Supporting Information

Synergetic Effect of H^+ Adsorption and Ethylene Functional Group of Covalent Organic Frameworks on the CO_2 Photoreduction in Aqueous Solution

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Materials and methods

Materials. The starting materials for COF synthesis were purchased from The Shanghai Tensus Bio-techCo., Ltd. Other reagents and solvents applied in the synthesis and photocatalysis were purchased from Aladdin and Sigma-Aldrich, and used without pretreatments.

PXRD patterns were recorded on a Siemens D5005 diffractometer with Cu KR (λ = 1.5418 Å) radiation in the range of 1–50°. ICP spectroscopy was conducted on Agilent 7500a Inductively Coupled Plasma Mass Spectrometry (ICP-MS 7500). TEM images were recorded on a JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV. SEM images were recorded on XL-30 ESEM-FEG Scanning Electron Microscope. The elemental mappings of the samples were determined by EDX equipped on SEM with the type of Genesis 2000. UV–Vis absorption spectroscopy was obtained on U-3010 spectrophotometer (Hitachi, Japan). Infrared spectra were obtained from KBr pellets in a wavelength ranging from 4000-400 cm^{-1} on a Nicolet 380 FT-IR spectrophotometer. XPS was performed using an Escalab 250 instrument. Nitrogen gas porosimetry measurements were performed on a automatic volumetric adsorption equipment (ASIQM0G002-3) and porosity analyzer after the samples were outgassed under a vacuum at 100 °C for 12 h. Emission lifetime measurements were performed on photon technology international quanta master/time master TM 400 phosphorescence/fluorescence Spectrofluoromete. The gas product in photocatalytic reaction was measured by Shimadzu Gas Chromatography.

The COF simulation was performed using Materials Studio software. All simulations were performed using spin-polarized DFT/GGA, where the PBE exchange-related functions were implemented in DMol3 (package). Simulation of the X-ray diffraction pattern of the COF was performed using a Reflect Tools. The DFT pore size distribution was obtained from the adsorption/desorption isotherm by using a slit hole model. All of the above calculations were carried out using the Gaussian 16 package.[1]

Synthesis of 2, 4, 6-tri(4-vinylbenzoyl)-s-triazine

1,4-Phthalaldehyde (1.6 g, 12 mmol), KOH (0.68 g, 4 mmol) and methanol (150 mL) were added into a 500 mL round-bottomed flask; then trimethyl-s-triazine (0.49 mg, 4 mmol) in 100 mL methanol was added via a constant-voltage funnel. The reaction was refluxed at 80 °C for 24 h. The solid product was collected by filtration and washed thoroughly with methanol and water sequentially. The crude product was purified by silica gel column chromatography using mixed solvents [v (ethyl acetate) : v (petroleum ether) = 1 : 1] as an eluent. Yield: 60.3%. ^{1}H NMR (DMSO-d_6, 600 MHZ, TMS) δ (ppm) 10.05 (s, 3H), 8.38 (d, J = 16.0 Hz, 3H)， 8.07 (d, J = 8.0 Hz, 6H), 8.00 (d, J = 8.0 Hz, 6H), 7.45 (d, J = 16.0 Hz, 3H).

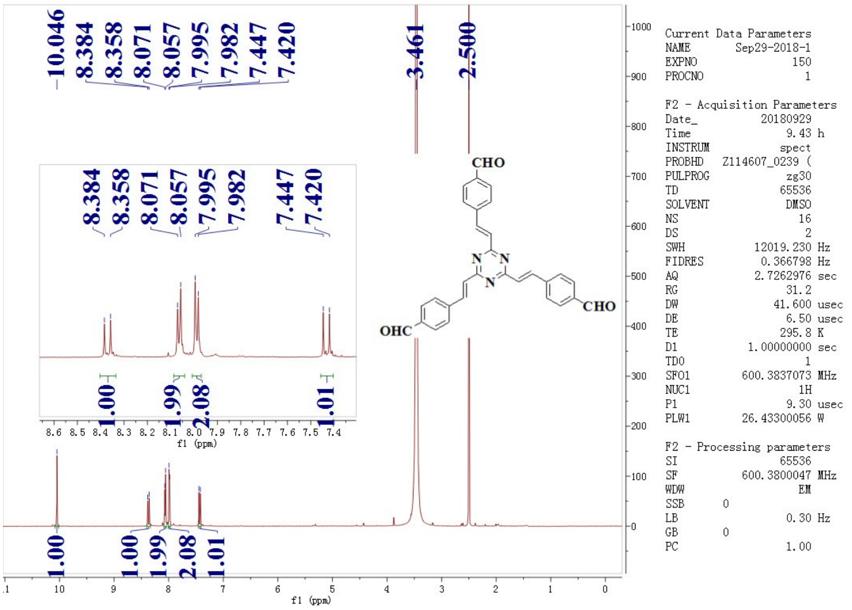

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Figure S1 ^{1}H NMR of 2, 4, 6-tri(4-vinylbenzoyl)-s-triazine.

