Metal-Organic Frameworks Based on Tetraphenylpyrazine Derived Tetracarboxylic Acid for Electrocatalytic Hydrogen Evolution Reaction and NACs Sensing

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Content

Table S1. Selected bond lengths (Å) and angles (°) for 1-6.

Compound 1					
Cd1-O1	2.391(4	Cd1-O2	2.376(4)	N1-C9	1.345(6)
Cd1-O3	2.240(4	O1-C16	1.261(7)	C2-C3	1.387(7)
O2-C16	1.247(7	O3-C1	1.253(7)	C1-C2	1.506(6)
O4-C1	1.252(7	N1-C8	1.335(6)	C7-H7	0.93
O1-Cd1-O1	133.7(2	O2-Cd1-O1	88.67(1)	C16-O1-Cd1	90.6(4)
O2-Cd1-O2	80.9(2)	O3-Cd1-O1	88.64(1)	C1-O3-Cd1	111.1(3)
Compound 2					
Pb1-O1	2.428(5	Pb1-O7	2.283(5)	C1-C2	1.509(1)
Pb1-O4	2.436(7	Pb1-O2	2.547(5)	Pb2-O3	2.324(6)
N1-C32	1.247(7	O3-C1	1.253(7)	C1-O2	1.260(9)
O4-C1	1.340(9	N1-C8	1.346(9)	Pb2-O5	2.398(5)
C1-O1-Pb1	133.7(2	O7-Pb1-O1	76.1(2)	O1-Pb1-O2	137.2(2)
O7-Pb1-O4	87.5(2)	O7-Pb1-O7	78.8(3)	O1-C1-O2	127.0(7)
Compound 3					
La1-O1	2.565(4)	La1-O3	2.638(6)	N1-C8	1.338(4)
La1-O4	2.543(4)	La1-O5	2.673(5)	N2-O26	1.335(4)
La1-O6	2.499(4)	La1-O7	2.559(5)	N1-C9	1.329(4)
O3-C19	1.255(4)	O4-C19	1.274(5)	N2-O27	1.337(4)
O1-La1-O3	70.83(1)	O1-La1-O5	142.76(7)	O4-La1-O3	50.27(9)
O3-La1-O5	139.57(1)	O1-La1-O4	82.63(1)	O5-La1-O7	118.02(9)
Compound 4					
Sr1-O1	2.537(2	Sr1-O3	2.717(2)	Sr2-O7	3.005(3)
Sr1-O10	2.508(2	Sr1-O87	2.547(3)	Sr2-O12	2.651(2)
Sr1-O88	2.709(2	Sr1-O89	2.647(2)	Sr2-O10	2.648(2)
Sr2-O3	2.539(2	Sr2-O4	2.518(2)	Sr2-O18	2.689(4)
O1-Sr1-Sr2	78.46(4	O1-Sr1-O2	24.29(7)	O1-Sr1-O89	70.96(7)
O1-Sr1-O3	48.60(6	O1-Sr1-O88	128.63(7)	O10-Sr1-O89	79.21(7)
Compound 5					
Ce1-O1	2.518(2)	Ce1-O2	2.606(2)	N1-C6	1.335(4)
Ce1-O3	2.518(2)	Ce1-O4	2.657(2)	C12-O3	1.218(5)
Ce1-O5	2.541(2)	Ce1-O6	2.495(19)	N1-C7	1.343(4)
Ce1-O7	2.522(19)	Ce1-O9	2.562(2)	C12-O2	1.314(5)
O3-Ce1-O1	76.60(8)	O4-Ce1-O1	132.61(7)	O5-Ce1-O4	50.06(7)
O4-Ce1-O3	147.95(8)	O5-Ce1-O2	122.62(8)	O6-Ce1-O1	79.55(7)
Compound 6					

Mn4-O5	2.319(3)	Mn4-O4	2.027(4)	Mn3-O9	2.201(4)
Mn4-O5	2.219(3)	Mn4-O4	2.027(4)	Mn3-O9	2.201(4)
Mn4-O6	2.217(3)	Mn3-O3	2.143(4)	Mn3-O3	2.143(4)
Mn4-O6	2.217(3)	Mn3-O5	2.208(4)	Mn3-O5	2.208(4)
O5-Mn4 -O5	96.13(17)	O4-Mn4-	97.12(15)	O5-Mn3-O5	85.83(19)
O6-Mn4 -O5	86.79(13)	O4-Mn4-	127.24(16	O3-Mn3-O3	162.4(2)

Symmetry code: 1. Cd = x, y, z; O2 = 1-x, 0.25+y, 0.25+z.; 2. Pb1= x, y, z; O4= -x, 1-y, 1-z.; 3. La1= x, y, z; O5= x, y, z; 4. Sr1= x, 1+ y, z; Sr2=1- x, 1-y, 1-z; 5. Ce1 = x, y, z; O1 = x, y, 1 + z; 6. Mn3= x, y, z; Mn4= x, y, z.

