Supporting Information

Pyridine polymer tubular connected with Polyoxometalates as bifunctional electrocatalysts for water Splitting

*Jihua Wang**, Hui Li**, Lige Gong*,Limin Dong, Yunhao Gu, Meijia Wang, BingHe Yang*

School of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin, 150080, China.School of Materials Science and Chemical Engineering, Harbin University of Science and Technology, Harbin, 150080, China. .*Corresponding author; **Co-author

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Electrode preparation

A mixture of active material and carbon black in a mass ratio of 2:1 was prepared, and thoroughly ground for 30 minutes. 5mg mixture was dissolved in a mixed solution of 100μL water and ethanol (1:3), and ultrasonic for 30 minutes to ensure uniform dispersion. Subsequently, the paste was coated onto a 1×1 cm^2 carbon cloth, dispense 10 μL of Nafion and dried.

Table S1. Selected bond lengths (Å) and bond angles (°) for compound 1.

Mo1-O6	1.635(11)	Mo1-O16	2.000(12)	Mo1-O18	1.817(11)
Mo1-O13	1.972(11)	Mo1-O2	1.820(12)	Mo1-O19	2.510(11)
Mo2-O12	1.988(11)	Mo2-O3	1.669(10)	Mo2-O7	1.796(11)
Mo2-O15	1.762(14)	Mo2-O2	1.997(13)	Mo2-O17	2.433(11)
Mo3-O1	1.658(10)	Mo3-O12	1.842(13)	Mo3-O14	2.003(13)
Mo3-O11	1.820(13)	Mo3-O17	2.493(11)	Mo3-O9	1.950(13)
Mo3-O5	2.502(11)	Mo4-O10	1.669(11)	Mo4-O16	1.816(12)
Mo4-O20	1.973(11)	Mo4-O15	2.012(13)	Mo4-O17	2.464(11)
Mo4-O9	1.829(13)	Mo4-O19	2.500(11)	Mo5-O4	1.648(10)
Mo5-O14	1.798(12)	Mo5-O21	1.946(12)	Mo5-O13	1.839(12)
Mo5-O7	2.015(11)	Mo5-O5	2.461(11)	Mo6-O8	1.678(10)
Mo6-O18	1.966(11)	Mo6-O20	1.808(12)	Mo6-O21	1.840(13)
Mo6-O11	1.952(12)	Mo6-O19	2.491(11)	Mo6-O5	2.447(11)
P1-O17	1.544(11)	P1-O19	1.469(11)	P1-O5	1.530(11)
O12-Mo2	1.988(11)	O13-Mo1	1.972(11)	O2-Mo2	1.997(13)
O17-Mo2	2.433(11)	O17-Mo4	2.464(11)	O17-O19	1.728(15)
O9-Mo3	1.950(13)	O19-O17	1.728(15)	O19-O5	1.737(15)
O5-Mo3	2.502(11)	O5-Mo5	2.461(11)	O5-Mo6	2.447(11)
O5-O19	1.737(15)	N2-C1	1.38(2)	N2-C4	1.37(2)
C1-H1	0.95	C1-C4	1.35(2)	C4-C1	1.35(2)
C4-H4	0.95	C6-H6	0.95	C6-C7	1.29(3)
C6-N1	1.33(3)	C7-H7	0.95	C7-C3	1.39(3)
N1-C2	1.20(4)	C2-H2	0.95	C2-C5	1.27(3)
C5-H5	0.95	C5-C3	1.47(4)	C3-H3	0.95
O6-Mo1-O16	99.0(7)	O6-Mo1-O18	103.8(7)	O6-Mo1-O13	100.1(7)
O6-Mo1-O2	102.6(7)	O6-Mo1-O19	158.7(6)	O16-Mo1-O19	63.9(5)
O18-Mo1-O16	85.4(5)	O18-Mo1-O13	153.7(6)	O18-Mo1-O2	96.6(6)
O18-Mo1-O19	64.1(5)	O13-Mo1-O16	80.2(5)	O13-Mo1-O19	89.7(5)
O2-Mo1-O16	157.2(7)	O2-Mo1-O13	88.7(5)	O2-Mo1-O19	96.4(6)
O12-Mo2-O2	81.5(6)	O12-Mo2-O17	64.6(5)	O3-Mo2-O12	97.6(6)
O3-Mo2-O7	103.4(7)	O3-Mo2-O15	103.0(7)	O3-Mo2-O2	99.2(6)
O3-Mo2-O17	157.5(5)	O7-Mo2-O12	157.6(7)	O7-Mo2-O2	87.6(5)
O7-Mo2-O17	96.6(6)	O15-Mo2-O12	86.5(5)	O15-Mo2-O7	96.1(6)
O15-Mo2-O2	155.9(7)	O15-Mo2-O17	64.1(6)	O2-Mo2-O17	91.8(5)
O1-Mo3-O12	101.6(6)	O1-Mo3-O14	100.9(6)	O1-Mo3-O11	103.0(7)
O1-Mo3-O17	159.5(5)	O1-Mo3-O9	102.6(7)	O1-Mo3-O5	157.5(5)
O12-Mo3-O14	156.1(7)	O12-Mo3-O17	64.9(5)	O12-Mo3-O9	86.5(5)
O12-Mo3-O5	97.4(6)	O14-Mo3-O17	91.2(6)	O14-Mo3-O5	62.8(5)
O11-Mo3-O12	96.6(7)	O11-Mo3-O14	86.3(5)	O11-Mo3-O17	94.2(7)
O11-Mo3-O9	152.9(8)	O11-Mo3-O5	62.5(6)	O17-Mo3-O5	42.7(3)

O9-Mo3-O14	80.7(6)	O9-Mo3-O17	62.7(5)	O9-Mo3-O5	90.4(6)
O10-Mo4-O16	103.5(7)	O10-Mo4-O20	101.3(6)	O10-Mo4-O15	100.7(6)
O10-Mo4-O17	157.2(6)	O10-Mo4-O9	103.0(7)	O10-Mo4-O19	160.7(5)
O16-Mo4-O20	87.5(5)	O16-Mo4-O15	154.5(7)	O16-Mo4-O17	97.1(6)
O16-Mo4-O9	96.0(6)	O16-Mo4-O19	66.2(5)	O20-Mo4-O15	80.0(5)
O20-Mo4-O17	89.2(5)	O20-Mo4-O19	63.2(5)	O15-Mo4-O17	60.8(5)
O15-Mo4-O19	88.3(5)	O17-Mo4-O19	40.7(4)	O9-Mo4-O20	153.9(7)
O9-Mo4-O15	86.1(5)	O9-Mo4-O17	64.7(6)	O9-Mo4-O19	94.5(6)
O4-Mo5-O14	103.5(7)	O4-Mo5-O21	101.3(6)	O4-Mo5-O13	102.6(6)
O4-Mo5-O7	100.3(6)	O4-Mo5-O5	160.2(5)	O14-Mo5-O21	89.7(6)
O14-Mo5-O13	94.4(6)	O14-Mo5-O7	155.4(7)	O14-Mo5-O5	66.0(6)
O21-Mo5-O7	79.5(6)	O21-Mo5-O5	63.3(5)	O13-Mo5-O21	154.0(7)
O13-Mo5-O7	86.5(5)	O13-Mo5-O5	95.1(6)	O7-Mo5-O5	89.4(5)
O8-Mo6-O18	99.8(6)	O8-Mo6-O20	102.6(7)	O8-Mo6-O21	103.7(7)
O8-Mo6-O11	101.5(7)	O8-Mo6-O19	158.4(5)	O8-Mo6-O5	159.4(5)
O18-Mo6-O19	63.0(5)	O18-Mo6-O5	90.8(5)	O20-Mo6-O18	86.1(5)
O20-Mo6-O21	95.0(6)	O20-Mo6-O11	154.4(8)	O20-Mo6-O19	65.2(5)
O20-Mo6-O5	95.7(6)	O21-Mo6-O18	155.6(6)	O21-Mo6-O11	87.5(5)
O21-Mo6-O19	95.4(6)	O21-Mo6-O5	64.8(5)	O11-Mo6-O18	81.5(6)
O11-Mo6-O19	89.2(7)	O11-Mo6-O5	62.4(6)	O5-Mo6-O19	41.2(3)
O17-P1-O17	180.0(11)	O19-P1-O17	110.1(6)	O19-P1-O17	69.9(6)
O19-P1-O19	180.0(11)	O19-P1-O5	70.8(6)	O19-P1-O5	109.2(6)
O5-P1-O17	72.6(6)	O5-P1-O17	107.4(6)	O5-P1-O5	180.0(12)
Mo3-O12-Mo2	137.4(8)	Mo5-O14-Mo3	138.9(9)	Mo4-O16-Mo1	138.5(8)
Mo1-O18-Mo6	141.4(7)	Mo6-O20-Mo4	140.0(7)	Mo6-O21-Mo5	138.6(9)
Mo3-O11-Mo6	142.3(10)	Mo5-O13-Mo1	139.3(8)	Mo2-O7-Mo5	139.5(8)
Mo2-O15-Mo4	141.2(9)	Mo1-O2-Mo2	136.9(9)	Mo2-O17-Mo3	92.8(4)
Mo2-O17-Mo4	93.3(4)	Mo4-O17-Mo3	91.7(4)	P1-O17-Mo2	124.6(6)
P1-O17-Mo3	122.1(6)	P1-O17-Mo4	123.5(6)	P1-O17-O19	53.0(5)
O19-O17-Mo2	129.2(7)	O19-O17-Mo3	133.9(6)	O19-O17-Mo4	70.7(5)
Mo4-O9-Mo3	140.6(9)	Mo4-O19-Mo1	90.9(4)	Mo6-O19-Mo1	91.1(4)
Mo6-O19-Mo4	90.8(4)	P1-O19-Mo1	124.2(6)	P1-O19-Mo4	125.3(6)
P1-O19-Mo6	124.2(6)	P1-O19-O17	57.1(5)	P1-O19-O5	56.3(5)
O17-O19-Mo1	136.2(7)	O17-O19-Mo4	68.5(5)	O17-O19-Mo6	125.9(6)
O17-O19-O5	91.3(7)	O5-O19-Mo1	127.5(7)	O5-O19-Mo4	134.5(7)
O5-O19-Mo6	68.1(5)	Mo5-O5-Mo3	91.6(4)	Mo6-O5-Mo3	92.3(4)
Mo6-O5-Mo5	92.3(4)	P1-O5-Mo3	122.3(6)	P1-O5-Mo5	125.4(6)
P1-O5-Mo6	123.6(6)	P1-O5-O19	53.0(5)	O19-O5-Mo3	127.0(7)
O19-O5-Mo5	137.1(7)	O19-O5-Mo6	70.8(5)	C4-N2-C1	118.2(14)
N2-C1-H1	119.1	C4-C1-N2	121.8(15)	C4-C1-H1	119.1
N2-C4-H4	120	C1-C4-N2	120.0(15)	C1-C4-H4	120
C7-C6-H6	119.4	C7-C6-N1	121(2)	N1-C6-H6	119.4
C6-C7-H7	119.1	C6-C7-C3	122(2)	C3-C7-H7	119.1

C2-N1-C6	120(3)	N1-C2-H2	116.9	N1-C2-C5	126(2)
C5-C2-H2	116.9	C2-C5-H5	120.5	C2-C5-C3	119.0(18)
C3-C5-H5	120.5	C7-C3-C5	111(2)	C7-C3-H3	124.5
C5-C3-H3	124.5				

Table S2. Selected bond lengths (Å) and bond angles (°) for compound 2.

