(7)#1–Ni(1)–N(1)	91.49(10)	O(5)–Ni(2)–N(4)#2	87.19(10)
O(1)–Ni(1)–N(1)	89.71(10)	O(3)–Ni(2)–N(4)#2	90.79(10)
O(2W)–Ni(1)–N(1)	87.03(10)	O(3W)–Ni(2)–N(4)#2	93.16(11)
O(1W)–Ni(1)–N(1)	90.04(11)	N(7)–Ni(2)–N(4)#2	178.69(10)
N(5)–Ni(1)–N(1)	176.79(11)	O(4W)–Ni(2)–N(4)#2	89.68(10)

Symmetry code for 2: #1 $x + 1, y, z + 1$, #2 $–x – 1, –y + 2, –z – 1$.

3 $C_{58}H_{58}N_8Ni_2O_{17}$

Ni(1)–O(1)	2.0234(17)	Ni(2)–O(5)#1	2.0237(18)
Ni(1)–O(1W)	2.0598(19)	Ni(2)–O(2W)	2.054(2)
Ni(1)–N(2)	2.116(2)	Ni(2)–N(4)	2.118(2)
Ni(1)–N(1)	2.120(2)	Ni(2)–N(3)	2.129(2)
Ni(1)–O(11)	2.1436(18)	Ni(2)–O(3)	2.1351(19)
Ni(1)–O(12)	2.1444(17)	Ni(2)–O(4)	2.1438(17)
O(1)–Ni(1)–O(1W)	97.86(8)	O(5)#1–Ni(2)–O(2W)	97.20(8)
O(1)–Ni(1)–N(2)	88.29(8)	O(5)#1–Ni(2)–N(4)	89.29(8)
O(1W)–Ni(1)–N(2)	92.09(9)	O(2W)–Ni(2)–N(4)	92.45(9)
O(1)–Ni(1)–N(1)	93.33(8)	O(5)#1–Ni(2)–N(3)	93.34(8)
O(1W)–Ni(1)–N(1)	87.55(8)	O(2W)–Ni(2)–N(3)	87.68(9)
N(2)–Ni(1)–N(1)	178.38(8)	N(4)–Ni(2)–N(3)	177.33(8)
O(1)–Ni(1)–O(11)	98.59(7)	O(5)#1–Ni(2)–O(3)	98.37(8)
O(1W)–Ni(1)–O(11)	163.54(7)	O(2W)–Ni(2)–O(3)	164.42(7)
N(2)–Ni(1)–O(11)	88.75(8)	N(4)–Ni(2)–O(3)	87.39(9)
N(1)–Ni(1)–O(11)	91.15(8)	N(3)–Ni(2)–O(3)	91.77(8)
O(1)–Ni(1)–O(12)	159.70(8)	O(5)#1–Ni(2)–O(4)	159.62(8)
O(1W)–Ni(1)–O(12)	102.14(7)	O(2W)–Ni(2)–O(4)	102.91(7)
N(2)–Ni(1)–O(12)	87.56(8)	N(4)–Ni(2)–O(4)	86.64(8)
N(1)–Ni(1)–O(12)	90.97(8)	N(3)–Ni(2)–O(4)	90.73(8)
O(11)–Ni(1)–O(12)	61.46(7)	O(3)–Ni(2)–O(4)	61.52(7)
O(1)–Ni(1)–C(48)	129.27(8)	O(5)#1–Ni(2)–C(9)	129.03(8)
O(1W)–Ni(1)–C(48)	132.80(8)	O(2W)–Ni(2)–C(9)	133.67(8)
N(2)–Ni(1)–C(48)	87.59(8)	N(4)–Ni(2)–C(9)	86.10(8)
N(1)–Ni(1)–C(48)	91.50(8)	N(3)–Ni(2)–C(9)	91.88(8)
O(11)–Ni(1)–C(48)	30.79(7)	O(3)–Ni(2)–C(9)	30.76(7)
O(12)–Ni(1)–C(48)	30.67(7)	O(4)–Ni(2)–C(9)	30.76(7)

