

Supporting Information

Fluorination covalent organic frameworks for metal-free visible-light driven CO₂ reduction

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1. General Information

1.1 Characterization methods

The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. The powder X-ray diffraction (PXRD) patterns were measured on Rigaku SmartLab operating at (40 kV, 150 mA) with a scan rate of 8 °/min from 2 ° to 60 °. Field emission scanning electron microscopy (SEM) images and field emission transmission electron microscopy (TEM) images were obtained on JSM-7500F at an acceleration voltage of 5 kV and Tecnai G2 F20 at an acceleration voltage of 200 kV, respectively. CO₂ sorption of the polymers was measured by Micromeritics ASAP 2020. Solid UV-Vis spectra were recorded on a UV-visible absorption spectroscopy (Shimadzu, UV-2700). All experiments were carried out at room temperature. Contact angle measurements were measured by Krüss DSA-30. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al K α X-ray source (1486.6 eV) operated at 100 W. Samples were analyzed under vacuum ($P < 10^{-8}$ mbar) with a pass energy of 150 eV (survey scans) or 30 eV (high-resolution scans).

Electrochemical measurements were carried out on a CHI660e electrochemical work station with an ITO conductive glass (1 cm*1 cm) coated with the synthesized samples (the coated area is 1 cm²) as the working electrode, a Ag/AgCl electrode (saturated KCl solution) as the reference electrode, a platinum plate as the counter electrode. The coated samples were prepared by mixing photocatalyst (5 mg) and Nafion solution (30 μ L, 5 wt%) in ethanol (1 mL), then dried in air. The Mott-Schottky tests were carried out in 0.1 M TBABF₆ acetonitrile solution, with the measured potentials calibrated by ferrocene/ferrocenium (Fc/Fc⁺ $E_{red/ox} = 0.49$ V). Linear sweep voltammograms measurements were performed in 0.1 M TBABF₆.

The condition of photocatalytic experiments :The Schenk tube was placed under a 300 W xenon lamp (130 mW/cm²). All experiments were carried out right over the stirrer by 5 cm with a constant stirring speed of 500 rpm. The room temperature was maintained between 20 and 25 °C using air conditioners, and potential heating of the solution was prevented using the exhaust fan of the photocatalytic box and an extra electric fan.

1.2 Experimental Section/Methods

Materials

Tris(1,10-phenanthroline)ruthenium(II) Bis(hexafluorophosphate) was purchased from Energy Chemical Co., Ltd.; 1,2-Dichlorobenzene, 2,3,5,6-Tetrafluoroterephthalaldehyde, Thieno[3, 2-b]thiophene-2,5-dicarboxaldehyde, 4,4',4''-(1,3,5-Triazine-2,4,6-Triyl)Trianiline, and Terephthalaldehyde were purchased from Shanghai Adamas Reagent Co., Ltd.. CO₂ gas (99.99% purity) was purchased from Liquefied Air (Hangzhou) Co., Ltd.. N, N-dimethylformamide (DMF), acetonitrile, ethanol, and triethanolamine were purchased from J&K Scientific Ltd..

Synthesis of N3-COF: The COF was prepared by a slight modification of our earlier procedure.^[1]

About 17 mg of terephthalaldehyde (0.1 mmol) was dissolved in 3 mL of analytical grade ethanol in a Pyrex tube, to this, 3.0 mL of O-dichlorobenzene was added and stirred until a clear solution was observed. Then, about 30 mg of 2,4,6-Tris(4-aminophenyl)-s-triazine (0.1 mmol) and 250 μ L of aqueous acetic acid (3 M) were added to the reaction mixture and contents were stirred for 30 mins. The pyrex tube along with its contents was flash frozen in a liquid nitrogen bath and sealed. The tube was placed in an oven and heated to 120°C and was left undisturbed

for 3 days. The product, a yellow powder was washed with copious amounts of MeOH, DMF, Acetone, dioxane and THF. Yield 53%.