Mo1-O2	1.919(12)	Mo1-O7	1.810(12)	Mo1-O10	1.659(11)
Mo1-O13	1.940(13)	Mo1-O14	1.876(13)	Mo1-O21	2.403(13)
Mo2-O4	1.954(10)	Mo2-O9	1.855(11)	Mo2-O12	1.649(11)
Mo2-O16	1.937(12)	Mo2-O19	1.800(14)	Mo2-O22	2.390(13)
Mo3-O2	1.845(11)	Mo3-O6	1.645(11)	Mo3-O16	1.853(13)
Mo3-O18	1.961(13)	Mo3-O20	1.891(14)	Mo3-O22	2.403(14)
Mo4-O4	1.822(11)	Mo4-O8	1.968(10)	Mo4-O11	1.650(10)
Mo4-O13	1.828(12)	Mo4-O15	1.925(11)	Mo4-O21	2.400(13)
Mo5-O1	1.660(13)	Mo5-O8	1.829(10)	Mo5-O9	1.935(10)
Mo6-O3	1.675(14)	Mo6-O7	1.972(13)	Mo6-O15	1.840(13)
Mo6-O21	2.491(14)	Mo7-O5	1.659(13)	Mo7-O19	1.953(15)
Mo7-O20	1.863(15)	O14-Mo8	1.920(10)	Mo8-O14	1.920(10)
Mo8-O17	1.649(17)	Mo8-O18	1.823(11)	P1-O21	1.579(14)
P1-O22	1.566(14)	N1-H1	0.88	N1-C3	1.328(18)
N1-C5	1.37(2)	C1-H1A	0.95	C1-C2	1.34(2)
C1-C4	1.37(2)	C2-H2	0.95	C2-C5	1.39(2)
C3-H3	0.95	C3-C4	1.39(2)	C4-H4	0.95
C5-H5	0.95	C6-H6	0.95	C6-C7	1.31(2)
C6-C10	1.36(3)	C7-H7	0.95	C7-N2	1.36(3)
C8-H8	0.95	C8-C9	1.32(3)	C8-N2	1.36(3)
C9-H9	0.95	C9-C10	1.40(3)	C10-H10	0.95
N2-H2A	0.88	O2-Mo1-O13	82.0(6)	O2-Mo1-O21	88.8(6)
O7-Mo1-O2	153.6(7)	O7-Mo1-O13	86.8(6)	O7-Mo1-O14	93.0(6)
O7-Mo1-O21	64.9(6)	O10-Mo1-O2	102.2(6)	O10-Mo1-O7	103.4(7)
O10-Mo1-O13	100.7(6)	O10-Mo1-O14	102.5(5)	O10-Mo1-O21	157.9(5)
O13-Mo1-O21	61.4(6)	O14-Mo1-O2	87.8(5)	O14-Mo1-O13	156.1(7)
O14-Mo1-O21	97.0(5)	O4-Mo2-O22	88.0(6)	O9-Mo2-O4	86.7(4)
O9-Mo2-O16	154.4(7)	O9-Mo2-O22	95.9(6)	O12-Mo2-O4	100.5(6)
O12-Mo2-O9	103.1(6)	O12-Mo2-O16	101.0(7)	O12-Mo2-O19	105.2(7)
O12-Mo2-O22	159.5(6)	O16-Mo2-O4	80.7(5)	O16-Mo2-O22	61.7(6)
O19-Mo2-O4	153.7(7)	O19-Mo2-O9	93.1(6)	O19-Mo2-O16	88.7(6)
O19-Mo2-O22	65.8(6)	O2-Mo3-O16	90.9(7)	O2-Mo3-O18	88.0(5)
O2-Mo3-O20	154.5(7)	O2-Mo3-O22	92.0(6)	O6-Mo3-O2	102.5(7)
O6-Mo3-O16	102.9(7)	O6-Mo3-O18	101.0(5)	O6-Mo3-O20	102.5(7)
O6-Mo3-O22	159.8(5)	O16-Mo3-O18	155.7(7)	O16-Mo3-O20	88.2(6)
O16-Mo3-O22	62.3(6)	O18-Mo3-O22	93.5(5)	O20-Mo3-O18	82.6(6)

O20-Mo3-O22	65.2(6)	O4-Mo4-O8	88.2(4)	O4-Mo4-O13	92.7(6)
O4-Mo4-O15	153.9(7)	O4-Mo4-O21	92.6(6)	O8-Mo4-O21	92.3(5)
O11-Mo4-O4	103.5(6)	O11-Mo4-O8	101.1(5)	O11-Mo4-O13	102.9(7)
O11-Mo4-O15	101.9(6)	O11-Mo4-O21	159.1(5)	O13-Mo4-O8	155.0(7)
O13-Mo4-O15	87.0(6)	O13-Mo4-O21	62.7(6)	O15-Mo4-O8	81.5(5)
O15-Mo4-O21	64.2(6)	O1-Mo5-O8	102.4(5)	O1-Mo5-O9	99.9(6)
O8-Mo5-O8	93.4(7)	O8-Mo5-O9	157.0(6)	O8-Mo5-O9	87.5(5)
O9-Mo5-O9	82.8(7)	O3-Mo6-O7	98.5(6)	O3-Mo6-O15	104.7(6)
O3-Mo6-O21	155.5(4)	O7-Mo6-O7	82.2(9)	O7-Mo6-O21	92.4(6)
O7-Mo6-O21	61.2(5)	O15-Mo6-O7	86.4(6)	O15-Mo6-O7	155.5(7)
O15-Mo6-O15	95.3(9)	O15-Mo6-O21	63.1(5)	O15-Mo6-O21	97.8(6)
O15-Mo6-O21	97.8(6)	O21-Mo6-O21	46.9(6)	O5-Mo7-O19	101.9(6)
O5-Mo7-O20	103.7(6)	O19-Mo7-O19	81.2(9)	O20-Mo7-O19	153.7(7)
O20-Mo7-O19	87.5(6)	O20-Mo7-O20	92.5(10)	Mo3-O2-Mo1	141.0(7)
Mo4-O4-Mo2	141.3(7)	Mo1-O7-Mo6	140.2(8)	Mo5-O8-Mo4	138.5(7)
Mo2-O9-Mo5	139.9(8)	Mo4-O13-Mo1	140.3(10)	Mo1-O14-Mo8	138.8(7)
Mo6-O15-Mo4	139.9(8)	O14-Mo8-O14	82.8(6)	O17-Mo8-O14	101.3(6)
O17-Mo8-O18	102.1(6)	O18-Mo8-O14	156.2(7)	O18-Mo8-O14	88.1(5)
O18-Mo8-O18	91.5(7)	Mo3-O16-Mo2	139.2(10)	Mo8-O18-Mo3	139.4(8)
Mo2-O19-Mo7	140.8(8)	Mo7-O20-Mo3	140.6(8)	O21-P1-O21	77.7(10)
O22-P1-O21	101.9(8)	O22-P1-O21	179.6(8)	O22-P1-O22	78.4(11)
Mo1-O21-Mo6	93.2(5)	Mo4-O21-Mo1	95.1(5)	Mo4-O21-Mo6	92.6(4)
P1-O21-Mo1	124.7(7)	P1-O21-Mo4	125.2(7)	P1-O21-Mo6	117.6(7)
C3-N1-H1	119.9	C3-N1-C5	120.1(15)	C5-N1-H1	119.9
C2-C1-H1A	118.5	C2-C1-C4	123.0(16)	C4-C1-H1A	118.5
C1-C2-H2	120.8	C1-C2-C5	118.5(14)	C5-C2-H2	120.8
N1-C3-H3	119.1	N1-C3-C4	121.9(14)	C4-C3-H3	119.1
C1-C4-C3	116.8(14)	C1-C4-H4	121.6	C3-C4-H4	121.6
N1-C5-C2	119.7(14)	N1-C5-H5	120.2	C2-C5-H5	120.2
C7-C6-H6	118.9	C7-C6-C10	122.1(18)	C10-C6-H6	118.9
C6-C7-H7	120.2	C6-C7-N2	119.6(17)	N2-C7-H7	120.2
C9-C8-H8	119.3	C9-C8-N2	121(2)	N2-C8-H8	119.3
C8-C9-H9	120.6	C8-C9-C10	118.7(18)	C10-C9-H9	120.6
C6-C10-C9	118.4(17)	C6-C10-H10	120.8	C9-C10-H10	120.8
C7-N2-C8	119.5(18)	C7-N2-H2A	120.2	C8-N2-H2A	120.2
Mo2-O22-Mo3	95.6(5)	P1-O22-Mo2	126.0(7)	P1-O22-Mo3	125.1(7)

Table S3. Selected bond lengths (Å) and bond angles (°) for compound 3.

Mo1-O1	1.649(7)	Mo1-O2	1.833(8)	Mo1-O5	1.972(8)
Mo1-O6	1.823(8)	Mo1-O6	1.977(8)	Mo1-O8	2.480(11)
Mo1-O7	2.467(11)	Mo2-O2	1.983(7)	Mo2-O3	1.646(7)
Mo2-O4	1.817(8)	Mo2-O4	1.993(8)	Mo2-O5	1.830(8)
Mo2-O8	2.468(11)	Mo2-O8	2.471(11)	P1-O8	1.530(11)

P1-O7	1.54(2)	O2-Mo2	1.983(7)	O4-Mo2	1.993(8)
O6-Mo1	1.977(8)	O8-Mo2	2.468(11)	O8-O8	1.765(15)
O8-O7	1.774(16)	N1-C2	1.125(13)	N1-N2	1.17(2)
N3-N4	1.534(16)	N3-C2	1.709(15)	N3-C1	1.37(3)
N4-C1	1.26(2)	C2-N1	1.125(13)	C2-N3	1.709(15)
O1-Mo1-O2	102.4(4)	O1-Mo1-O5	101.0(4)	O1-Mo1-O6	102.4(5)
O1-Mo1-O6	100.7(5)	O1-Mo1-O8	158.5(4)	O1-Mo1-O7	158.9(5)
O2-Mo1-O5	87.5(3)	O2-Mo1-O6	155.6(5)	O2-Mo1-O8	64.8(4)
O2-Mo1-O7	95.7(5)	O5-Mo1-O6	80.5(4)	O5-Mo1-O8	62.8(4)
O5-Mo1-O7	90.4(4)	O6-Mo1-O2	94.5(4)	O6-Mo1-O5	155.5(5)
O6-Mo1-O6	88.1(5)	O6-Mo1-O8	96.1(5)	O6-Mo1-O8	90.8(5)
O6-Mo1-O7	63.4(4)	O6-Mo1-O7	65.1(4)	O7-Mo1-O8	42.0(5)
O2-Mo2-O4	80.5(4)	O2-Mo2-O8	90.4(4)	O2-Mo2-O8	63.4(4)
O3-Mo2-O2	99.3(5)	O3-Mo2-O4	103.4(5)	O3-Mo2-O4	98.4(5)
O3-Mo2-O5	103.8(5)	O3-Mo2-O8	158.7(4)	O3-Mo2-O8	157.8(4)
O4-Mo2-O2	87.7(3)	O4-Mo2-O4	156.6(7)	O4-Mo2-O5	96.1(4)
O4-Mo2-O8	63.4(4)	O4-Mo2-O8	91.2(5)	O4-Mo2-O8	65.4(4)
O4-Mo2-O8	96.8(5)	O5-Mo2-O2	154.9(5)	O5-Mo2-O4	86.6(3)
O5-Mo2-O8	64.5(4)	O5-Mo2-O8	95.6(5)	O8-Mo2-O8	41.9(4)
O8-P1-O8	70.4(4)	O8-P1-O8	179.997(2)	O8-P1-O8	109.6(4)
O8-P1-O8	179.997(1)	O8-P1-O8	180.0(8)	O8-P1-O7	70.6(4)
O8-P1-O7	109.4(4)	O7-P1-O7	179.997(1)	Mo1-O2-Mo2	138.7(6)
Mo2-O4-Mo2	138.5(6)	Mo2-O5-Mo1	139.9(6)	Mo1-O6-Mo1	138.7(6)
Mo2-O8-Mo1	92.3(4)	Mo2-O8-Mo1	92.4(4)	Mo2-O8-Mo2	92.4(4)
P1-O8-Mo1	123.4(6)	P1-O8-Mo2	123.6(6)	P1-O8-Mo2	123.8(6)
P1-O8-O8	54.8(2)	P1-O8-O8	54.8(2)	P1-O8-O7	54.9(6)
O8-O8-Mo1	127.2(7)	O8-O8-Mo1	134.9(8)	O8-O8-Mo2	69.1(5)
O8-O8-Mo2	127.6(8)	O8-O8-Mo2	135.4(9)	O8-O8-Mo2	69.0(5)
O8-O8-O8	90.2(9)	O8-O8-O7	90.1(5)	O7-O8-Mo1	68.6(6)
O7-O8-Mo2	135.1(6)	O7-O8-Mo2	127.2(6)	C2-N1-N2	135.3(17)
N4-N3-C2	151.0(14)	C1-N3-N4	51.1(11)	C1-N3-C2	99.9(13)
C1-N4-N3	57.8(12)	N1-C2-N1	180(3)	N1-C2-N3	89.3(10)
N1-C2-N3	90.7(10)	N3-C2-N3	180.0(13)	N1-N2-C1	105.6(19)
N4-C1-N3	71.1(14)	N4-C1-N2	178(3)	N2-C1-N3	108.3(18)
Mo1-O7-Mo1	92.2(5)	P1-O7-Mo1	123.7(4)	P1-O7-O8	54.5(6)
O8-O7-Mo1	69.4(4)	O8-O7-Mo1	127.5(4)	O8-O7-Mo1	135.2(4)
O8-O7-Mo1	135.3(4)	O8-O7-O8	89.6(9)		