Symmetry code for 3: #1 $x – 1, y, z – 1$

4 $C_{78}H_{76}N_{12}Ni_3O_{26}$

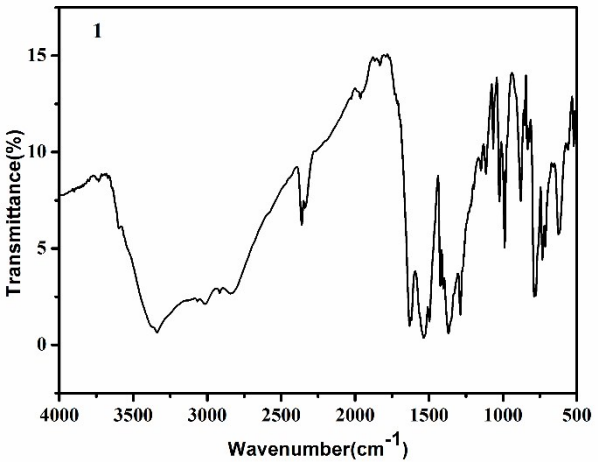
Ni(1)–O(1)#1	2.0334(17)	Ni(2)–O(3)#2	2.0232(17)
Ni(1)–O(1)	2.0334(17)	Ni(2)–O(2W)	2.038(2)
Ni(1)–O(1W)#1	2.0992(18)	Ni(2)–N(6)	2.106(2)
Ni(1)–O(1W)	2.0993(18)	Ni(2)–N(3)	2.107(2)
Ni(1)–N(1)	2.133(2)	Ni(2)–O(6)	2.1196(17)
O(1)#1–Ni(1)–O(1)	180.0	O(3)#2–Ni(2)–O(2W)	89.30(8)

O(1)#1–Ni(1)–O(1W)#1	90.37(7)	O(3)#2–Ni(2)–N(6)	109.54(8)
O(1)–Ni(1)–O(1W)#1	89.63(7)	O(2W)–Ni(2)–N(6)	90.94(9)
O(1)#1–Ni(1)–O(1W)	89.63(7)	O(3)#2–Ni(2)–N(3)	93.03(8)
O(1)–Ni(1)–O(1W)	90.37(7)	O(2W)–Ni(2)–N(3)	174.26(9)
O(1W)#1–Ni(1)–O(1W)	180.0	N(6)–Ni(2)–N(3)	93.22(9)
O(1)#1–Ni(1)–N(1)	92.69(8)	O(3)#2–Ni(2)–O(6)	156.32(7)
O(1)–Ni(1)–N(1)	87.31(8)	O(2W)–Ni(2)–O(6)	84.13(8)
O(1W)#1–Ni(1)–N(1)	92.19(8)	N(6)–Ni(2)–O(6)	93.34(8)
O(1W)–Ni(1)–N(1)	87.81(8)	N(3)–Ni(2)–O(6)	91.67(8)
O(1)#1–Ni(1)–N(1)#1	87.31(8)	O(3)#2–Ni(2)–O(5)	97.28(7)
O(1)–Ni(1)–N(1)#1	92.69(8)	O(2W)–Ni(2)–O(5)	86.99(8)
O(1W)#1–Ni(1)–N(1)#1	87.81(8)	N(6)–Ni(2)–O(5)	153.08(8)
O(1W)–Ni(1)–N(1)#1	92.19(8)	N(3)–Ni(2)–O(5)	87.51(8)
N(1)–Ni(1)–N(1)#1	179.999(1)	O(6)–Ni(2)–O(5)	59.74(7)

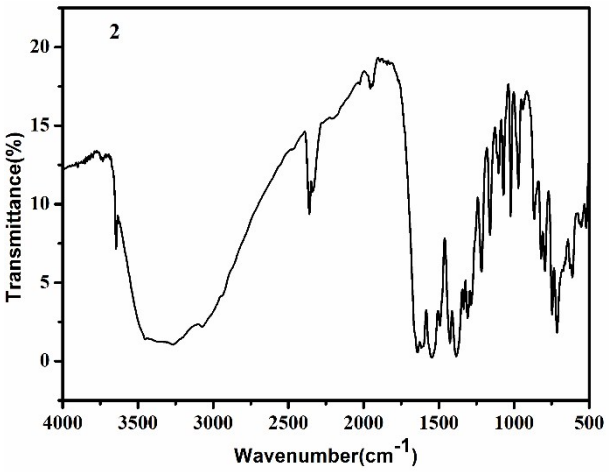
Symmetry code for 4: #1 $-x, -y + 2, -z + 1$, #2 $x + 1, y, z$, #3 $x - 1, y, z$.

