Supporting Information

Enhancing CO$_2$ electroreduction to ethylene via microenvironment regulation in boron-imidazolate frameworks

Chen Lu [ab], Qin-Long Hong[a], Hai-Xia Zhang[a]* and Jian Zhang[a]*

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China.*
[b] *University of Chinese Academy of Sciences, Beijing 100049, P. R. China*

1. Experimental methods.

1.1 *Preparation of Catalyst.*

All chemical reagents were used as purchased without further purification.

1.2 *Synthesis of KBH(mim)₃ ligands.*

The KBH(mim)$_3$ ligands were synthesized based on a reported procedure with a slight modification.[1] The mixture of KBH$_4$ (1.080 g, 0.02 mol) and 2-methylimidazole (5.050 g, 0.06 mol) were placed in a nitrogen-filled flask and heated to 210 °C under stirring. During the heating process, the mixture of solids was melted and hydrogen gases were generated. About 45 min, the evolution of gas ceased. Then cooled to room temperature, the product KBH(mim)$_3$ was obtained as off-white solid.

1.3 *Synthesis of BIF-151*

The mixture of KBH(mim)$_3$ (0.044g), 2-fouric acid (0.044g) and cupric acetate (0.026g), in a water (H$_2$O, 1 mL)/N-methylacetamide (2 mL)/2-butyl alcohol (2 mL) solution were placed in a 20 mL vial. The sample was heated at 80 °C for 4 days, and then cooled to room temperature. After washing with ethanol and distilled water, the bluish violet crystals were obtained.

1.4 *Synthesis of BIF-152*

The mixture of KBH(mim)$_3$ (0.045g), 3-fouric acid (0.044g) and cupric nitrate (0.026g), in a water (H$_2$O, 2 mL)/N,N-dimethylacetamide (2 mL)/methyl alcohol (1 mL) solution were placed in a 20 mL vial. The sample was heated at 80 °C for 1 days, and then cooled to room temperature. After washing with ethanol and distilled water, the bluish violet crystals were obtained.

1.5 *Synthesis of BIF-153*

The mixture of KBH(mim)$_3$ (0.045g), 2-thiophenecarboxylic acid (0.047g) and cupric nitrate (0.055g), in a water (H$_2$O, 1 mL)/N, N-dimethylformamide (2 mL)/methyl alcohol (2 mL) solution were placed in a 20 mL vial. The sample was heated at 80 °C for 4 days,

and then cooled to room temperature. After washing with ethanol and distilled water, the bluish violet crystals were obtained.

1.6 Synthesis of BIF-154

The mixture of KBH(mim)$_3$ (0.045g), 3-thiophenecarboxylic acid (0.047g) and cupric nitrate (0.055g), in a water (H$_2$O, 1 mL)/N-methylacetamide (2 mL)/isopropyl alcohol (2 mL) solution were placed in a 20 mL vial. The sample was heated at 80 °C for 3 days, and then cooled to room temperature. After washing with ethanol and distilled water, the bluish violet crystals were obtained.

1.7 Electrochemical measurements.

The electrochemistry CO$_2$ reduction reaction was performed in a two-compartment electrochemical cell, which was separated by a Nafion-117 proton exchange membrane. The glassy carbon electrode (GCE) was used as working electrode; the platinum net and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. The electrochemical measurements were performed in a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co., China) at ambient temperature and pressure with a mixed aqueous solution of 0.05 M CsCO$_3$ and 0.1 M KCl (v:v = 1:1) as the electrolyte. Either high-purity Ar or CO$_2$ were bubbled in electrolyte to prepare CO$_2$-free or CO$_2$-saturated electrochemical study, respectively. 5 mg of electrocatalysts (BIF-151) were dispersed into the mixture of 50 μL Nafion117, 450 μL ethanol, with assistance of ultrasonication for at least 30 min to achieve a homogeneous ink. 50 uL of the catalyst ink was pipette onto the glassy carbon electrode (S = 1 cm^2) with a loading of 0.5 mg cm^{-2}.

1.8 Gas products analysis.

The electrolysis experiments were performed in a two-compartment electrochemical cell consisting of working and counter electrode compartments. During the electrochemical tests, the cathodic compartment was continuously purged with CO$_2$ at a constant flow rate of 20 sccm and was connected the inlet directly into the gas-sampling loop of gas

chromatograph (GC, SHIMADZU Instruments) for the periodic quantification of the gas-phase products. The electrolyte in the cathodic compartment was purged with CO_2 for least 30 min before the electrolysis experiments. N_2 (99.999%) was used as the carrier gas. A flame ionization detector (FID) was used to quantify CO, CH_4, C_2H_4, C_2H_6 concentration and a thermal conductivity detector (TCD) was used to quantify H_2 concentration.

The Faradic efficiencies of gaseous products were calculated using the following equations[2]:

Faradic efficiency of the gas product = $Q_i / Q_{total} \times 100\%$ $\qquad$ (1)

$Q_i = Z_i \times F \times N_i$ $\qquad$ (2)

$Q_{total} = I \times t$ $\qquad$ (3)

$N_i = N_{total} \times V_i$ $\qquad$ (4)

Based on the ideal gas law:

$N_{total} = P_0 \times V_0 / (R_0 \times T_0)$ $\qquad$ (5)

$V_o = G \times t$ $\qquad$ (6)

Where i represents CO, CH_4, C_2H_4, C_2H_6 or H_2; Z_i is the number of electrons required to form a molecule of product i; F is Faraday's constant (96,485 C mol^{-1}); N_i is the moles of product i in the GC gas-sampling loop; I is the recorded current; t is the time required to fill GC gas-sampling loop; N_{total} is the moles of all gases in the GC gas-sampling loop; P_0 is atmospheric pressure (1.013×10^5 Pa); V_0 is the volume of the GC sampling loop; R_0 is the ideal gas constant (8.314 J mol^{-1} K^{-1}); T_0 is reaction temperature (298 K); G is the volumetric flow rate.