Table S4. Selected bond lengths (Å) and bond angles (°) for compound 4.

Mo1-O1	1.66(5)	Mo1-O4	1.82(4)	Mo1-O4	2.00(4)
Mo1-O9	1.85(4)	Mo1-O12	2.03(5)	Mo1-O12	2.42(4)
Mo2-O2	1.98(4)	Mo2-O3	1.87(4)	Mo2-O3	1.83(5)
Mo2-O9	1.98(5)	Mo2-O11	1.68(4)	Mo2-O11	2.43(4)

Mo3-O2	1.85(4)	Mo3-O3	1.98(4)	Mo3-O3	1.68(4)
Mo3-O10	2.01(5)	Mo3-O12	1.84(5)	Mo3-O12	2.42(4)
Mo4-O0AA	1.84(4)	Mo4-O0AA	2.01(4)	Mo4-O0AA	2.01(5)
Mo4-O8	2.42(4)	Mo4-O10	1.82(5)	Mo4-O10	1.68(5)
P1-O8	1.54(8)	P1-O13	1.54(4)	P1-O13	1.98(4)
O4-Mo1	2.00(4)	O0AA-Mo4	2.01(4)	O0AA-Mo4	2.01(5)
O8-Mo4	2.42(4)	O13-Mo1	2.42(4)	O13-Mo1	2.43(4)
O13-Mo3	2.42(4)	N1-C1	1.32(10)	N1-C1	1.39(8)
C1-N2	1.32(9)	C1-N3	1.32(9)	C1-N3	1.36(11)
N4-C2	1.27(11)	O1-Mo1-O4	105(2)	O1-Mo1-O4	102(2)
O1-Mo1-O9	102(2)	O1-Mo1-O12	99(2)	O1-Mo1-O13	169.5(19)
O4-Mo1-O4	85(2)	O4-Mo1-O9	97.4(19)	O4-Mo1-O12	79.7(18)
O4-Mo1-O12	154.7(19)	O4-Mo1-O13	85.7(18)	O4-Mo1-O13	80.4(16)
O9-Mo1-O4	153.9(19)	O9-Mo1-O12	87.5(19)	O9-Mo1-O13	73.9(17)
O12-Mo1-O13	71.7(16)	O2-Mo2-O9	82.4(19)	O2-Mo2-O13	81.8(16)
O3-Mo2-O2	155.4(19)	O3-Mo2-O9	86.9(19)	O3-Mo2-O13	73.9(16)
O2AA-Mo2-O2	86(2)	O2AA-Mo2-O3	96(2)	O2AA-Mo2-O9	156.1(19)
O2AA-Mo2-O13	86.3(18)	O9-Mo2-O13	71.6(16)	O11-Mo2-O2	101(2)
O11-Mo2-O3	103(2)	O11-Mo2-O2AA	104(2)	O11-Mo2-O9	99(2)
O11-Mo2-O13	170(2)	O2-Mo3-O3	155.1(19)	O2-Mo3-O10	84(2)
O2-Mo3-O13	85.7(17)	O3-Mo3-O10	81.4(18)	O3-Mo3-O13	72.1(16)
O1AA-Mo3-O2	102(2)	O1AA-Mo3-O3	101(2)	O1AA-Mo3-O10	101(2)
O1AA-Mo3-O12	104(2)	O1AA-Mo3-O13	172.4(18)	O10-Mo3-O13	80.5(17)
O12-Mo3-O2	96(2)	O12-Mo3-O3	89.4(19)	O12-Mo3-O10	155.0(19)
O12-Mo3-O13	74.6(17)	O0AA-Mo4-O0AA	87(3)	O0AA-Mo4-O2AA	155.4(19)
O0AA-Mo4-O8	71.8(16)	O0AA-Mo4-O8	74.5(17)	O2AA-Mo4-O0AA	81.4(18)
O2AA-Mo4-O8	81.3(16)	O10-Mo4-O0AA	155(2)	O10-Mo4-O0AA	98(2)
O10-Mo4-O2AA	85.2(19)	O10-Mo4-O8	85.7(18)	O14-Mo4-O0AA	100(2)
O14-Mo4-O0AA	102(2)	O14-Mo4-O2AA	101(2)	O14-Mo4-O8	171(2)
O14-Mo4-O10	103(2)	O13-P1-O8	109.6(19)	O13-P1-O13	109(2)
Mo3-O2-Mo2	152(3)	Mo2-O3-Mo3	125(2)	Mo1-O4-Mo1	152(3)
Mo4-O0AA-Mo4	124(2)	Mo2-O2AA-Mo4	151(3)	Mo4-O8-Mo4	89(2)
P1-O8-Mo4	125.7(14)	Mo1-O9-Mo2	125(2)	Mo4-O10-Mo3	153(3)
Mo3-O12-Mo1	124(2)	Mo1-O13-Mo2	89.1(14)	Mo1-O13-Mo3	89.5(14)
Mo3-O13-Mo2	89.1(14)	P1-O13-Mo1	126(3)	P1-O13-Mo2	125(2)
P1-O13-Mo3	126(2)	C1-N1-N4	110(7)	N1-C1-N3	126(8)
N2-C1-N1	107(7)	N2-C1-N3	127(8)	C1-N2-C2	107(7)
C2-N4-N1	104(7)	N4-C2-N2	112(7)		

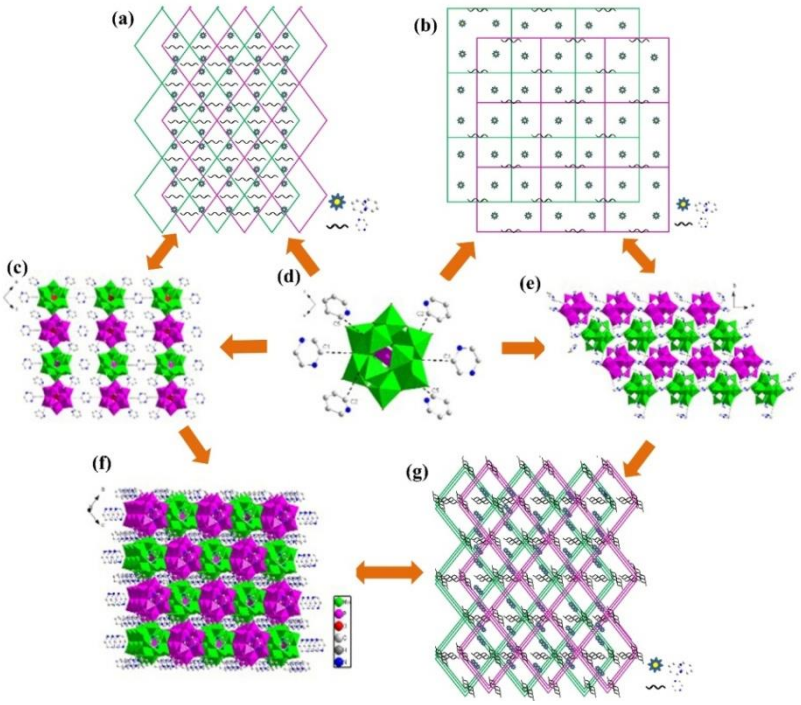

Figure S1.(a) Palisade surface of compound 1 (b) The grid surface of compound 1 (c) Two-dimensional plane view from the B-axis direction (d) monomer diagram of compound 1 (e) Two-dimensional plane view from the C-axis direction (f) three-dimensional stacking diagram of compound 1 (g) three-dimensional simplified view of compound 1.

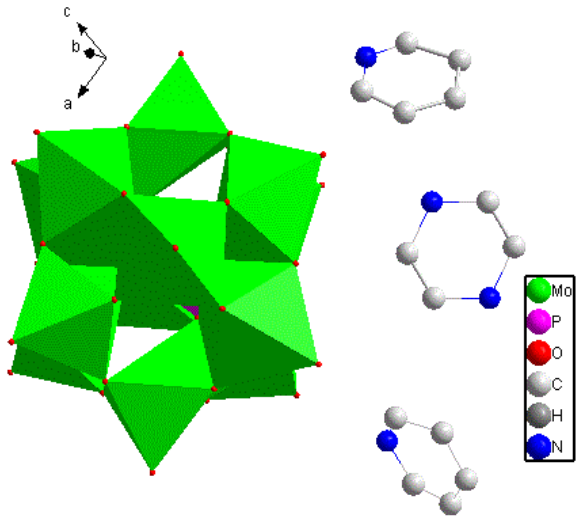

Figure S2.Monomer diagram of compound 1,ignore hydrogen.

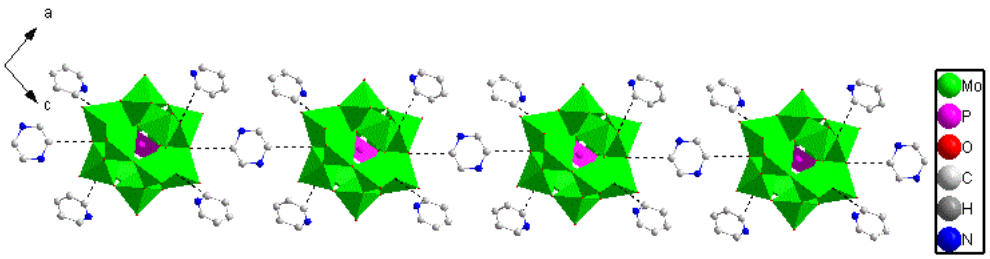

Figure S3.One-dimensional chain structure A of compound 1,ignore hydrogen.

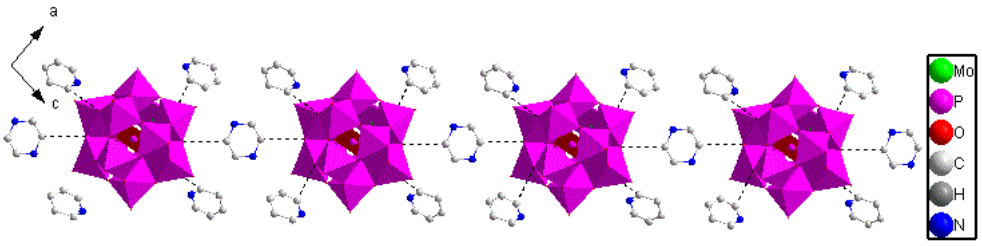

Figure S4.One-dimensional chain structure B of compound 1,ignore hydrogen.

