Electronic Supplementary Information

Modulating Hydrophilicity and Conductivity of Covalent Organic Frameworks for Enhanced Oxygen Evolution Reaction

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Experimental detail

Material and general method. There was no need to purify pharmaceuticals or chemical reagents before use. Sun Chemical Technology Co. (Shanghai, China) provided the following products: Tp, Tfmb, Nda, mesitylene, and *o*-dichlorobenzene (*o*-DCB). The supplier of acetone was Chongqing Chuandong Chemical (Group) Co., Ltd, located in Chongqing, China. *N*, *N*-Dimethylformamide (DMF), methanol, ethanol, CH_3COOH, $Co(CH_3COO)_2{\cdot}4H_2O$, and tetrahydrofuran (THF) were obtained from Guangdong Guanghua Sci-Tech Co., Ltd (Guangdong, China). KOH and KCl were purchased from Xilong Scientific Co., Ltd. in Guangdong, China.

Scanning electron microscope (SEM) from TESCAN MIRA LMS, Czech Republic was used to obtain SEM images, while a Thermo Scientific K-Alpha (Thermo Fisher Scientific, USA) was used to perform X-ray photon-electron spectroscopy (XPS) measurements. The X-ray diffraction (XRD) spectra were collected on a Rigaku Ultima IV (Rigaku, Japan). A Nicolet 670 Fourier Transform-Infrared Spectrometer (FT-IR) (Nicolet, America) was used to record FTIR spectra (KBr), and a Quantachrome Autosorb IQ3 (Quantachrome Instruments, USA) was used to measure N_2 adsorption-desorption isotherms and pore size distributions at 77 K. A Discovery SDT 650 (TA, America) was used to obtain thermogravimetric analysis curves. A contact angle goniometer (JY-82C, Chengde Dingsheng Testing Machine Testing Equipment Co., Ltd. China) was used to measure the water contact angle.

Synthesis

COF-Tfmb$_{50}$ was used as an example. 63.3 mg of Tp (0.3 mmol), 35.6 mg of Nda (0.225 mmol), and Tfmb (0.225 mmol, 72.3 mg) were ultrasonically dispersed in 6 mL of a mixture of o-dichloroethane and mesitylene (1:1, 6 mL). Then, 0.6 mL of 6 M acetic acid was added. After three freeze-extract-thaw cycles, the tubes were sealed and heated at 120 °C for 3 days. The precipitate was collected via filtration, separated, and washed with methanol and DMF. The COF-Tfmb$_{50}$ was synthesized and subsequently purified using THF and acetone Soxhlet extraction for 24 hours. The resulting yellow powder was dried under vacuum at 80°C for 12 hours, yielding a final product with 83% purity. COF-Tfmb$_{0}$, COF-Tfmb$_{33}$, COF-Tfmb$_{67}$, and COF-Tfmb$_{100}$ were synthesized using the same procedure as COF-Tfmb$_{50}$ by varying the amounts of Nda and Tfmb according to the molar ratio.

A mixture of 100 mg of COF-Tfmb$_{x}$ and 100 mg of $Co(CH_3COO)_2 \cdot 4H_2O$ was mixed in 10 mL of ethanol (EtOH). The suspension was kept for 12 hours at 50 °C while being agitated at 200 rpm. To get the Co-COF-Tfmb$_{x}$, the resulting product was filtered out, cleaned with deionized water and EtOH, and dried at 60 °C under vacuum.

Electrochemical Characterization

All electrochemical measurements were performed in 1 M KOH solution (pH = 14) using a CHI 660E electrochemical workstation. Electrochemical characterization was performed in a standard three-electrode electrochemical cell using graphite rods and Ag/AgCl (1 M KOH) as counter and reference electrodes, respectively, and a sample-coated glassy carbon (GC) electrode as the working electrode. The potentials of all measurements were calibrated to RHE according to the following equation: $E_{RHE} = E_{Ag/AgCl} + 0.1989\ V + 0.059\ pH$, and the current densities were normalized to the effective geometric surface area of the Co-COF-Tfmb$_{x}$-coated GCs. Linear sweep voltammetry (LSV) measurements were confidently performed to determine the OERs at a scanning rate of 5 mV/s and corrected to 95% iR. Tafel plots were derived from the obtained polarization OER curves and confidently fitted to the equation $\eta = b \log j + a$ (where η is overpotential, j is current density, b is Tafel slope, and a is Tafel constant). Electrochemical impedance spectroscopy (EIS) was confidently performed at a potential of 1.60 V from 10^5 Hz to 0.01 Hz with an AC voltage of 5 mV. Electrode stability was confidently assessed by chronopotentializing the electrode during 24 hours of continuous OER electrolysis.

