Supporting Information for

Temperature-induced Structural Diversity of Metal-Organic Frameworks and Their Applications in Selectively Sensing of Nitrobenzene and Electrocatalyzing Oxygen Evolution Reaction

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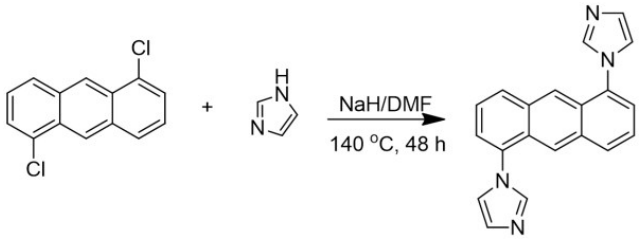
Contents

Electrocatalytic method for OER

Electrochemical measurements were carried out on a CHI-660E electrochemical workstation in a standard three electrode system with a scan rate of 5 mV s^{-1} by using 1.0 M KOH (pH = 14) electrolyte, in which platinum wire was served as the counter electrode while Ag/AgCl was employed as the reference electrode. The Working electrode was prepared through loading the as-prepared samples onto the surface of the GCE, then electrochemically preconditioned with 10 cyclic voltam-metric scans to reach a steady state before LSV tests. All measured potentials were converted to the reversible hydrogen electrode (RHE) potential based on the equation E(RHE) = E(Ag/AgCl) + 0.059 pH + 0.197 V. Electrochemical impedance spectra (EIS) were recorded at the open circuit potential in potentiostatic mode in a frequency range from 100 kHz to 0.1 Hz with an AC amplitude of 5 mV. The charging current versus the scan rate was directly proportional to Cdl, and the electrochemical active surface area could be evaluated from the slope. All measurements were conducted at room temperature unless otherwise stated.



Scheme S1 Synthetic route for ligand **L1**

Table S1 Comparisons of some MOF-based sensors for NB among various NACs.

MOFs	Medium	K_{sv}/M^{-1}	λ_{Ex}/nm	LOD	Refs	Selectivity
UPC-21	DMSO	4.42×10^5	330	0.0949 ppm	*Sci. Rep*., 2016, **6**, 20672	no
$[Tb_2(H_2L)_3(H_2O)2]\cdot 21H_2O$	EtOH	2.5×10^4	265	0.467 μM	*J. Mater. Chem. A*, 2017, **5**, 1952	no
Tb^{3+}@NENU-522	DMF	-	333	100 ppm	*Inorg. Chem. 2015, **54**, 3290*	no
Zn-MOFs	-	<504.6	360	-	*Cryst. Growth Des.,* 2016, **16**, *4539*	no
Ln-MOFs	H_2O	$617/754 \times 10^{-2}$ ppm^{-1}	320	-	*Dalton Trans.* 2015, **44**, 14594	no
$[Zn(L)_2]\cdot 3DMF\cdot 5H_2O$	MeOH	-	-	-	*Inorg. Chem.*, 2013, **52**,12323	no

[InRu(dcbpy)$_3$]-[$(CH_3)_2NH_2$]·6H_2O	MeOH	-	400 (solid)	-	*Cryst. Growth Des.,* 2013, **13**, 5466	no
$Zn_4O(L)_2$ ($H_2O)_3$] 3DMA 3EtOH 6H_2O	EtOH	-	350	-	*Chem. Commun.,* 2011, **47**, 12137	no
$Eu_3(MFDA)_4(NO_3)$(1a)	DMF	-	336		*Dalton Trans.* 2013, **42**, 5718	no
[Tb(TTCA)(DMA)(H_2O)]·7DMA·9.5H_2O	EtOH	-	370	0.025 mM	Chem. Commun., *2013, **49**, 11113*	no
[Zn_2(L)(bipy)($H_2O)_2$]·($H_2O)_3$($DMF)_2$ (**1**)	CH_3CN	-	350	5–200 ppm	*Dalton Trans. 2013, **42**, 12865*	yes
Zn-MOF (**1'**)	-	-	280	-	*J. Am.Chem. Soc.,* 2011, **133**, 4153	yes
Co-MOFs	***H_2O***	***3.28×10^4 - 6.15×10^4***	***270 nm***	***3.3 μM***	***This work***	***yes***

Table S2 Selected bond lengths (Å) and angles (°) for MOFs **1 - 4**.