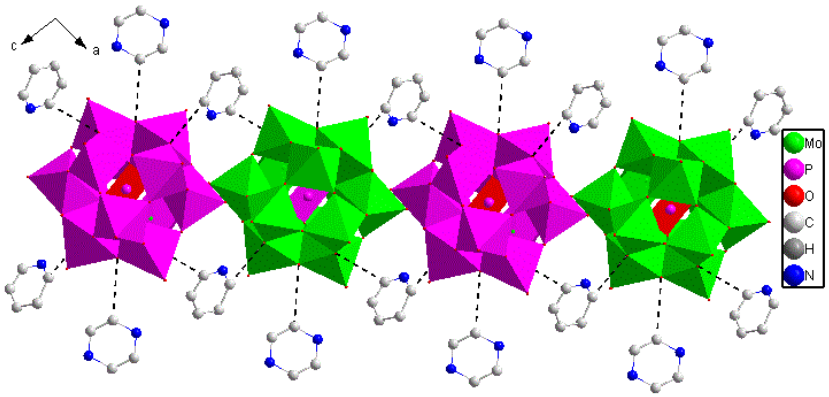

Figure S5.One-dimensional chain structure C of compound 1,ignore hydrogen.

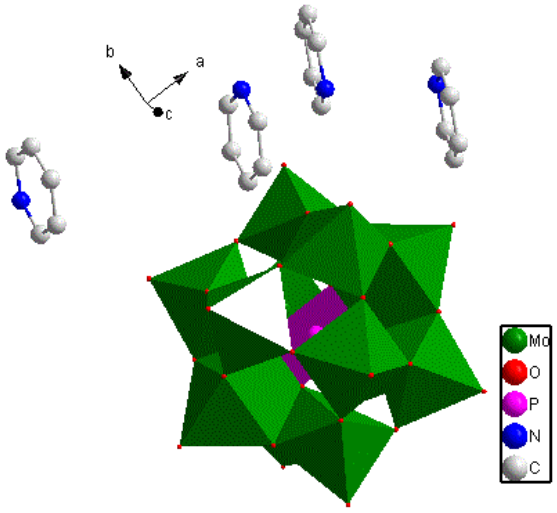

Figure S6.Monomer diagram of compound 2,ignore hydrogen.

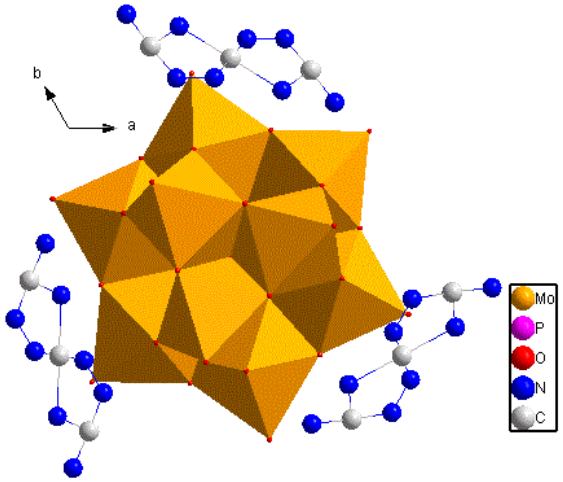

Figure S7.The monomer diagram of compound 3 ignores the water molecules and hydrogen elements

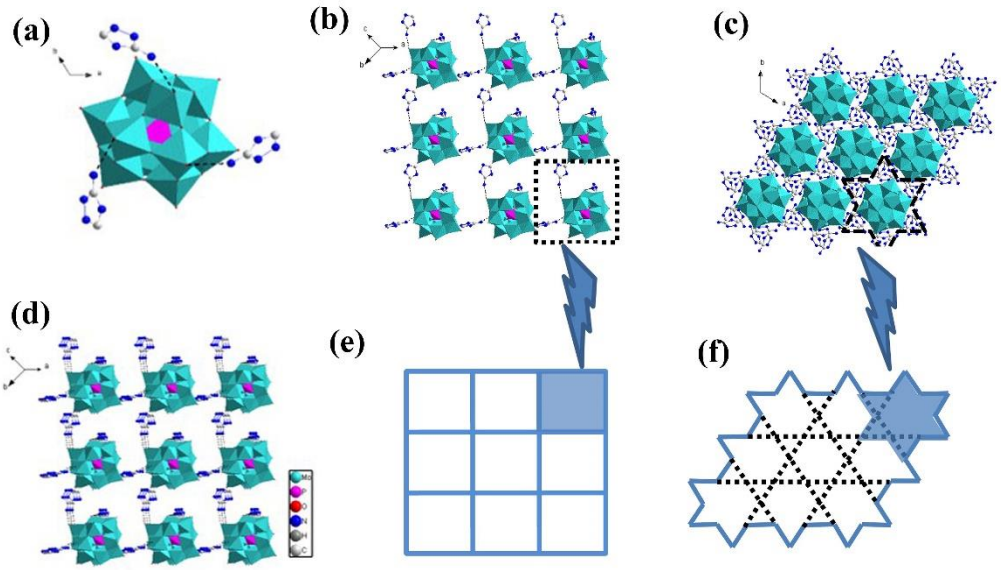

Figure S8.(a) Monomer diagram of compound 4.(b) Two-dimensional plan of compound 4.(c) two-dimensional plan of compound 4 as viewed from the C-axis.(d) three-dimensional stack diagram of compound 4.(e) Two-dimensional plane simplified view of compound 4.(f) two-dimensional simplified view from the C-axis.

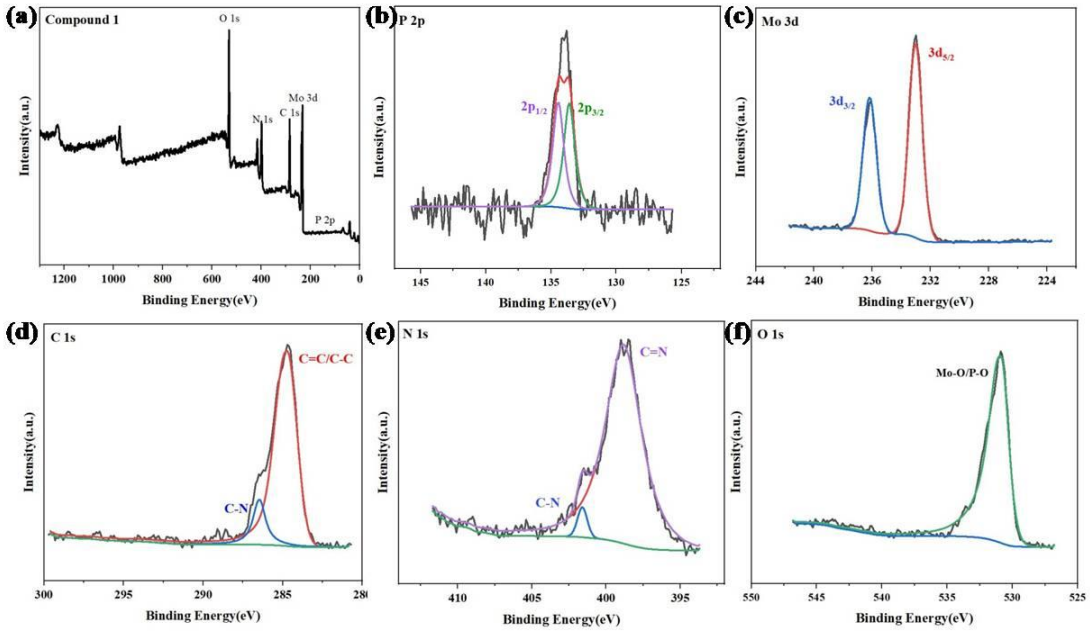

Figure S9. The XPS spectrum of 1.

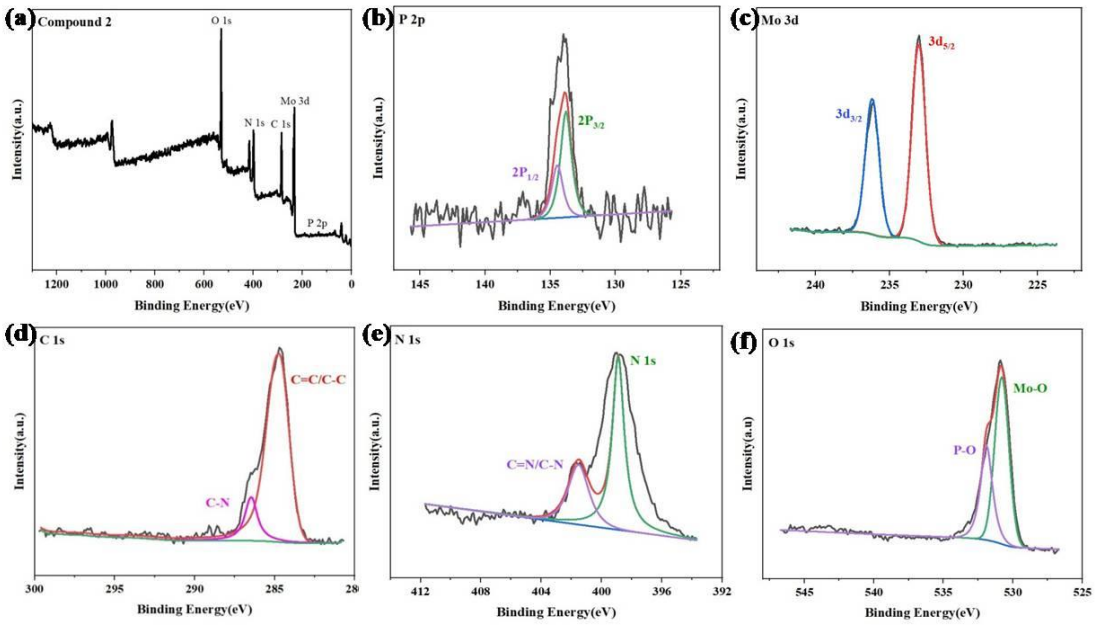

Figure S10. The XPS spectrum of 2.

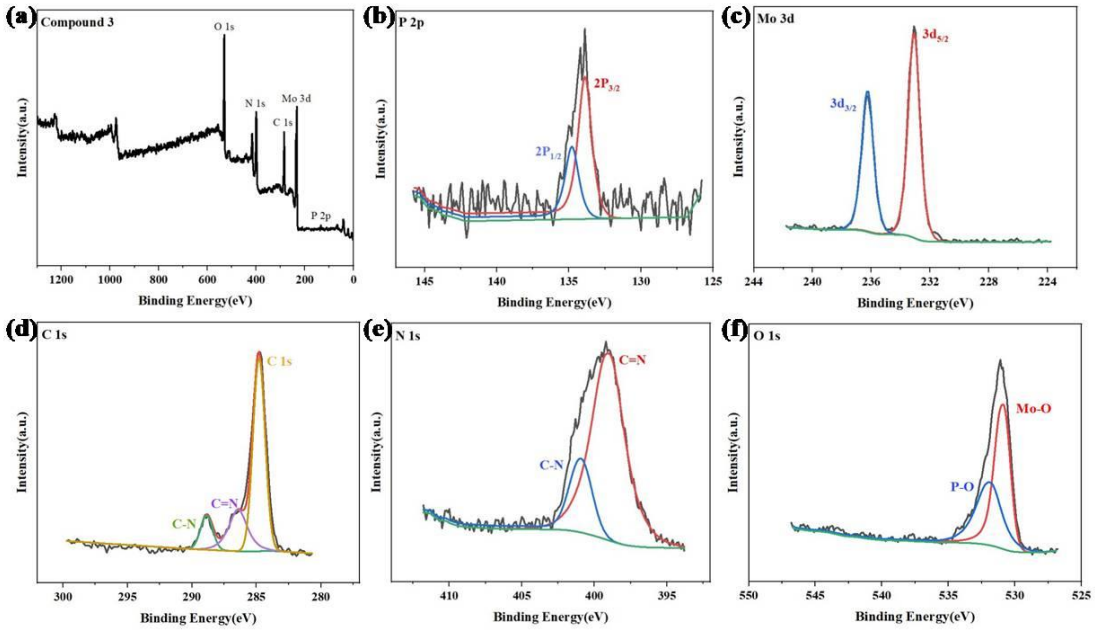

Figure S11. The XPS spectrum of 3.