The working electrode material was prepared as follows: the prepared Co-COF-$Tfmb_x$ material (1 mg) was dispersed in a Nafion mixture (ethanol: water: 5% Nafion = 100 μL: 100 μL: 10 μL). After approximately 60 minutes of sonication, 2.4 μL of the mixture was dropped onto a glassy carbon electrode (3 mm effective diameter). Finally, room temperature drying of the working electrodes was performed. The glassy carbon electrodes were meticulously polished with aluminum oxide powder of 1.5 μm, 500 nm, and 50 nm to ensure a pristine electrode surface before use.

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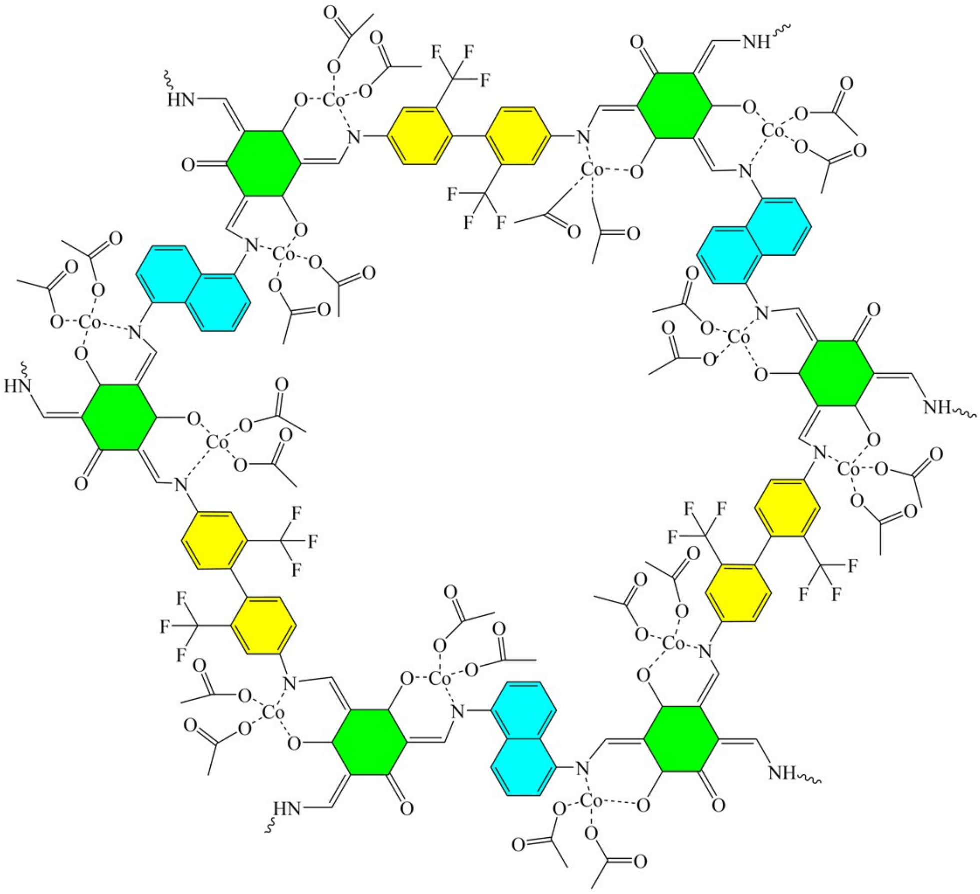
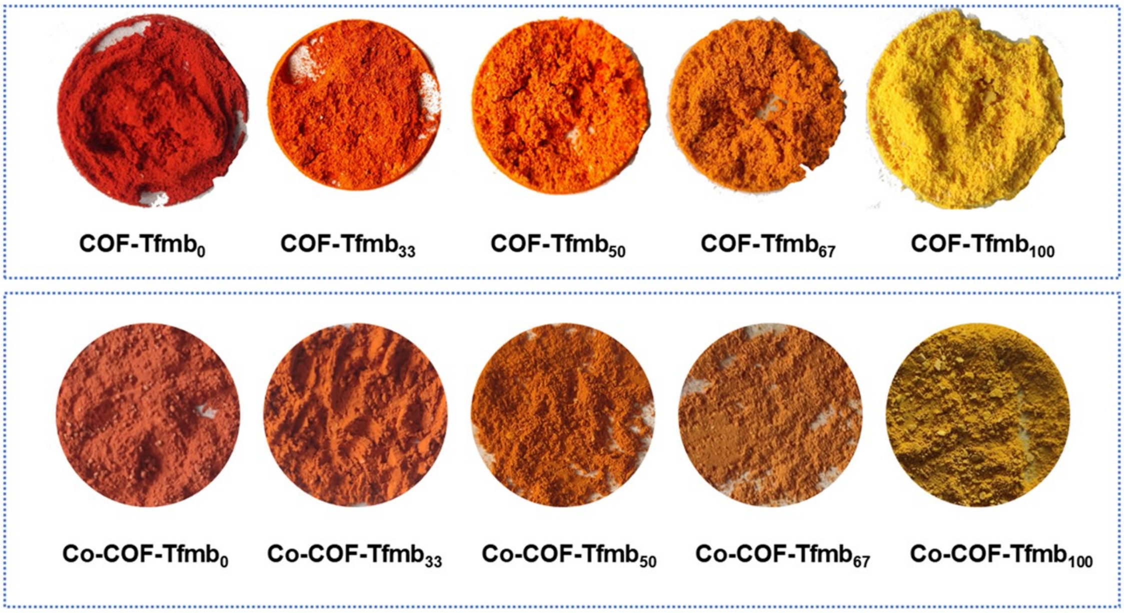


