Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Axial Cl/Br atom-mediated CO_2 electroreduction performance in a stable porphyrin-based metal-organic framework

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Experimental Procedures

Synthesis of NNU−17 and NNU−18

All chemicals and reagents were obtained from commercial sources. TIPP (22 mg, 0.025 mmol) and $CdCl_2 \cdot 2.5\ H_2O$ (45.7 mg，0.20 mmol) were dissolved in the mixed solvent ($DMF:H_2O=5:2$, V=7 mL) and stirred 10 minutes. Above mixture was sealed and heated at 120 ^oC for 72h. Dark violet plate crystals of **NNU−17** were isolated and collected (~57% yield based on TIPP). TIPP (22 mg, 0.025 mmol) and $CdBr_2 \cdot 4H_2O$ (68.8 mg，0.20 mmol) were dissolved in the mixed solvent ($DMF:H_2O=5:2$, V=7 mL). Above mixture was stirred 10 minutes and sealed in a 10 mL glass vial, and then kept 120 ^oC for 72h. After cooling to room temperature at 10 $^oC/h$, violet crystal samples of **NNU−18** were obtained and isolated (~69% yield based on TIPP).

Single−Crystal X−ray Crystallography

NNU−17 and NNU−18 were measured on SSRF BL17B diffractometer at National Facility for Protein Science Shanghai (NFPS) at 100k. All of them were solved using direct methods by SHELXT and refined by SHELXL−2014 program within Olex^2. Anisotropic temperature parameters were used to refine all nonhydrogen atoms. Hydrogen atoms were located at calculated positions. NNU−17 and NNU−18 were corrected with the SQUEEZE program and a part of PLATON software was utilized to check the space group of crystal owing to solvent molecule molecules disorder. Crystallographic data for NNU−17 and NNU−18 were summarized and showed in (Table S1).

Characterizations and instruments

IR spectra ranging from 4000 to 400 cm^{-1} were recorded on a Bruker Tensor 27 FT/IR spectrophotometer utilizing KBr pellets. Thermogravimetric analyses (TGA) were performed on a Netzch STA449F3 analyser under an oxygen atmosphere from room temperature to 700 °C (heating rate was 10 °C min^{-1}). PXRD data (5−50 °) were collected by a D/max 2500VL/PC diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54060 Å).

Electrochemical measurements

All electrocatalysis tests of these catalysts were carried out on the electrochemical workstation (Bio−Logic) using the standard three−electrode configuration (Ag/AgCl and carbon electrode as the reference and counter electrode, respectively) in an airtight H−type cell injected with 0.5 M $KHCO_3$ solution. The total volume of the H−type cell is 100 mL (50 ml on each side). In order to enhance the conductivity of the MOF catalysts, the acetylene black (AB) was introduced in the pure MOF crystals by grinding the mixture. In many reported works, Nafion solution as a dispersion solution was generally employed to form a uniform ink with MOF and AB, which was propitious to attach to the surface of carbon paper. The preparation process of the working electrode is as follows. 10 mg AB and 10 mg pure MOF crystal as catalyst were ground uniformly, and added the 0.5% Nafion solution (1000 μL). In order to mix evenly, the mixture needs sonication over 30 min. Then, the mixture was dropped on a carbon paper (1 cm × 1 cm) and the mixture loading density was about 1 mg / cm^2. After the natural drying, the working electrode (total area, 1 cm × 2 cm) can be used for test.

At a scan rate of 5 mV s^{-1}, LSV mode was utilized to obtain the polarization curves in ECR experiments. The polarization curves of the working electrode were recorded under the inert atmosphere (Ar gas) and the CO_2 (99.999%), respectively. The FE experiments were performed from −0.6 V to −1.2 V (*vs*. RHE) in the 0.5 M $KHCO_3$ solution (both the cathode and the anode contain 25 ml), bubbling with CO_2 (99.999%) atmosphere about 40 min when the pressure relief valve displays 0.5 MPa, and the calculation about FE of catalysts were shown in supporting information. Based on the Nernst equation: E (*vs*. RHE) = E (*vs*. Ag/AgCl) + 0.1989 V + 0.059 × pH, the test results were reported versus reversible hydrogen electrode. To evaluate the ECSA, the double−layer capacitance (C_{dl}) were recorded by cyclic voltammograms (CVs) with various scan rates from 20 to 200 mV s^{-1}. EIS experiments was executed range from 1000 kHz to 0.1 Hz at −1.0 V *vs*. RHE using an AC voltage with 10 mV amplitude. H_2 and CO from commercial purchase were used to plot standard working curve. The purity of the H_2 is at least 99.999 %, and the purity of the CO is at least 99.99%.

Products detection

The generated gaseous products were analyzed by a gas chromatography (GC−7900, CEAULIGHT, China) equipped with a flame ionization detector (FID) and a thermal conductivity (TCD) with the helium as carrier gas. The generated gas was analyzed offline by injected into GC after collecting the generated gas. The details as follow, when the reaction reached about 5 coulombs, we utilized gas-tight syringes (Hamilton) to inject 500 μL into the GC, and calculated the faradaic efficiency according to the formula in supporting information. The results of isotope−labeled experiments ($^{13}CO_2$ instead of CO_2) were analyzed by GC−MS. (7890A and 5875C, Agilent). After reaction, the liquid products were collected and quantified by NMR (Bruker AVANCEAV III 400) spectroscopy. The specific operation is as follows: 0.5 mL electrolyte after reaction (−1.0 V) was mixed with 0.1 μL dimethyl sulfoxide (DMSO, 99.99%, internal standard) and 0.1 mL D_2O. Solvent pre−saturation technique was implemented to suppress the water peak. The ICP results after reactions were measured on ICPMS (Agilent 7700). The UV−Vis spectra were recorded on UV−Vis instrument (Beijing Purkinje, TU−1900). The halogen anions were detected and analyzed by IC (LC-2010 PLUS, shimadzu. Japan). The standard solution was obtained from commercial purchase.

Reaction product analysis and calculation

The calculation of faradaic efficiency

For CO,

$$\text{FE=} \frac{2F \times n_{co}}{Q} \times 100\% \quad \text{(Equation 1)}$$

For H_2,

$$\text{FE=} \frac{2F \times n_{H_2}}{Q} \times 100\% \quad \text{(Equation 2)}$$

where F is the Faraday constant (F = 96485 C mol^{-1}), n_{co} is the moles of produced CO and n_{H_2} is the moles of produced H_2, Q is the charge passed (C).