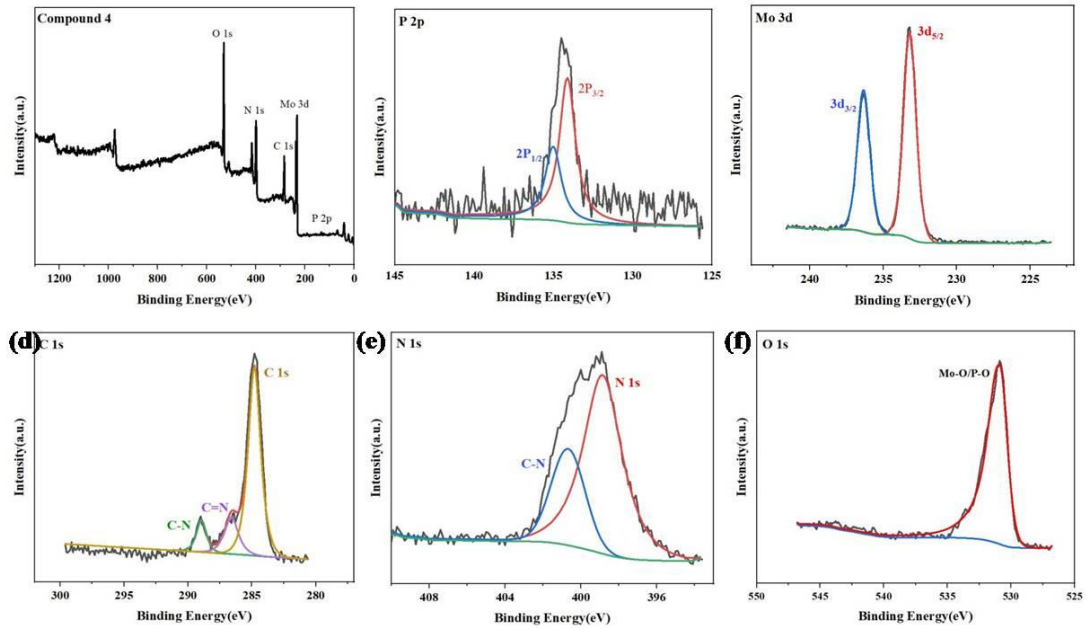

Figure S12. The XPS spectrum of 4.

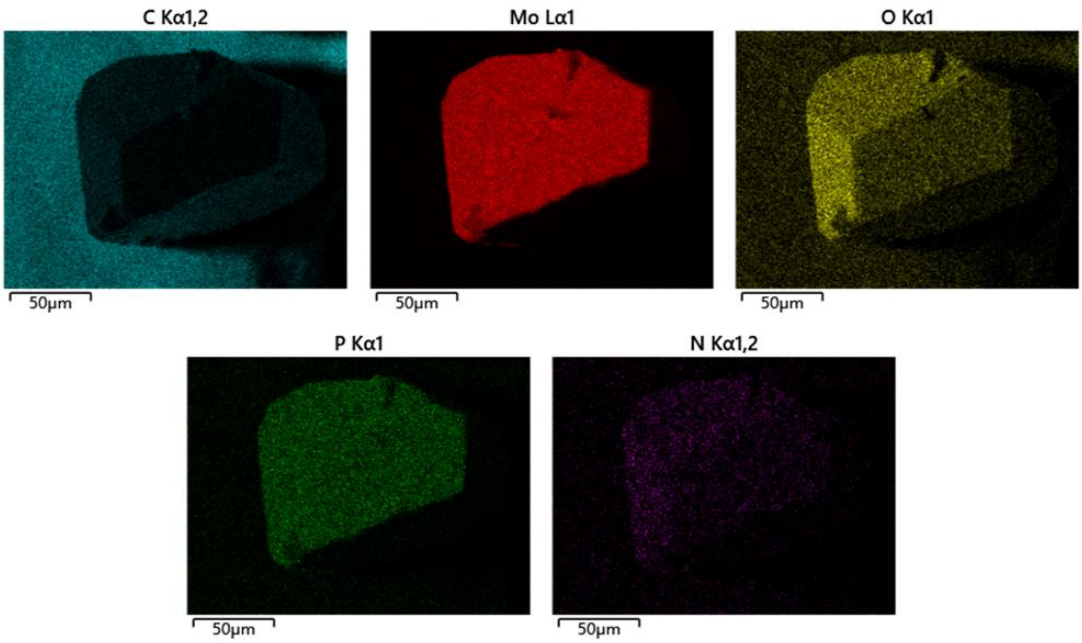

Figure S13.EDS mapping images of compound 1.

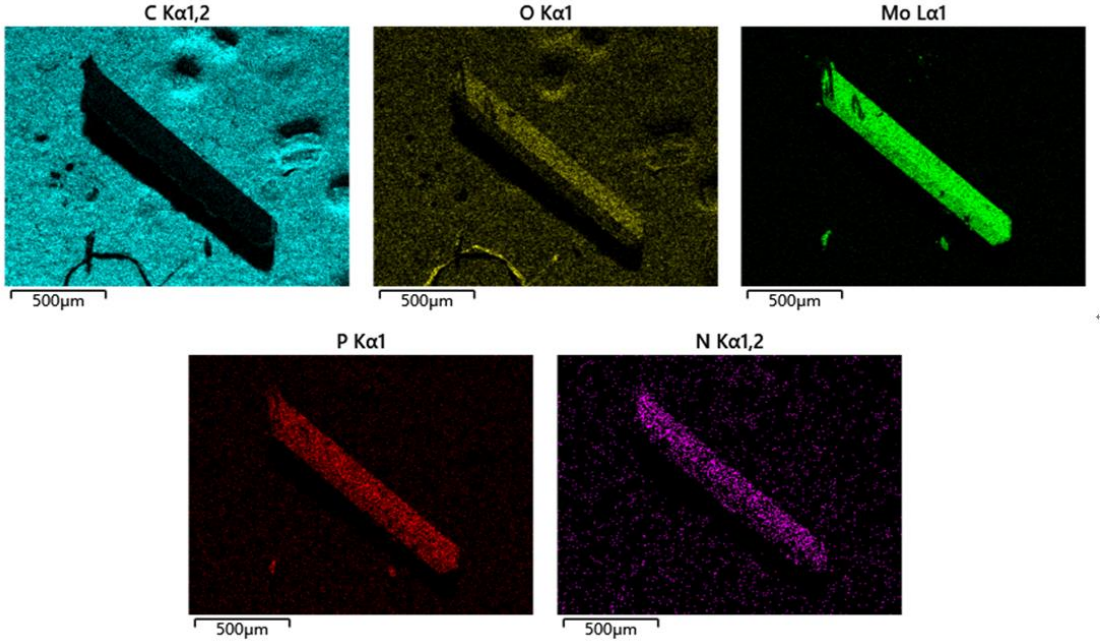

Figure S14. EDS mapping images of compound 3.

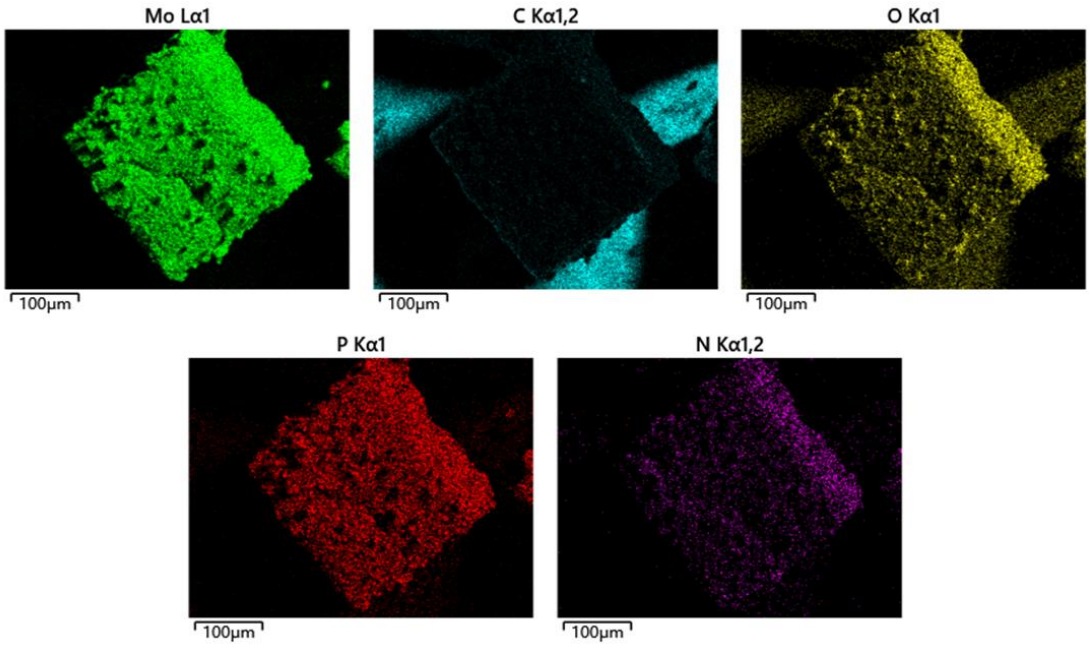

Figure S15. EDS mapping images of compound 4.

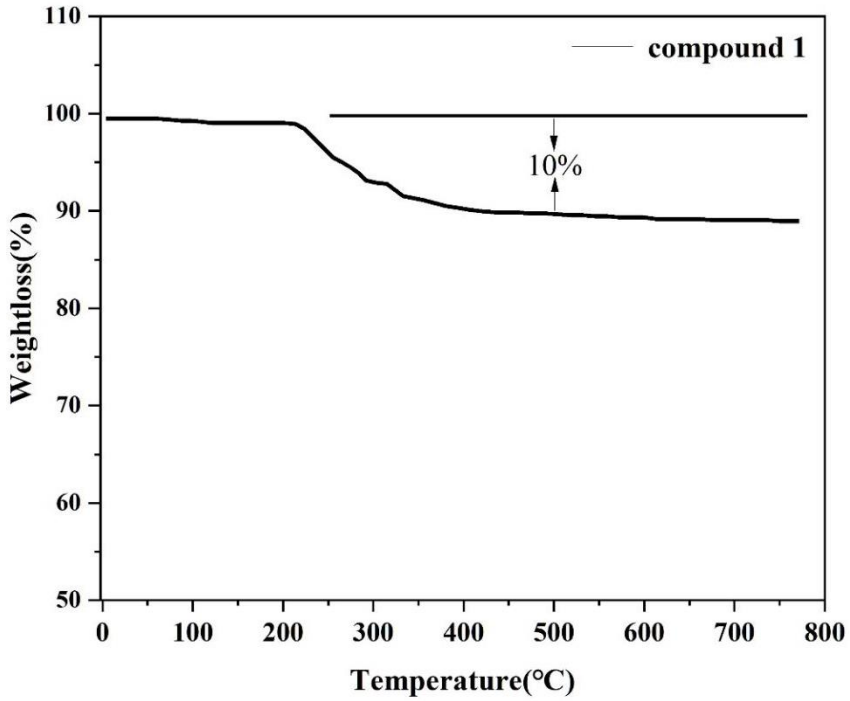

Figure S16. The TGA thermogram for compound 1.