Synthesis of N3F4-COF:

About 20 mg of 2,3,5,6-Tetrafluoroterephthalaldehyde (0.1 mmol) was dissolved in 3 mL of analytical grade ethanol in a Pyrex tube, to this, 3.0 mL of O-dichlorobenzene was added and stirred until a clear solution was observed. Then, about 30 mg of 2,4,6-Tris(4-aminophenyl)-s-triazine (0.1 mmol) and 250 μ L of aqueous acetic acid (3 M) were added to the reaction mixture and contents were stirred for 30 mins. The pyrex tube along with its contents was flash frozen in a liquid nitrogen bath and sealed. The tube was placed in an oven and heated to 120°C and was left undisturbed for 3 days. The product, a orange red powder was washed with copious amounts of MeOH, DMF, Acetone, dioxane and THF. Yield 56%.

General Procedure for Photocatalytic CO₂ Reduction.

To a 25 mL Schlenk tube, photocatalyst (2 mg), [Ru(phen)₃](PF₆)₂ (2 mg), TEOA (0.5 mL), BIH (0.05 mM), H₂O (1 mL) and acetonitrile (3 mL) were successively added. Then, the reaction mixture

was sonicated to allow the polymer to disperse evenly in the whole solution for 15 min. Air in the Schlenk tube was replaced by CO₂ through the freeze-pump-thaw method. Then, the reaction tube was sealed and placed under a 300W Xenon lamp ($\lambda \geq 420\text{nm}$) for desired time at room temperature. After the reaction, partial gaseous products (1 mL) were taken from the tube using a syringe and then analyzed by gas chromatography with a TCD detector.

Recycling test Procedure

After the first reaction for 1h, the reaction mixture was used recycling, just released the gas in the Schlenk tube. And then air in the Schlenk tube was replaced by CO₂ through the freeze-pump-thaw method again and reused for the next run. After the fourth run, an equal amount of photosensitizer is added to the Schlenk tube, and then repeat the above steps to finish the fifth run reaction.

2. Supplementary Figures

2.1 Characterization of the structure composition and morphology

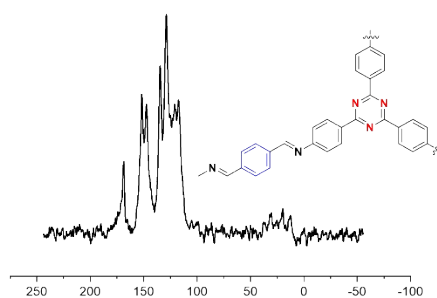


Figure S1. CP/MAS ¹³C NMR of N3-COF

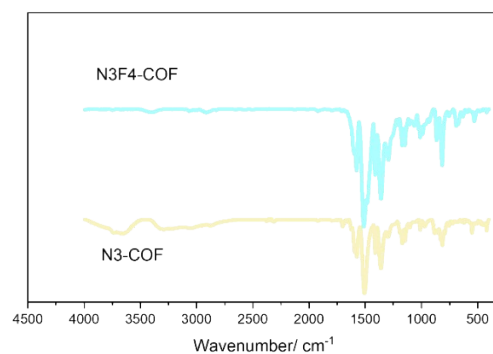


Figure S2. FTIR spectra of N3F4-COF and N3-COF

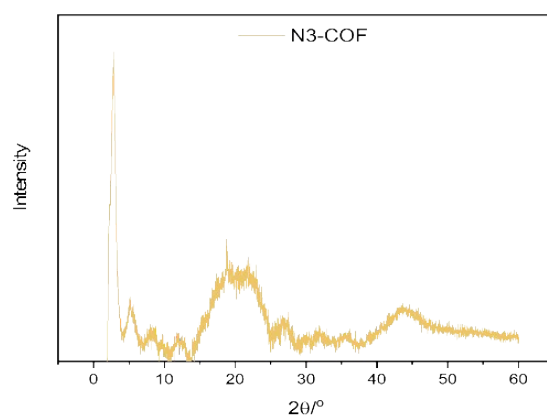


Figure S3. XRD patterns of N3-COF.