Table S2 The contents of different elements in Ni@NC 1 and Ni@NC 4

	Ni@NC 1	Ni@NC 4
Ni%	54.41	63.84
C%	38.33	30.86
N%	2.06	0.86
O%	2.02	3.77
H%	0.52	0.67
S%	2.66	0



(a)



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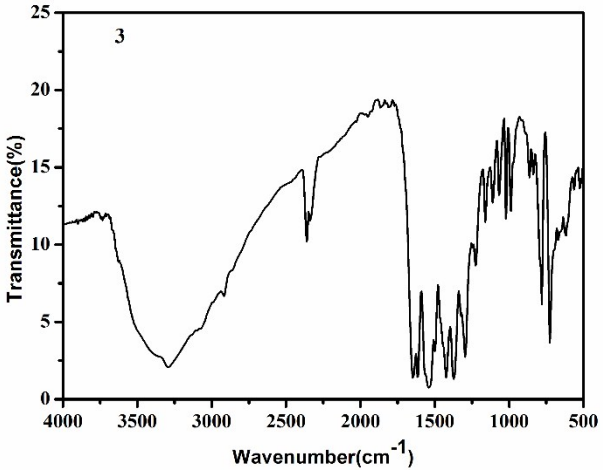
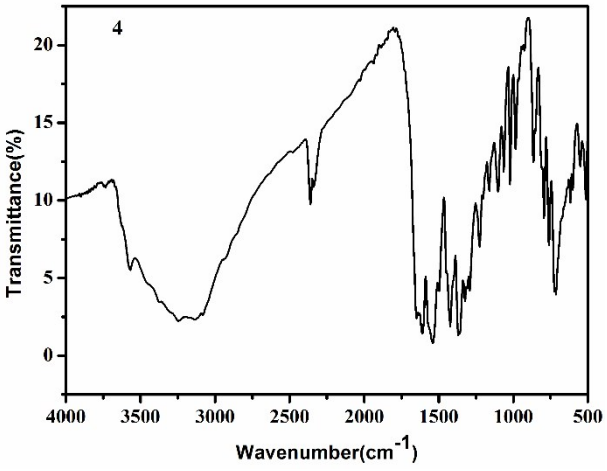


(c)



(d)

Fig. S1. The IR spectra of complexes 1–4**.**

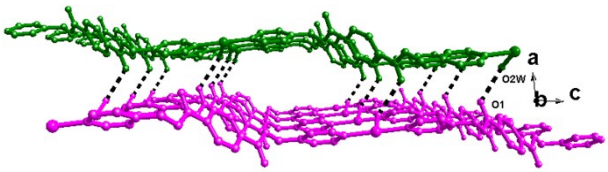


Fig. S2 3D supramolecular framework of complex **1.**

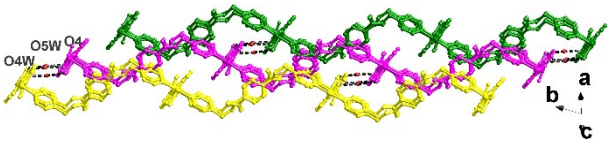


Fig. S3 3D supramolecular framework of **2.**

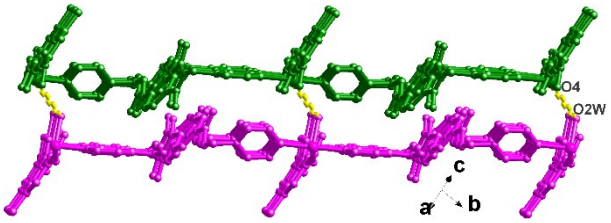


Fig. S4 3D supramolecular framework of **3**.