Partial current density ($j_{product}$) of each product was calculated as follows:

$j_{product} = j_{total} \times FE_{product}$ (Equation 3)

where j_{total} is the average total current density (mA cm^{-2}) during electrolysis.

The TOF for CO was calculated as follow:

$$TOF = \frac{I_{product}/NF}{m_{cat} \times \omega / M_{Cd}} \times 3600 \quad \text{(Equation 4)}$$

$I_{product}$: partial current for certain product, CO;

N: the numbers of electron transferred for product formation, which is 2 for CO;

F: Faraday constant, 96485 C mol^{-1};

m_{cat}: catalyst mass in the electrode, g;

ω: Cd loading in the catalyst;

M_{Cd}: atomic mass of Cd, 112.4 g mol^{-1}.

Computation details

All calculations were performed using Gaussian 09 program.[1] The B3LYP functional was used with a standard 6-31+G(d) basis set (SDD basis set for Cd) to optimize the geometries of all the structures.

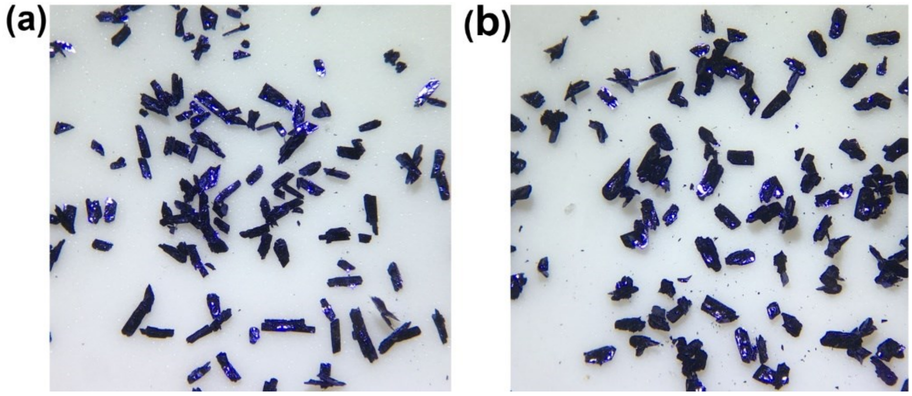

Figure S1. The images of (a) NNU-17 and (b) NNU-18 under optical microscope.

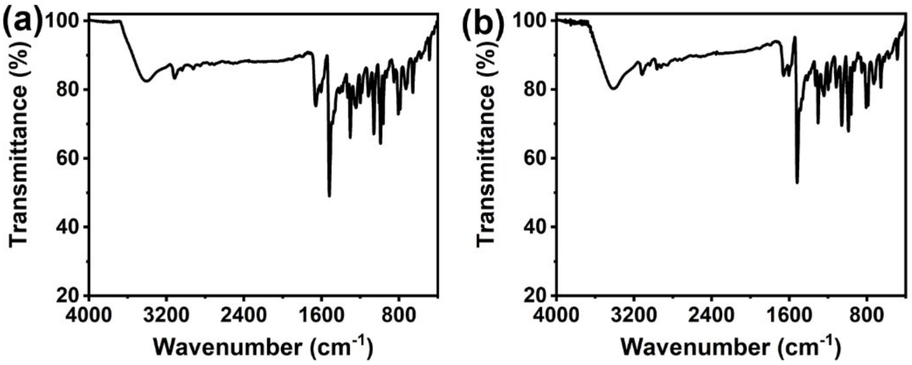

Figure S2. The IR spectra of (a) NNU-17 and (b) NNU-18. (NNU-17, KBr pellets, v/cm^{-1}): 3408 (w), 3110 (w), 3036 (w), 2919 (w), 2850 (w), 2754 (w), 2702 (w), 1907 (w), 1803 (w), 1604 (m), 1517 (s), 1234 (s), 1196 (m), 1057 (s), 991 (s), 964 (s), 809 (s), 724 (s), 659 (s), 490 (m). (NNU-18, KBr pellets, v/cm^{-1}): 3410 (m), 3112 (m), 2962 (w), 2923 (w), 2852 (w), 2752 (w), 2703 (w), 1911 (w), 1796 (w), 1604 (m), 1521 (s), 1242 (s), 1203 (m), 1058 (s), 996 (s), 958 (s), 803 (s), 723 (s), 656 (s), 487 (m).