		1			
Co1-O1	2.1062(15)	Co1-O2	2.1174(15)	Co1-N3	2.1244(17)
Co2-O3	2.1128(15)	Co2-O4	2.0933(15)	Co2-N1	2.1727(18)
O1-Co1- O1	180.00(7)	O1-Co1-O2	96.17(6)	$O1^1$-Co1-O2	83.83(6)
O1-Co1-N3	88.31(7)	O1-Co1-$N3^1$	91.69(7)	O2-Co1-O2	180.00
O2-Co1-N3	87.54(6)	$O2^1$-Co1-N3	92.46(6)	N3-Co1-N3	180.0
O3-Co2-O3	180.00	O3-Co2- N1	91.48(7)	$O3^2$-Co2-N1	88.52(7)
symmetry code:1 = 1-x, 1-y, 1-z; 2 = 2-x, 1-y, 1-z;					
		2			
Co2-O3	2.109(2)	Co2-O4	2.096(2)	Co2-N1	2.171(3)
Co1-O1	2.104(2)	Co1-O2	2.117(2)	Co1-N3	2.121(3)
O3-Co2-O3	180.0	O3-Co2-N1	88.58(11)	O3-Co2-$N1^1$	91.42(11)
O4-Co2-O3	97.23(10)	O4-Co2-$O3^1$	87.66(10)	O4-Co2-$O4^1$	180.0
O4-Co2-N1	91.45(11)	$O4^1$-Co2-N1	88.55(11)	N1-Co2-$N1^1$	180.00(16)
O1-Co1-$O1^2$	180.00(11)	O1-Co1-$O2^2$	83.94(10)	O1-Co1-O2	96.06(10)
O1-Co1-N3	88.30(11)	$O1^2$-Co1-N3	91.70(11)	O2-Co1-$O2^2$	180.00(10)
O2-Co1-$N3^2$	92.36(10)	O2-Co1-N3	87.64(10)	$N3^2$-Co2-N3	180.0
symmetry code: 1 = 2-x, 1-y, 2-z; 2 = 1-x, 1-y, 2-z.					
		3			
Co1-O1	2.1162(12)	Co1-N1	2.1409(15)	Co1-N4	2.1513(15)
O1-Co1-O1	180.0	O1-Co1-$N1^1$	87.18(5)	O1-Co1-N1	92.82(5)
O1-Co1-N4	86.43(5)	$O1^1$-Co1-$N4^3$	93.56(5)	$O1^1$-Co1-$N4^2$	86.44(5)
N1-Co1-$N1^1$	180.00(6)	N1-Co1-$N4^3$	90.78(6)	N1-Co1-$N4^2$	89.22(6)

$N1^{1}$-Co1-$N4^{2}$	90.78(6)	$N4^{2}$-Co1-$N4^{3}$	180.00(4)		
symmetry code: 1 = -x, 1-y, -z; 2 = +x, 3/2-y, 1/2+z; 3= -x, -1/2+y, -1/2-z.					
		4			
Co1-O1	2.1086(16)	Co1-O5	2.132(2)	Co1-N1	2.1002(19)
O1-Co1-$O1^{1}$	180.0	O1-Co1-$O5^{1}$	91.58(7)	O1-Co1-O5	88.42(7)
O5-Co1-$O5^{1}$	180.0	N1-Co1-O1	88.29(8)	$N1^{1}$-Co1-O1	91.71(8)
$N1^{1}$-Co1-$O5^{1}$	93.24(8)	$N1^{1}$-Co1-O5	86.75(8)	N1-Co1-$N1^{1}$	180.0
symmetry code: 1 = 1-x, -y, 1-z.					