1.9 *Liquid products analysis.*

Liquid products were analyzed by offline Ion chromatograph (CIC-D100, Qingdao Shenghan Instrument Co., China). After an hour of electrolysis, an aliquot (500 uL) of electrolyte containing CO_2 reduction products was diluted to 10 mL, the diluted electrolyte was injected into ion chromatography for testing. The formic acid (HCOOH) signals of known concentration of HCOOH in five standard solutions were first determined, and then

a linear regression standard curve was produced using ratio of their HCOOH peak area and the known concentration of the HCOOH in standard solutions.

The faradaic efficiencies of liquid products were calculated using the following equations:

Faradic efficiency of the liquid product $= \dfrac{C \times V \times n \times F}{I \times t} \times 100\%$

Where C is the concentration of the liquid product in the NMR sample; V is the liquid volume in the cathodic chamber; n is the number of electrons required to form a molecule of formic acid; F is Faraday's constant; I is the recorded current; t is time of analysis.
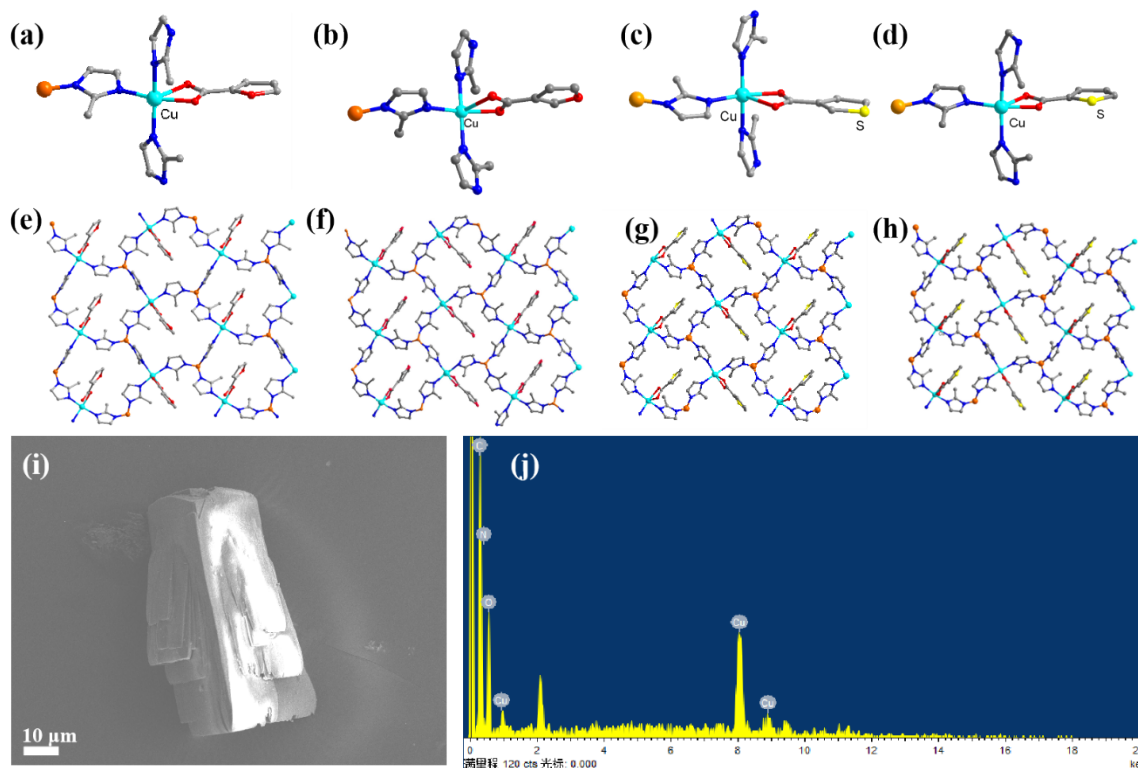
2.Supporting Figures.