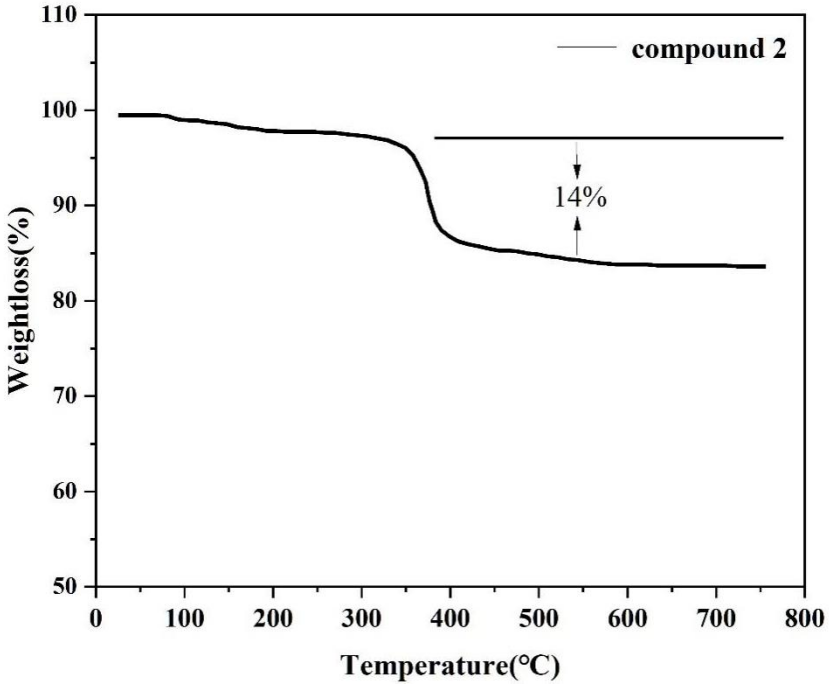

Figure S17. The TGA thermogram for compound 2.

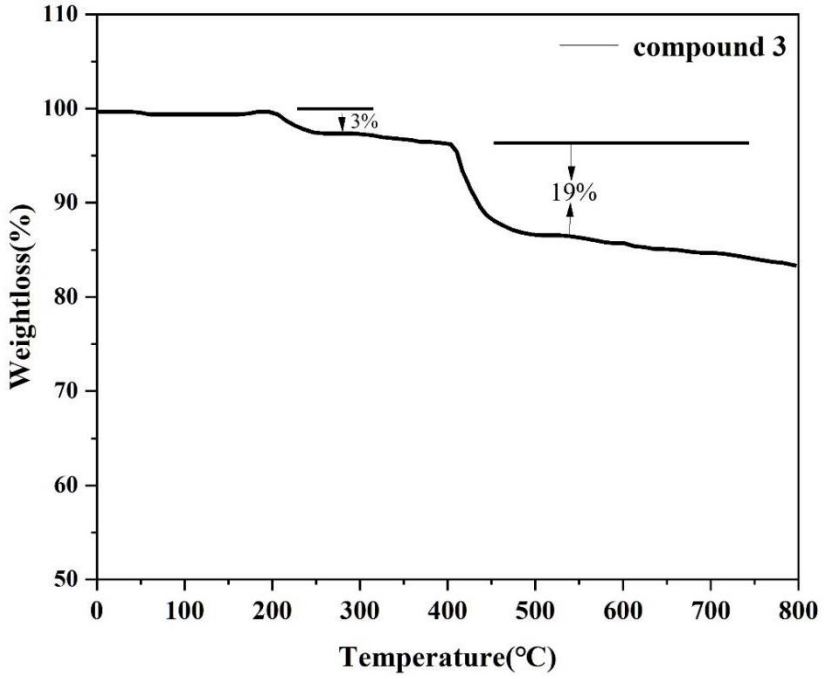

Figure S18. The TGA thermogram for compound 3.

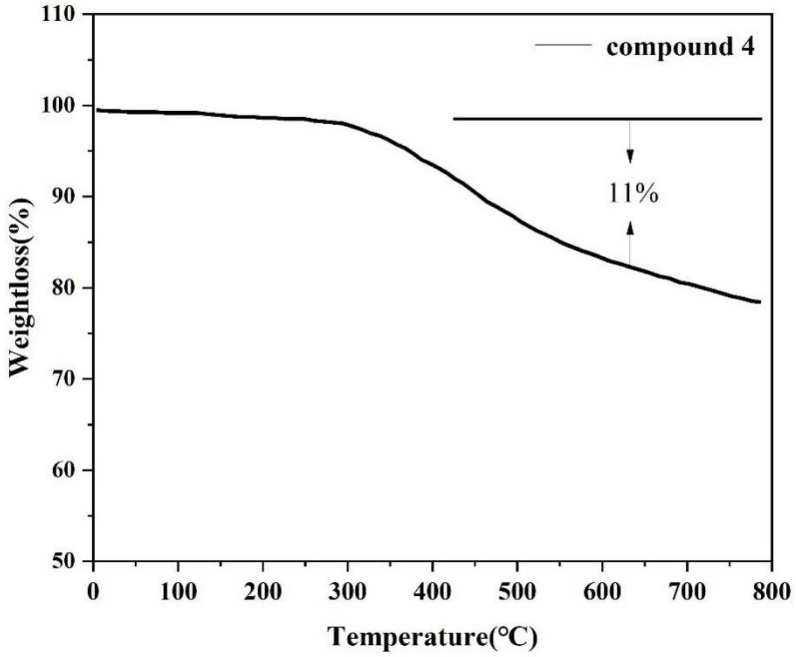

Figure S19. The TGA thermogram for compound 4.

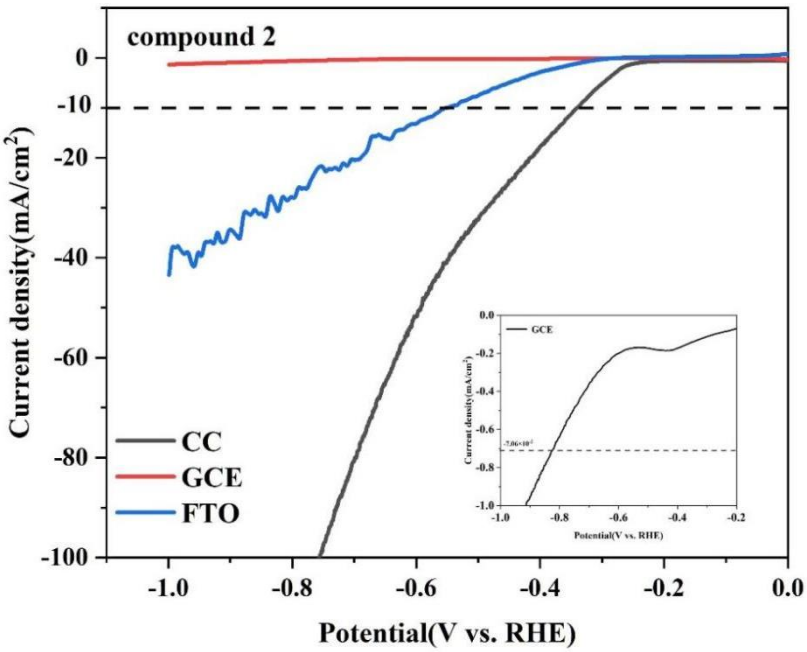

Figure S20.LSV curves of compound 2 in 0.5M H_2SO_4 solution with different collector fluids.

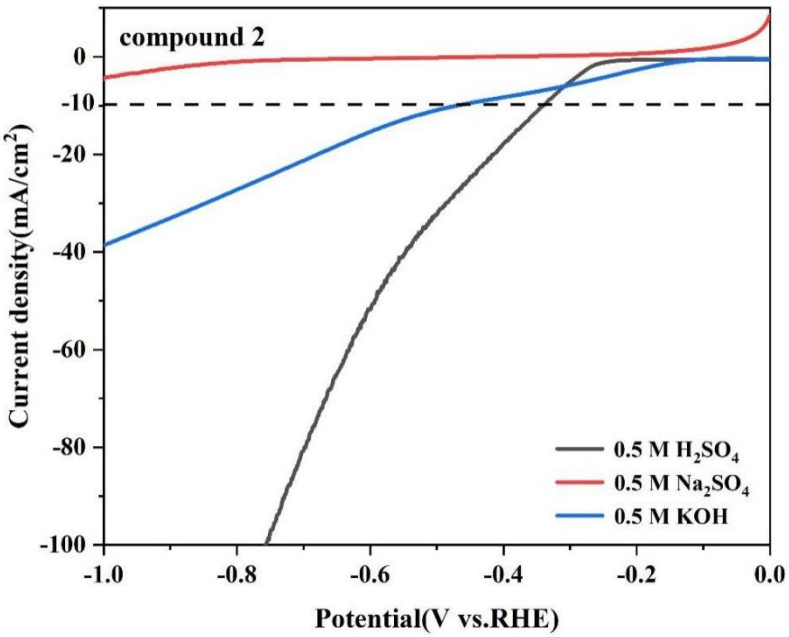

Figure S21.LSV curves of compound 2 under neutral (0.5M Na_2SO_4), alkaline (0.5M KOH), and acidic (0.5M H_2SO_4) conditions.

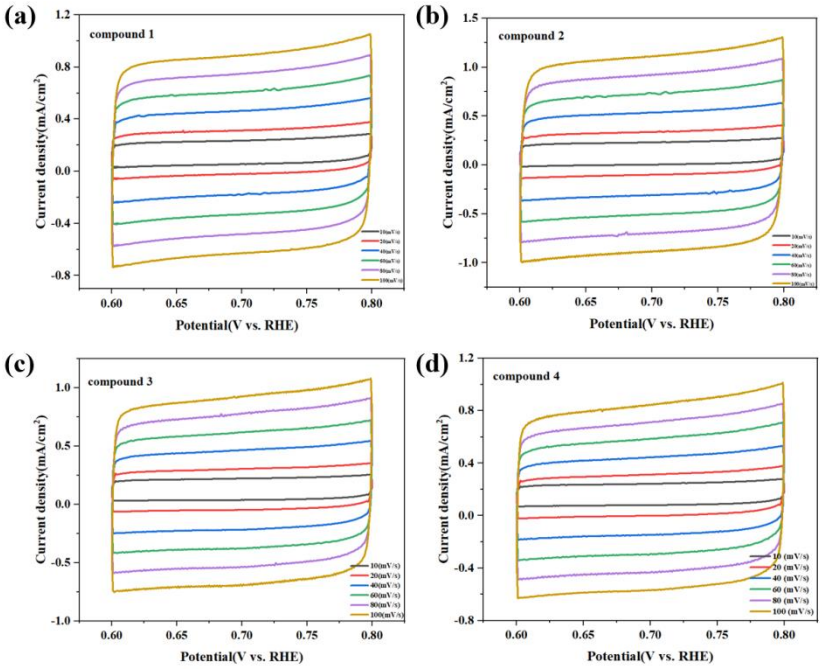

Figure S22.CV curves of four compounds.