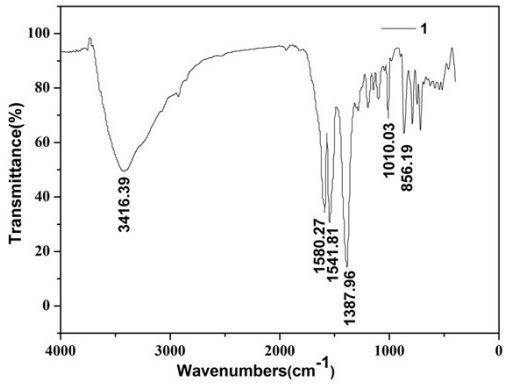

Fig. S1 Infrared spectrum of 1.

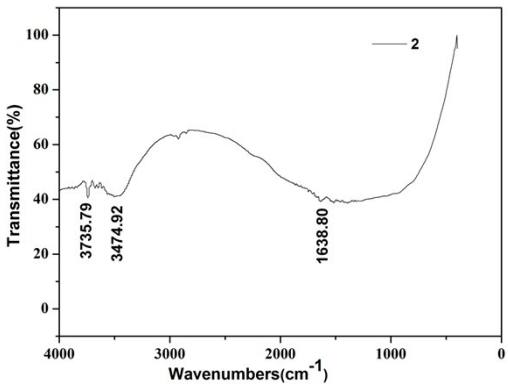

Fig. S2 Infrared spectrum of 2.

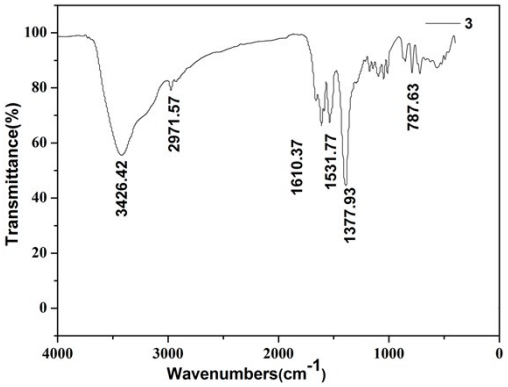

Fig. S3 Infrared spectrum of 3.

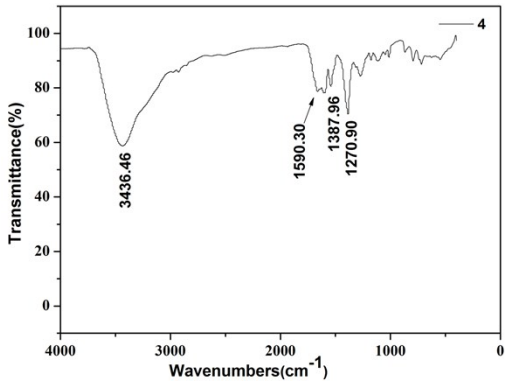

Fig. S4 Infrared spectrum of 4.

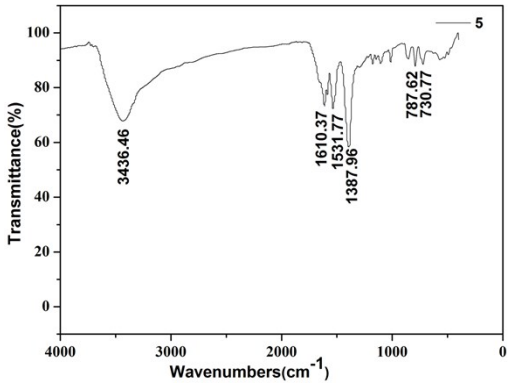

Fig. S5 Infrared spectrum of 5.