Synthesis of COF-TVBT-PA

The precursors of 2, 4, 6-tri(4-vinylbenzoyl)-s-triazine (TVBT) and P-phenylenediamine (PA) were synthesized according to a reported procedure and detailed synthesis step was provided in supporting information. TVBT (47.2 mg, 0.1 mmol) and PA (16.2 mg, 0.15 mmol) were put in a cylindrical glass tube (20 cm of length, ϕ_{in} = 0.8 cm, ϕ_{out} = 1.0 cm) and were mixed with mesitylene, dioxane (3.6 ml 5:1, v/v) and 0.3 ml 6 M glacial acetic acid, then sonicated for 15 minutes to get a homogenous dispersion. After degased by three freeze-pump-thaw cycles, the tube was sealed off and then heated at 120 °C for 3 days. The bright red precipitates were collected by filtration and rinsed with N, N-dimethylformylamide (DMF) and acetone in turn. Finally, the powders were steepened in the mixed solvent of acetone and dichloroethane (1:1 in v/v) to exchange for 8 h, and then dried at 100 °C for 24 h.

Cyclic Voltammetry

The cyclic voltammetry of COF-TVBT-PA was tested in an electrochemical workstation (CHI 760e, China) with a three-electrode system. The working electrode is a GC electrode (d = 3mm), a platinum wire as the auxiliary electrode and an Ag/AgCl electrode as the reference electrode. 5 mg of the samples and 5 mg of carbon black (Vulcan XC-72R) were dispersed in 0.6 mL of solution containing 300 μL of 0.5 wt% Nafion solution, 150 μL of water and 150 μL of ethanol, followed by sonication for 60 min until a suspension was formed. After sonication, 5 μL of as-prepared suspension was drop-cast onto the GC electrode. Then, the working electrode was dried spontaneously under ambient temperature. The final mass loading of the catalysts is about 0.59 $mg \cdot cm^{-2}$. The electrochemical measurements were tested in methyl cyanide solution.

Photocurrent Measurements

Photocurrent measurements were performed using an electrochemical workstation (ParStat MC multichannel potentiostats, Germany) with a three-electrode configuration. The working electrodes (1 cm ×1 cm) were prepared by spreading aqueous slurries of various samples on ITO glass substrate. Ag/AgCl electrode and Pt-wire electrode were employed as the reference and counter electrode, respectively. Irradiation was carried out by using a 300-W xenon lamp. The Tetrabutylammonium Hexafluorophosphate (0.1 M) in Acetonitrile solution was used as the electrolyte.

Photocatalytic Experiment.

In a quartz tube (10 mL), catalyst (5 mg) was dispersed in the solution containing 0.1M $NaHCO_3$ (3.5 mL), MeOH (0.5 mL), ascorbic acid (50 mg). This mixture system was bubbled with pure CO_2 gas for 20 min. The temperature of the reaction solution was maintained at 25 °C controlled by a flow of water during the reaction. Then, the system is irradiated under visible light using a PLS-SXE300 Xe lamp with an AM 1.5 cut-off filter. To detect the yield of CO gas, gas (500 μL) in the middle of the test tube was emigrated using a syringe and injected into FID detector by argon as carrier gas. The volume of the generated CO was calculated by comparing the integrated area of the signals of CO with a calibration curve. Both the injector and detector temperatures were set to 60 °C. The retention time of hydrogen was 1.9 min. To detect the formation of hydrogen from the reaction mixture, the gas (1000 μL) of the headspace of the test tube was transferred using a syringe and injected into TCD detector through a 5Å molecular sieve column, with argon acting as both carrier gas and reference gas. The volume of the hydrogen produced was calculated by comparing the integrated area of the signals of hydrogen with a calibration curve. The injector and detector temperatures were set to 60 °C. The retention time of hydrogen was 0.7 min.

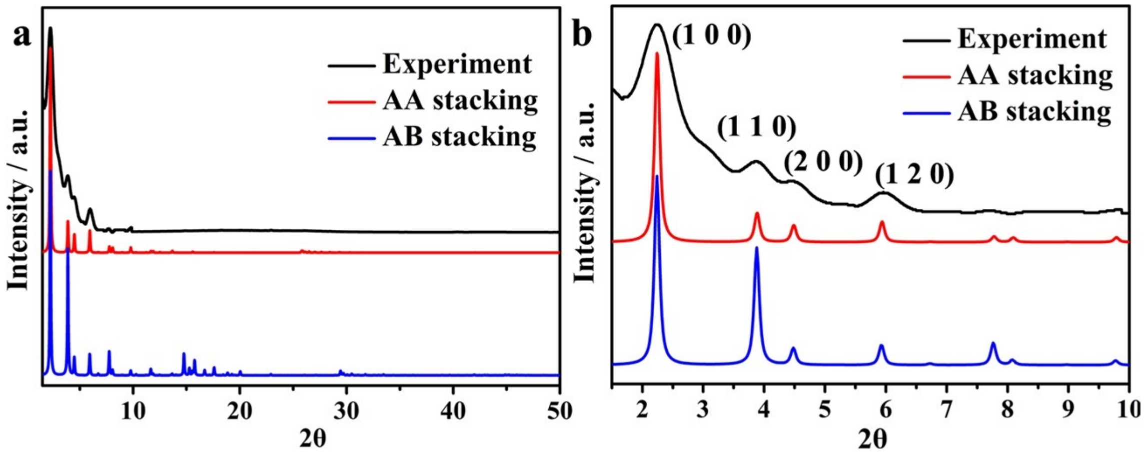

Figure S2 (a) PXRD of experiment, AA stacking and AB stacking. (b) The enlargement of PXRD and plane reflection information.