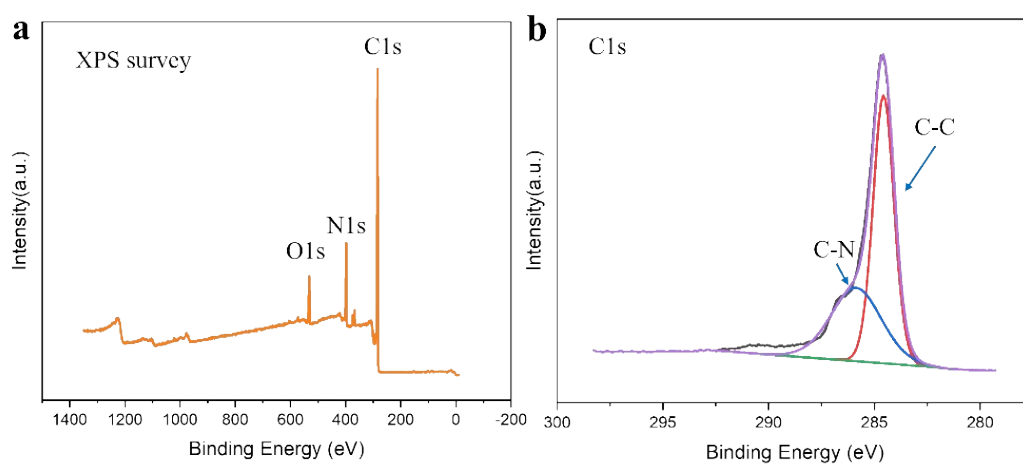


Figure S4. XPS patterns of N3-COF.(a) XPS survey; (b) C1s

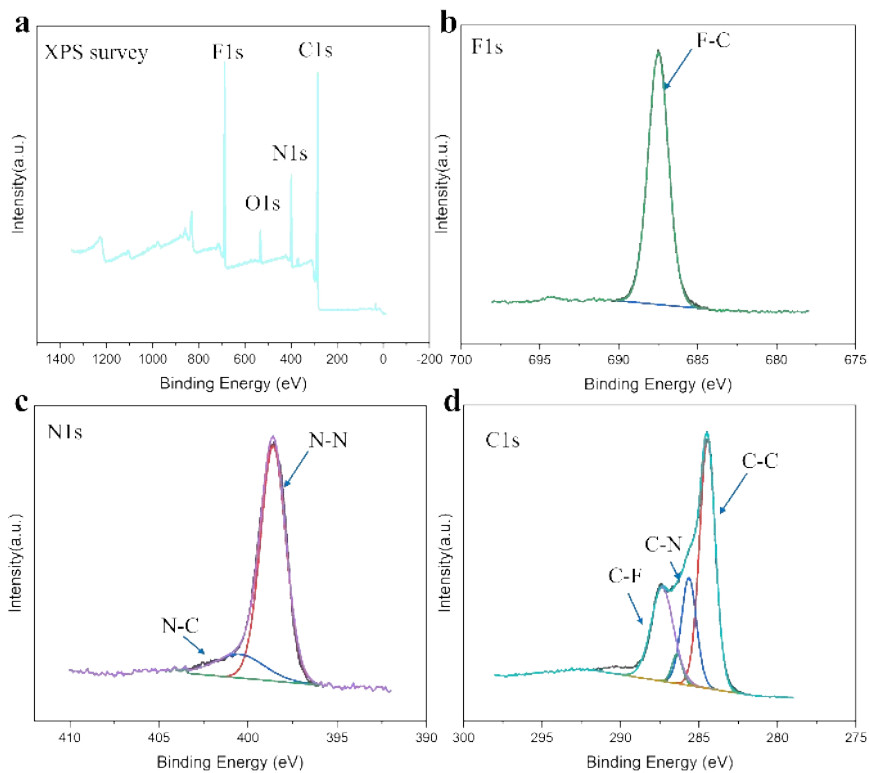


Figure S5. XPS patterns of N3F4-COF. (a) XPS survey; (b) F1s; (c) N1s; (d) C1s

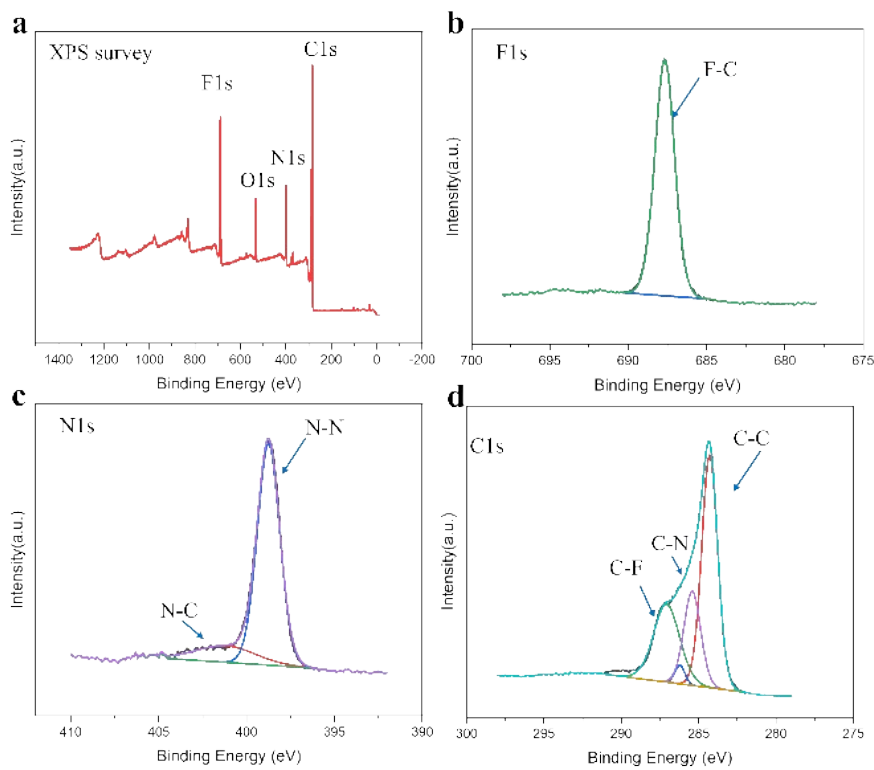