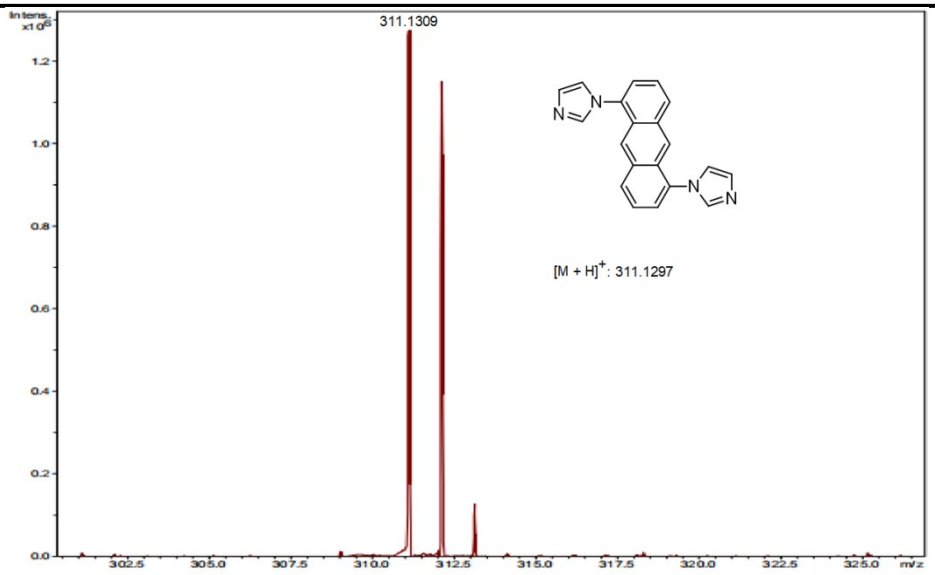


Fig. S1 The HRMS (ESI) spectrum of **L1**

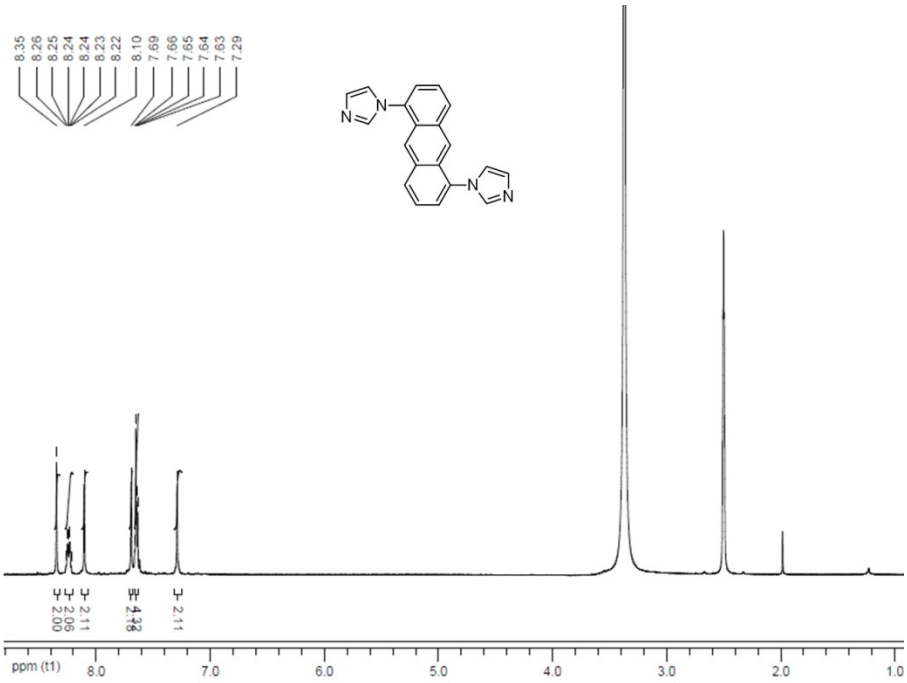


Fig. S2 ^{1}H NMR (400 MHz) spectrum of **L1** in DMSO-d_6.