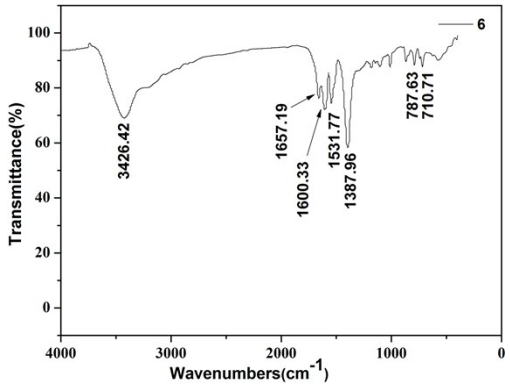

Fig. S6 Infrared spectrum of 6.

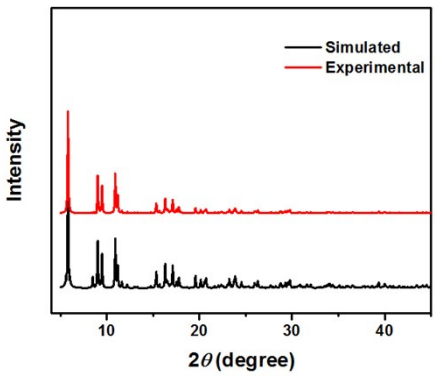

Fig. S7 PXRD patterns of 1

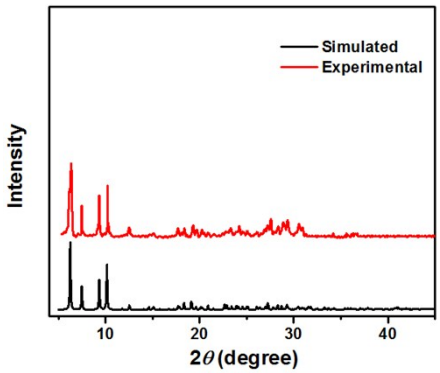

Fig. S8 PXRD patterns of 2.

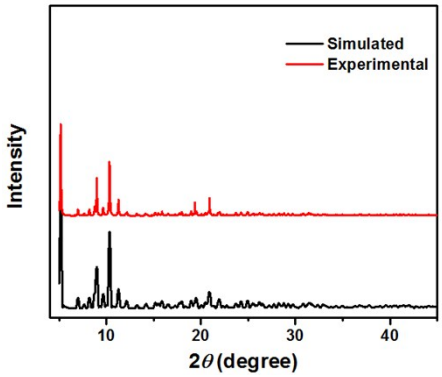

Fig. S9 PXRD patterns of 3.

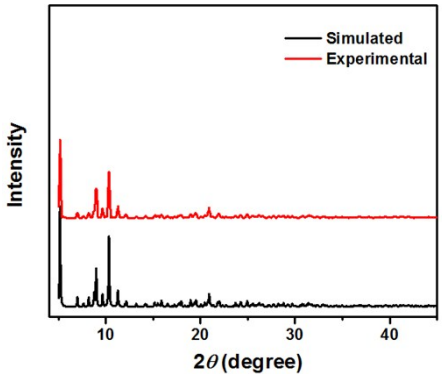

Fig. S10 PXRD patterns of 4.

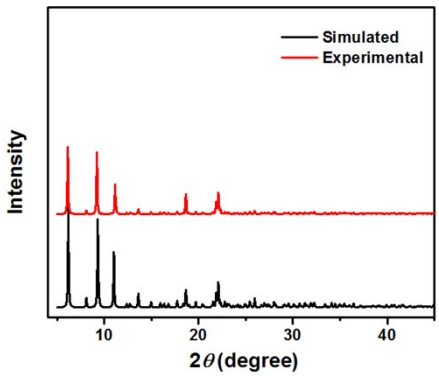

Fig. S11 PXRD patterns of 5.

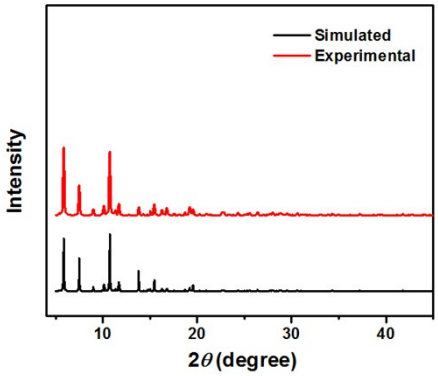

Fig. S12 PXRD patterns of 6.

