Supporting Information

Integration of Strong Electron Transporter Tetrathiafulvalene into Metalloporphyrin-Based Covalent Organic Framework for Highly Efficient Electroreduction of CO₂

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**S1. Materials and characterization methods**

**S1.1 Materials and Synthetic procedures**

All reagents were purchased from commercial sources without further purification. P-nitrobenzaldehyde (98%) and SnCl$_2$·2H$_2$O (98%) were purchased from Aladdin, pyrrole (99%) was purchased from Adamas, 2, 3, 6, 7-tetra (4-formylphenyl) tetrathiafulvalene (95%) was purchased from HWRK CHEM, Co(OAc)$_2$·4H$_2$O (98%) was purchased from Alfa, benzyl alcohol (99%) was purchased from Macklin. Acetic anhydride, o-dichlorobenzene, propionic acid, acetone, chloroform, concentrated hydrochloric acid, chlorobenzene and DMF, K$_2$CO$_3$, NaHCO$_3$, NaOAc, acetic acid, dioxane were purchased from Sinopharm Chemical Reagent Co., Ltd, Carbon Paper (Toray), LION Ketjenblack (ECP600JD).

**Synthesis of 5, 10, 15, 20-tetrakis (para-aminophenyl)-21H, 23H-porphyrin (TAPP):**

Following a modified procedure from reference.$^{S1}$

(1) **Synthesis of 5,10,15,20-tetrakis (p-nitrophenyl)-21H, 23h-porphyrin (TNPP):**

In a 500 mL flask, p-nitrobenzaldehyde (11 g, 0.07 mol), propionic acid (300 mL) and acetic anhydride (12 mL) were added and heat to 145 °C to reflux with stirring. Then the mixed solution with 5 mL of pyrrole and 10 mL of propionic acid was added and continue refluxing under stirring for 1h. After that cooled to room temperature and stand undisturbed for 24 h. Then the crude product was affording through vacuum filtered, then washed with 100 mL water for 6 times. Put the crude product in a 80°C vacuum oven for overnight to drying to obtain purple-black solid. After that, the solid was mixed with 80 mL of pyridine and refluxed for 1 h, then cooled to room temperature and stored at -4°C overnight to get black precipitate. Then the solvent was removed through vacuum filtered and washed the filter cake with acetone for several times until the filtrate become colorless, yielding bright purple product TNPP.

(2) **Synthesis of 5, 10, 15, 20-tetrakis (para-aminophenyl)-21H, 23H-porphyrin (TAPP):**

The second step is the reduction of nitro to amino groups. 2.2 g of TNPP was dissolved in 100 mL of concentrated hydrochloric acid. 25 mL of concentrated hydrochloric acid solution containing 9.3 g of SnCl$_2$·2H$_2$O was added dropwise to the
porphyrin solution within 10 min at room temperature under stirring, and then the temperature was raised to 70 °C for 1h. The dark green solid was separated by ice bath cooling, the hydrochloride was dispersed in 200 mL of deionized water, neutralized with concentrated ammonia to pH = 9, and the solid was collected by centrifugation and dried under vacuum at 70 °C. The product was extracted with 300 mL chloroform by using a Soxhlet extractor, and solvent was concentrated to 20 mL by rotary evaporation, it was recrystallized by adding 100 mL of diethyl ether to obtain of bright purple TAPP crystal.

**Synthesis of 5,10,15,20-tetrakis (4-aminophenyl) porphinato cobalt(II) (Co-TAPP):**

Co-TAPP was synthesized according to reference and slightly modified.\(^2\) TAPP (200 mg, 0.30 mmol) and NaOAc (108 mg, 1.3 mmol) were added mixed solution with 63 mL of chlorobenzene and 45 mL of DMF, then Co(OAc)\(_2\)·4H\(_2\)O (200 mg, 0.3 mmol) was added. After equipping with a Soxhlet apparatus with a paper thimble containing K\(_2\)CO\(_3\) (1.1 g, 8.0 mmol), the reaction mixture was stirred under nitrogen at reflux for 24 h. Upon cooling, the Soxhlet apparatus was replaced with a distillation setup, and the solvent was removed under vacuum. The resulting dark solid was suspended in CHCl\(_3\) (100 mL) and transferred to a Buchner funnel with a glass frit, and the solvent was removed through vacuum filtration. The crude product was then washed thoroughly with water three times, saturate NaHCO\(_3\) solution one times, and then water again three times. The resulting dark purple microcrystalline powder was dried under high vacuum overnight.