Figure S1 (a-d) the coordination environments of BIF-151 to 154. (e-h) 2D structures of BIF-151 to 154. (i) SEM image of BIF-151. (j) EDS of BIF-151.
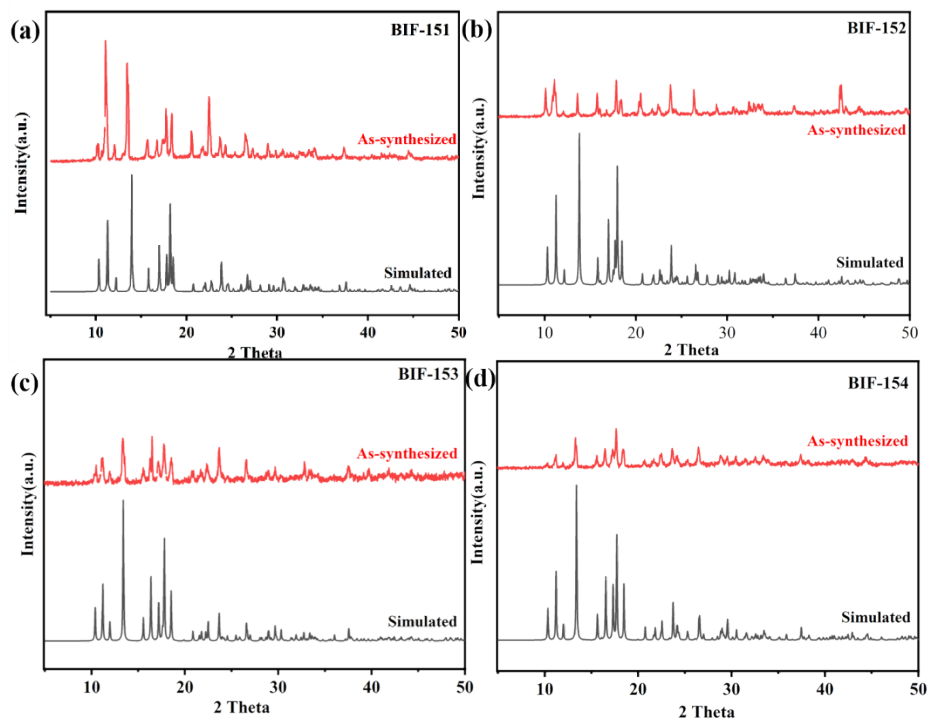
Figure S2 The powder XRD patterns of simulated and as-synthesized (a) BIF-151, (b) BIF-152, (c) BIF-153 and (d) BIF-154.
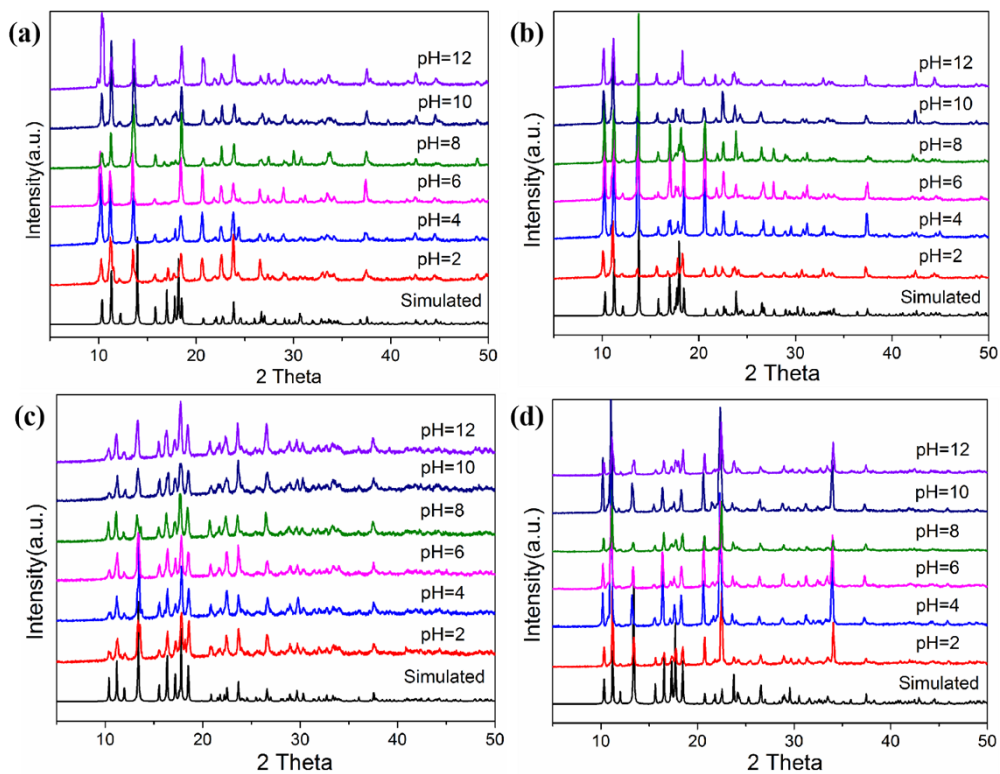

Figure S3 The powder XRD patterns of (a) BIF-151, (b) BIF-152, (c) BIF-153 and (d)
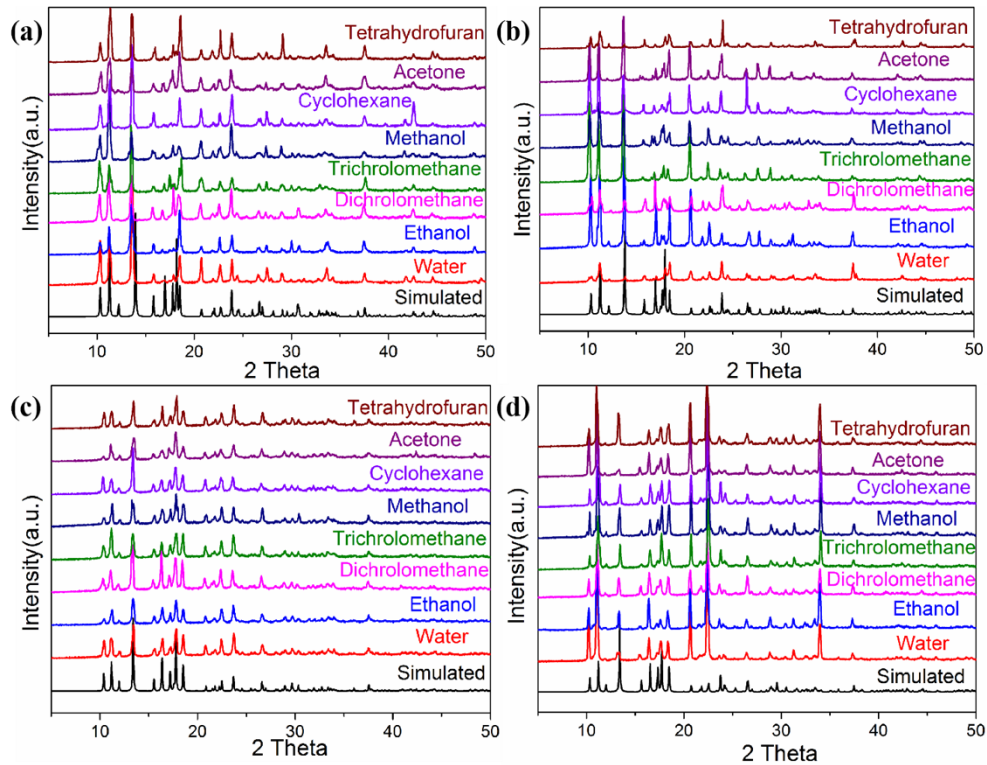
BIF-154 with different pH values.