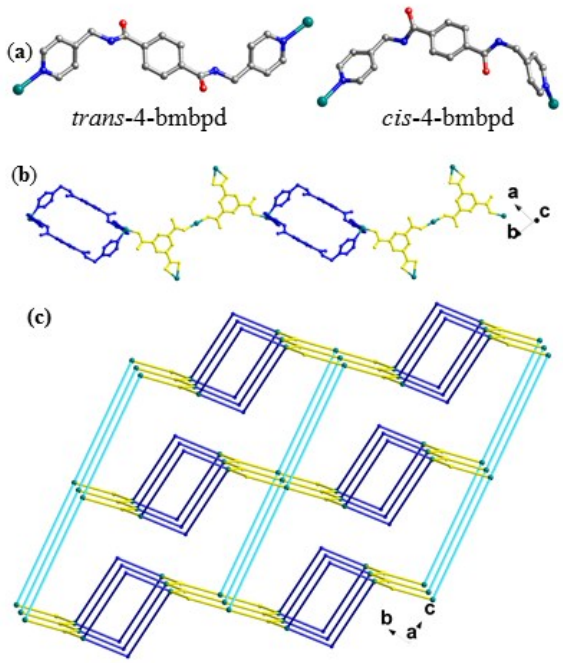
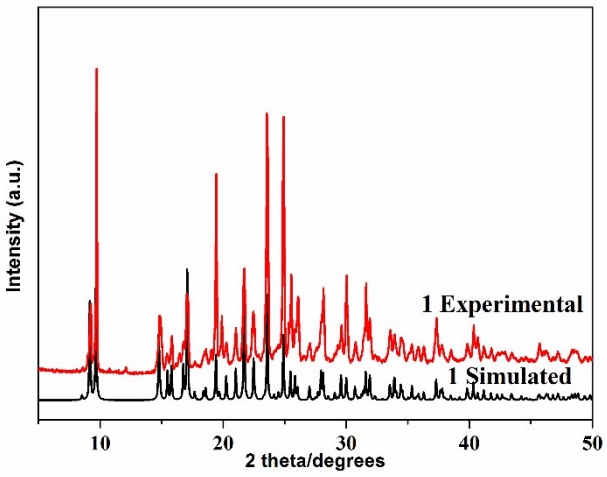
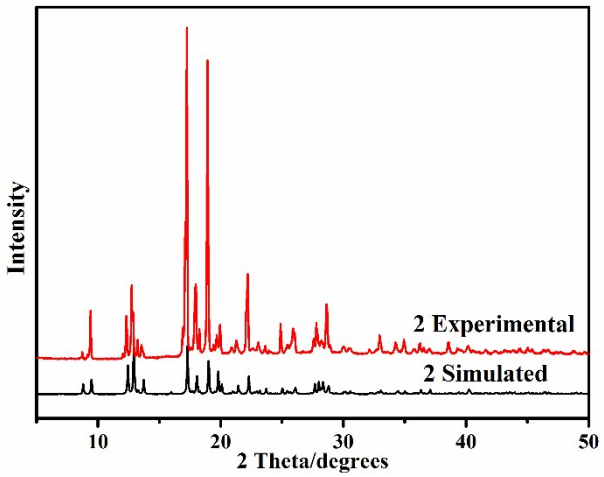


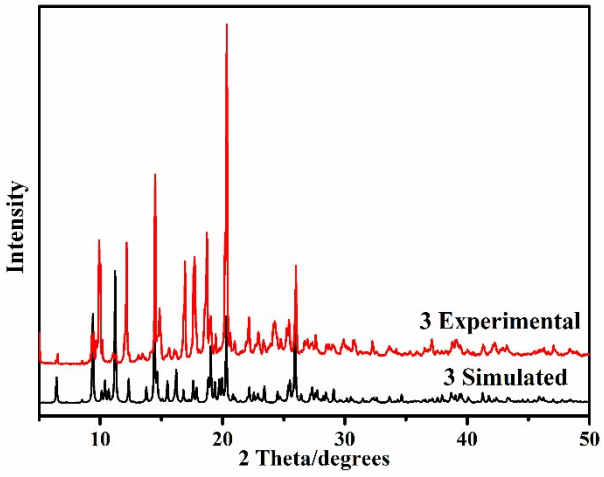
Fig. S5. (a) The coordination modes of the *trans*- and *cis*-4-bmbpd ligand in **4.** (b) The 1D chain in 4. (c) The simplified 3D (2,3,4,4)-connected framework of **4**.