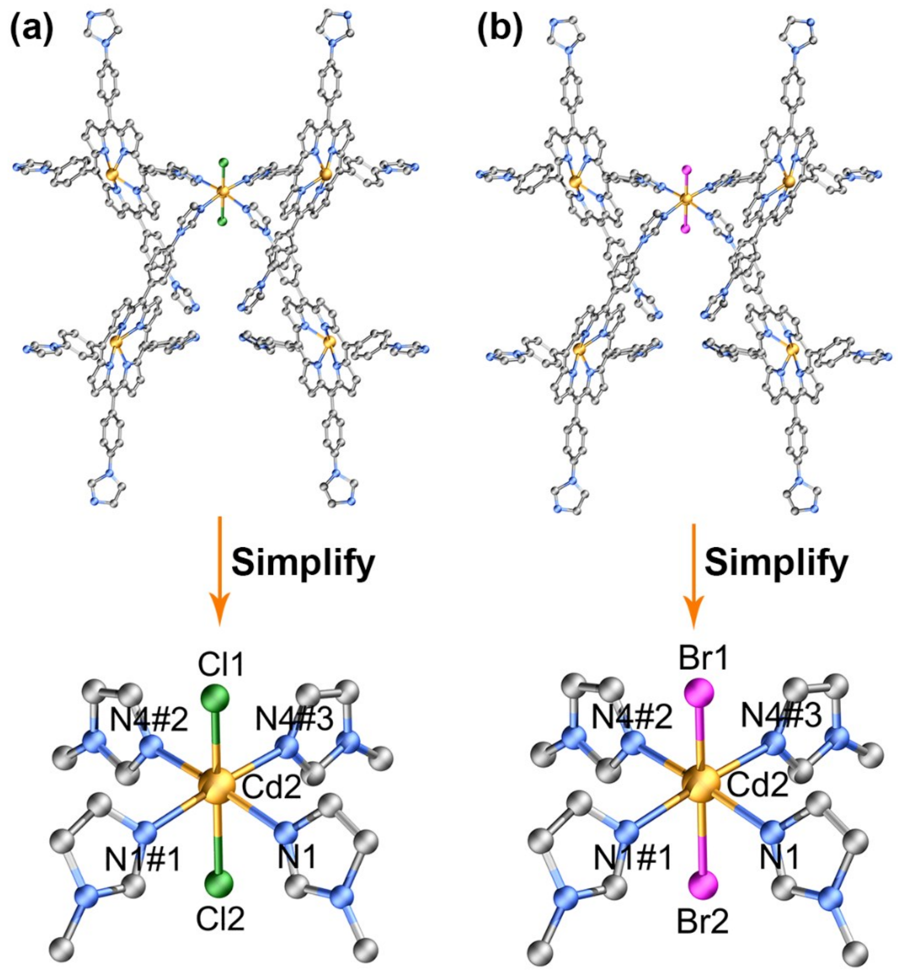

Figure S3. The coordination environment for Cd2 ions in NNU-17 and NNU-18. The simplified modes are at the bottom.

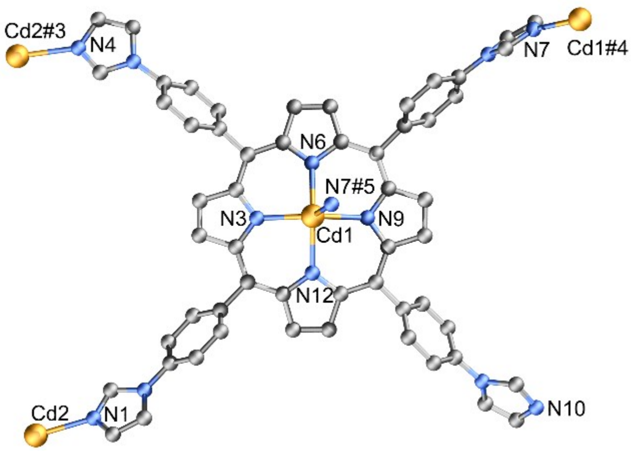

Figure S4. The Cd-TIPP coordination environment in NNU-17/NNU-18.

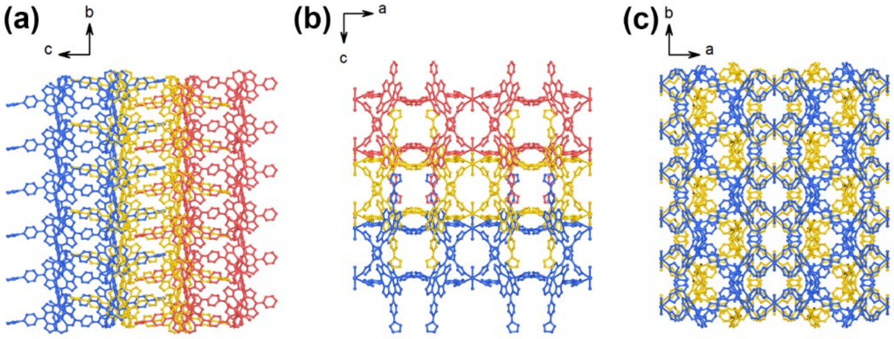

Figure S5. View of the structure of NNU-17/NNU-18 along *a*, *b*, *c* axis.

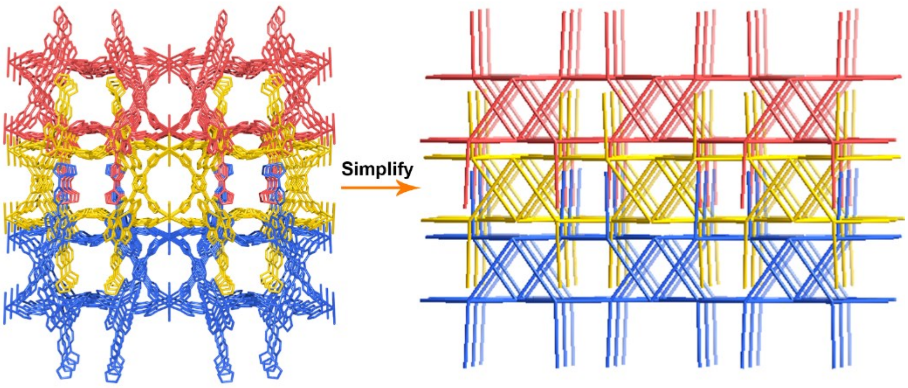

Figure S6. Schematic diagram of structure simplification： 2D + 2D → 3D interdigitated architecture of NNU-17/NNU-18.

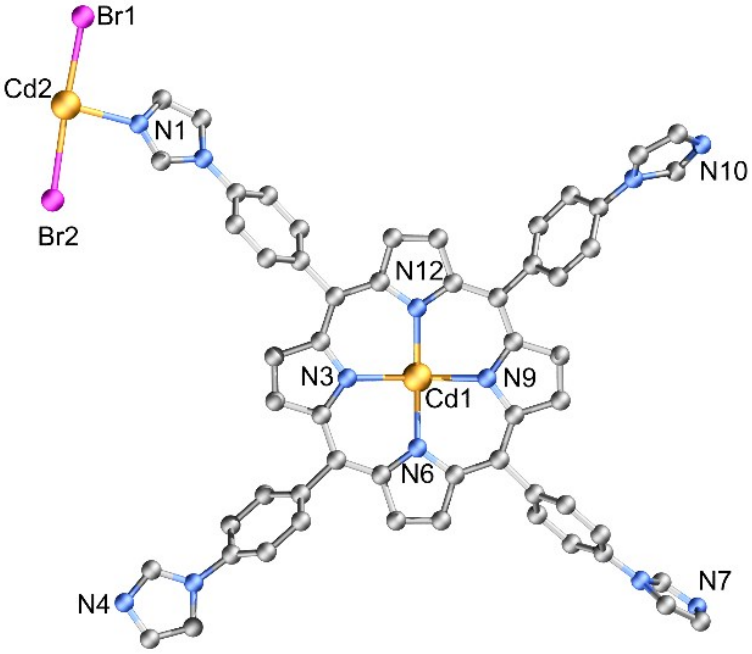

Figure S7. The asymmetric unit of NNU-18.