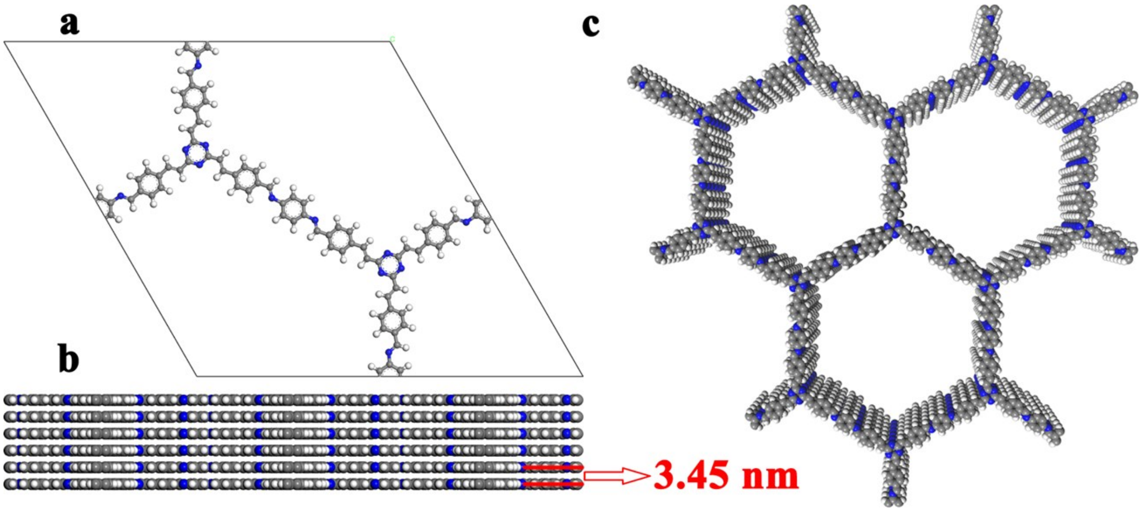

Figure S3 Space filling models showing AA stacking of COF-TVBT-PA: unit cell (a), side view (b) and top view (c); carbon (grey), nitrogen (blue), oxygen (red) and hydrogen (white).

Table S1. Fractional atomic coordinates for the unit cell of COF-TVBT-PA calculated based on staggered AA model.

Space group	P6/m		
Unit cell	a = b= 45.4367 Å, c = 3.4519, α = β = 90°, γ = 120°		
atom	x	y	z
N1	0.30934	-0.32288	0.00000
N2	0.46065	0.53298	0.00000
C3	0.34271	-0.29895	0.00000
C4	1.26469	0.61676	0.00000
C5	1.23869	0.62476	0.00000
C6	0.40066	0.60247	0.00000
C7	0.43601	0.62508	0.00000
C8	0.45868	0.61273	0.00000

C9	0.44665	0.57769	0.00000
C10	0.41144	0.55507	0.00000
C11	0.38876	0.56737	0.00000
C12	0.47117	0.56536	0.00000
C13	0.48121	0.51709	0.00000
C14	0.51700	0.53553	0.00000
C15	0.53543	0.51845	0.00000
H16	1.25878	0.59061	0.00000
H17	1.24560	0.65130	0.00000
H18	0.44664	0.65227	0.00000
H19	0.48573	0.63065	0.00000
H20	0.40137	0.52786	0.00000
H21	0.36174	0.54932	0.00000
H22	0.49793	0.58396	0.00000
H23	0.53112	0.56294	0.00000
H24	0.56293	0.53301	0.00000

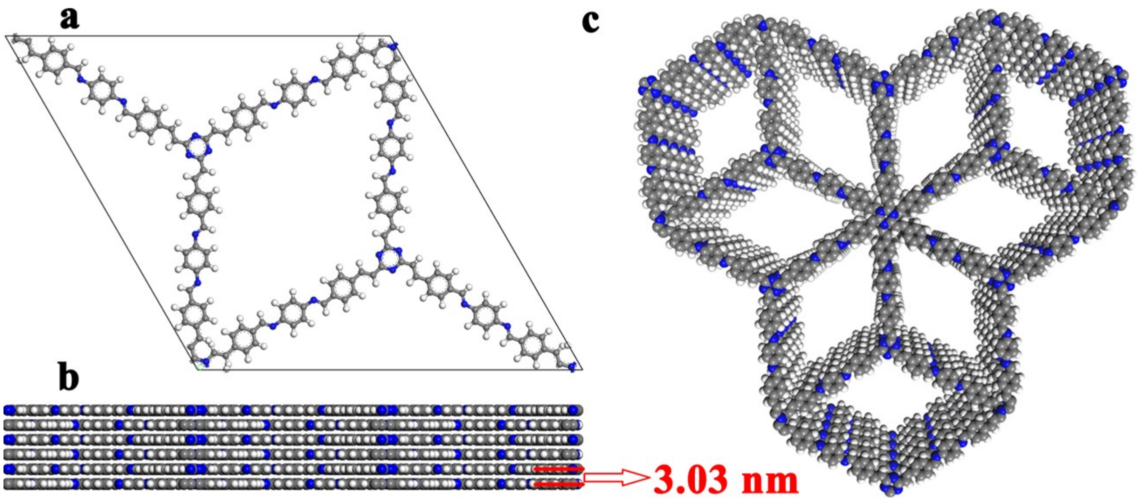

Figure S4 Space filling models showing AB stacking of COF-TVBT-PA: unit cell (a), side view (b) and top view (c); carbon (grey), nitrogen (blue), oxygen (red) and hydrogen (white).

Table S2. Fractional atomic coordinates for the unit cell of COF-TVBT-PA calculated based on staggered AB model.