Figure S6. XPS patterns of reused N3F4-COF. (a) XPS survey; (b) F1s; (c) N1s; (d) C1s

N3-COF

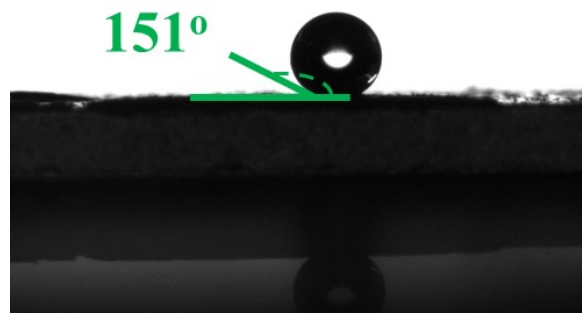


Figure S7. Contact angle measurement of water for N3-COF.

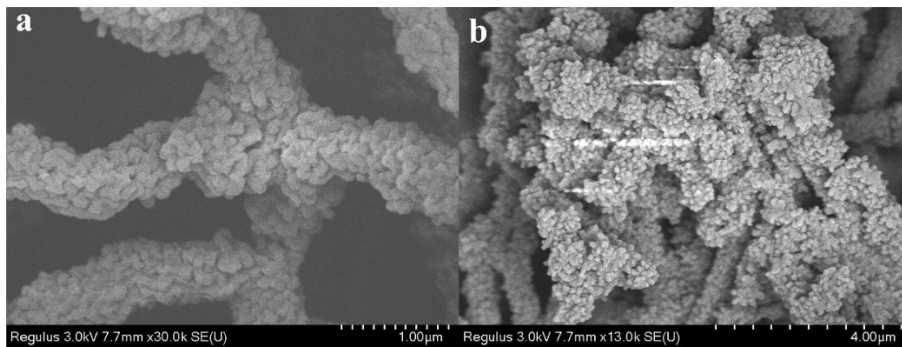


Figure S8. SEM image of N3-COF (a) and (b).