**Synthesis of TTF-Por(Co)-COF:**

For the synthesis of TTF-Por(Co)-COF, 15.5 mg of TTF-Ph-CHO (0.025 mmol) and 18 mg of Co-TAPP (0.025 mmol) were added to a Pyrex tube measuring 10 × 8 mm (o.d × i.d) and dispersed in a solvent mixture of benzyl alcohol, o-dichlorobenzene and 6 M acetic acid (15:5:2 v:v:v, 2 mL). After sonication for 15 minutes the tube was flash frozen at 77 K (liquid N\(_2\) bath). After one freeze-pump-thaw cycle the system was evacuated to an internal pressure of 50 mTorr and flame sealed. Upon sealing, the length of the tube was reduced to approximately 18~20 cm. The reaction was heated at 120 ºC for 3d yielding a dark purple precipitate at the bottom of the tube, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor
and thoroughly washed with dioxane (24 h) and acetone (24 h). Following that, the product was washed five times with liquid CO$_2$. The system was then heated up to 45 ºC to bring about the supercritical state of CO$_2$ and slowly bled to ambient pressure. Finally the product was evacuated at 100 ºC for 12 h at 10$^{-2}$ mTorr to yield activated sample. Finally, the product was evacuated at 150 ºC under dynamic vacuum overnight to yield activated sample.

**Synthesis of TTF-Por(2H)-COF:**

TTF-Por(2H)-COF was prepared under the similar conditions of TTF-Por(Co)-COF with TAPP as monomer instead of Co-TAPP.

**Synthesis of COF-366-Co:**

COF-366-Co was synthesized according to reference.$^{S2}$

A Pyrex tube measuring 10 × 8 mm (o.d × i.d) was charged with Co-TAPP (18 mg, 0.025 mmol), BDA (10 mg, 0.075 mmol), 1,2-dichlorobenzene (1 mL), butanol (1 mL), and 6 M aqueous acetic acid (0.25 mL). After sonication for 15 minutes the tube was flash frozen at 77 K (liquid N$_2$ bath). After one freeze-pump-thaw cycle the system was evacuated to an internal pressure of 50 mTorr and flame sealed. Upon sealing, the length of the tube was reduced to approximately 18~20 cm. The reaction was heated at 120 ºC for 48 h yielding a dark purple precipitate at the bottom of the tube, which was isolated by filtration. The wet sample was then transferred to a Soxhlet extractor and thoroughly washed with dioxane (24 h) and acetone (24 h). Following that, the product was washed five times with liquid CO$_2$. The system was then heated up to 45 ºC to bring about the supercritical state of CO$_2$ and slowly bled to ambient pressure. Finally the product of COF-366-Co was evacuated at 100 ºC for 18 h at 10$^{-2}$ mTorr to yield activated sample.
S1.2 Characterization methods

Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex 600 diffractometer using Cu Kα radiation (λ = 0.154 nm). N₂ adsorption-desorption isotherm and the Brunauer-Emmett-Teller (BET) surface area measurements were measured by using Micromeritics ASAP 2460 instrument. CO₂ adsorption-desorption isotherms were measured by using Micrometrics ASAP 2020 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher) using an Al Kα source (15 kV, 10 mA). Infrared (IR) spectra were recorded using KBr pellets on a PerkinElmer Spectrum One in the range of 400-4000 cm⁻¹. Elemental analyses of C, H, S and N were carried out on an Elementar Vario EL III analyzer. The gas chromatography measurements were performed on the Agilent 7820A gas chromatograph (GC) equipped with FID and TCD. Scanning electron microscope (SEM) were recorded by a FEIT 20 working at 10 KV. Transmission electron microscope (TEM) images were taken on a FEI TECNAI G2 F20 microscope equipped EDS detector at an accelerating voltage of 200 kV. XAFS measurement and data analysis: XAFS spectra at the Co K-edge was collected at BL14W1 station in Shanghai Synchrotron Radiation Facility (SSRF). The Co K-edge XANES data were recorded in a transmission mode. The Nyquist plots were obtained by the electrochemical impedance spectroscopy (EIS) measurement which was conducted by applying AC voltage with 5 mV amplitude in a frequency range from 100 mHz to 100 kHz. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere with heating rate of 10 °C min⁻¹ to 800 °C by using an SDT Q600 thermogravimetric analyser. Analysis of Co content in TTF-Por(Co)-COF was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Ultima 2 analyzer (Jobin Yvon). ¹H NMR and Solid-state ¹³C NMR spectra was performed at AVANCE III Bruker Biospin spectrometer, operating at 400 MHz. The conductivity of COF powder pellets was measured with a two-probe method using Keithley 4200. The pellets of COFs pellets were pressed at a pressure of approximately 1 GPa. And Figure 1 is referred to Lan’s work.¹³
S2. Electrochemical measurements

The electrochemical measurements were performed in a H-type cell with two compartments separated by anion exchange membrane (Nafion-117) by chi700e at room temperature. One compartment contained 70 mL electrolyte (0.5 M KHCO$_3$ aqueous solution made from DI water) and Pt foil as counter electrodes, another with the same electrolyte, Ag/AgCl electrode in saturated KCl solution as reference electrodes and working electrode. Typically, 5 mg of the catalyst and 2 mg ketjenblack were dispersed in 1 mL of isopropanol and 40 μL of Nafion binder solution (5 wt%) under sonication for 1 h to form a homogeneous ink. Then 60 μL of the catalyst ink was loaded onto the carbon fiber paper electrode with 1×1 cm$^2$. During the electrochemical measurements, the electrolyte solution was purged with CO$_2$ for 30 min to achieve the CO$_2$-saturated solution (pH = 7.6). Linear sweep voltammetry (LSV) was performed with a scan rate of 10 mV s$^{-1}$ from 0 V to -1.0 V vs. RHE in CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte. All measured potentials were converted to reversible hydrogen electrode (RHE) scale using the following equation:

$$E_{\text{vs. RHE}} = E_{\text{vs. Ag/AgCl}} + 0.059 \times \text{pH} + 0.197 \text{ V}.$$

CO$_2$ gas was delivered at an average rate of 30 ml/min (at room temperature and ambient pressure) and routed into the gas sampling loop (1 mL) of a gas chromatograph. The gas phase composition was analyzed by GC every 15 min. The separated gas products were analyzed by a thermal conductivity detector (for H$_2$) and a flame ionization detector (for CO, CH$_4$). The liquid products were analyzed afterwards by quantitative NMR (Bruker AVANCE AV III 400). Solvent presaturation technique was implemented to suppress the water peak.

Faradaic efficiency calculation for CO.

$$FE = \frac{J_{CO}}{J_{total}} = \frac{\nu_{CO} \times N \times F}{J_{total}}$$

$J_{CO}$: partial current density for CO production;

$J_{total}$: total current density;

$N$: the number of electron transferred for product formation, in which it is 2 for CO;

$\nu_{CO}$: the production rate of CO (measured by GC);

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

FE: Faradaic efficiency for CO production.
Evaluation of turnover frequency (TOF, h\(^{-1}\)) for CO

\[
TOF = \frac{I_{\text{product}}}{m_{\text{cat}} \times \omega / M_{\text{metal}}} \times 3600
\]