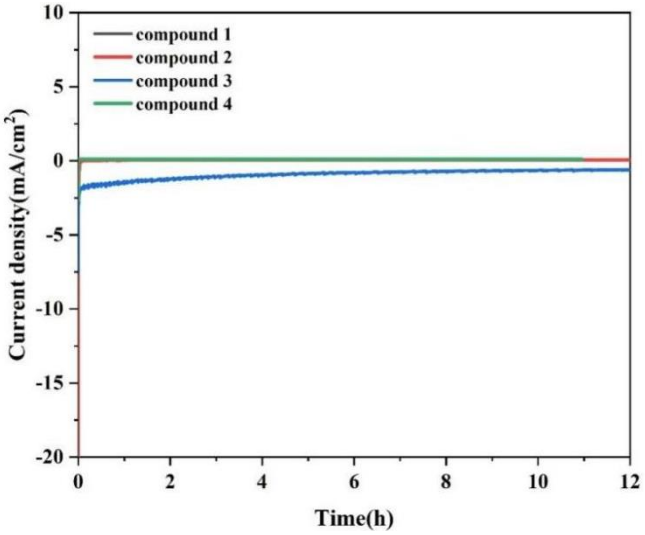

Figure S23. IT of four compounds.

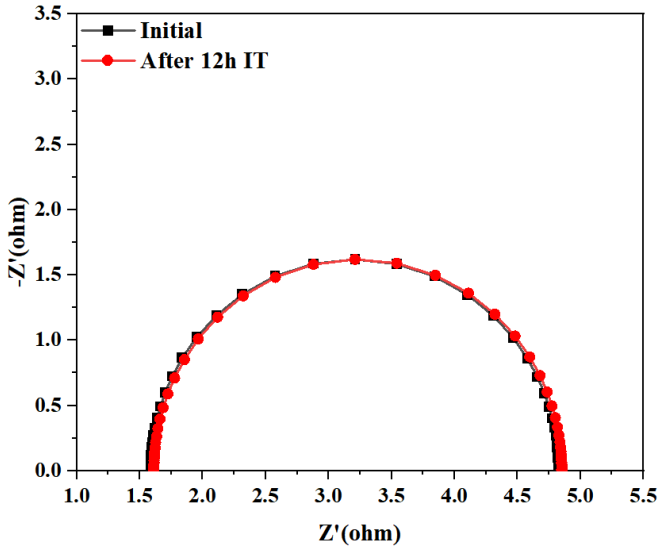

Figure S24. EIS before and after 12h IT of compound 2.

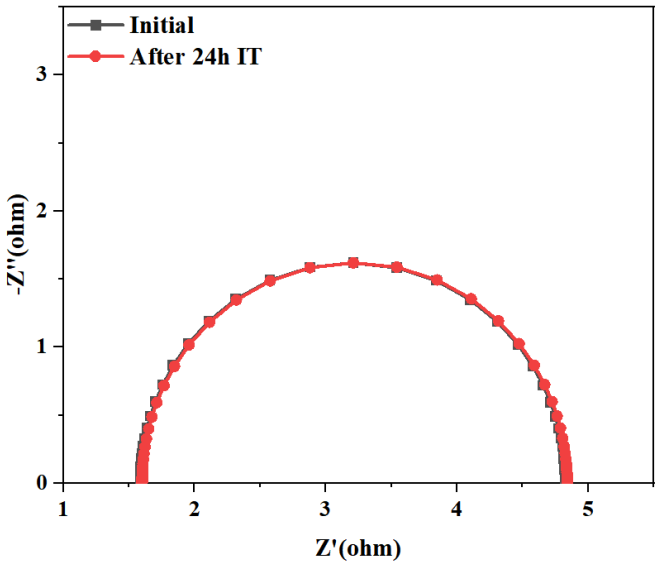

Figure S25. EIS before and after 24h IT of compound 2.

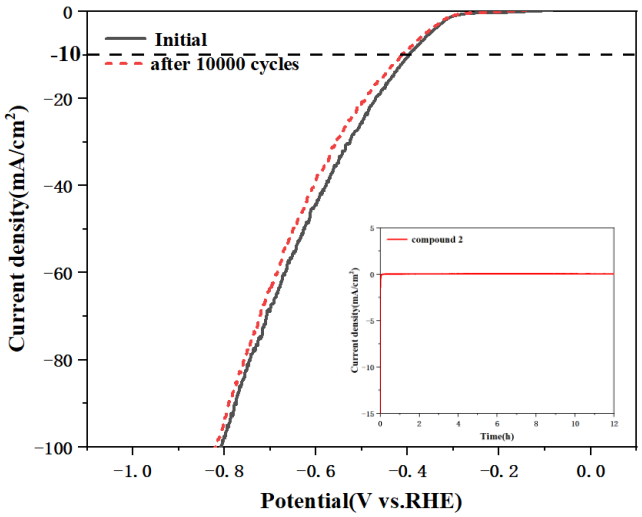

Figure S26. LSV curve for compound 2 before and after 10,000 CV cycles.

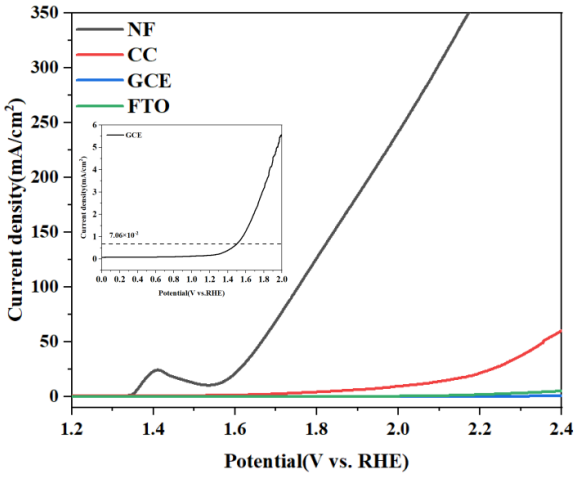

Figure S27. LSV curves of compound 2 in 0.5M KOH solution with different collector fluids.

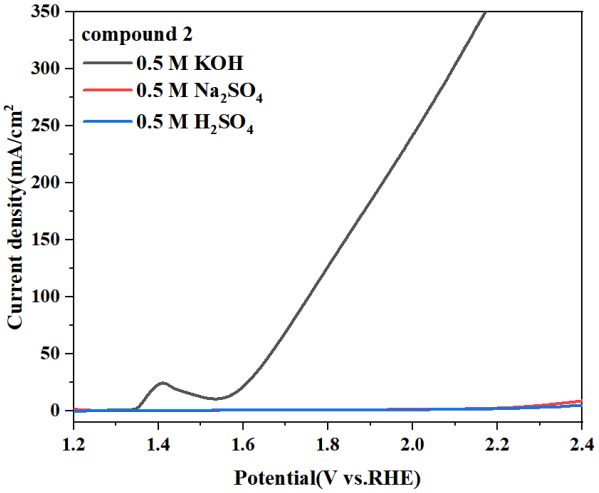

Figure S28. LSV curves of compound 2 under neutral (0.5M Na_2SO_4), alkaline (0.5M KOH), and acidic (0.5M H_2SO_4) conditions.

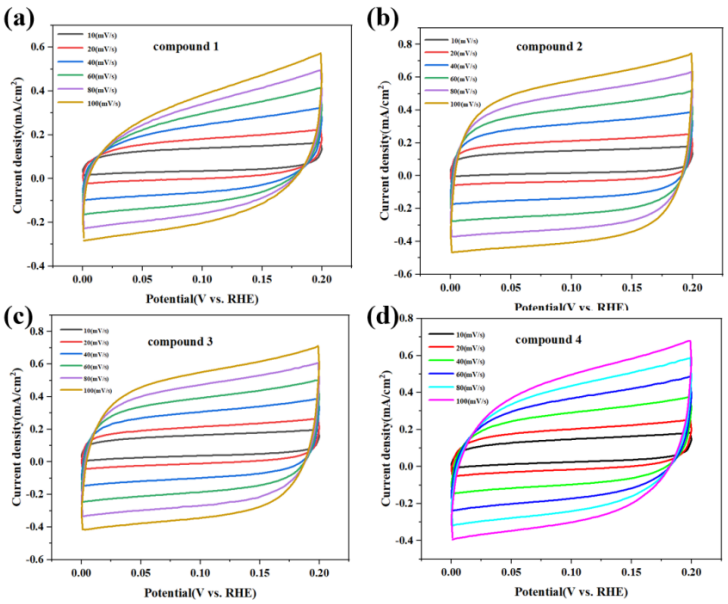

Figure S29. CV curves of four compounds.

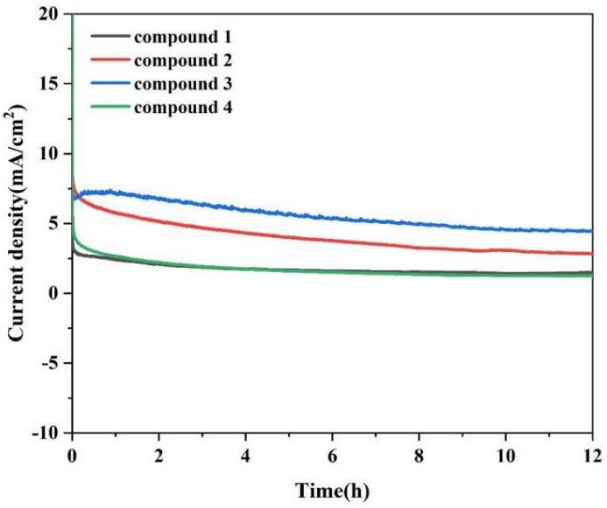

Figure S30. IT of four compounds.

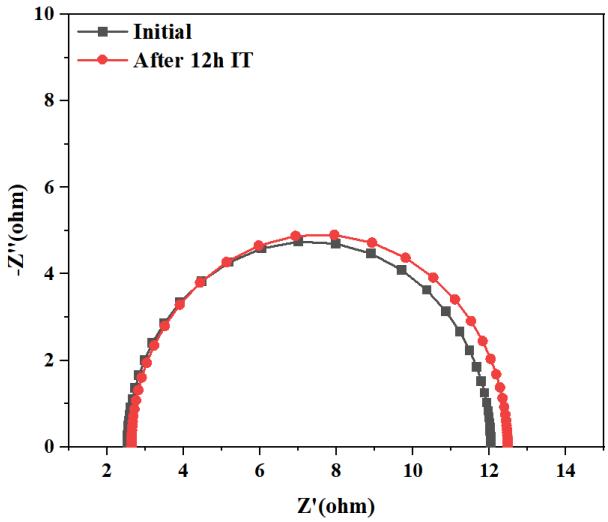

Figure S31. EIS before and after 12h IT of compound 2.

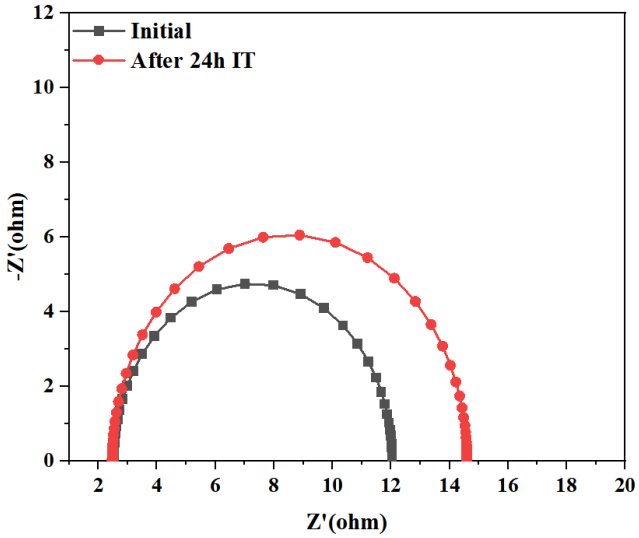

Figure S32. EIS before and after 24h IT of compound 2.