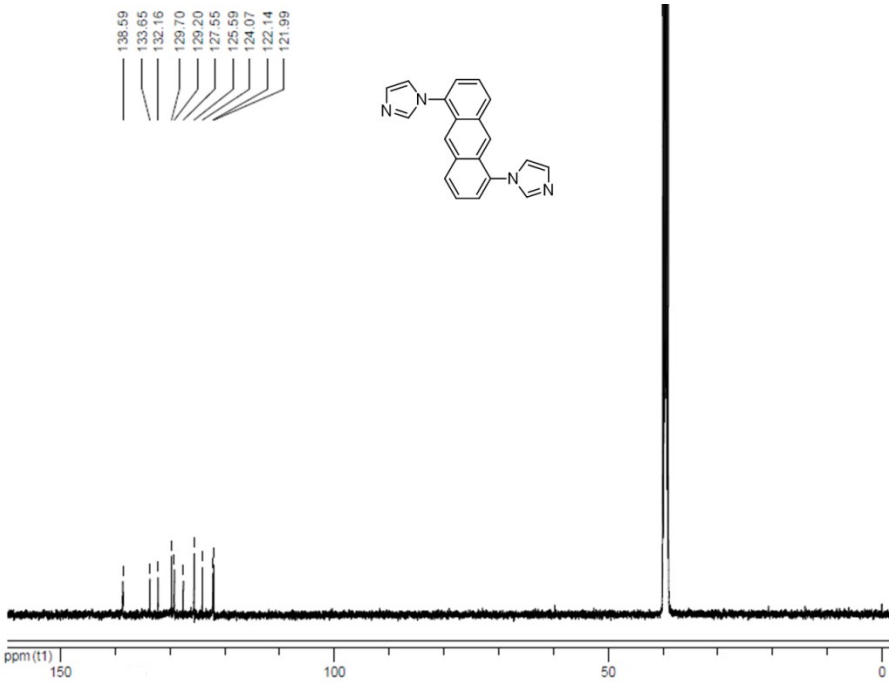


Fig. S3 ^{13}C NMR (100 MHz) spectrum of **L1** in DMSO-d_6.

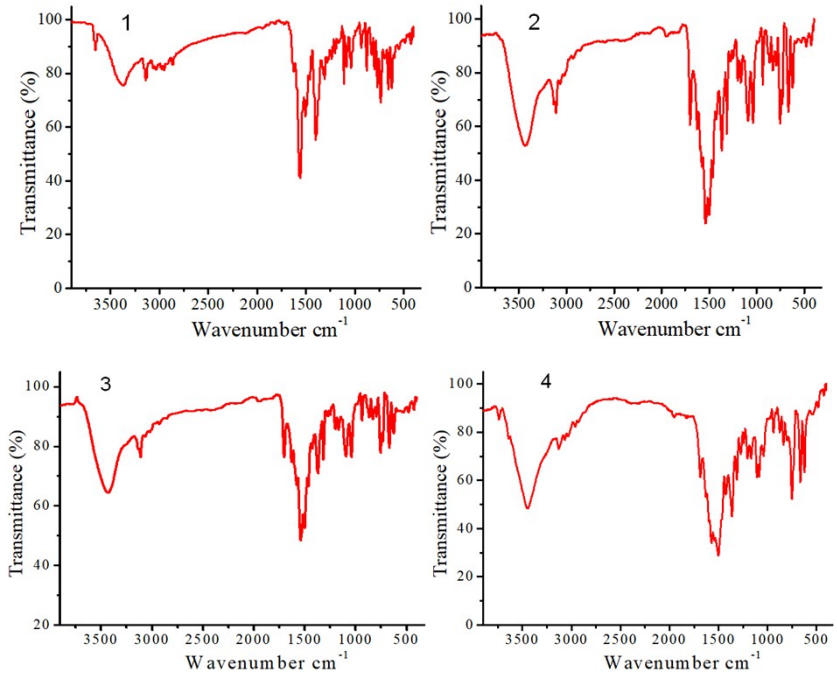
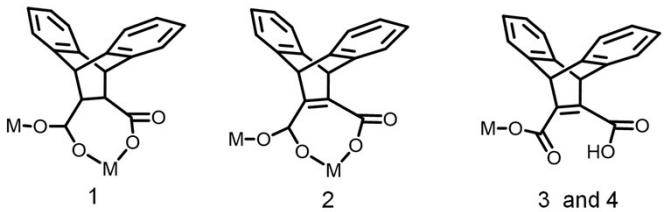


Fig. S4 IR spectra of **1 - 4**



Scheme 2 Coordination modes of dibenzobarrelene derived carboxylate ligands in MOFs **1 - 4**.

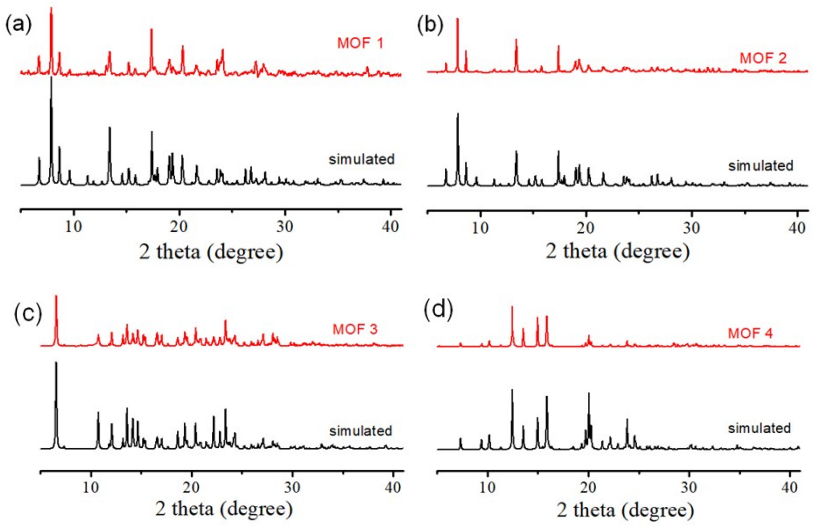


Fig. S5 PXRD patterns of the experimental (red solid lines) and simulated samples (black solid lines), a - d for MOFs **1** - **4**, respectively.