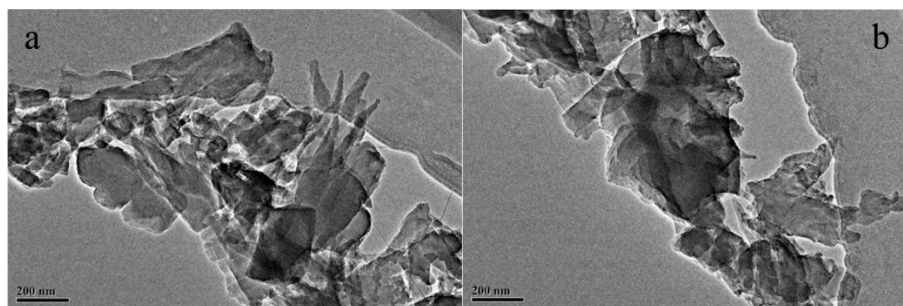


Figure S9. TEM image of N3F4-COF (a) and (b).

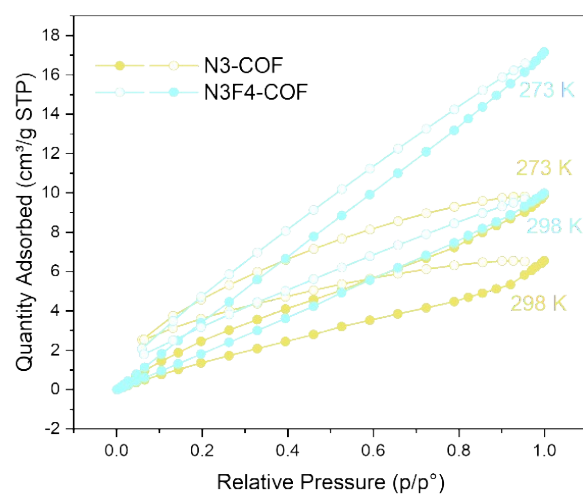


Figure S10. CO₂ uptakes at 273 K and 298 K for N3-COF and N3F4-COF.

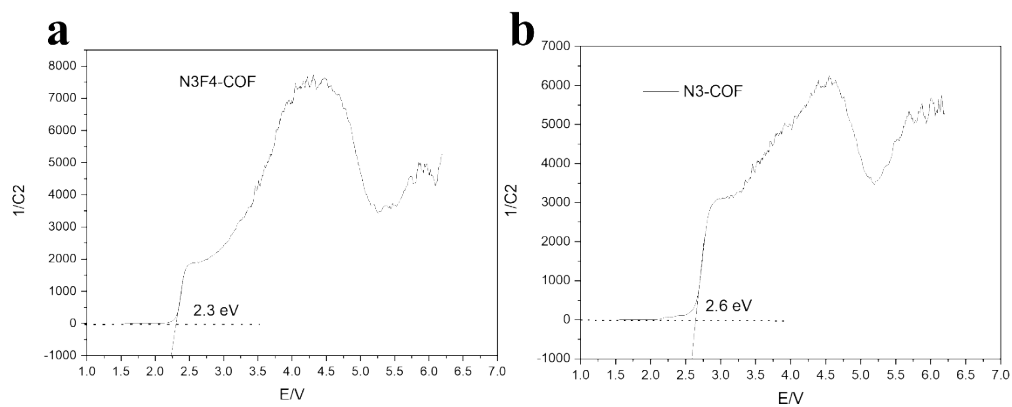


Figure S11. Tauc plots of (a)N3F4-COF and (b)N3-COF derived from the corresponding DRS.