\(I_{\text{product}}\): partial current for certain product, CO;

\(N\): the number of electron transferred for product formation, in which it is 2 for CO;

\(F\): Faradaic constant, 96485 C mol\(^{-1}\);

\(m_{\text{cat}}\): catalyst mass in the electrode, g;

\(\omega\): metal loading in the catalyst;

\(M_{\text{metal}}\): atomic mass of metal.
S3. Computational method

All the density functional theory (DFT) calculations were performed via the Vienna Ab initio Simulation package (VASP),\textsuperscript{84–88} and the projector-augmented plane wave (PAW) pseudopotentials were used for the elements involved.\textsuperscript{89} The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) was used to treat the exchange-correlation between electrons.\textsuperscript{810} We calculated finite clusters (as shown in Figure S1 and Figure S2) instead of periodic structures due to the limitation of the computational resource. The clusters are separated from their periodic images in all directions by a vacuum space of 10 Å. A cutoff energy of 500 eV and the Gamma point k-mesh were chosen. The convergence in the energy and force were set to be $10^{-4}$ eV and 0.01 eV/Å.

![Figure S1. Relaxed structure of TTF-Por(Co)-COF.](image1)

![Figure S2. Relaxed structure of COF-366-Co.](image2)
S4. Supporting Figures and Tables:

Figure S3. The PXRD patterns of TTF-Por(2H)-COF.

Figure S4. The PXRD patterns of COF-366-Co.
Figure S5. Comparison of FT-IR spectra of TTF-Por(2H)-COF and TTF-Por(Co)-COF with the monomer TTF-Ph-CHO, TAPP, and Co-TAPP.

Figure S6. Solid-state $^{13}$C NMR spectra for the activated sample of TTF-Por(2H)-COF.
Figure S7. TGA for the TTF-Por(Co)-COF under nitrogen atmosphere.

Figure S8. Electrical measurements of TTF-Por(Co)-COF were performed using two-electrode in air at a constant temperature of 298 K and in the absence of light. The electrical conductivity is calculated to be $1.32 \times 10^{-7}$ S m$^{-1}$. ($\sigma = \frac{L}{R \times \pi (d/2)^2}$, $L = 0.57$ mm, $d = 2.5$ mm, $R = 8.76 \times 10^8$ $\Omega$).
Figure S9. Electrical measurement of COF-366-Co was performed using two-electrode in air at a constant temperature of 298 K in the absence of light. The electrical conductivity is calculated to be $6.5 \times 10^{-9}$ S m$^{-1}$. ($\sigma = \frac{L}{R \cdot \pi (d/2)^2}$, $L = 0.76$ mm, $d = 2.5$ mm, $R = 2.38 \times 10^{10}$ $\Omega$).

Figure S10. Current-voltage measurements of TTF-Por(Co)-COF according to the space charge-limited current (SCLC) model. $I$-$V$ trace of single crystal exhibiting two different regimes, marked for Ohmic ($I \propto V^n = 1$), and Child´s ($I \propto V^n = 2$) regime.
Figure S11. Current-voltage measurements of COF-366-Co according to the space charge-limited current (SCLC) model. $I-V$ trace of single crystal exhibiting two different regimes, marked for Ohmic ($I \propto V^n = 1$), and Child’s ($I \propto V^n = 2$) regime.

Figure S12. Electrochemical impedance spectroscopy (EIS) of TTF-Por(Co)-COF and COF-366-Co, which were mixed with Ketjenblack (ECP600JD) tested at FTO.
Figure S13. The XPS Co 2p spectra of Co-TAPP and TTF-Por(Co)-COF (up) and TTF-Por(Co)-COF after catalysis (down).
Figure S14. The XPS S 2p spectra of TTF-Por(Co)-COF catalysis before (a) and (b) after CO₂RR.