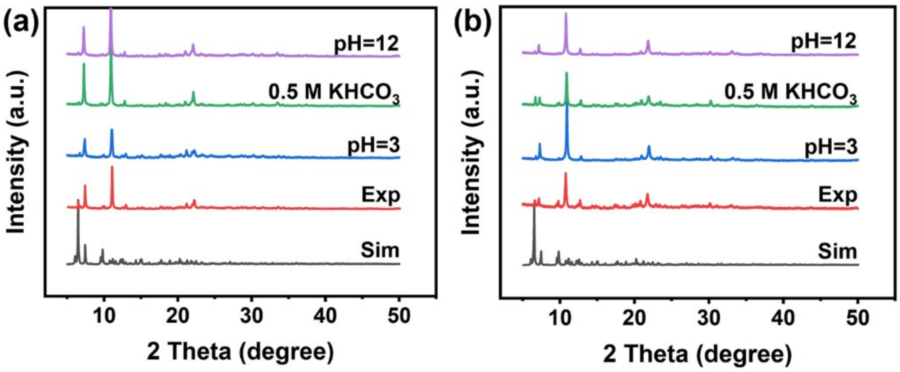

Figure S8. PXRD patterns of (a) NNU-17 and (b) NNU-18 in different pH solutions ranging from 3−12 and 0.5 M $KHCO_3$ for 24 h. “Sim”: simulated pattern and “Exp”: as−synthesized sample.

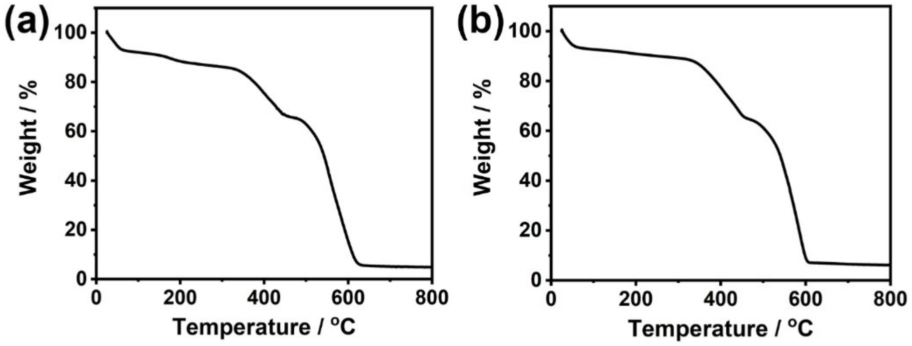

Figure S9. The TGA curves of (a) NNU-17 and (b) NNU-18 measured in air from room temperature to 800°C at the heating rate of 10 °C·min⁻¹.

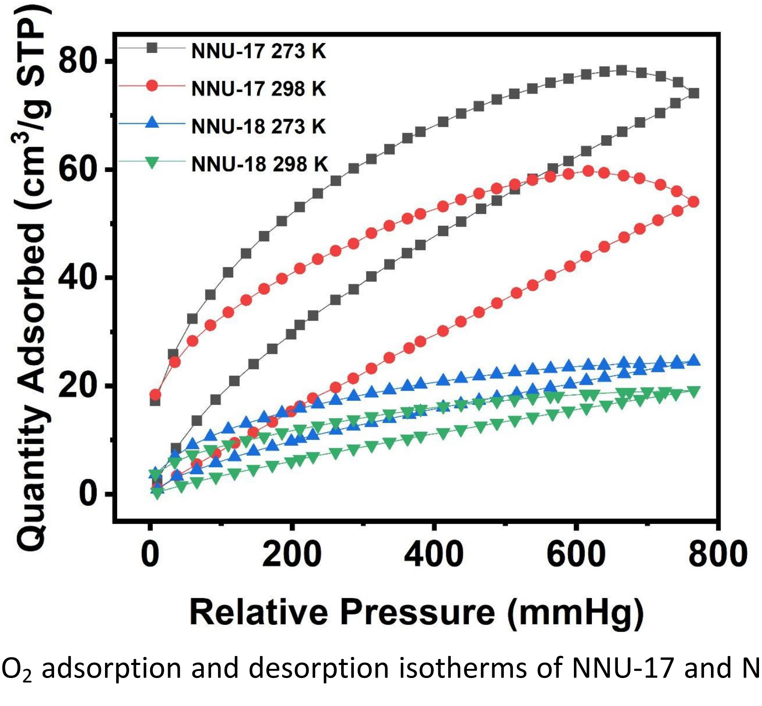

Figure S10. CO_2 adsorption and desorption isotherms of NNU-17 and NNU-18 at 273 K and 298K, respectively.

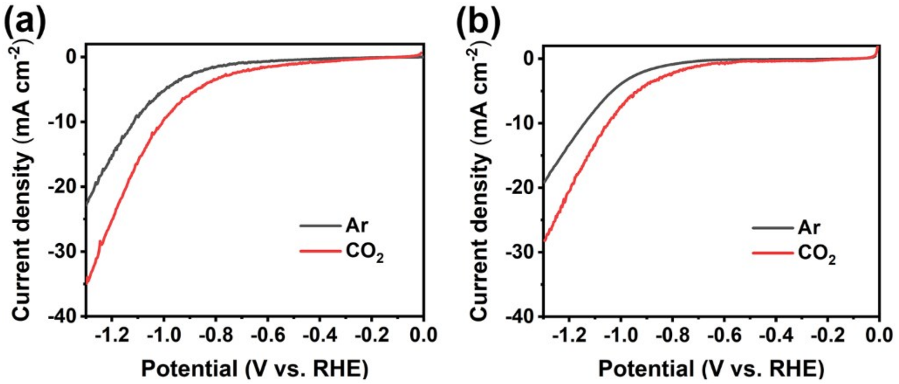

Figure S11. Linear sweep voltammetric curves of (a) NNU-17 and (b) NNU-18 in Ar-saturated and CO_2-saturated 0.5 M $KHCO_3$ aqueous solution.