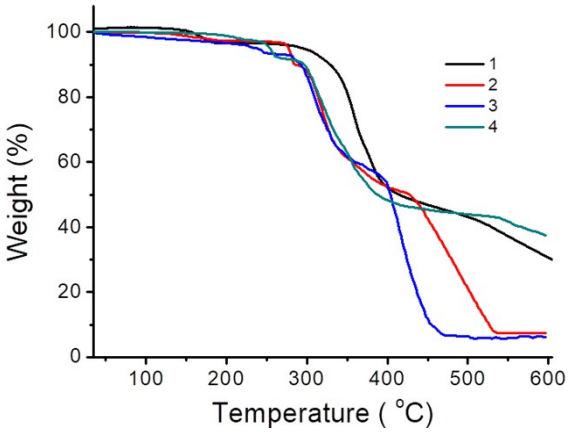


Fig. S6 TG curves for compounds **1** - **4**

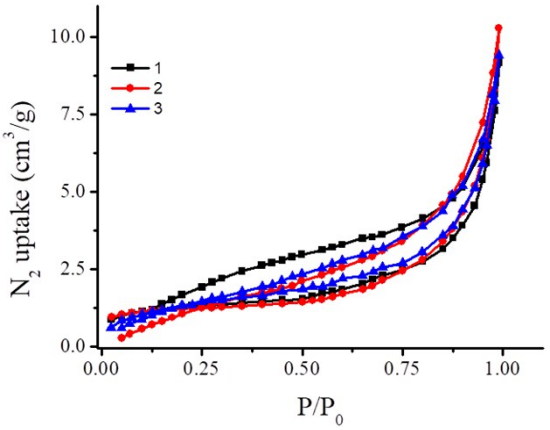


Fig. S7 The nitrogen sorption isotherms of samples **1** - **3** at 77 K.

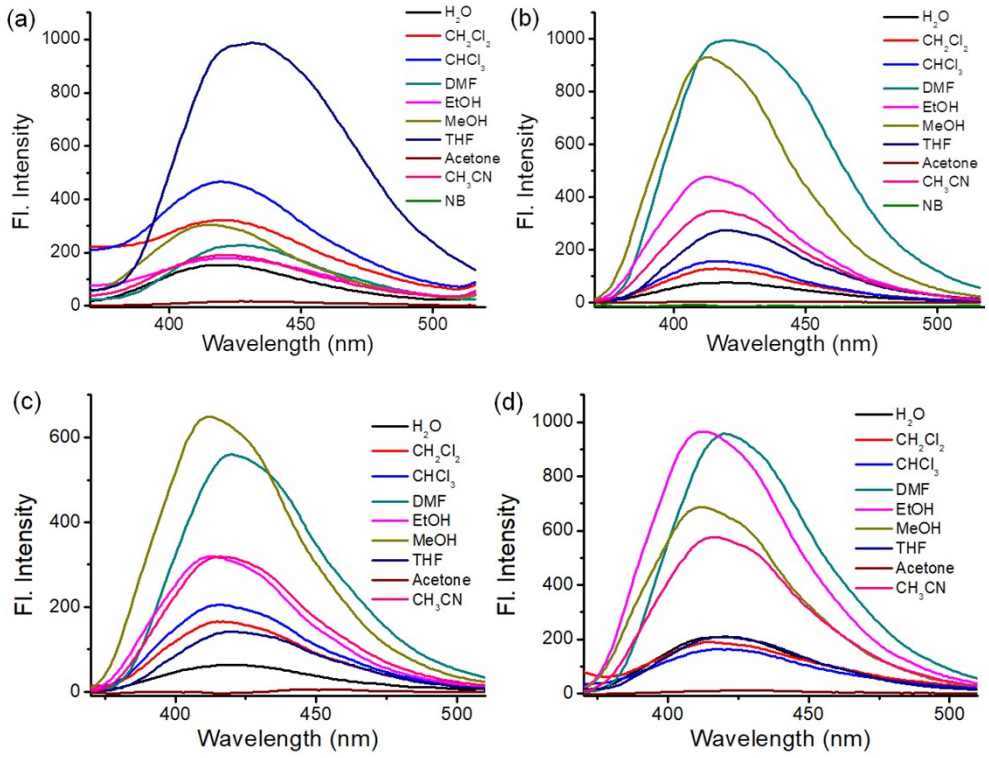


Fig. S8 Emission profiles of MOFs in different solvents (a - d for **1** - **4**, respectively), λ_{ex}: 270 nm.