Space group	P63/m		
Unit cell	a = b= 45.5077 Å, c = 6.0646, α = β = 90°, γ = 120°		
atom	x	y	z
N1	−0. 35694	0. 34424	0. 25000
N2	−0. 20909	0. 19683	0. 25000
C3	−0. 32350	0. 36780	0. 25000
C4	−0. 40215	0. 28417	0. 25000
C5	−0. 42782	0. 29258	0. 25000

C6	-0.26756	0.26767	0.25000
C7	-0.23218	0.28988	0.25000
C8	-0.20990	0.27711	0.25000
C9	-0.22233	0.24203	0.25000
C10	-0.25758	0.21981	0.25000
C11	-0.27987	0.23253	0.25000
C12	-0.19821	0.22925	0.25000
C13	-0.18898	0.18049	0.25000
C14	-0.15321	0.19848	0.25000
C15	-0.13480	0.18137	0.25000
H16	-0.40841	0.25794	0.25000
H17	-0.42057	0.31918	0.25000
H18	-0.22123	0.31708	0.25000
H19	-0.18281	0.29473	0.25000
H20	-0.26798	0.19258	0.25000
H21	-0.30692	0.21477	0.25000
H22	-0.17141	0.24758	0.25000
H23	-0.13893	0.22584	0.25000
H24	-0.10734	0.19607	0.25000
N25	-0.03426	-0.02434	0.25000
N26	0.26051	0.13007	0.25000
C27	-0.02535	0.00883	0.25000
C28	-0.01765	-0.06821	0.25000
C29	-0.05146	-0.09444	0.25000
C30	0.13112	0.06869	0.25000
C31	0.14341	0.10392	0.25000
C32	0.17830	0.12690	0.25000
C33	0.20163	0.11531	0.25000
C34	0.18947	0.08021	0.25000
C35	0.15461	0.05721	0.25000
C36	0.23836	0.14015	0.25000

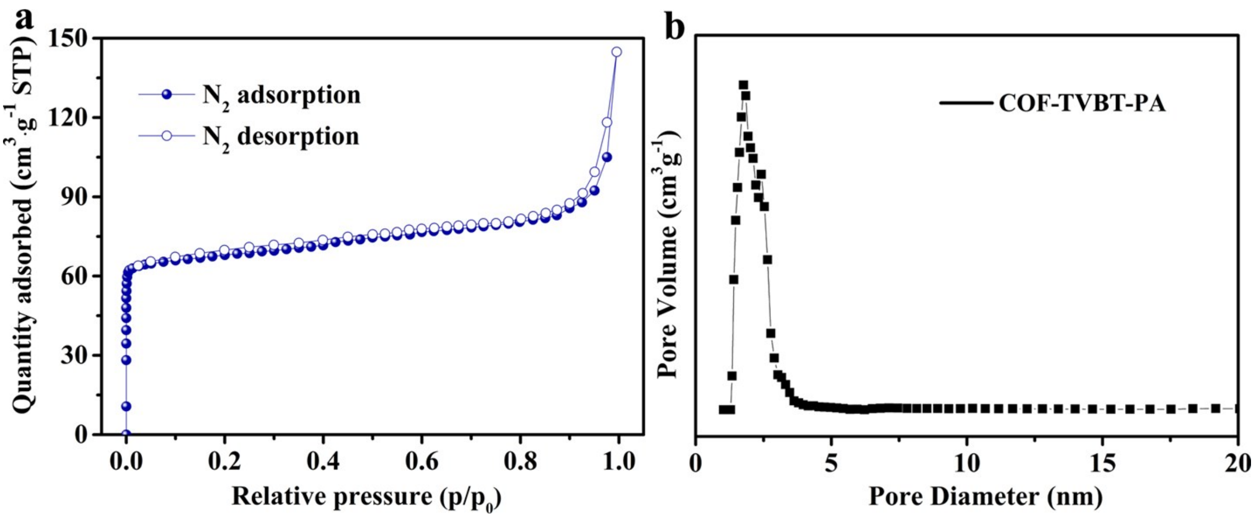

Figure S5 Gas isotherms adsorption. (a) N_2 adsorption–desorption isotherms for pure COF-TVBT-PA. (b) pore size of pure COF-TVBT-PA.

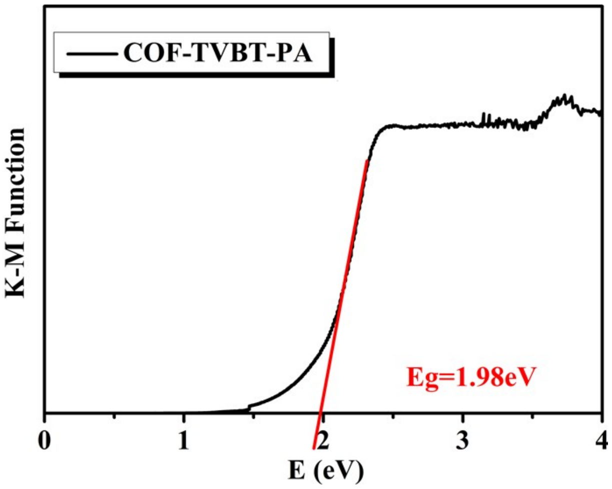

Figure S6 Band structure diagram for COF-TVBT-PA.