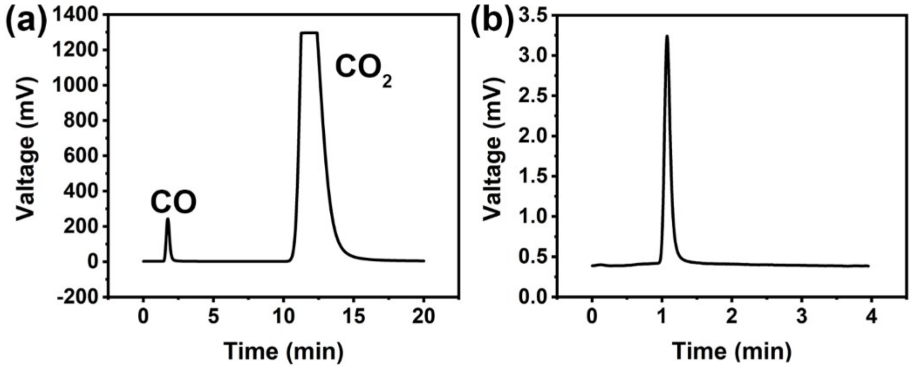

Figure S12. (a) The gas products (CO) was detected by FID detector, (b) and the H_2 was detected by TCD detector.

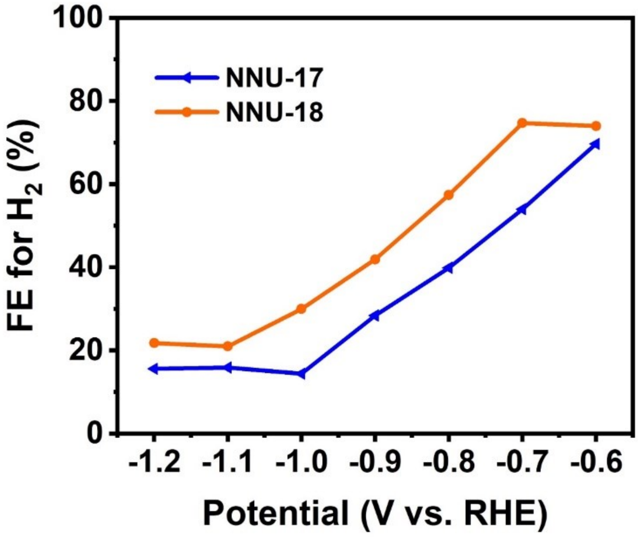

Figure S13. FE(H_2) of NNU-17 and NNU-18 at various applied potentials in CO_2-saturated 0.5 M KHCO3 aqueous solution.

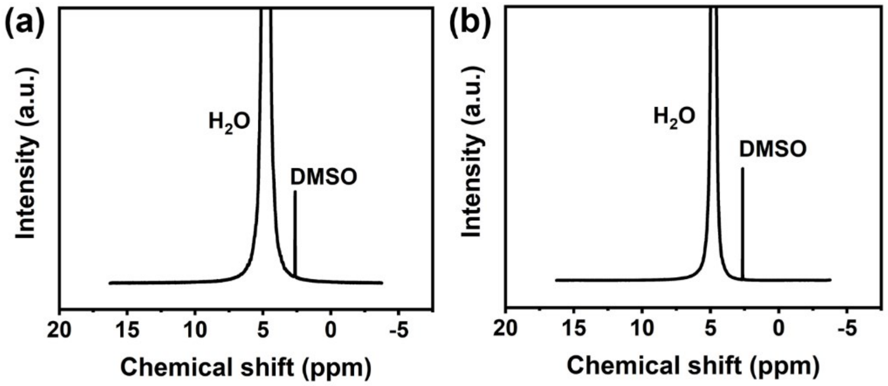

Figure S14. ^1H nuclear magnetic resonance spectroscopy for the liquid product of (a) NNU-17 and (b) NNU-18 after CO_2 reduction.

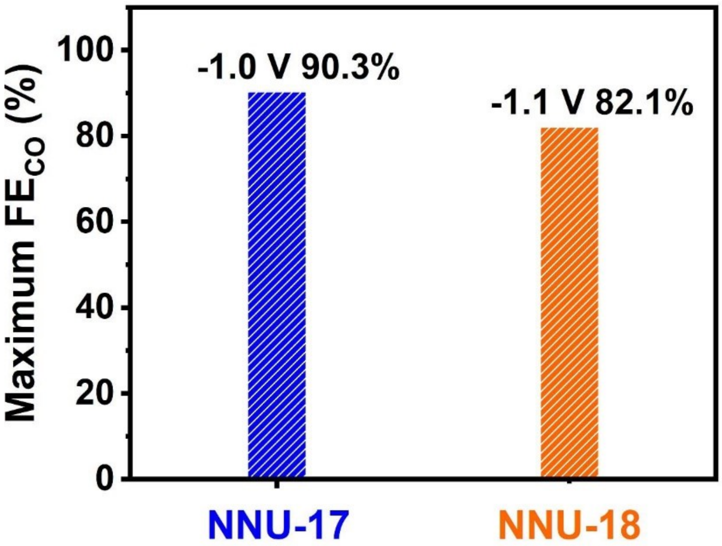

Figure S15. The maximum FE_{CO} appears at different potential.

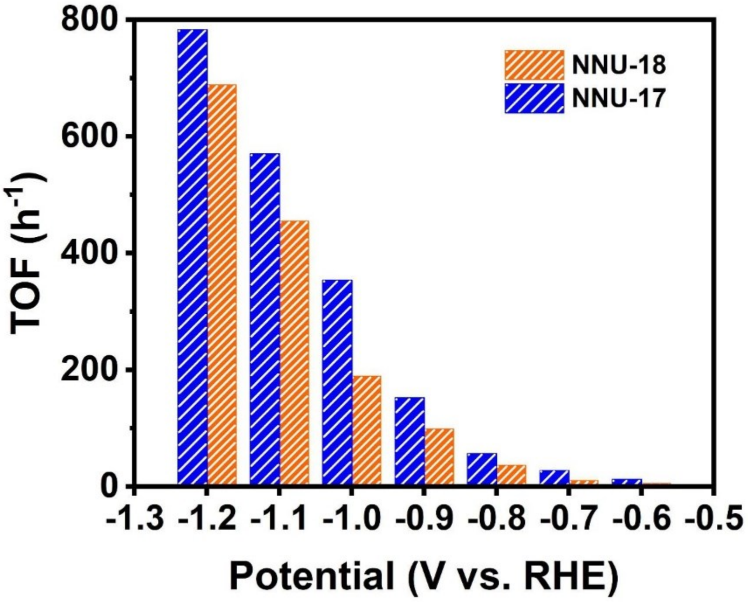

Figure S16. TOF (CO) of NNU-17 and NNU-18 in CO_2-saturated 0.5 M $KHCO_3$ aqueous solution.