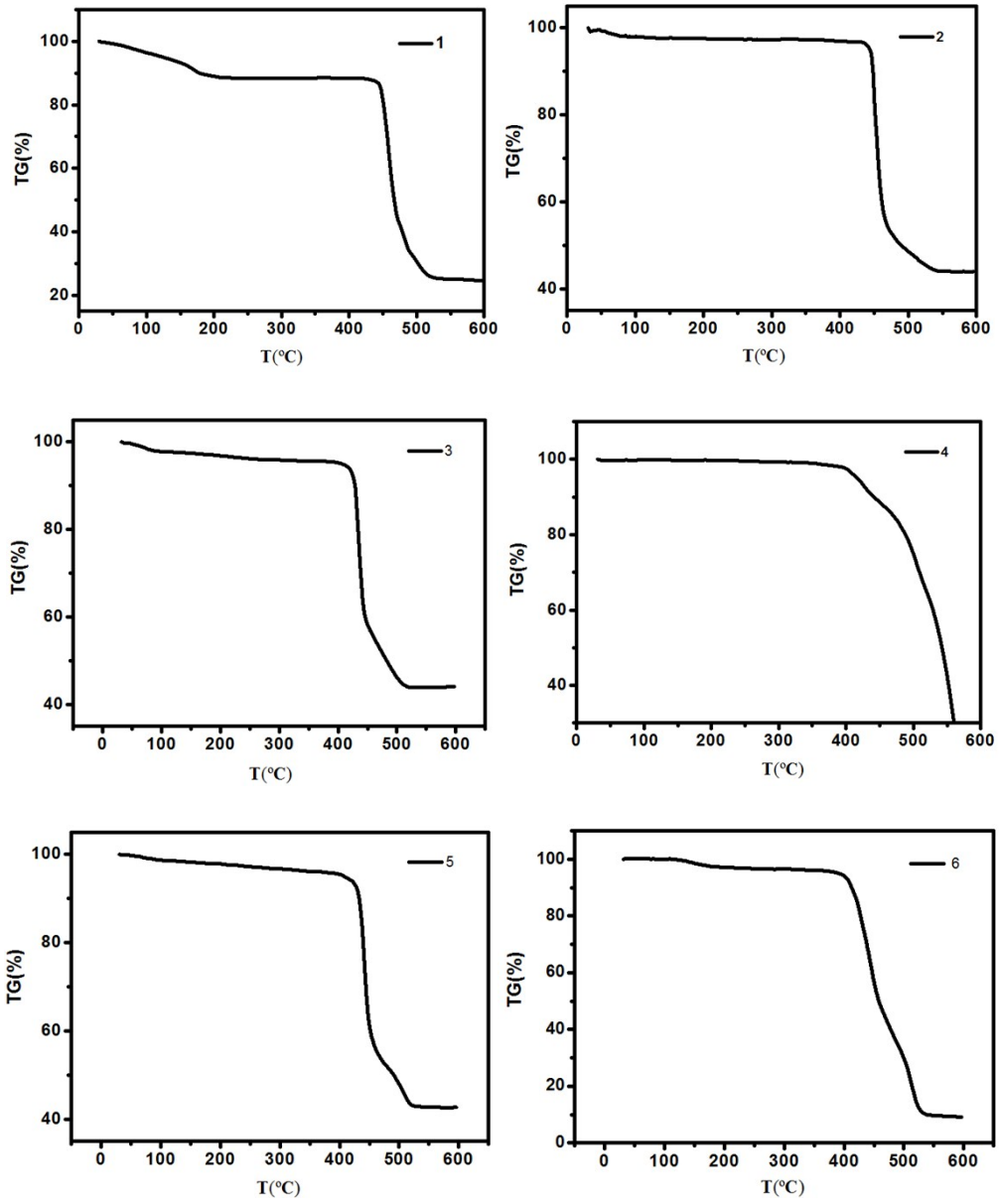

Fig. S13 TGA plots of 1 - 6.

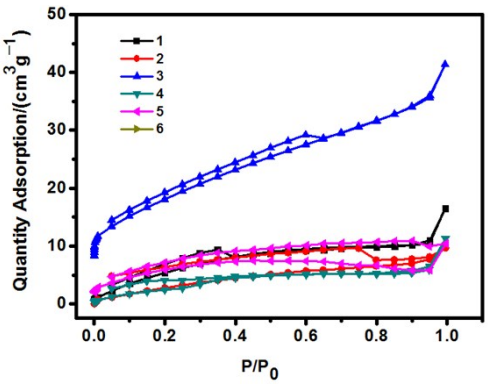

Fig. S14 N_2 adsorption isotherm of 1 - 6 at 77 K.