Figure S4 The powder XRD patterns of (a) BIF-151, (b) BIF-152, (c) BIF-153 and (d) BIF-154 in different solvents.
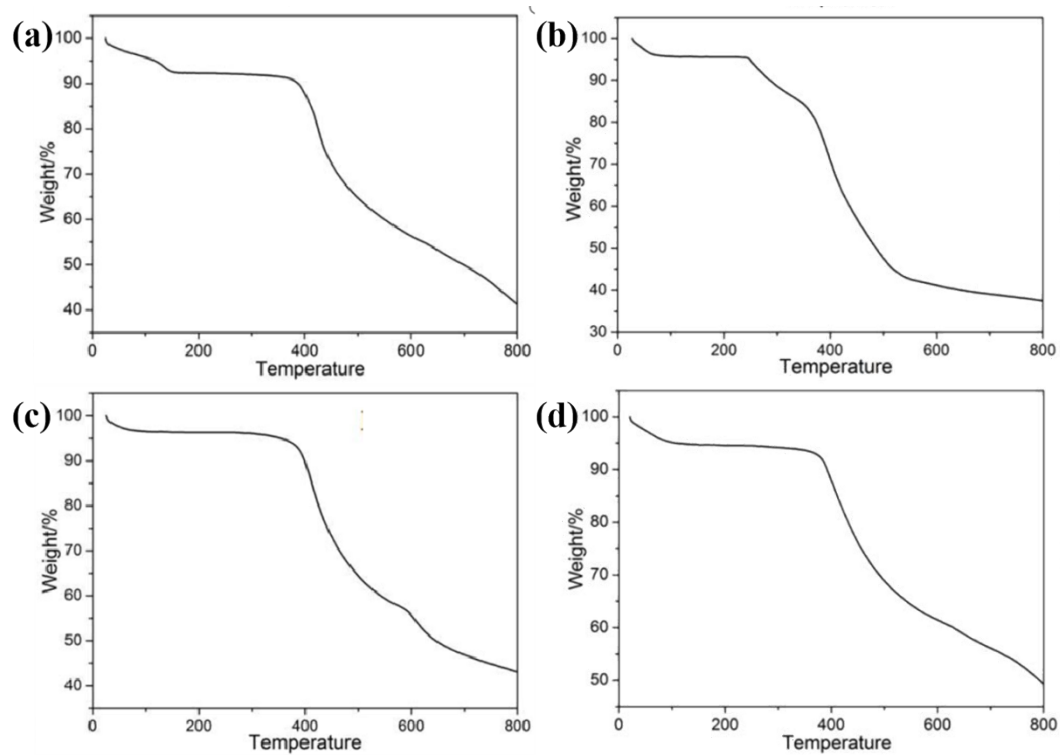
Figure S5 The thermogravimetric analysis plots of (a) BIF-151, (b) BIF-152, (c) BIF-153 and (d) BIF-154.
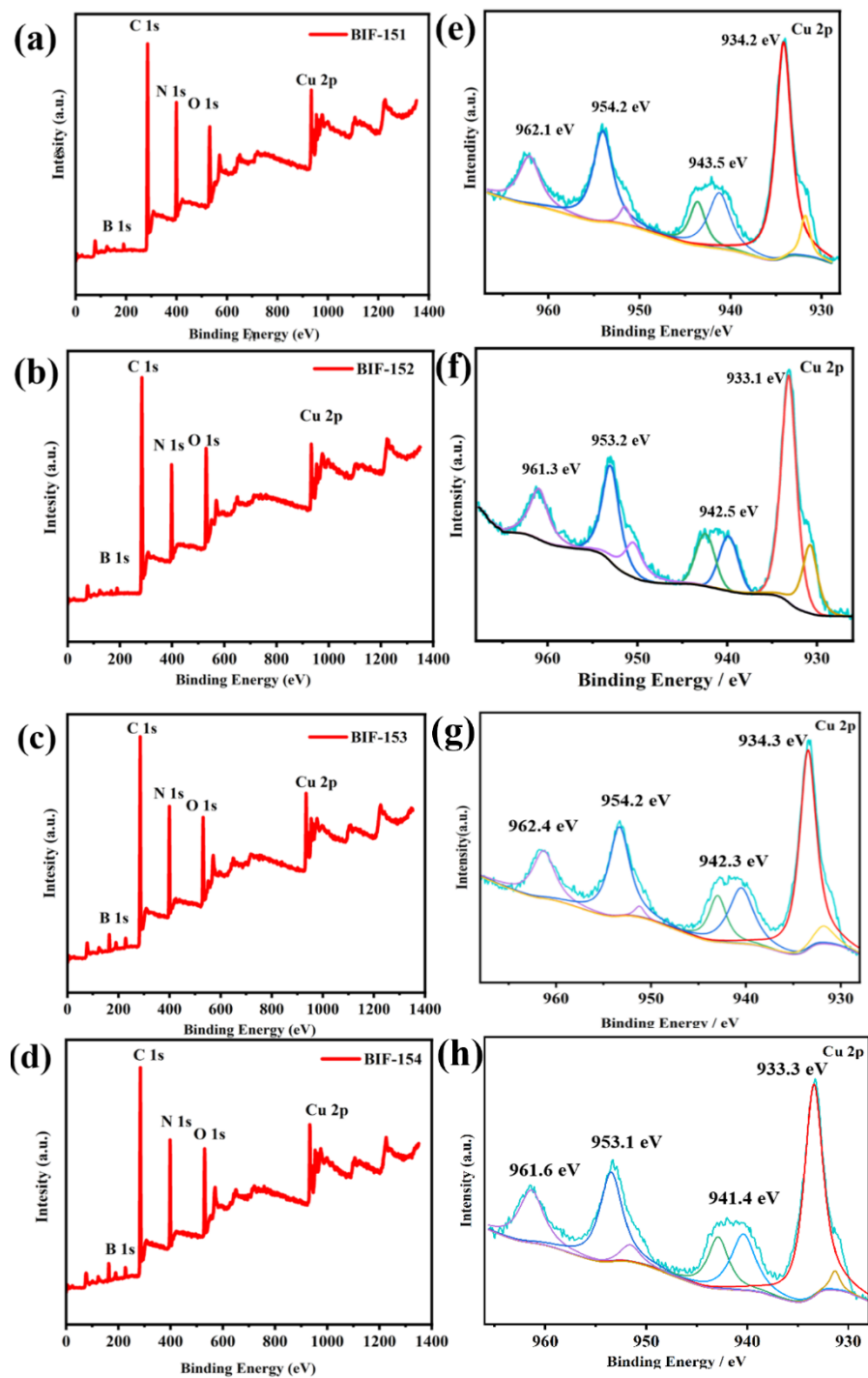
Figure S6 The X-ray photoelectron spectroscopy (XPS) measurements. (a-d) survey spectra and (e-h) Cu 2p spectra of BIF-151, BIF-152, BIF-153 and BIF-154.