Figure S1. Structure of the Co-COF-Tfmb$_x$ complex.



COF-Tfmb$_0$ COF-Tfmb$_{33}$ COF-Tfmb$_{50}$ COF-Tfmb$_{67}$ COF-Tfmb$_{100}$

Co-COF-Tfmb$_0$ Co-COF-Tfmb$_{33}$ Co-COF-Tfmb$_{50}$ Co-COF-Tfmb$_{67}$ Co-COF-Tfmb$_{100}$

Figure S2. Comparison Color COF-Tfmb$_x$ and Co-COF-Tfmb$_x$.

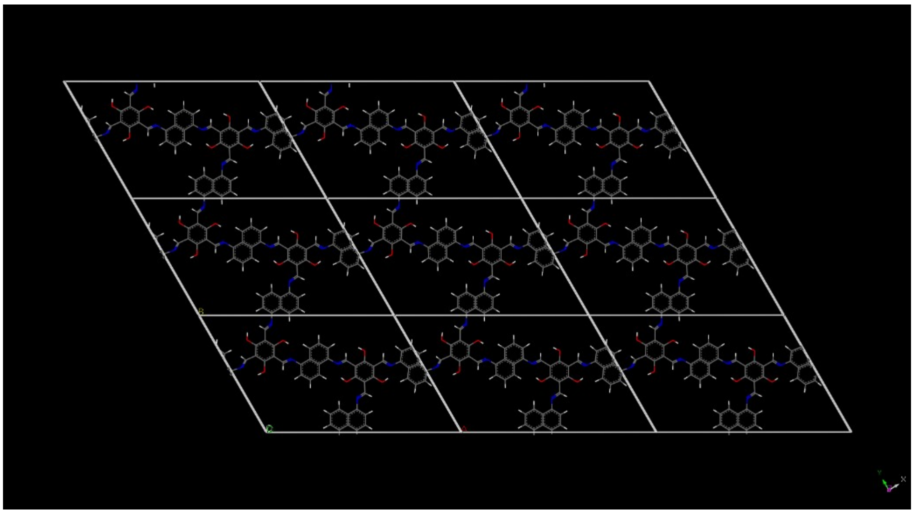


Figure S3. Structural Simulation of Co-COF-Tfmb$_0$ (calculated: a=26.1165, b=18.0868, c=3.5505 Å).