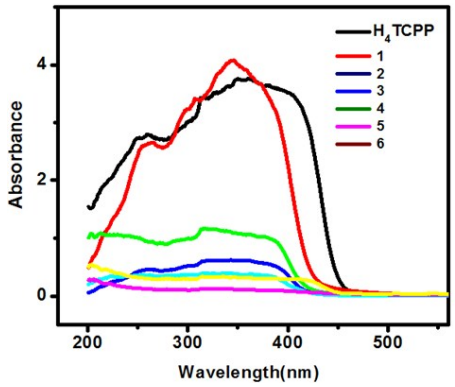

Fig. S15 Solid-state absorption spectra of H_4TCPP and 1 – 6.

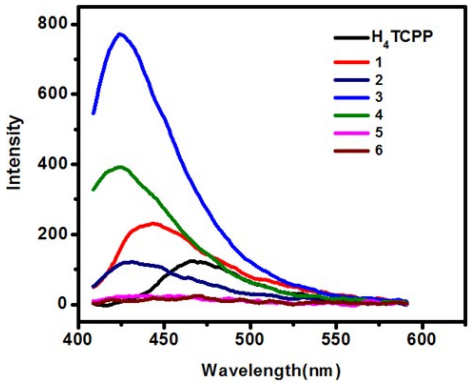

Fig. S16 Solid-state emission spectra of H_4TCPP and 1 - 6.