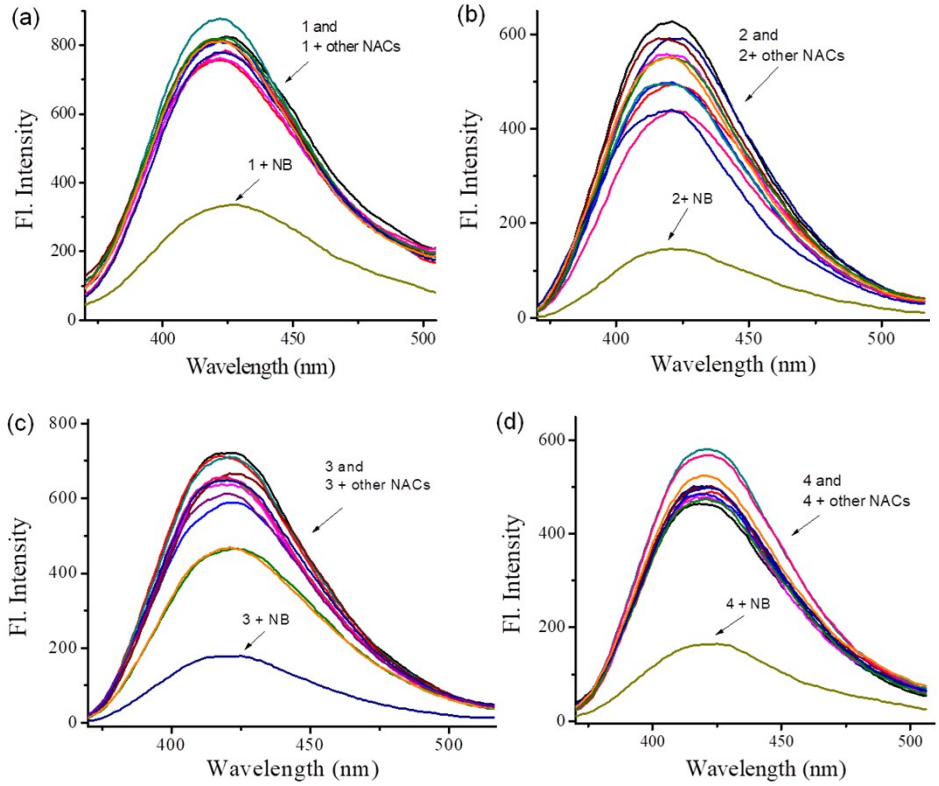


Fig. S9 Emission profile of MOFs (0.3 mg in 3 mL water) toward various NACs (16.7 μM) in water, (a - d for **1** - **4**, respectively). The other NACs include 4-NP, TNP, 2-NP, 4-CNB, 4-NTol, 2-NPA, 3-NP, 4-DNA, 4-NPA, 2, 4-NPH and 4-NBA, λ_{ex}: 270 nm.