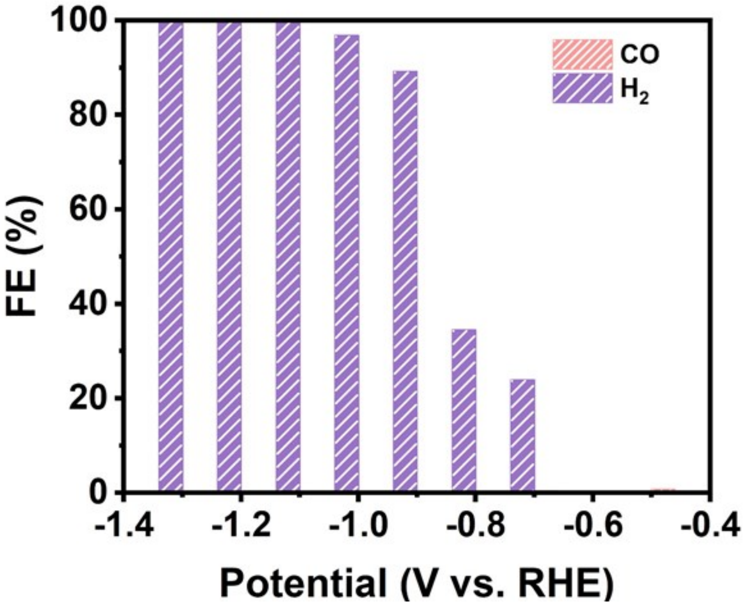

Figure S17. Carbon paper produces hydrogen gas without CO over the potential range.

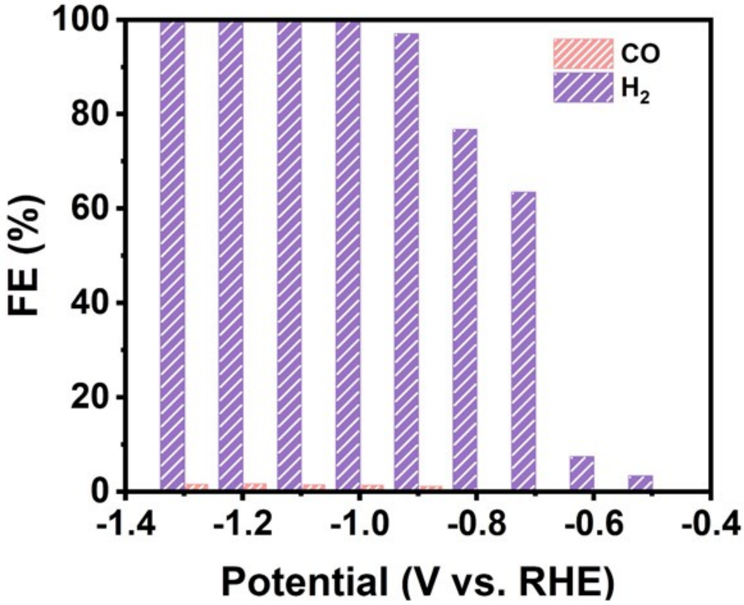

Figure S18. Acetylene black produces hydrogen gas without CO over the potential range.

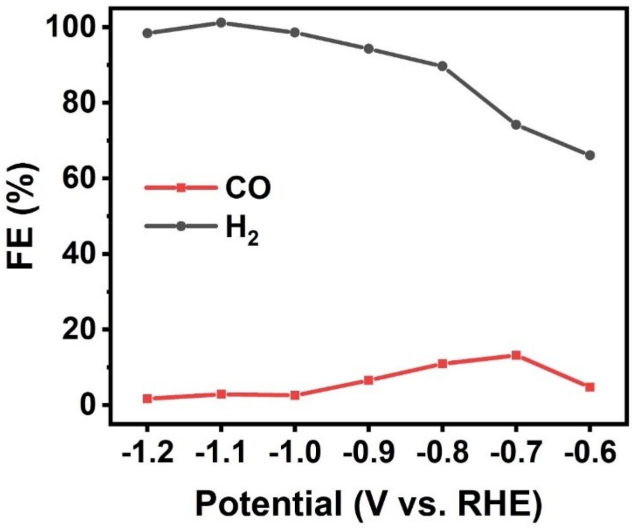

Figure S19. The faradaic efficiencies of TIPP ligand at various applied potentials in CO_2-saturated 0.5 M $KHCO_3$ aqueous solution.