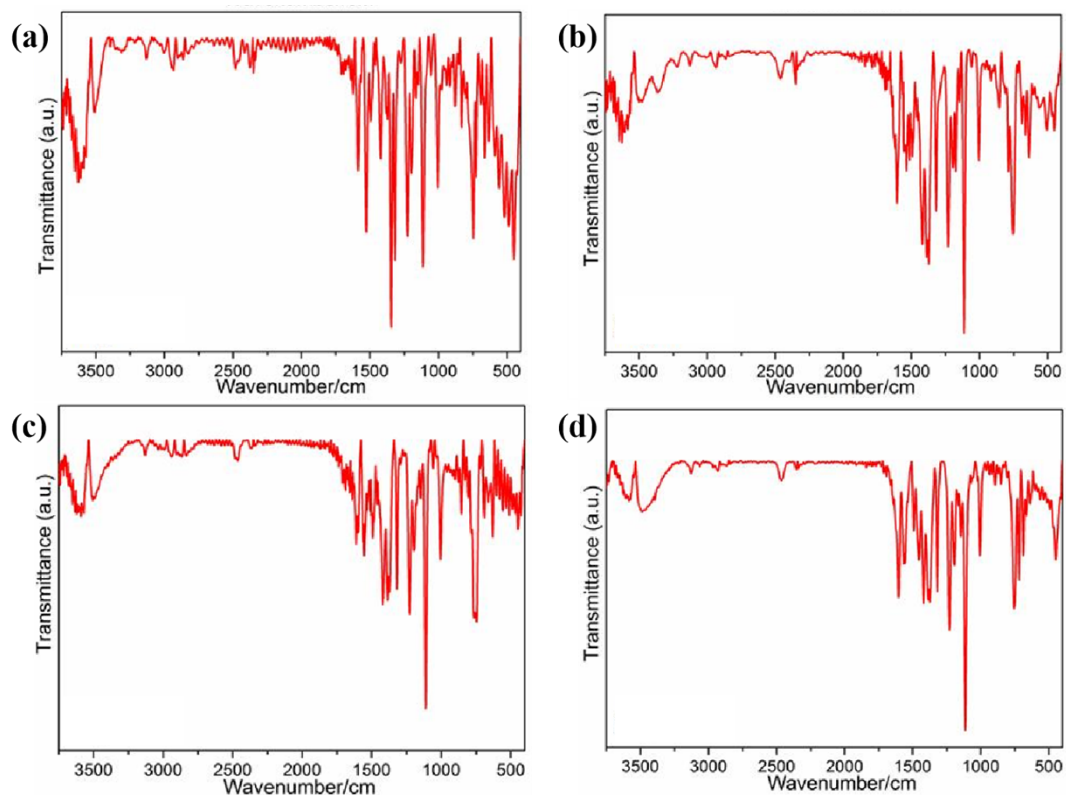
Figure S7 FT-IR analysis of (a) BIF-151, (b) BIF-152, (c) BIF-153 and (d) BIF-154.
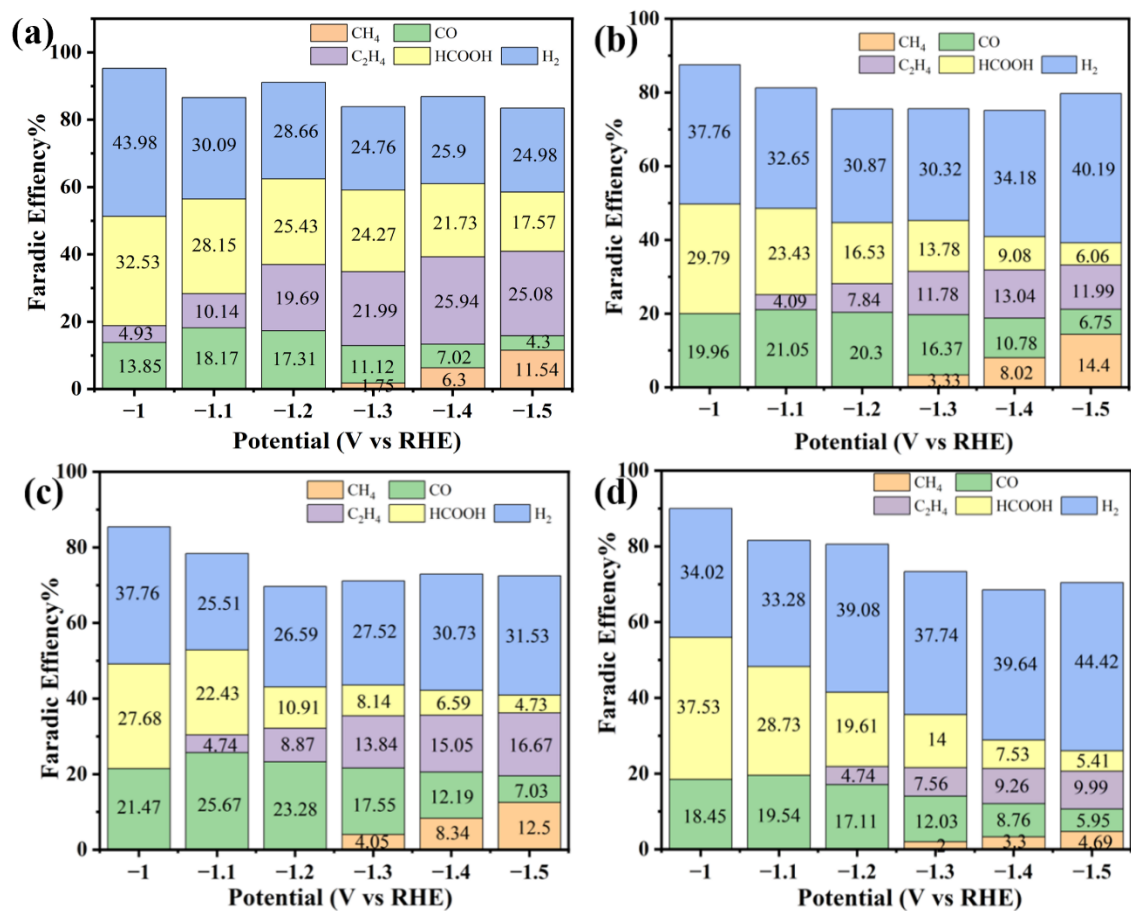
Figure S8 The FE of gas products and liquid products of (a) BIF-151, (b) BIF-152, (c) BIF-153 and (d) BIF-154 electrocatalyst at different applied potentials in CO_2 saturated electrolyte.