Intensity (a.u.)
1 Experimental
1 Simulated
10
20
30
40
50
2 theta/degrees

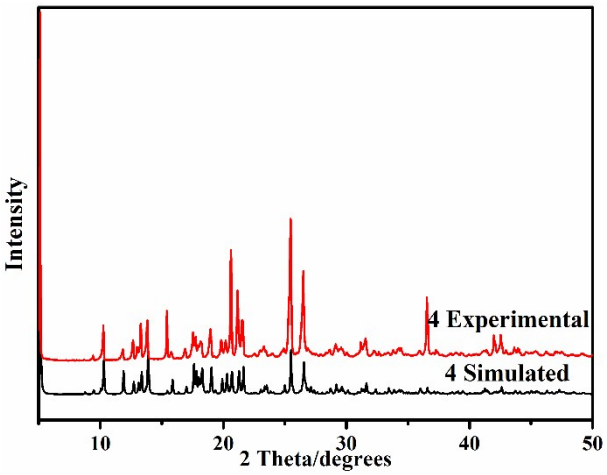
(a)


Intensity
2 Experimental
2 Simulated
10
20
30
40
50
2 Theta/degrees

(b)


Intensity
3 Experimental
3 Simulated
10
20
30
40
50
2 Theta/degrees

(c)



(d)

Fig. S6. The PXRD patterns of complexes **1–4.**

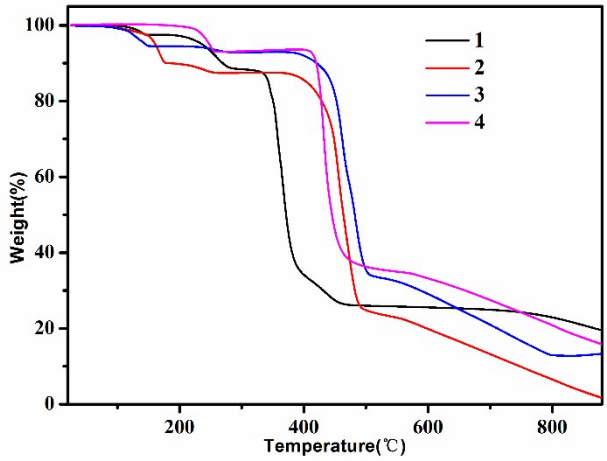
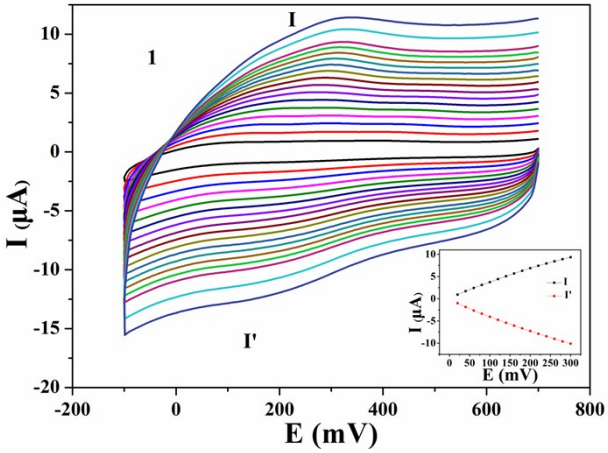
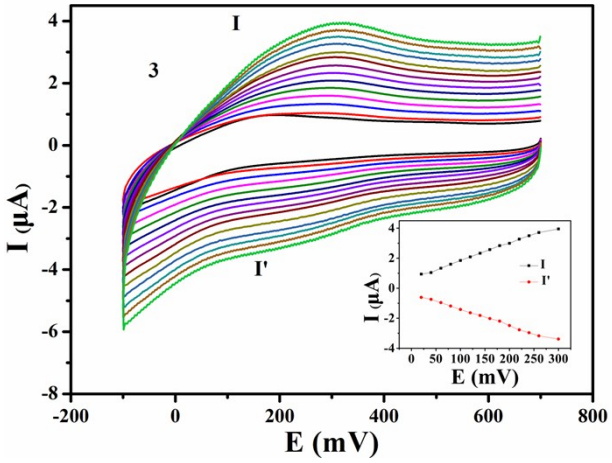