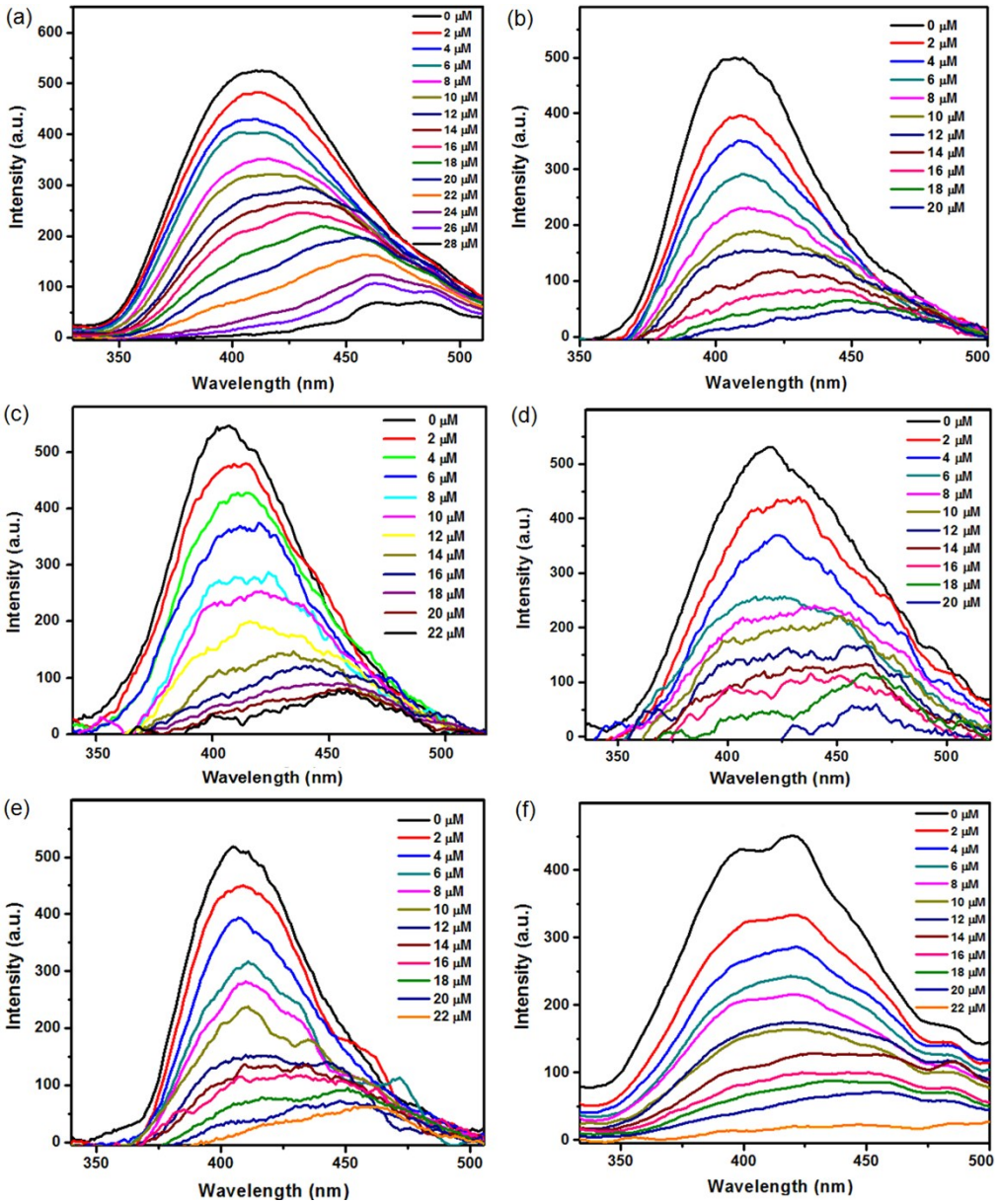

Fig. S17 The emission spectra of MOFs 1 - 6 (0.5 mg in 2 mL H_2O) titrated with TNP in water.