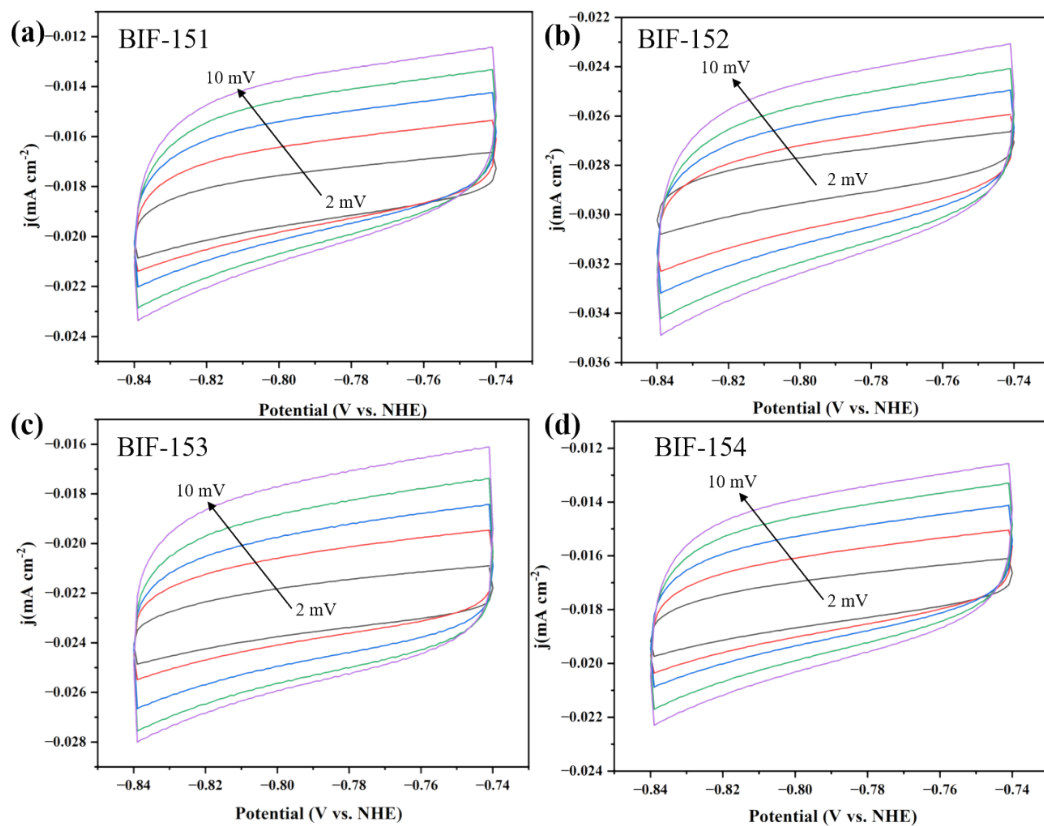
Figure S9 (a-d) Cyclic voltammagrams curves of BIF-151, BIF-153, BIF-153 and BIF-154 electrocatalysts taken over a range of scan rates in the potential window -0.74 ~ -0.84 V (vs. RHE).
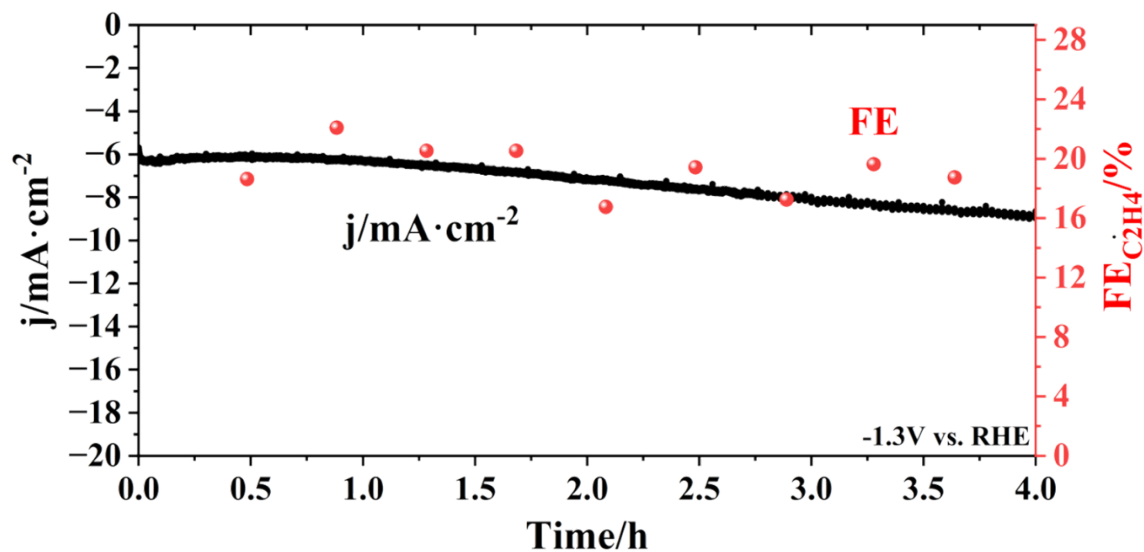
Figure S10 Chronoamperometric and corresponding FE_{C2H4} for the BIF-151 catalysts at -1.3 V (vs. RHE) in CO_2 saturated electrolyte, respectively.