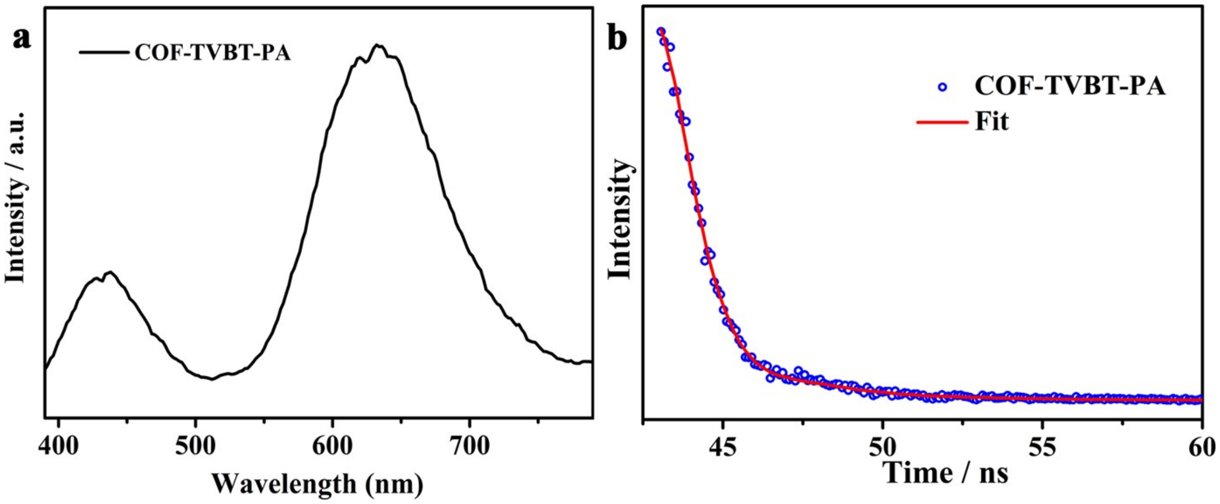

Figure S7 (a) Steady-state PL for COF-TVBT-PA. (b) Transient PL decay for COF-TVBT-PA. Fitted lifetimes of the fluorence decay profiles: A_1% = 87.6 %, τ_1 = 0.52, A_2% = 12.4 %, τ_2 = 3.67.

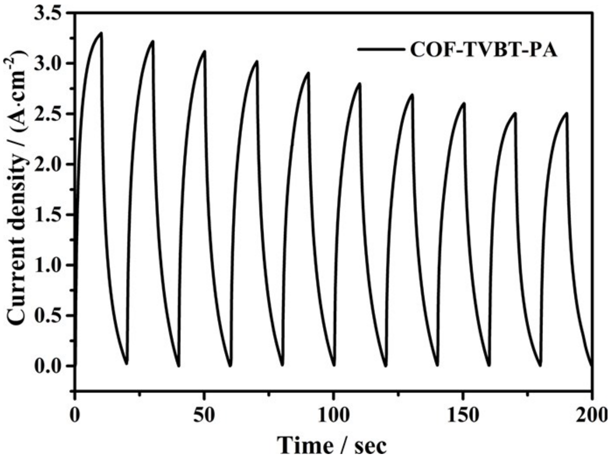

Figure S8 Transient photocurrent responses of COF-TVBT-PA.

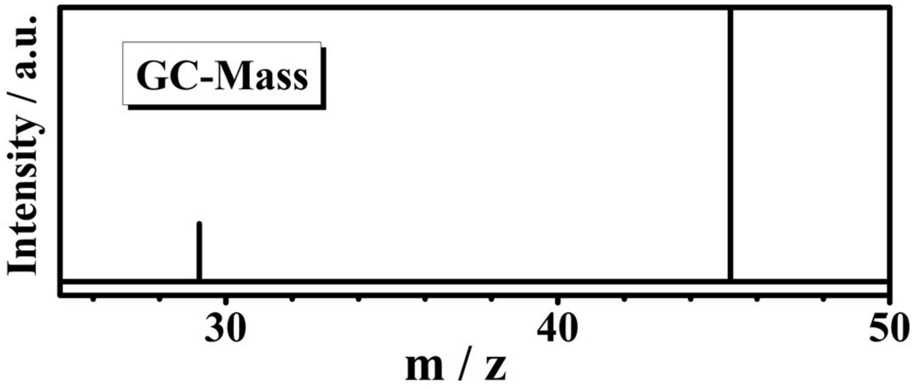

Figure S9 The GC-Mass result of isotopic experiment under $^{13}CO_2$ atmosphere.

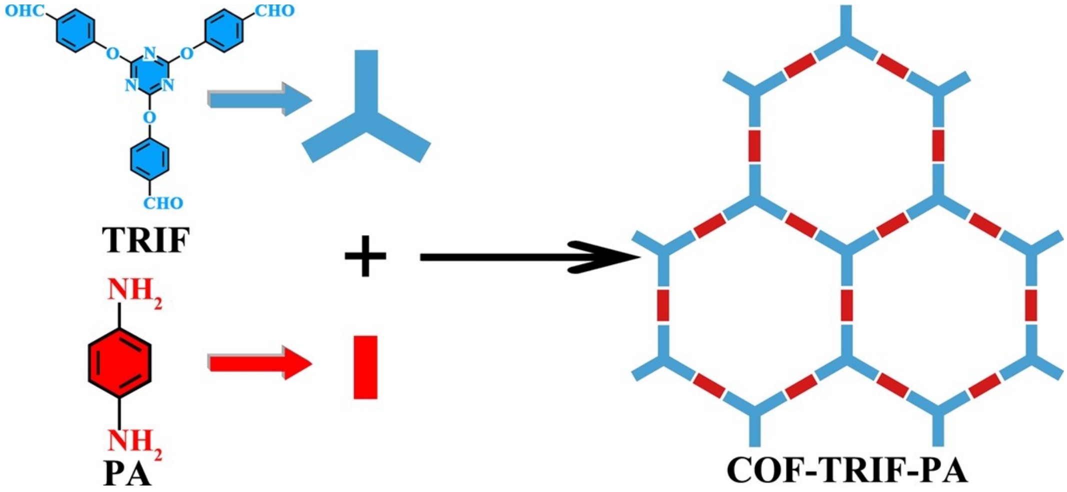

Figure S10 Synthesis diagram of COF without C=C band named as COF-TRIF-PA.