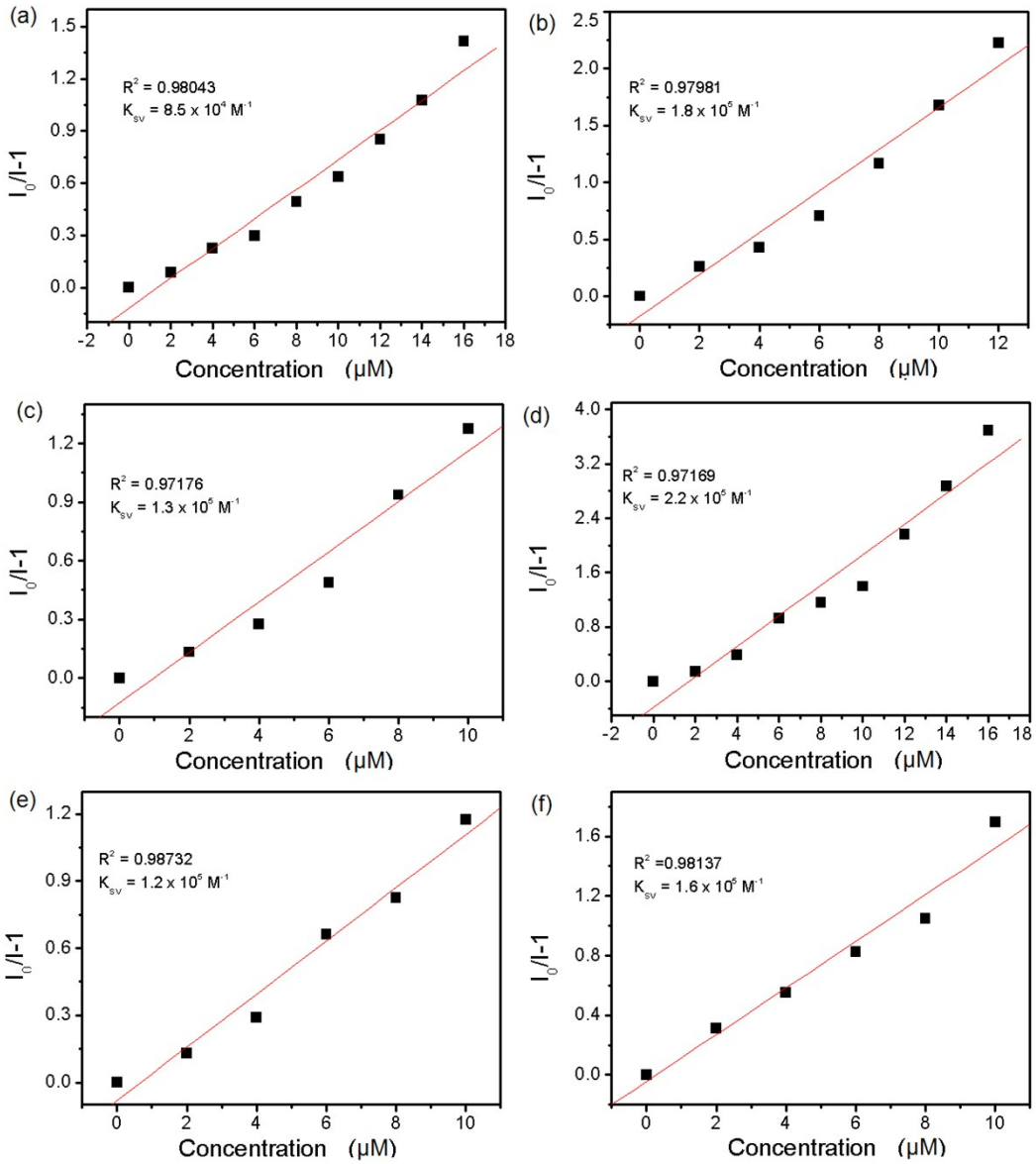

Fig. S18 Stern - Volmer plots of the fluorescent quenching of MOFs 1 - 6 with TNP, respectively. The solid lines represent fit to the concentration-resolved data using the Stern - Volmer equation. The fluorescence intensity was monitored at 432 nm.

Table S2. The corresponding data of 1 – 6 evaluated from nitrogen adsorption.

Complex	BET(m^2/g)	Pore volumes (cm^3/g)	pore size(μm)
1	4.493	0.0255	3.819
2	4.193	0.01491	3.408
3	18.325	0.06396	3.406
4	1.675	0.01745	3.405
5	3.642	0.01612	4.304
6	31.128	0.07064	3.405

Table S3. Comparison of electrocatalytic activities of 1 – 6.

catalyst	dimensionality	η_{10} * (mV)	V_{onset} (mV)	Solution (1M)	Tafel Slope
H_4TCPP	2D	486	380	KOH	435
1	3D	423	348	KOH	400
2	3D	449	362	KOH	253
3	3D	545	336	KOH	485
4	3D	487	319	KOH	362
5	3D	457	244	KOH	273
6	3D	452	350	KOH	360

*η_{10} is defined as overpotential measured for a current of 10 mA cm^{-2}.

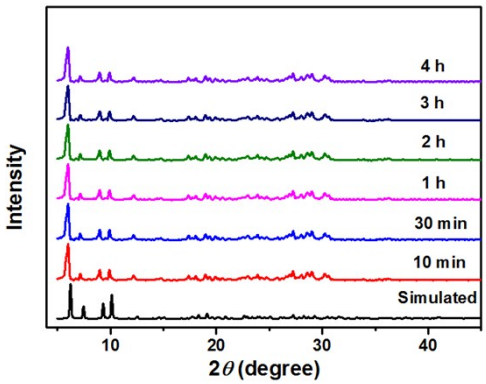

Fig. S19 PXRD patterns of 2 immersed in 1M KOH at different time.

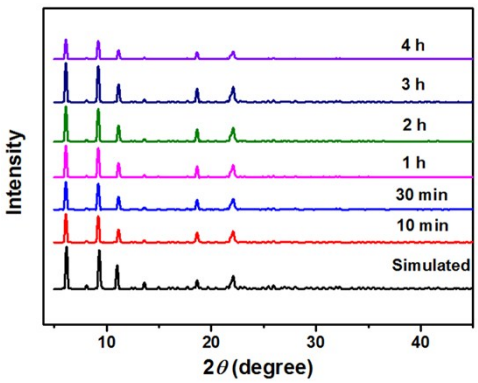

Fig. S20 PXRD patterns of 5 immersed in 1M KOH at different time.

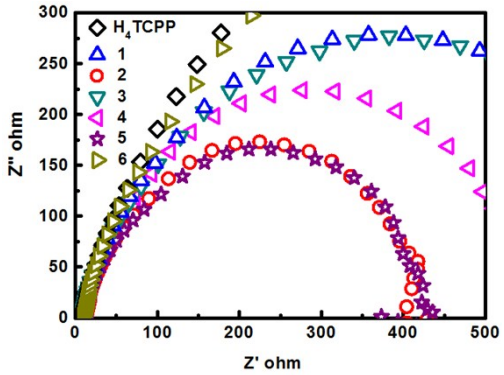

Fig. S21 Electrochemical impedance spectra (EIS) of 1 - 6 and H_4TCPP