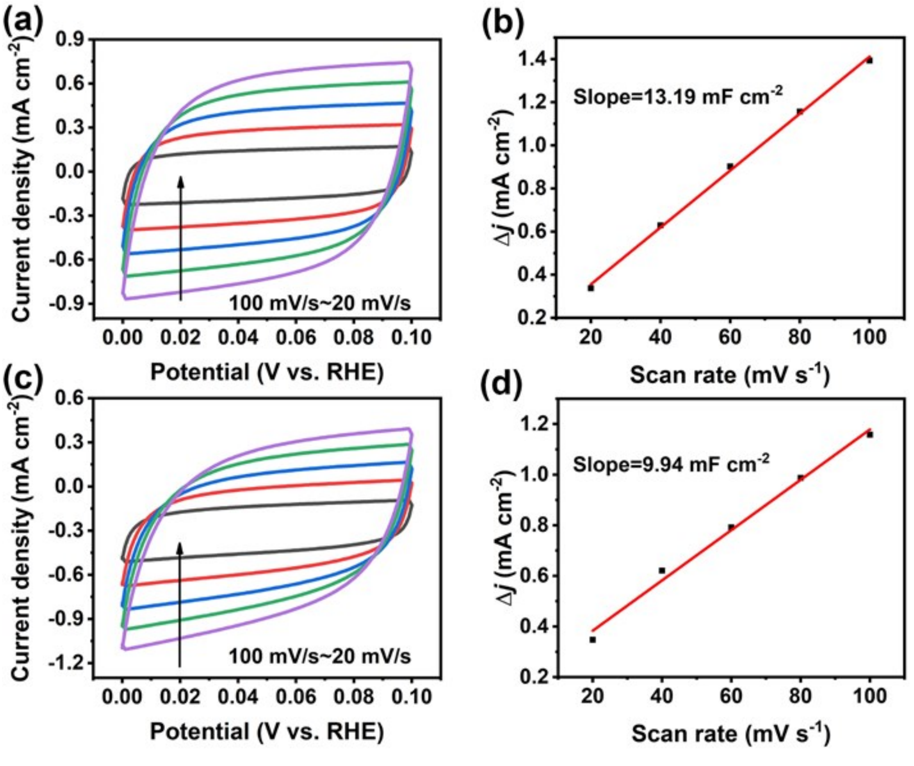

Figure S20. Cyclic voltammertrys (CV) curves in the region of 0.00 ~ 0.10 V *vs*. RHE at various scan rate (100 ~ 20 mV s^{-1}) and corresponding capacitive current at 0.05 V as a function of scan rate for NNU-17 (a and b) and NNU-18 (c and d).

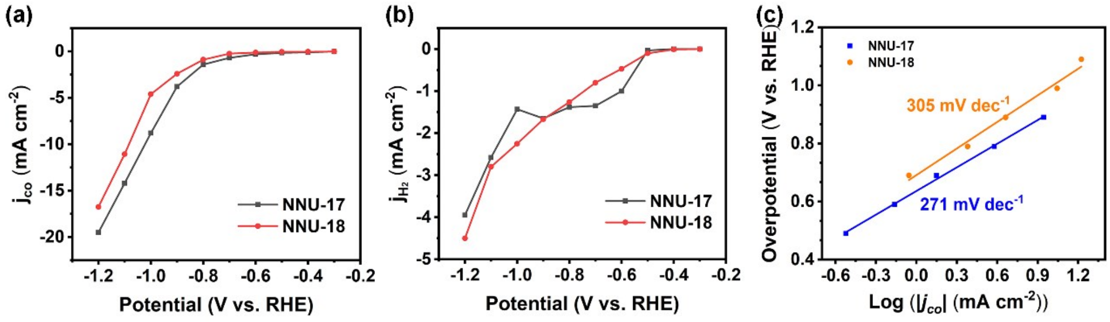

Figure S21. (a) Partial CO and (b) H_2 current density (based on geometric surface area) plots of NNU-17 and NNU-18 in CO_2-saturated 0.5 M $KHCO_3$ aqueous solution. (c) Tafel slopes of NNU-17 and NNU-18 in CO_2-saturated 0.5 M $KHCO_3$ aqueous solution.

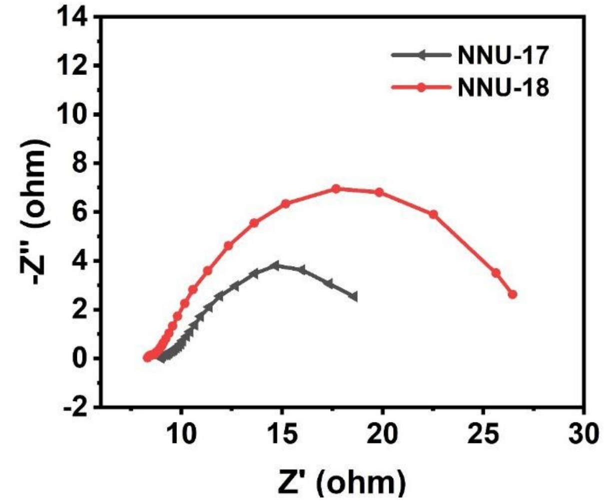

Figure S22. Nyquist plots of electrocatalysts over the frequency ranging from 1000 kHz to 0.1 Hz at -1.0 V vs. RHE.

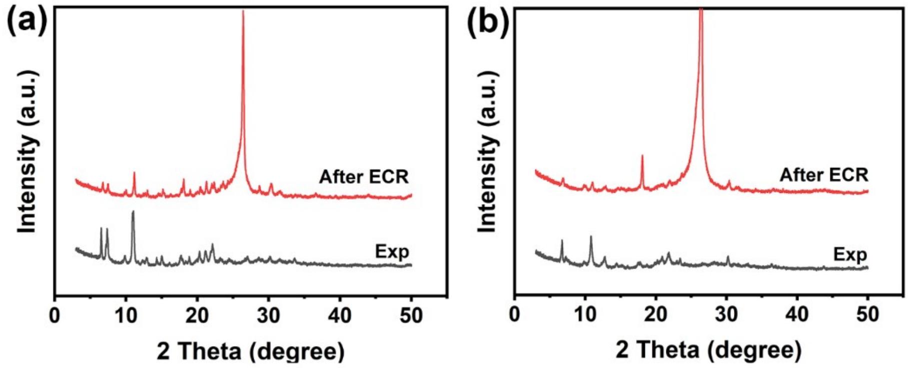

Figure S23. The PXRD pattern of (a) NNU-17 and (b) NNU-18 after ECR (EXP: as-synthesized crystal samples; 26^{o} is assigned to C-conductive substrate).

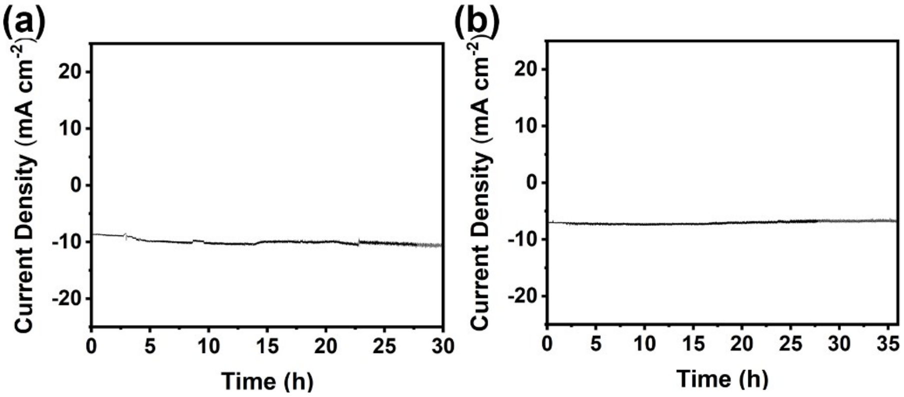

Figure S24. Durability test of (a) NNU-17 and (b) NNU-18 at the potential of −1.0 V vs. RHE.