Electrocatalytic stability for the BIF-151 was also characterized by using chronoamperometric and related FE_{C2H4} curves. At the applied potential of -1.3 V, BIF-151 exhibited no obvious degradation of current density during the first hour, then showed a low downward trend after one hour. During the first 4 hours test, its FE_{C2H4} value could maintain a relatively good level.

Figure S11 PXRD patterns of BIF-151(black: simulated; red: in electrolyte solution of 0.05 M CsCO3 and 0.1 M KCl (v:v = 1:1); blue: after 4 hours electrocatalytic stability test)

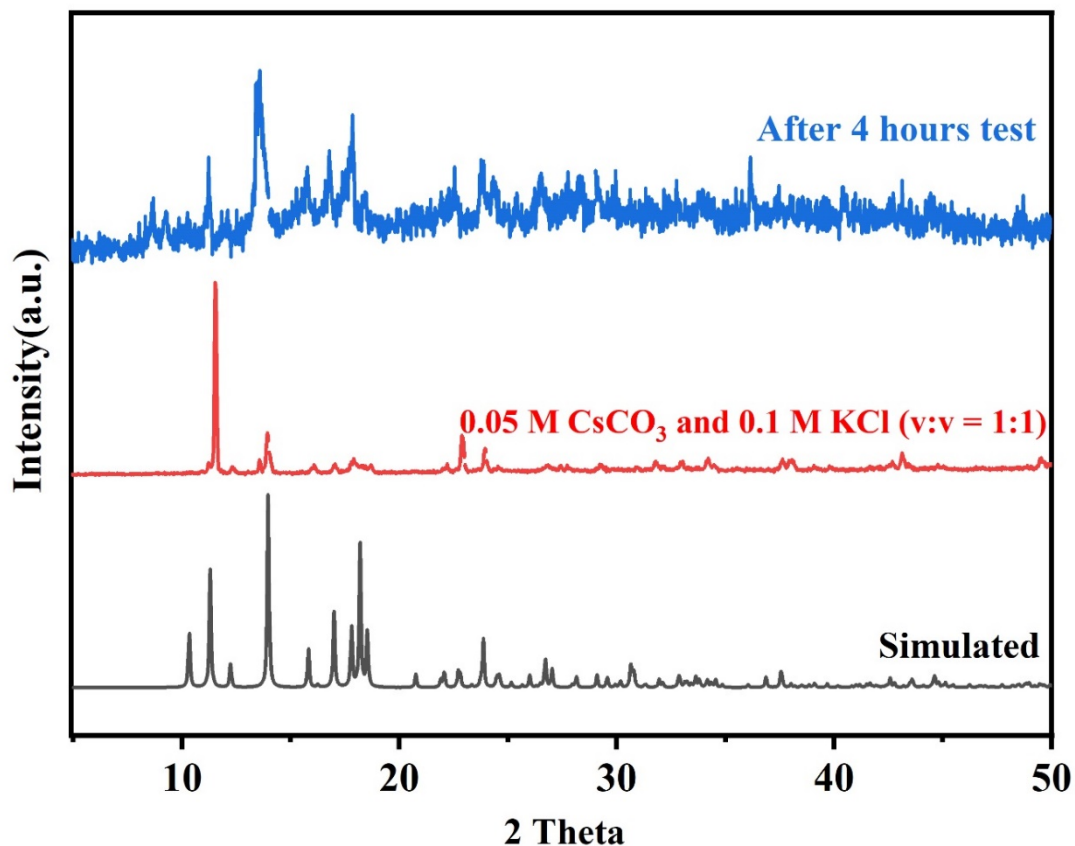Table S1. Summary of crystal data and structural refinements for BIF-151 and BIF-152.

Compound reference	BIF-151	BIF-152
Empirical formula	$C_{18}H_{19}BCuN_6O_3$	$C_{17}H_{19}BCuN_6O_3$
Formular weight	429.74	429.73
Temperature/K	103.2(4)	100.0(3)
Crystal system	monoclinic	monoclinic
Space group	*Ia*	*Ia*
a/Å	12.6893(3)	12.5552(2)
b/Å	8.8027(2)	8.81030(10)
c/Å	17.1269(4)	17.1609(2)
α/°	90	90
β/°	92.777(2)	92.0380(10)
γ/°	90	90
Volume/Å³	1910.83(8)	1897.05(4)
Z	4	4
ρ_{calc}g/cm³	1.48	1.505
μ/mm⁻¹	6.299	6.374
F(000)	876	884
Radiation	GaKα (λ = 1.3405)	GaKα (λ = 1.3405)