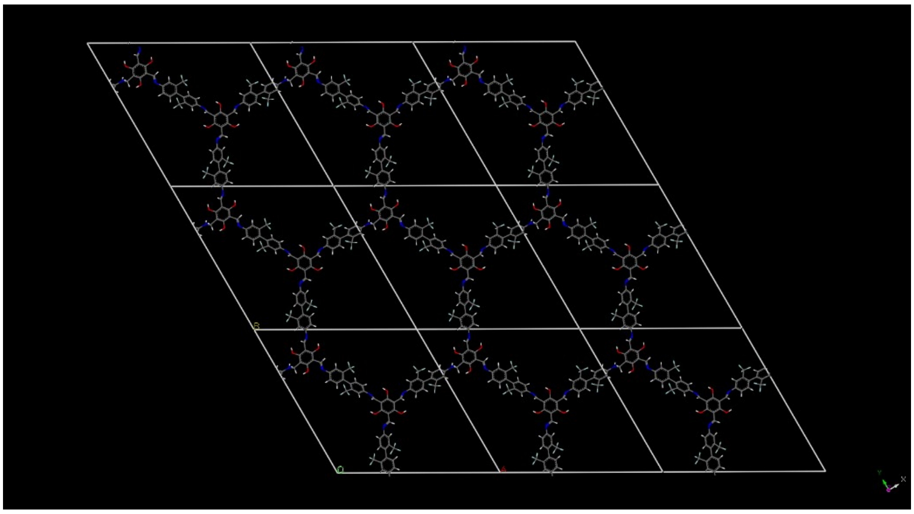


Figure S4. Structural Simulation of Co-COF-Tfmb$_{100}$ (calculated: a=26.1165, b=18.0868, c=3.5505 Å).

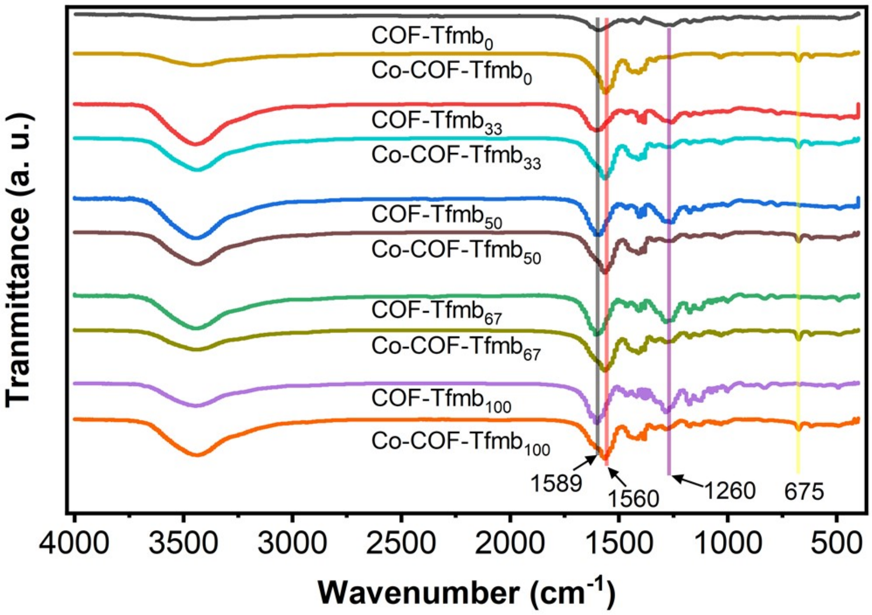


Figure S5. FT-IR spectra of COF-Tfmb$_x$ before and after cobalt modification.