Table S3. Variation of Reference Experiments Conditions[a]

Entry	CO (μmol·g^{-1})	H_2 (μmol·g^{-1})	Sel. (%)[b]
1[c]	22.48	0.02	99.9
2[d]	< 0.01	< 0.01	—
3[e]	< 0.01	< 0.01	—
4[f]	< 0.01	< 0.01	—
5[g]	< 0.01	0.89	—
6[h]	2.63	0.53	83.2
7[i]	< 0.01	0.23	—
8[j]	0.95	0.76	55.6
9[k]	0.11	< 0.01	—
10[l]	1.42	< 0.01	—
11[m]	< 0.01	< 0.01	—
12[n]	0.80	< 0.01	—
13[o]	< 0.01	< 0.01	—

[a] Reaction conditions: 0.1 M $KHCO_3$ (3.5 mL), ascorbic acid (50 mg), CO_2 (1 atm), photocatalyst (5 mg), methanol (0.5 ml), 20 °C, 3 h, and AM 1.5. [b] Selectivity = $n_{CO}/n_{(CO+H2)} \times 100$. [c] Using COF-TVBT-PA. [d] Without COF-TVBT-PA. [e] Without ascorbic acid. [f] In dark. [g] Using Ar to replace CO_2 and using H_2O to replace $KHCO_3$. [h] Using TEOA to replace ascorbic acid. [i] Using EDTA to replace ascorbic acid. [j] Using H_2O to replace $KHCO_3$. [k] Using methanol to replace $KHCO_3$. [l] Using 0.5 ml 0.1 M $KHCO_3$ to replace 0.5 ml methanol. [m] Using PA to replace COF-TVBT-PA. [n] Using TVBT to replace COF-TVBT-PA. [o] Using COF-TFPA to replace COF-TVBT-PA.

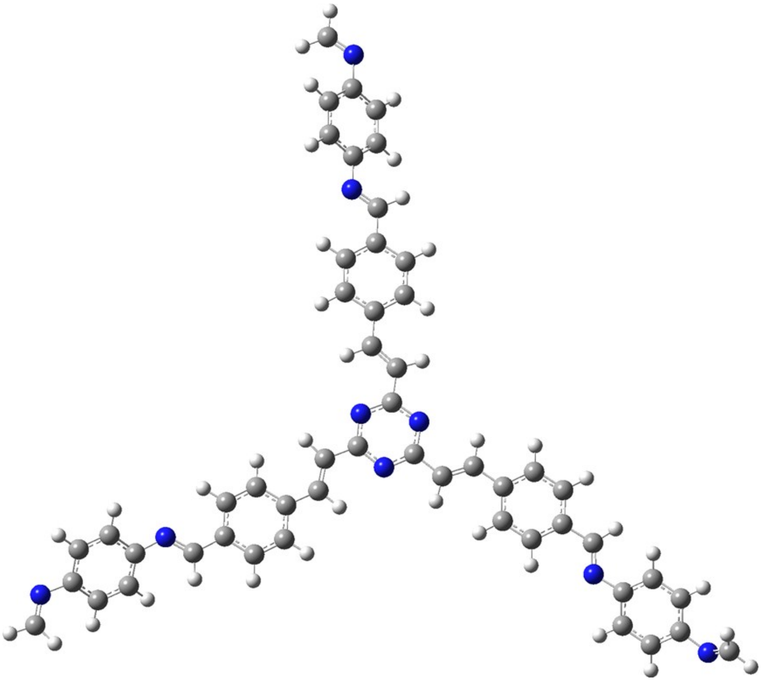

Figure S11 Computational model for COF-TVBT-PA with a cluster model. Carbon (grey), Nitrogen (blue), Oxygen (red) and Hydrogen (white).