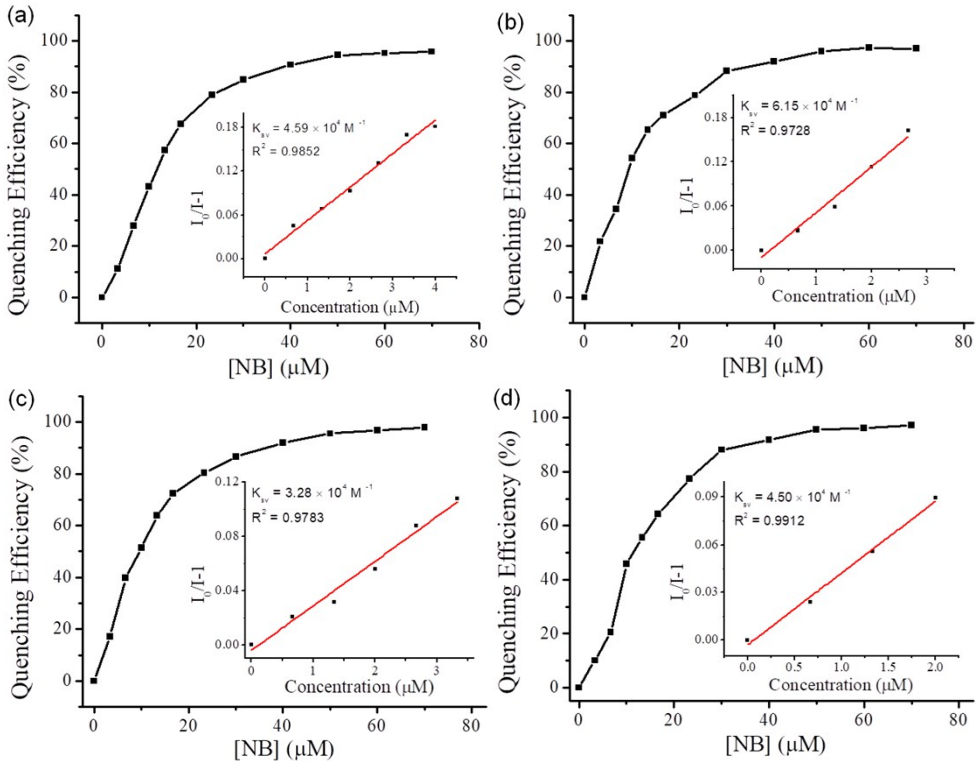


Fig. S10 The Stern - Volmer curves of MOFs with different concentrations of NB according to the titration curves (a - d for **1** - **4**, respectively). Insets: K_{sv} values calculated from data in a - d, respectively, λ_{ex}: 270 nm.

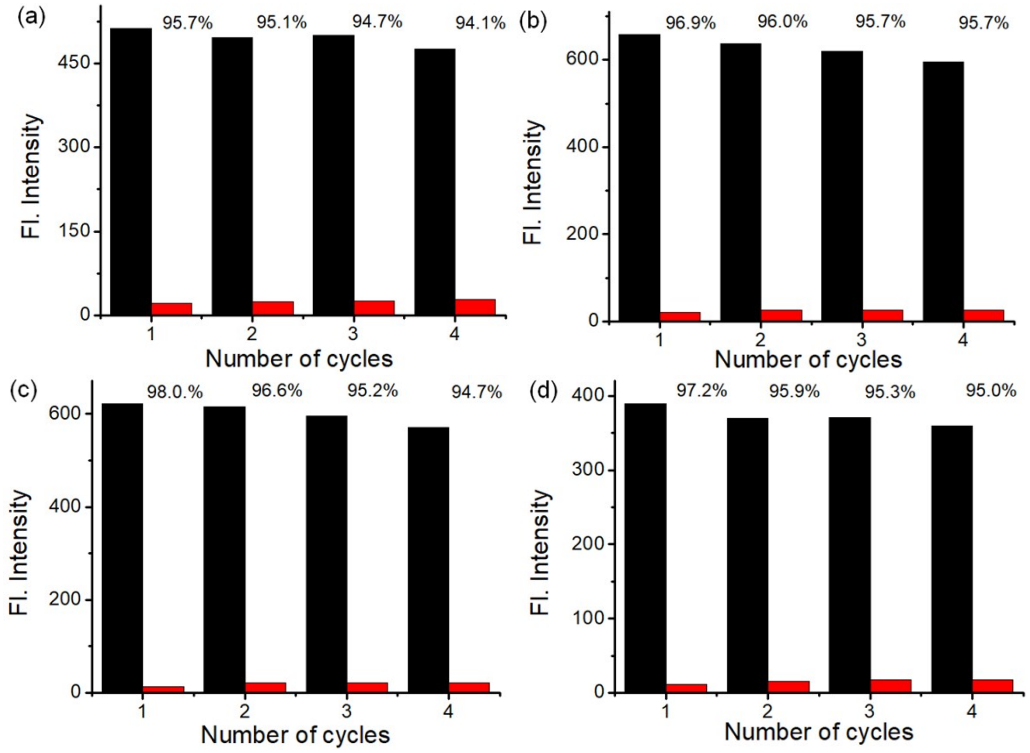


Fig. S11 Reproducible quenching ability of MOFs (a - d for **1** - **4**, respectively) in water and in the presence of NB (70 μM), black bars: free MOFs; red bars: free MOFs with NB (70 μM), fluorescence quenching efficiencies were listed in the upper part of panels a - d, respectively.