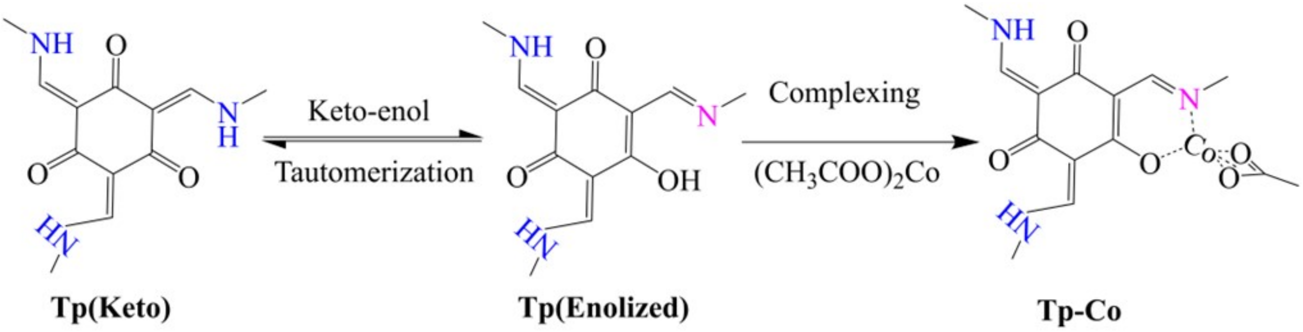


Figure S6. Structural tautomerization of keto to enol for coordination of Co^{2+} with N-salicylideneaniline moiety.