The bonding energy of sulphur at 168.6 eV (2p₃/₂) and 170.0 eV (2p₁/₂) are attributed to the existence of sulfonic acid groups in Nafion, which was introduced to the catalyst ink, while bonding energy at 163.9 eV (2p₃/₂) and 165.1 eV (2p₁/₂) can be ascribed to the S of TTF in TTF-Por(Co)-COF.⁵₁¹

Figure S15. N₂ sorption isotherms of TTF-Por(2H)-COF at 77 K (inset pore-size distribution profile). Solid symbols denote adsorption, open symbols denote desorption (P/P₀ = partial pressure).

The N₂ sorption revealed that TTF-Por(2H)-COF has Brunauer-Emmer Teller (BET) surface area 268 m² g⁻¹ and the pore size distribution around 0.66 and 1.1 nm.
Figure S16. N$_2$ sorption isotherms of COF-366-Co at 77 K. Solid symbols denote adsorption, open symbols denote desorption (P/P$_o$ = partial pressure).

Figure S17. The pore size distribution profiles of COF-366-Co based on NLDFT method.

The N$_2$ sorption revealed that COF-366-Co has Brunauer-Emmer Teller (BET) surface area 817 m$^2$ g$^{-1}$ and the pore size distribution around 1.2-2.0 nm.
Figure S18. CO$_2$ sorption isotherms of TTF-Por(2H)-COF measured at 298 K.

Figure S19. SEM images of TTF-Por(Co)-COF with scale bar 100 nm.
In Figure S20, the two high resolution N 1s peaks at 399.9 eV and 398.5 eV are attributed to Co-N₄ structure and C=N in TTF-Por(Co)-COF, respectively.⁵¹²

**Table S1.** CN, coordination number; R, distance between absorber and backscatter atoms; $\sigma^2$, Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); R factor is used to value the goodness of the fitting.

<table>
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<tr>
<th>Sample Path</th>
<th>CN</th>
<th>R(Å)</th>
<th>$\sigma^2(10^{-3}\text{Å}^2)$</th>
<th>R factor</th>
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<td>4</td>
<td>1.964</td>
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<td>TTF-Por(Co)-COF</td>
<td>Co-O</td>
<td>0.84±1.93</td>
<td>1.936</td>
<td>2.5±8.4</td>
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Figure S21. Corresponding EDS mapping of oxygen elements in selected area of TTF-Por(Co)-COF.

Figure S22. $^1$H NMR spectra of TTF-Por(Co)-COF for the electrolyte test after CO$_2$RR in CO$_2$-saturated 0.5 M KHCO$_3$. 
Figure S23. LSV curve in the N₂-saturated and CO₂-saturated 0.5 M KHCO₃ electrolyte at a scan rate of 10 mV s⁻¹ for TTF-Por(2H)-COF.

Figure S24. The selectivity and activity of the TTF-Por(Co)-COF and TTF-Por(2H)-COF were compared at -0.9 V vs. RHE using identical conditions.
Figure S25. Summary of CO TOFs at corresponding potentials for TTF-Por(Co)-COF.

Figure S26. Stability of TTF-Por(Co)-COF in CO$_2$-saturated 0.5 M KHCO$_3$ electrolyte at a potential of -0.7 V vs RHE during 10 h.
Figure S27. Normalized Co K-edge XANES spectra of the TTF-Por(Co)-COF and TTF-Por(Co)-COF-used.

Figure S28. Fourier transform EXAFS spectra of TTF-Por(Co)-COF and TTF-Por(Co)-COF-used.
<table>
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<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Applied potential (V vs RHE)</th>
<th>Faradaic efficiency of CO (%)</th>
<th>Reference</th>
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<td>TTF-Por( Co)-COF</td>
<td>0.5 M KHCO$_3$</td>
<td>-0.7</td>
<td>95</td>
<td>This work</td>
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<td>COF-366-Co</td>
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<td>70</td>
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<td>[Co$^{III}$N4H(Br)$_2$]$^+$</td>
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<td>OCP</td>
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S5. References