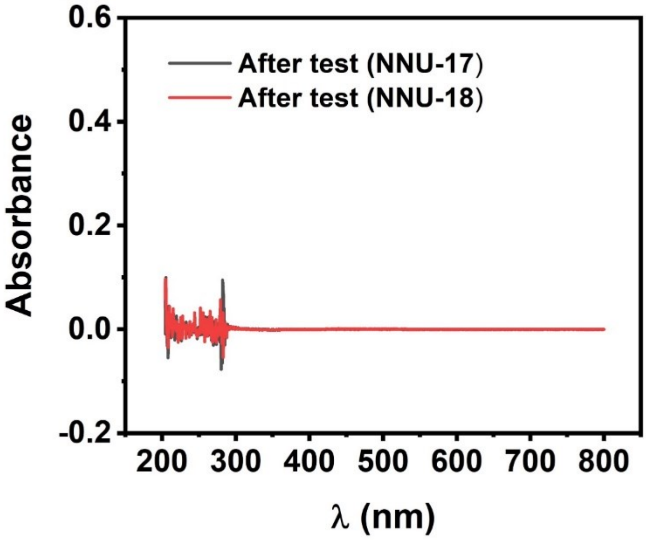

Figure 25. UV-Vis spectra of the solution after test for NNU-17 and NNU-18 at –1.0 V.

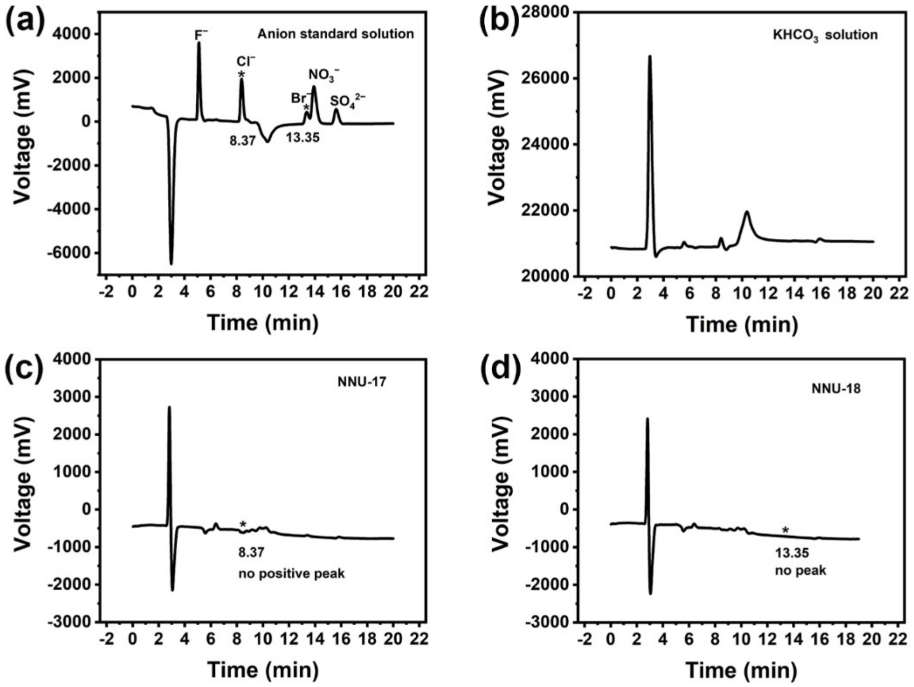

Figure S26. The ion chromatography analysis: (a) the standard solution, (b) $KHCO_3$ solution (the electrolyte before ECR reaction), (c) the electrolyte of NNU-17 and (d) NNU-18 after ECR test.

Table S1. Crystal data and structure refinement for NNU-17 and NNU-18.

Compounds	NNU-17	NNU-18
Empirical formula	$C_{112}H_{72.7}Cd_3Cl_{1.3}N_{24}O_{0.7}$	$C_{112}H_{74.7}Br_{1.3}Cd_3N_{24}O_{0.7}$
Formula weight	2152.21	2202.65
Crystal system	Orthorhombic	Orthorhombic
Space group	*Cmca*	*Cmca*
a (Å)	47.491(2)	47.7736(13)
b (Å)	18.5114(10)	18.5513(5)
c (Å)	27.2738(13)	27.2877(8)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	23977(2)	24184.1(12)
Z	8	8
D_{calc}(Mg·m^{-3})	1.192	1.213
Abs.coeff.(mm^{-1})	0.766	1.259
F(000)	8675.0	8878.0
Reflns collected	79777	71527
Independent reflns	11698	11143
GOF on F^2	1.090	1.032
R_{int}	0.1285	0.0746
R_1 [$I > 2\sigma(I)$][a]	0.0896	0.0627
wR_2 [$I > 2\sigma(I)$][a]	0.1771	0.1724
R_1(all data)[b]	0.1252	0.0672
wR_2(all data)[b]	0.1901	0.1778

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o^2)^2|^{1/2}$.

CCDC numbers: 1993105 (NNU-17) and 1993106 (NNU-18).

Table S2. ICP-MS analysis of solution after electroreduction (−1.0 V) of CO_2 for NNU-17 and NNU-18.

After reaction (−1.0 V)		Content determination
NNU-17	Cd	＜1 ppb (detection limit)
NNU-18	Cd	＜1 ppb (detection limit)

Table S3. The calculated interaction energy between CO_2 and coordinated halogen ions in NNU-17 and NNU-18.

The calculated interaction energy	
Br-C	-3.67 kcal/mol
Cl-C	-5.55 kcal/mol

Reference:

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 09, Revision E.01., Gaussian, Inc., Wallingford CT, 2013.