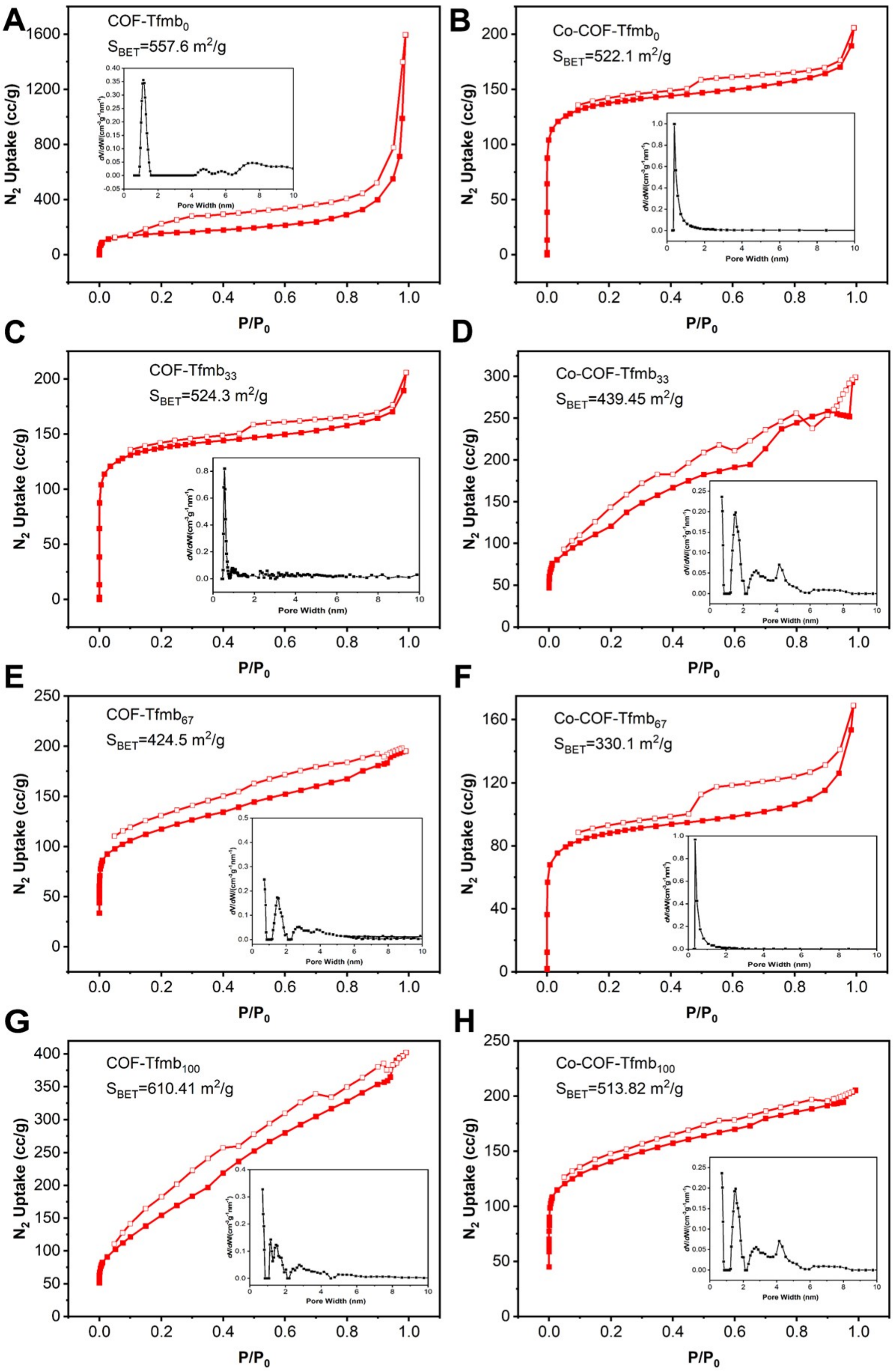


Figure S7. N_2 sorption isotherms of (A) COF-Tfmb$_0$, (C) COF-Tfmb$_{33}$, (E) COF-Tfmb$_{67}$ (G) COF-Tfmb$_{100}$, (B) Co-COF-Tfmb$_0$, (D) Co-COF-Tfmb$_{33}$, (F) Co-COF-Tfmb$_{67}$, (H) Co-COF-Tfmb$_{100}$. Insets in (A-H) are the pore-size distributions.