2Θ range for data collection/°	8.988 to 105.856	8.966 to 113.808
Index ranges	$-15 \leq h \leq 15, -10 \leq k \leq 10,$ $-20 \leq l \leq 20$	$-15 \leq h \leq 15, -11 \leq k \leq 11, -21$ $\leq l \leq 20$
Reflections collected	16315	16779
Independent reflections	3360 [R_{int} = 0.0328, R_{sigma} = 0.0248]	3566 [R_{int} = 0.0432, R_{sigma} = 0.0266]
Data/restraints/parameters	3360/2/256	3566/2/256
Goodness-of-fit on F^2	1.044	1.051
Final R indexes [I >=2σ (I)]	R_1 = 0.0267, wR_2 = 0.0674	R_1 = 0.0383, wR_2 = 0.0993
Final R indexes [all data]	R_1 = 0.0279, wR_2 = 0.0677	R_1 = 0.0395, wR_2 = 0.1000

Table S2. Summary of crystal data and structural refinements for BIF-153 and BIF-154.

Compound reference	BIF-153	BIF-154
Empirical formula	$C_{17}H_{19}BCuN_6O_2S$	$C_{17}H_{19}BCuN_6O_2S$
Formular weight	445.98	445.81
Temperature/K	100.0(3)	298.69(10)
Crystal system	monoclinic	monoclinic
Space group	Ia	Ia
a/Å	12.9474(2)	17.1231(3)
b/Å	8.91440(10)	8.8768(2)
c/Å	17.0439(3)	13.2163(3)
α/°	90	90
β/°	94.7990(10)	92.837(2)
γ/°	90	90
Volume/Å³	1960.28(5)	2006.39(7)
Z	4	4
ρ_{calc}g/cm³	1.511	1.482
μ/mm⁻¹	6.795	6.633
F(000)	916	924
Radiation	GaKα (λ = 1.3405)	GaKα (λ = 1.3405)
2Θ range for data collection/°	9.054 to 113.772	8.992 to 102.404
Index ranges	$-16 \leq h \leq 16, -11 \leq k \leq 11,$ $-21 \leq l \leq 18$	$-19 \leq h \leq 19, -10 \leq k \leq 9, -15 \leq$ $l \leq 15$
Reflections collected	16234	9342
Independent reflections	3732 [R_{int} = 0.0564, R_{sigma} = 0.0411]	2891 [R_{int} = 0.0363, R_{sigma} = 0.0312]
Data/restraints/parameters	3732/2/258	2891/2/256
Goodness-of-fit on F^2	1.054	1.04
Final R indexes [I >=2σ (I)]	R_1 = 0.0496, wR_2 = 0.1197	R_1 = 0.0458, wR_2 = 0.1247
Final R indexes [all data]	R_1 = 0.0518, wR_2 = 0.1209	R_1 = 0.0480, wR_2 = 0.1269

Table S3: The product distribution table of BIF-151, BIF-152, BIF-153 and BIF-154 electrocatalysts at different applied potentials in CO_2-saturated 0.5 M $CSCO_3$ and 0.1M KCl (V:V=1:1) electrolyte, respectively.

Sample	Potential/V vs. RHE	FE_{C2H4} %	FE_{CO} %	FE_{CH4} %	FE_{HCOOH} %	FE_{H2} %	Gas
BIF-151	-1.0	4.93	13.85	0	32.53	43.98	CO_2
	-1.1	10.14	18.17	0	28.15	30.09	
	-1.2	19.69	17.31	0	25.43	28.66	
	-1.3	21.99	11.12	1.75	24.27	24.76	
	-1.4	25.94	7.02	6.3	21.73	25.9	

	-1.5	25.08	4.30	11.54	17.57	24.98	
BIF-152	-1.0	0.00	19.96	0.00	29.79	37.76	CO_2
	-1.1	4.09	21.05	0.00	23.43	32.65	
	-1.2	7.84	20.30	0.00	16.53	30.87	
	-1.3	11.78	16.37	3.33	13.78	30.32	
	-1.4	13.04	10.78	8.02	9.08	34.18	
	-1.5	11.99	6.75	14.40	6.06	40.49	
BIF-153	-1.0	0.00	21.47	0.00	27.68	36.25	CO_2
	-1.1	4.74	25.67	0.00	22.43	25.51	
	-1.2	8.87	23.28	0.00	10.91	26.59	
	-1.3	13.84	17.55	4.05	8.14	27.52	
	-1.4	15.05	12.19	8.34	6.59	30.73	
	-1.5	16.67	7.03	12.50	4.73	31.53	
BIF-154	-1.0	0.00	18.45	0.00	37.53	34.02	CO_2
	-1.1	0.00	19.54	0.00	28.73	33.28	
	-1.2	4.74	17.11	0.00	19.61	39.08	
	-1.3	7.56	12.03	2.00	14.00	37.74	
	-1.4	9.26	8.76	3.30	7.53	39.64	
	-1.5	9.99	5.95	4.69	5.41	44.42	

Reference

[1] a) B. H. Hamilton, K. A. Kelly, W. Malasi and C. J. Ziegler, *Inorg. Chem.* 2003, **42**, 3067-3073; b) S. Trofimenko, *J. Am. Chem. Soc.,* 1967, **89**, 3170-3177; c) S. Trofimenko, *J. Coord. Chem.* 1972, **2**, 75-77; d) P. Shao, W. Zhou, Q.-L. Hong, L. Yi, L. Zheng, W. Wang, H.-X. Zhang, H. Zhang and J. Zhang, *Angew. Chem. Int. Ed.,* 2021, **60**,16687-16692.

[2] H.B. Yang, S.-F. Hung, S. Liu, K. Yuan, S. Miao, L. Zhang, X. Huang, H.-Y. Wang, W. Cai, R. Chen, J. Gao, X. Yang, W. Chen, Y. Huang, H.M. Chen, C.M. Li, T. Zhang and B. Liu, *Nature Energy*, 2018, **3**, 140-147.