Table S1. Some representative metal-free photocatalytic CO₂ reduction performance using CMP and COF-based porous organic polymers

Catalyst	Sacrificial reagent	Light source	Major product evolution rate (mmol g ⁻¹ h ⁻¹)	Reference
N3F4-COF	H ₂ O/ BIH/ TEOA	300 W Xe lamp (λ > 420 nm)	CO: 4.7 H ₂ : 1.8	This work
N3-COF	H ₂ O/ BIH/ TEOA	300 W Xe lamp (λ > 420 nm)	CO: 0.8 H ₂ : 0.01	This work
TAPA-PQ	H ₂ O/ BNAH/ TEA	300 W Xe lamp (λ > 420 nm)	CH ₄ :2.15	S2
CMP-BT	H ₂ O/ TEOA	white light (λ ≥ 420 nm)	CO:1.2 H ₂ :0.27	S3
OXD-TPA	H ₂ O vapour	300 W Xe Lamp (λ>420 nm)	CO:0.038	S4
PEosinY-1	H ₂ O vapour	300 W Xe lamp (λ>420 nm)	CO:0.033	S5
TAPBB-COF	H ₂ O	(200 ≤ λ ≤ 1000 nm)	CO:0.025	S6
TT-COF	TEA	400 nm ≤ λ ≤ 750 nm)	CO:0.25	S7
TPE-PT	H ₂ O	300 W Xe lamp full spectrum	CH ₄ :0.0106	S8
CT-COF	H ₂ O	λ ≥ 420 nm	CO:0.103	S9
N ₃ -COF	H ₂ O vapour	λ ≥ 420 nm	CH ₃ OH:5.7 × 10 ⁻⁴	S10

Table S2. Some representative state-of-art catalysts for photochemical CO₂ reduction to syngas formation

Catalyst	Photosensitizer /Cocatalyst	Sacrificial reagent	Light source	Major product CO evolution rate (mmol g ⁻¹ h ⁻¹)	CO selectivity (%)	Reference
N3F4-COF	[Ru(phen) ₃](PF ₆) ₂	H ₂ O/BIH/TEOA	300 W Xe lamp (λ > 420 nm)	4.7	72%	This work
N3-COF	[Ru(phen) ₃](PF ₆) ₂	H ₂ O/BIH/TEOA	300 W Xe lamp (λ > 420 nm)	0.8	99%	This work
Zn-Co ₃ O ₄	Ru(bpy) ₃	TEOA/H ₂ O	300 W Xe lamp (λ ≥ 420 nm)	36.3	70.9%	S11
MOF-Co	Ru(bpy) ₃	TEOA/H ₂ O	Xe lamp (λ ≥ 420 nm)	1.14	47.3	S12
Vo-HCo ₃ O ₄ /OMN C	[Ru(phen) ₃](PF ₆) ₂	TEOA/H ₂ O	300 W Xe lamp (λ > 420 nm)	220	65.15	S13
Co/C	Ru(bpy) ₃	TEOA/H ₂ O	300 W Xe lamp (λ > 400 nm)	0.45	64.3	S14
Ni-Co ₃ O ₄ NSDHN	Ru(bpy) ₃	TEOA/H ₂ O	LED light (36W, λ = 450 nm)	89.1	52.4	S15
bp-Co-COF _{4.25}	Ru(bpy) ₃ Cl ₂	TEOA	300W Xe lamp (with a UV cutoff filter, ≥420nm)	5.64	33.3%	S16
COF-367-Co NSs	Ru(bpy) ₃ Cl ₂	Ascorbic acid	300W Xe lamp	10.16	78	S17
Co-TAPT-1	Ru(bpy) ₃ Cl ₂	TEOA/H ₂ O	300W Xe lamp	8.39	41.7	S18

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