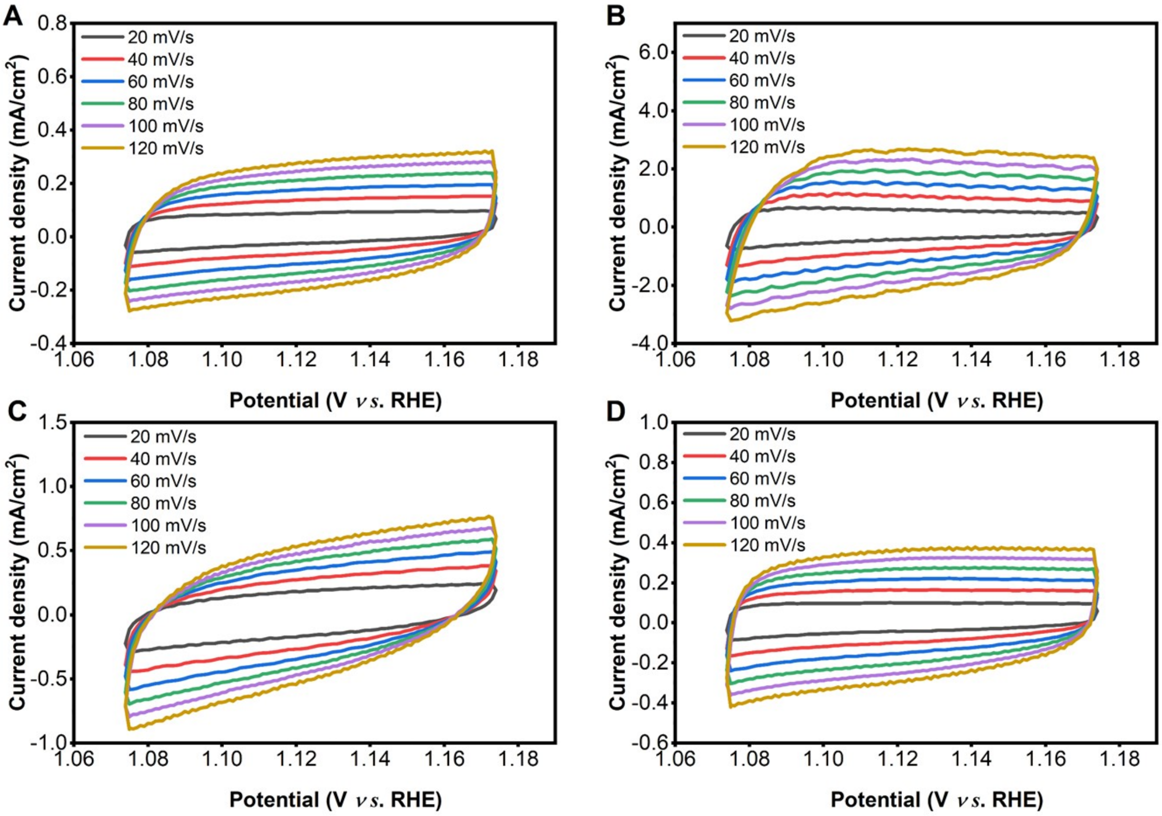


Figure S8. Cyclic voltammetry of (A) Co-COF-Tfmb$_0$, (B) Co-COF-Tfmb$_{33}$, (C) Co-COF-Tfmb$_{67}$ and (D) Co-COF-Tfmb$_{100}$ at different scan rates in 0.1 M phosphate buffer in the non-Faradaic potential region 0.1 M phosphate buffer solution.

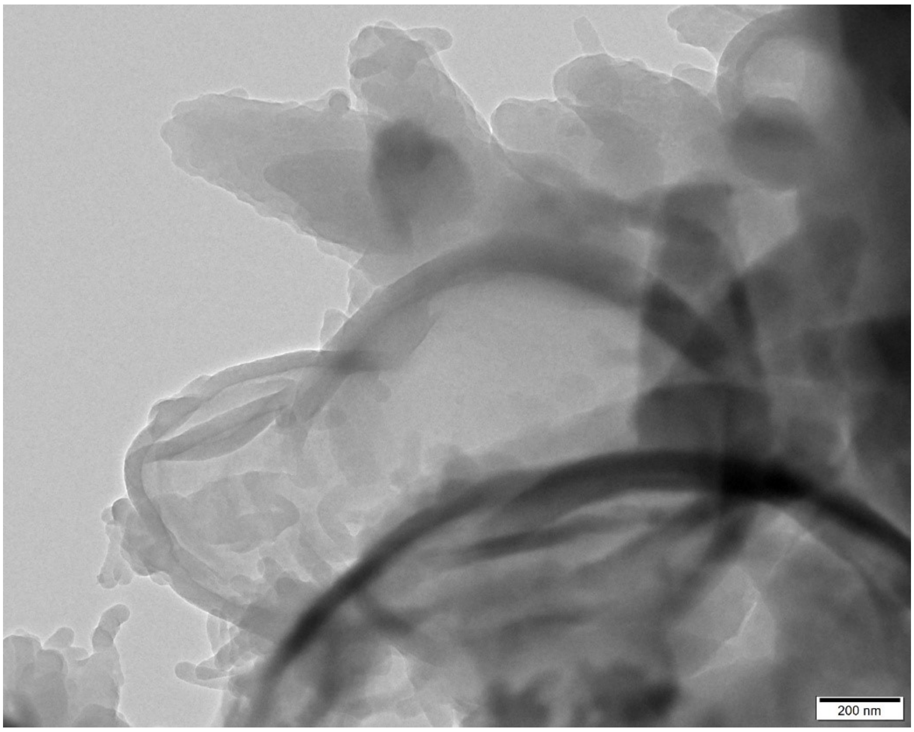


Figure S9. TEM of Co-COF-Tfmb$_{50}$ after OER reaction.

Table S1 Quantitative table of elemental contents (C, N, O, F, Co) from XPS for all five samples

Sample	C%	N%	O%	F%	Co%
COF-Tfmb$_0$	55.19	2.04	32.77	0.5	9.5
COF-Tfmb$_{33}$	56.84	1.94	30.96	1.98	8.28
COF-Tfmb$_{50}$	60.89	2.38	26.18	3.99	6.56
COF-Tfmb$_{67}$	64.42	2.98	23.11	4.33	5.16
COF-Tfmb$_{100}$	58.69	2.88	25.31	6.6	6.53

Table S2 Activity and stability of Co-COF-Tfmb$_{50}$ compared to that of other similar materials reported previously.