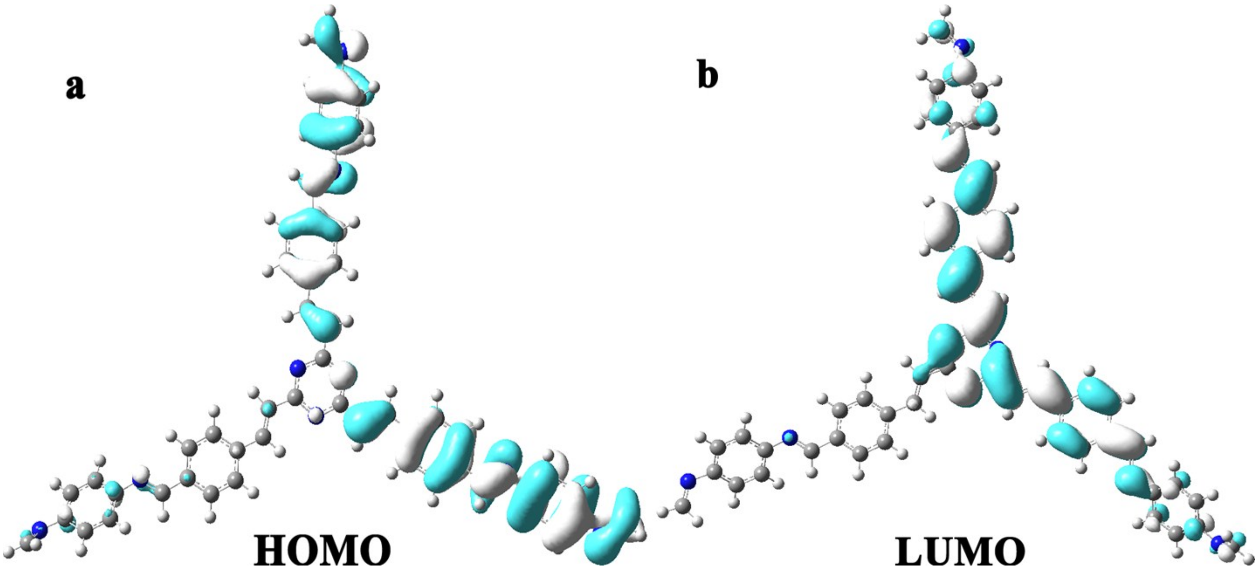

Figure S12 The orbital composition analysis of COF-TVBT-PA with HOMO (a) and LUMO (b). Carbon (grey), Nitrogen (blue), Oxygen (red) and Hydrogen (white).

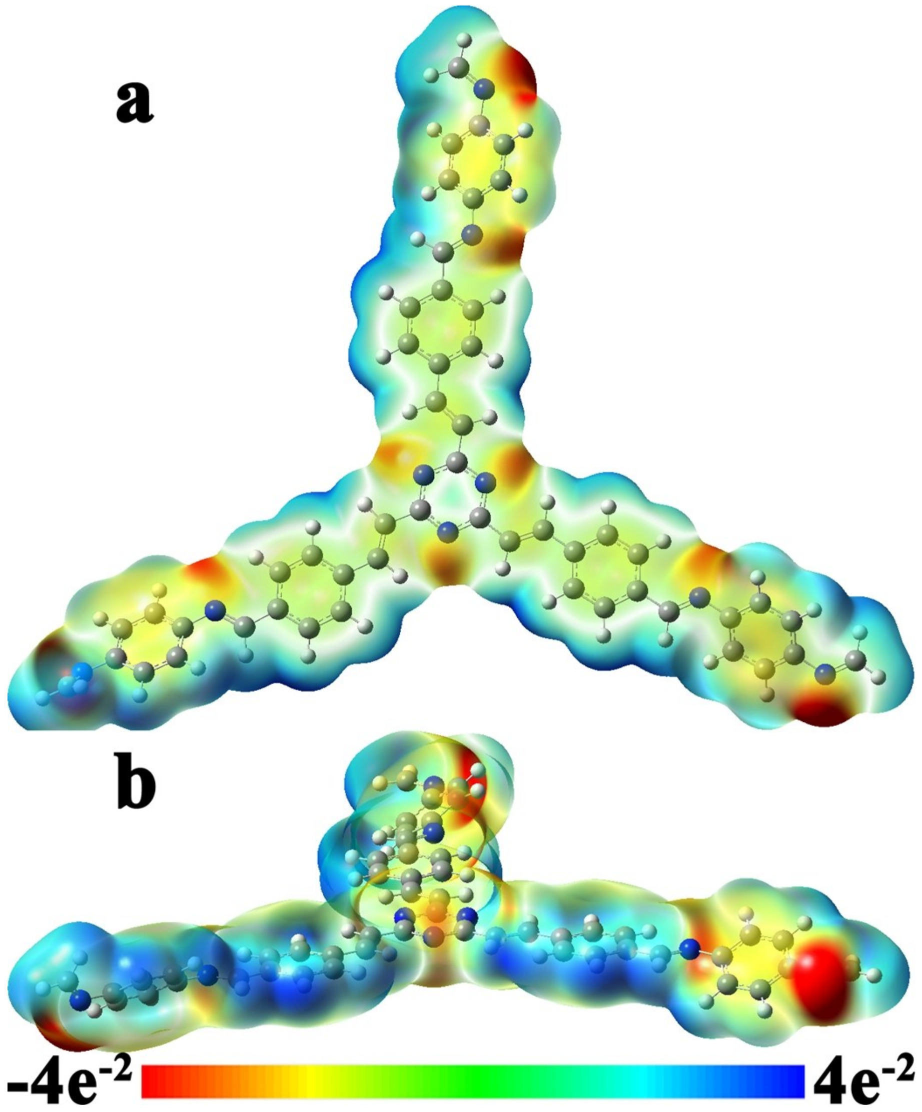

Figure S13 Electrostatic potential of COF-TVBT-PA with top view (c) and side view (d). Carbon (grey), Nitrogen (blue), Oxygen (red) and Hydrogen (white).