Table S3 OER activities of some Co-based materials and MOFs

Catalysts	**η mV@10 mA cm^{-2}**	**Tafel Slopes**	**Solution**	References
1	***411***	***52***	***1M KOH***	***This work***
2	***406***	***62***		
3	***438***	***60***		
4	***398***	***59***		
CoCo LDH	393	59	1M KOH	*Nat. Commun.,* 2014, **5**, 4477
NiCo LDHs	367	40	1M KOH	*Nano Lett.,* 2015, **15**, 1421–1427.
MAF-X27-OH	387	60	1M KOH	*J. Am. Chem. Soc*., 2016, **138**, 8336
Co_3O_4	465	91	1M KOH	*ACS Appl. Mater. Interfaces.,* **2017**, **9**, 7193
ZIF-67	400	108.8	1M KOH	*Adv. Funct. Mater.,* 2017, **27**, 1702546.
Pb-MOF	1.70 V	106.2	1M KOH	Dalton Trans., 2016, **45**, 61
$[Co_4(MOO_4)(eim)_6]$	210@1 mA cm^{-2} 490@10 mA cm^{-2}	144/219	0.5 M $KHCO_3$/ PBS pH=7	Angew. Chem. Int. Ed., 2019, **131**, 145
Co-ZIF-9 [a]	400	193	0.1 M PBS pH = 7	Nanoscale, 2014, **6**, 9930
UTSA-16	408	77	1M KOH	*ACS Appl. Mater. Interfaces.,* 2017, **9**, 7193
CoFe-MOF-74	280	56	1M KOH	ACS Energy Lett., 2018, **3**, 2520
$A_{2.7}B$-MOF-$FeCo_{1.6}$	288	39	1M KOH	*Adv. Energy Mater.*, 2018, **8**, 1801564
Fe/$Ni_{2.4}$/$Co_{0.4}$-MIL-53	236@20 mA cm^{-2}	52.2	1M KOH	*Angew. Chem. Int. Ed.*, 2018, **57,** 1888
NiFe-UMNs	260	30	1M KOH	*Nano Energy*, 2018, **44**, 345
CoFe-UMNs	350	31	1M KOH	
Bulk NiFe-MOFs	420	61	1M KOH	
NiCo-UMOFNs	250	42	1M KOH	*Nat. Energy*, 2016, **1**, 16184
Ni-UMOFNs	321	65	1M KOH	
Bulk NiCo-MOFs	317	61	1M KOH	

[a] Substrate: FTO electrode; others catalysts were loaded on glass carbon electrode (GCE).

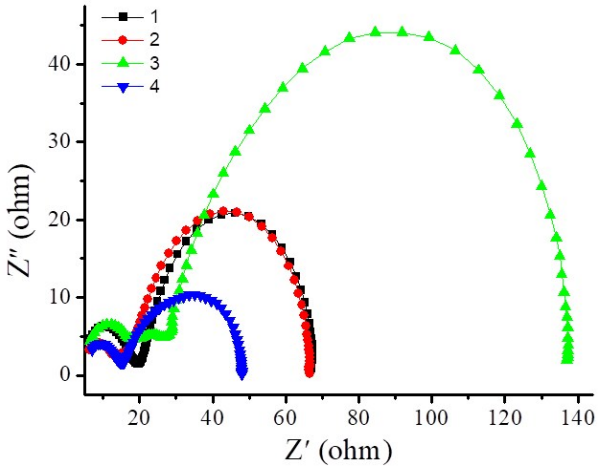


Fig. S12 Electrochemical impedance spectra (EIS) of **1 - 4**.

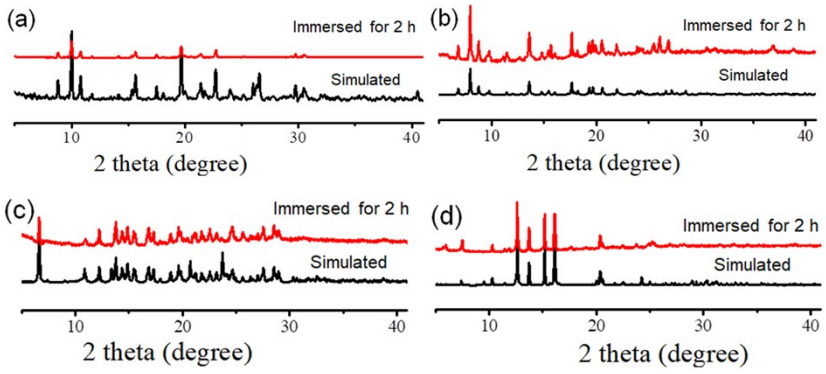


Fig. S13 PXRD patterns of **1 - 4** immersed in 1M KOH for 2h