Supplementary Information for

Efficient electrochemical reduction of CO₂ to CO in flow cell device by a pristine Cu₅tz₆-cluster-based metal-organic framework[†]

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EXPERIMENTAL SECTION

Materials and characterization

All reagents and chemicals were obtained commercially and used without further purification. 3,5-Diphenyl-1H-1,2,4-triazole (3,5-Ph₂-tzH, 98%) was from Aladdin. Methanol (\geq 99.5%,), dichloromethane (99.5%), potassium hydroxide (KOH, 99%) were purchased from Greagent. Tetrakis(acetonitrile) copper(I) tetrafluoroborate (Cu(CH₃CN)₄BF₄, 97%), n-hexane (97%, SafeDry) were from Adamas. Ethanol (EtOH, \geq 99.7%) and acetone (99.5%) were from Sinopharm Chemical Reagent Co.,Ltd. Nafion solution (5 wt %) was purchased from Sigma-Aldrich while anion exchange membrane was from Shanghai Hesen Electric Co., Ltd. Carbon paper (YSL-30T) was purchased from Suzhou Sinero Technology Co., Ltd..

 N_2 aborption and Brunauer-Emmett-Teller (BET) Analysis. The N₂ adsorption isotherms were recorded at 77 K by using a micromeritics ASAP 2020 surface area and porosity analyzer. Before the adsorption measurements, the freshly prepared samples (~50 mg) of **CuTz-1** was soaked in 20 mL of DCM three times over 1 h (20 min each) and subsequently immersed in 20 mL n-hexane three times over 1h (20 min each).¹

Thermogravimetric analysis (TGA). TGA was carried out in an N₂ atmosphere with a heating rate of 10 °C/min from 40 °C to 800 °C on a NETZSCH STA 449 F3 Jupiter instrument.

Element Analysis. Transmission electron microscope (TEM) images and energy dispersive spectroscopy (EDS) mapping results were collected using a FEI Tecnai G2 F20 S-TWIN FEGTEM with an accelerating voltage of 200 kV.

Fourier Transform Infrared (FTIR) Spectroscopy. The IR spectra in the range of 400–4000 cm⁻¹ were recorded on ground powder of samples using a Thermo Nicolet 6700 FTIR spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory.

Raman Spectroscopy. Raman spectra of samples were collected on a Horiba XploRA Raman spectrometer with an excitation line of 532 nm at 10% laser power. The measurements were conducted with a loading value of 3-4, comprising 3 accumulations, an exposure time of 10 seconds, and an average of 10 scans per region. Throughout the measurement process, CO_2 flowed continuously through the flow cell at a rate of 20 standard cubic centimeters per minute (SCCM). The Raman spectra were recorded from the open circuit potential (OCP) to -1.2 V, with a voltage interval of -0.1 V for subsequent measurements.²

X-ray photoelectron spectroscopy (XPS). The XPS data were recorded on a Thermo SCIENTIFIC SCALAB 250Xi using monochromatic Al K α (1486.6 eV) X-ray radiation at room temperature. The anode was operated at 24.2 W with a typical spot size of 650 µm. The binding energies obtained from XPS were calibrated using the C 1s binding energy peak (284.8eV) as a reference. Background measurements for the samples were corrected, and they were placed on an absolute scale following standard procedures. The quantitative XPS analysis was performed using the Avantage software.

Operando attenuated total reflectance surface-enhanced infrared absorption spectroscopy (*ATR-SEIRAS*). In this study, ATR-SEIRAS was conducted using a purged NICOLET 6700 FT-IR spectrometer equipped with the LingLu accessory and a midband MCT detector. A silicon hemispherical window (F530-8) served as the single-reflection attenuated total reflection (ATR) accessory for the FTIR investigation, with the working electrode gently placed on top of the window. The experimental setups are illustrated in Figure S8. Measurement parameters included a 4 cm⁻¹ resolution and 100 scans. This configuration facilitated the detection of eCO₂RR intermediate formation and changes in the adsorption of various intermediates on the electrode surface and within the thin layer electrolyte. At the onset of the IR experiment, we captured a spectrum of the entire electrochemical cell, followed by a background spectrum. This step allowed for the subsequent subtraction of the electrolyte contribution in the next spectrum, while potential was applied during CO₂RR. The OPUS software was employed for spectral analysis, and absorption spectra were directly plotted at various potentials.