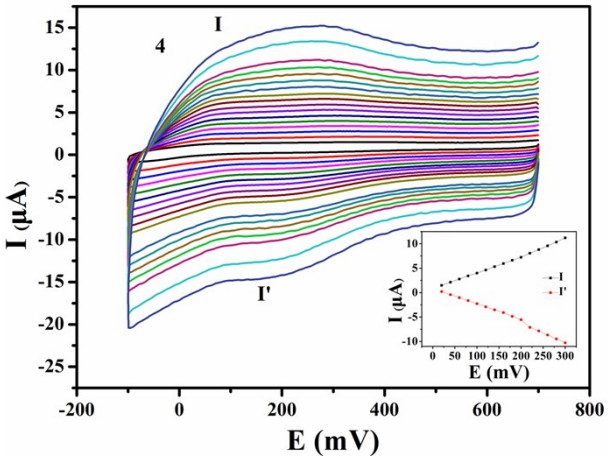
Fig. S7. The TG curves of complexes **1–4.**



(a)



(b)



(c)

Fig. S8. The cyclic voltammograms of **1**−CPE, **3**−CPE and **4**−CPE at different scan rates.

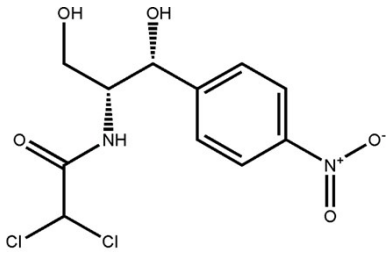


Fig. S9. The chemical structure of CAP**.**

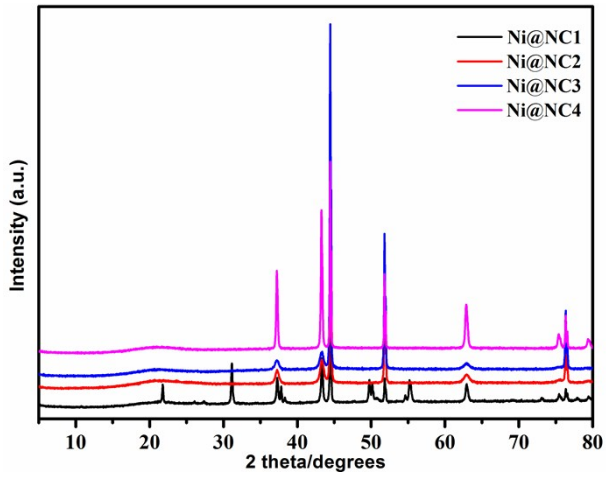


Fig. S10. The PXRD patterns of **Ni@NC1–4.**

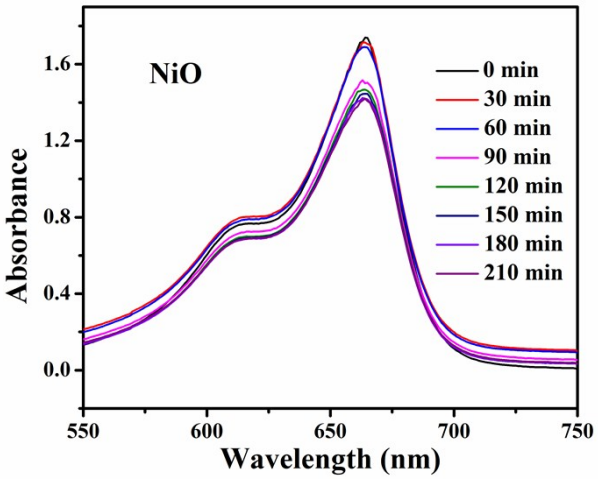


Fig. S11. Absorption spectra of the MB solution at the presence of NiO under UV irradiation.