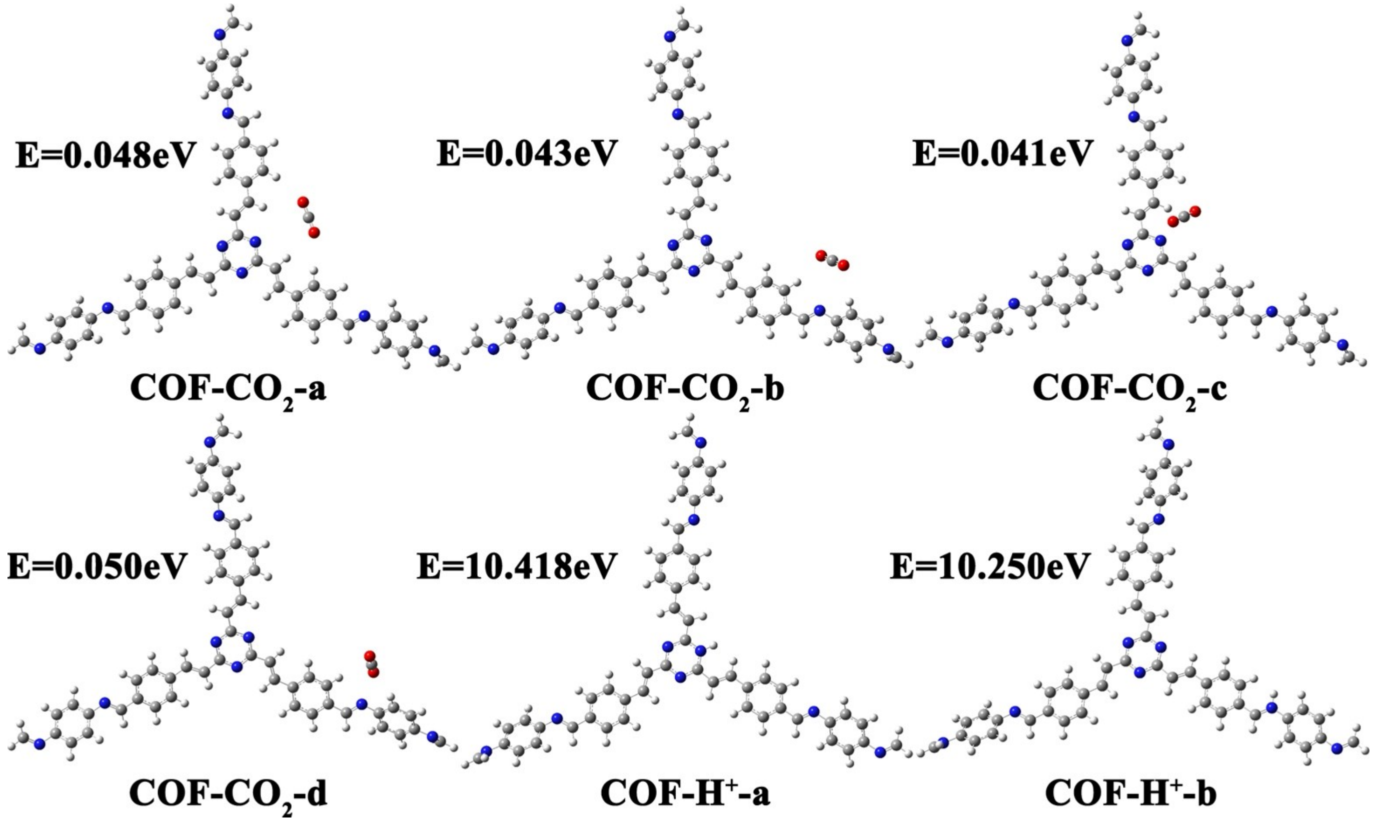

Figure S14 Geometry optimization for adsorption energy of COF-CO$_2$-a，COF-CO$_2$-b，COF-CO$_2$-c，COF-CO$_2$-d and COF-H$^+$-a、COF-H$^+$-b. Carbon (grey), Nitrogen (blue), Oxygen (red) and Hydrogen (white).

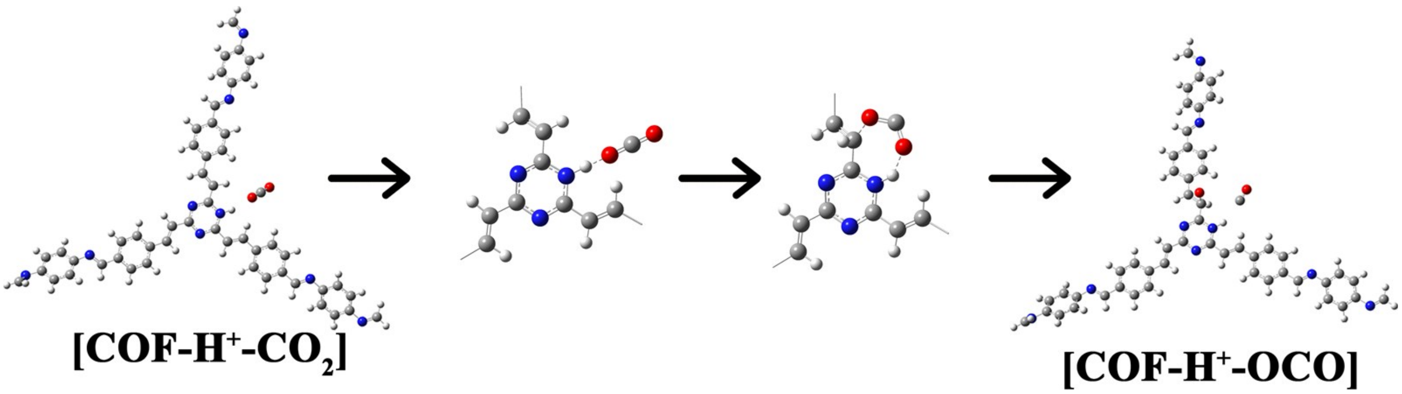

Figure S15 The CO$_2$ reduction inferential path from [COF-H$^+$-CO$_2$] to [COF-H$^+$-OCO]. Carbon (grey), Nitrogen (blue), Oxygen (red) and Hydrogen (white).

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian16 Revision B.01, Gaussian, Inc., Wallingford, CT, 2016.