X-ray absorption spectroscopy (XAS). X-ray absorption fine spectroscopy (XAFS) at Cu Kedge was collected at the 14W1 beamline at Shanghai Synchrotron Radiation Facility (SSRF). All XAFS data were analyzed using the program Demeter. The EXAFS oscillations were extracted from the normalized XAFS spectra by subtracting the atomic background using a quadratic spline fit to k^3 -weighted data, where k is the photoelectron wave number. The $\chi(k)$ functions were then Fourier transformed into R-space. The Fourier-transform window was in the k range 2-10 Å⁻¹.



Figure S1 Thermogravimetric analysis (TGA) curve of CuTz-1.



Figure S2 N₂ sorption and desorption isotherms of CuTz-1.



Figure S3 (a) Cyclic voltammetry curves (b) capacitive behaviors of CuTz-1 at various scan rate (10~50 mV S⁻¹), respectively.



Figure S4 FTIR spectra of CuTz-1 powder, CuTz-1 on carbon paper before electrocatalysis, CuTz-1 on carbon after electrocatalysis, and the carbon paper.



Figure S5 TEM images of CuTz-1 (a, b, and c) before and (d, e, and f) after electrocatalysis.





Figure S6 TEM and EDX-Mapping images of (a) CuTz-1 and (b) CuTz-1 after electrocatalysis at -0.8 V for 10 h in 1M KOH solution.



Figure S7 In situ Raman spectra from 400 to 1800 cm⁻¹ of CuTz-1 before and under CO₂RR potentials.



Figure S8 Operando attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) device diagram



Figure S9 XPS Cu 2p_{3/2} spectrum of CuTz-1 after electrocatalysis



Figure S10 Wavelet transforms (WT) contour plots of CuTz-1 (a) before and (b) after electrocatalysis.

Catalyst	Electrolyte	CO Selectivity(%)	E (V vs. RHE)	Partial Current Density of CO (mA/cm ²)	Cell type	References	
CuTz-1	1М КОН	62.7	-0.8	-35.1	Flow cell	This work	
CALF20	1M KOH	94.5	-0.97	-32.8	Flow	ACS Catal., 2021, 11, 7350-7357	
ZIF-8	1М КОН	61.1	-1.1	-20.0	cell		
Ag-MOF1	1М КОН	78.0	-1.08	28.45	Flow cell	Dalton Trans., 2024, 53, 3685-3689.	
Ag-MOF2	1М КОН	92.2	-0.98	29.51			
NiPc-NiO ₄	0.5 M KHCO ₃	98.4	-0.85	-34.5	H-cell	Angew. Chem. Int. Ed., 2021, 60, 17108-17114	
Ag@Al-PMOF	0.1 M KHCO ₃	55.8	-0.6	-5.2	H-type cell	Angew. Chem. Int. Ed., 2019, 58, 12632-12639.	
Al ₂ (OH) ₂ TCPP-Co	0.5 M K ₂ CO ₃	76	-0.7	-5.5	H-type cell	J. Am. Chem. Soc., 2015, 137, 44, 14129-14135.	
PcCu-O ₈ -Zn /CNT	0.1 M KHCO ₃	88	-0.7	-4.2	H-type	Nat. Commun., 2020, 11, 1409.	
PcZn-O ₈ -Zn/CNT	0.1 M KHCO ₃	63	-0.7	-1.2	cell		
[Cu(L)SO ₄]·H ₂ O	0.1 M KHCO3	77.5	-0.89	-3.2	H-type cell		
[Cu(L) ₂ (H ₂ O) ₂](CH ₃ COO) ₂	0.1 M KHCO ₃	64.6	-0.96	-2.1	H-type cell	ACS Appl. Mater. Interfaces 2022, 14, 13645-13652	
[Cu(L) ₂ (H ₂ O) ₂](ClO ₄) ₂	0.1 M KHCO ₃	50.5	-0.99	-1.9	H-type cell		

Table 1 Comparison of CO₂RR performance of CuTz-1 with other related MOFs.

Table 2 EXAFS fitting parameters of CuTz-1 before and after electrocatalysis.

sample	path	CN	R	σ ² ×(10 ⁻³ Å ²)	R factor
Before	Cu-N	2.7 ± 0.4	1.86 ± 0.01	4.3	0.046
After	Cu-N	2.6 ± 0.8	1.89 ± 0.02	4.6	0.007

Note: R is the distance between the absorber–scatterer pair, CN is the coordination number, σ^2 is the Debye-

Waller (disorder factor), Error: $\sigma^2 \le \pm 0.0047 \text{\AA}^2$ and R factor is a measure of the goodness of fit.

Supplementary References

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2. L. Li, X. Zhang, C. Liu, V. S. S. Mosali, J. Chen, A. M. Bond, Q. Gu and J. Zhang, *Appl. Catal. B Environ.*, 2023, **331**, 122597.