Sample	**Electrolyte**	**Performance**		**Ref.**
		Activity	Stability	
Co-COF-Tfmb$_{50}$	**1 M KOH**	**E = 362 mV at 10 mA cm^{-2}** **Tafel = 53 mV dec^{-1}**	**Decreased to 93% after 24 h test**	**This Work**
COF-C$_4$N	1 M KOH	E = 349 mV at 10 mA cm^{-2} Tafel = 64mV dec^{-1}	Decreased to 83.61% after 20 h test	1
C$_4$-SHz COF	1 M KOH	E = 320 mV at 10 mA cm^{-2} Tafel = 39 mV dec^{-1}	work efficiently for more than 11 h at of 10 mA cm^{-2}	2
JUC-630	1 M KOH	E = 400 mV at 10 mA cm^{-2} Tafel = 104 mV dec^{-1}	not available	3
Co-TpBpy	0.1 M Phosphate buffer	E = 400 mV at 1 mA cm^{-2} Tafel = 59 mV dec^{-1} TOF = 0.23s^{-1}	Decrease to 10% after 24 h test	4

Macro TpBpy-Co	0.1 M KOH	E = 380 mV at 10 mA cm^{-2} Tafel = 54 mV dec^{-1}	Slight negative shift (38 mV shift of the overpotential at 10 mA cm^{-2}) after 40000 s test	5
Ni$_{0.5}$Fe$_{0.5}$@COF-SO$_3$	0.1 M KOH	E = 308 mV at 10 mA cm^{-2} Tafel = 83mV dec^{-1}	Maintain current densities after 15 h test at 20, 50, and 100 mA cm^{-2}	6
CoS$_2$@BP-COP	1 M KOH	E = 270 mV at 10 mA cm^{-2} Tafel = 36 mV dec^{-1}	slight increase of 17 mV after 24 h	7
Co@COF-Pyr	1 M KOH	E = 450 mV at 10 mA cm^{-2} Tafel = 100 mV dec^{-1}	Increased by 6 mV again after 1000 cycles	8
COF-TpDb-TZ-Co	1 M KOH	E = 390 mV at 10 mA cm^{-2} Tafel = 82mV dec^{-1}	Increases by 2 mV after 1000 cycles	9
NiPcCOF	1 M NaOH	E = 410 mV at 10 mA cm^{-2} Tafel = 75 mV dec^{-1}	Decreased by merely 0.5% after 100 h test	10
COF-366-Co@CNT-0.4	1 M NaOH	E = 358 mV Tafel = 62 mV dec^{-1}	The η10 in the LSV profile almost remains unchanged after 2000 cycles	11
CoFeCOP/CNT-700	0.1 M KOH	E = 440 mV at 10 mA cm^{-2} Tafel = 98 mV dec^{-1}	The current density of CoFeCOP/CNT-700 is about 10 mA cm^{-2} with little loss in the 40,000 s test	12
JUC-627-NS@G-2	1 M KOH	E = 275 mV at 10 mA cm^{-2} Tafel = 132 mV dec^{-1}	Assessed at a current density of 10 mA cm^{-2} for 12 h and rise 7 %	13

IISERP-COF2-β	0.1 M KOH	E = 258 mV at 10 mA cm^{-2} Tafel = 38.9 mV dec^{-1}	slightly improved after potential scanning 500 cycles in Faradaic region (0.9–1.45 V)	14
Ni_3N + amorphous C + IISERP-COF3	1 M KOH	E = 230 mV at 10 mA cm^{-2} The amount of O_2 evolved (230 mmol h^{-1} g^{-1})	stable current could be generated over 20 h	15
Co_3O_4/NPC-2	1 M KOH	E = 330 mV at 10 mA cm^{-2} Tafel = 79 mV dec^{-1}	shows no obvious loss of current density after 3000 th cycles	16
Fe-SAC@COF	1 M KOH	E = 290 mV at 10 mA cm^{-2} Tafel = 40 mV dec^{-1}	maintains a stable current density at around 10 mA cm^{-2} for 24 h	17
O-Ni_3Fe-N-C	0.1 M KOH	E = 328 mV at 10 mA cm^{-2} Tafel = 52 mV dec^{-1}	Retain current desty after a long time operation (almost 75 h)	18

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