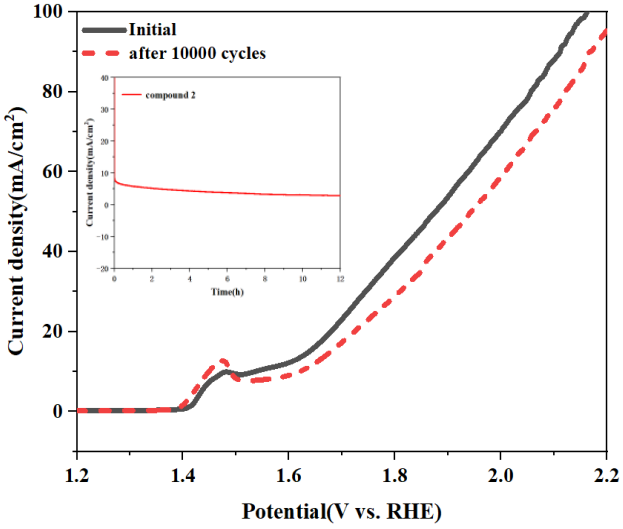

Figure S33. LSV curve for compound 2 before and after 10,000 CV cycles.

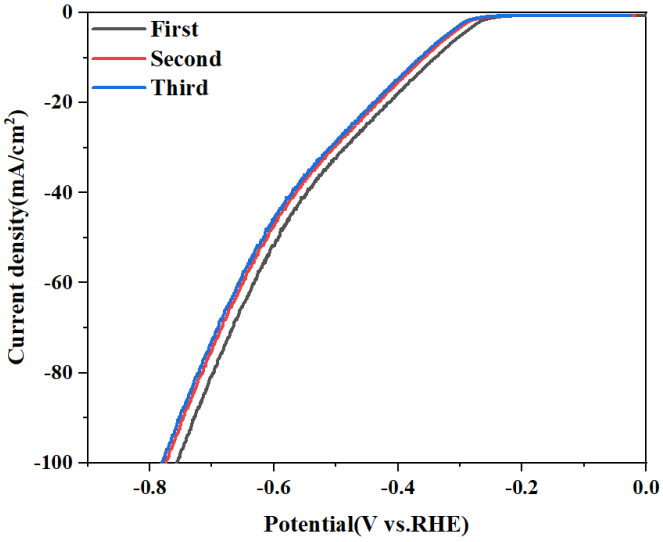

Figure S34. Reclaim the LSV after the test of HER.

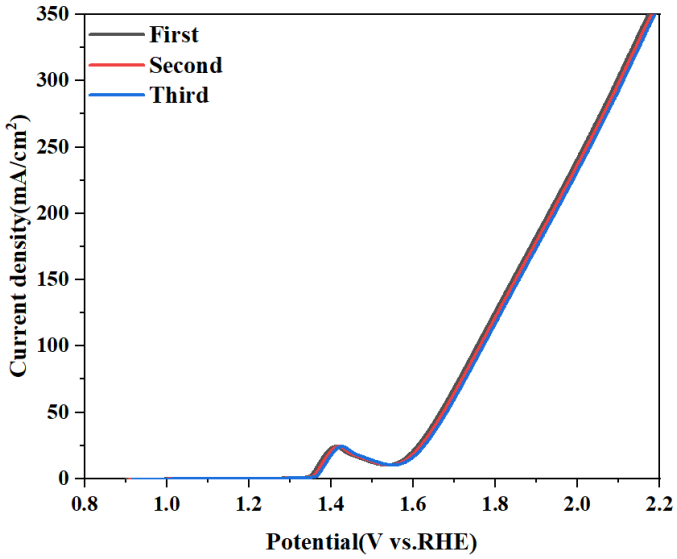

Figure S35. Reclaim the LSV after the test of OER.

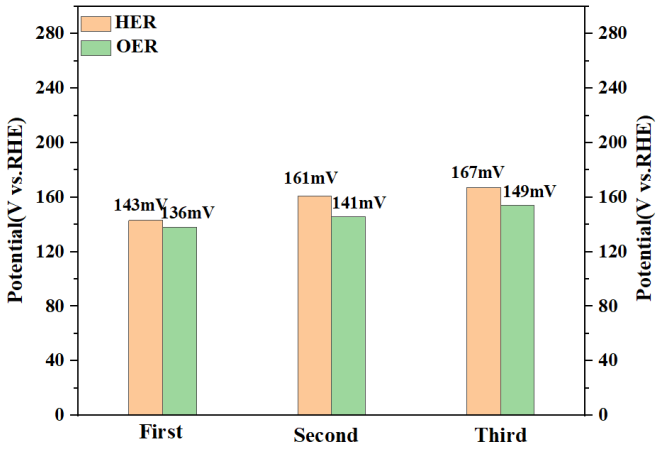

Figure S36. LSV before and after reclamation of compound 2.

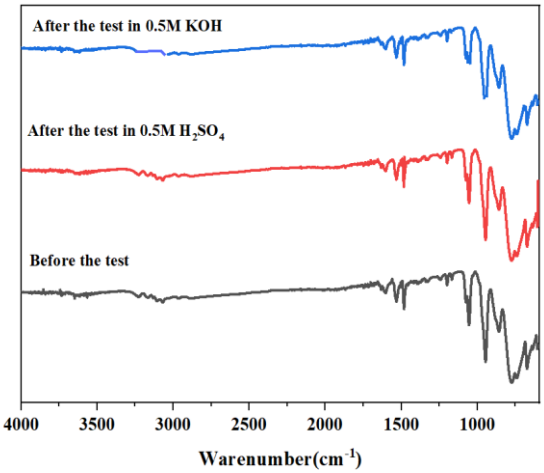

Figure S37. IR pattern after testing.

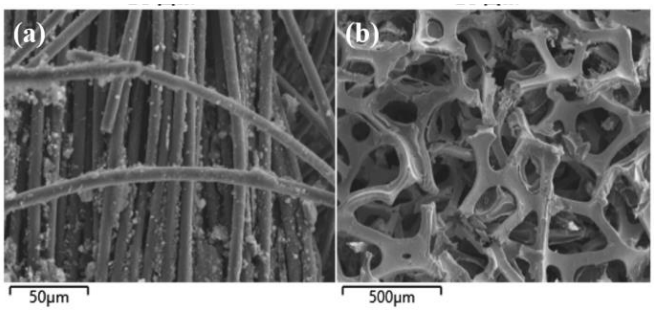

Figure S38. SEM spectra of (a) carbon cloth and (b) foam nickel electrodes after testing of compound 2.

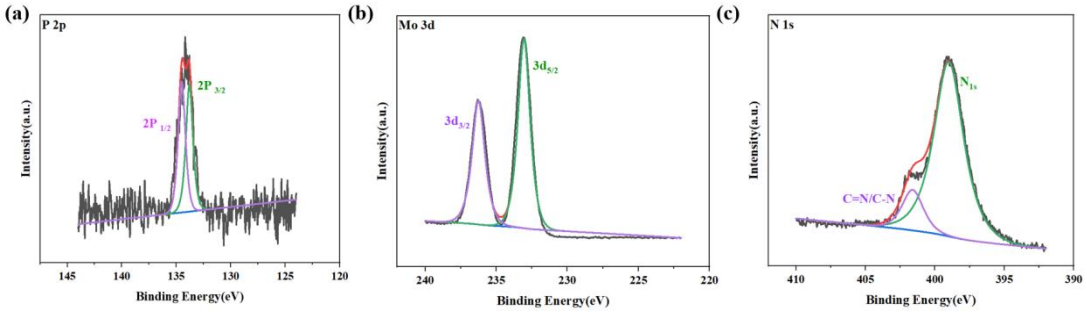

Figure S39. XPS after testing in 0.5M H_2SO_4 of compound 2.

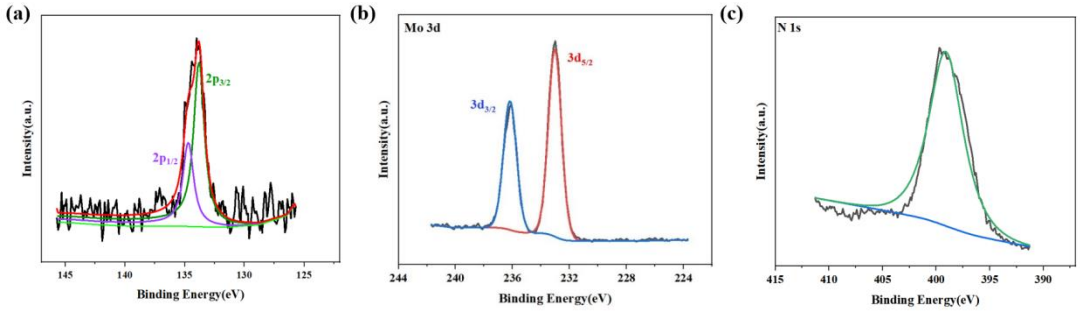

Figure S40. XPS after testing in 0.5M KOH of compound 2.

Table S5. ICP-MS determination results Concentration of Mo and N in electrolyte solution after electrochemical test.

sample	Value type	**Mo**	**N**	Electrolyte solution
Compound 2	Reported	/	/	0.5 M H_2SO_4
Compound 2	Reported	/	/	0.5 M KOH

Table S6. The EIS after fitting (In 0.5M H_2SO_4).

in 0.5M H_2SO_4	**Rs**	**Rct**	**CPE**
Compound 2	**1.588**	**3.238**	**0.0053**
Compound 3	**1.697**	**4.763**	**0.0052**
Compound 1	**1.562**	**4.902**	**0.0052**
Compound 4	**1.573**	**5.812**	**0.0063**
$H_3PMo_{12}O_{40}$	**1.595**	**4.677**	**0.0054**
pyrazine	**1.53**	**12.38**	**0.0068**

pyridine	**1.572**	**12.94**	**0.0067**
amitrole	**1.573**	**13.44**	**0.0066**
20%Pt/C	**1.557**	**2.139**	**0.0057**
Bare CC	**1.565**	**19.16**	**0.0084**

Table S7. The EIS after fitting (In 0.5M KOH).

in 0.5M KOH	**Rs**	**Rct**	**CPE**
Compound 2	**2.491**	**9.8**	**0.0002**
Compound 3	**2.675**	**11.85**	**0.0002**
Compound 1	**2.675**	**11.85**	**0.0002**
Compound 4	**2.197**	**14.31**	**0.0003**
$H_3PMo_{12}O_{40}$	**2.532**	**19.06**	**0.0004**
pyrazine	**2.48**	**21.09**	**0.00026**
pyridine	**2.618**	**16.21**	**0.0005**
amitrole	**2.685**	**28.14**	**0.0003**
RuO_2	**2.163**	**2.163**	**0.0004**
Bare NF	**2.822**	**40.92**	**0.0004**

Table S8. Compare with some polyoxometalates in the literature for Overall water-splitting.

catalyst	substrate	electrolyte	cell voltage (V) (10 mA cm^{-2})	Ref.
Ni_3S_2/$NiMo_2S_4$-POM/NF (POM=$H_3O_{40}PW_{12}\cdot xH_2O$)	NF	1M KOH	1.53	1
POM–$ZnFe_2O_4$ (POM=$(NH_4)_6P_2Mo_{18}O_{62}$)	NF	1M KOH	1.53	2
$NiCo_2S_4$@NiFe LDH	NF	1M KOH	1.60	3
Cu_3P@NF	NF	1M KOH	1.67	4
Ni_2P/CP	CFP	1M KOH	1.57	5
NiCoP/CC	CC	1M KOH	1.52	6
Mo_2C/CS	NF	1M KOH	1.73	7
Co_2P/Ni_2P-2%Mo	NF	1M KOH	1.56	8
NiFe LDH-POM/NF	NF	0.1M KOH	1.45	9
POM@ZnCoS NWs (POM=PW_{12}nanoparticles)	NF	1M KOH	1.64	10
$\{Cu(NH_4)_2NiMo_6O_{24}H_6\}$@HKUST-1	NF	1M KOH	1.61	11
$Co(OH)_2$/NiMoCA@CC	CC	1M KOH	1.52	12

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