Supporting Information

Tuning Charge Carrier Transport in Isostructural Covalent Organic Frameworks for Enhanced Photocatalytic CO₂ Reduction

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Section 1. Experimental Section

1.1 Materials.

Tetrakis(triphenylphosphine)palladium (98%), 3,6 dibromocarbazole (98%), 4-formylphenylboronic acid (99%) were purchased from Energy Chemical CO., Ltd. $Co(OAc)_2 \cdot 4H_2O$ (99%) and $Ni(OAc)_2 \cdot 4H_2O$ (99%) were purchased from J&K Scientific CO., Ltd. 5,10,15,20-tetra(p-amino-phenyl)porphyrin (H₂-TAPP-4NH₂) was purchased from Jilin Yanshen Technology Co., Ltd. Other solvents and reagents were purchased from local dealers. Unless otherwise stated, all chemicals were used without further purification.

1.2 Materials characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Thermo Scientific Nicolet iS10 spectroscope. Powder X-ray diffraction (PXRD) patterns were measured by a Bruker D8 ADVANCE instrument with monochromatized Cu Kα radiation operating at 40 kV and 40 mA. Solid-state ¹³C cross-polarization/magic-angle spinning solid-state nuclear magnetic resonance (CP/MAS ssNMR) spectra were collected on a Bruker AVANCE III HD 400MHz instrument. Thermogravimetric analysis (TGA) was conducted from 25 °C to 800 °C under N₂ protection with a heating rate of 10 °C/min using a NETZSCH STA449C thermal analyzer. UV-visible diffuse reflectance spectra (UV-vis DRS) were conducted on a Shimadzu UV-3600 instrument. Nitrogen adsorption and desorption isotherms were measured at 77 K by Autosorb-iQ-MP adsorption analyzer after degassing at 100 °C for 12 h. Surface areas were calculated based on Brunauer-Emmett-Teller (BET) method. Pore size distribution curves were obtained via non-local density functional theory (NLDFT) method. Scanning electron microscope (SEM) images were obtained on ZEISS Sigma 300. Transmission electron microscope (TEM) images were obtained on JEOL JEM 2100. X-ray photoelectron spectroscopy (XPS)

measurements were performed on the Thermo Scientific K-Alpha electron energy spectromete. All binding energies were referenced to the C 1s peak (284.8 eV) based on adventitious carbon. Steadystate photoluminescence and temperature-dependent photoluminescence spectra were recorded on a HITACHI F-7000 spectrophotometer. Time-resolved PL decay spectra were collected on an Edinburgh FS5 spectrophotometer. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was carried out on an Agilent ICP-OES 730 instrument.

1.3 Synthesis of 4,4',4'',4'''-([9,9'-bicarbazole]-3,3',6,6'-tetrayl)tetrabenzaldehyde (BCz-4CHO)



BCz-4CHO was synthesized according to previous literature with a slight modification.^[1] KMnO₄ (2.92 g, 90.0 mmol) was added to a solution of 3,6 dibromocarbazole (2.00 g, 30.0 mmol) in acetone (40 mL) and vigorously stirred under reflux for 9 h. After cooling to room temperature, add 100 mL of water and extract the mixture with DCM three times. Combine the organic layers, remove the solvent under reduced pressure, and wash the crude product with methanol to obtain BCz-4Br with a yield of 70%.

The as-synthesized BCz-4Br (0.65 g, 1.0 mmol), 4-formylphenylboronic acid (0.90 g, 6 mmol), and $K_2CO_3(2 \text{ g}, 14.5 \text{ mmol})$ were added to solution of THF (50 mL) and H_2O (8 mL). After being bubbled with nitrogen for 10 min, and Pd(PPh₃)₄ (0.25 g, 0.2 mmol) was added into the mixture, which was then stirred for 48 h at 90 °C under N₂ atmosphere. After cooling the reaction to room temperature,

H₂O was added to the mixture, which was then filtered under reduced pressure. The solid was washed twice with hot THF to obtain BCz-4CHO with a yield of 85%. The obtained NMR spectra are in good agreement with previously reported data. ¹H NMR (400 MHz, DMSO-*d*₆) δ (ppm): 10.08 (s, 4H), 9.09 (d, J = 1.9 Hz, 4H), 8.05 (s, 16H), 7.79 (dd, J = 8.6, 1.8 Hz, 4H), 6.96 (d, J = 8.6 Hz, 4H). ¹³C NMR(101 MHz, DMSO-*d*₆) δ (ppm): 193.17, 146.66, 140.49, 135.27, 133.39, 130.75, 127.88, 127.18, 123.10, 121.18, 109.92.





1.4 Synthesis of metalloporphyrin [M-TAPP-4NH₂ (M = Co, Ni, Zn, Cu)]i

M-TAPP-4NH₂ was synthesized according to previous literature with a slight modification.^[2] H₂-TAPP-4NH₂ (200 mg, 0.3 mmol) was dissolved in 90 mL CHCl₃ and 30 mL DMF, to which $Co(OAc)_2 \cdot 4H_2O$ (374 mg, 1.5 mmol) in 20 mL methanol was slowly added. The dark purple solution was stirred at reflux under N₂ for 24h. After cooling naturally, the solution was transferred into a separatory funnel and washed with water (3 × 100 mL). The organic layer was collected and dried over Na₂SO₄. The solvent was removed by rotary evaporator. The resulting green solid was named as Co-TAPP-4NH₂, dried under vacuum overnight. Ni-TAPP-4NH₂, Cu-TAPP-4NH₂, and Zn-TAPP-4NH₂ were synthesized using the same procedures as that of Co-TAPP-4NH₂ except Co(OAc)₂·4H₂O was replaced by M(OAc)₂·XH₂O.

1.5 Synthesis of BCz-Por(M)-COF (M = H₂, Co, Ni, Zn, Cu).

BCz-4CHO (74.9 mg, 0.1mmol) and M-TAPP-4NH₂ (0.1mmol) were put into a thick-walled pressure tube equipped with a vacuum switch (15 mL). Then a mixed solution of n-BuOH and o-DCB (6 mL, v/v=1:1) was added and ultrasonically dispersed for 30 min. Subsequently, 0.6 mL of 6M acetic acid (AcOH) was added into above mixture and sonicated again. After sealed and degassed by three freezepump-thaw cycles, the mixture was heated and stirred at 120 °C for 3 days. After cooling the reaction to room temperature, the precipitate was collected by filtration and successively washed with CH₃OH, THF, and acetone, and dried under vacuum at 60 °C for 24 h, finally affording BCz-Por(M)-COF.

1.6 Photocatalytic reduction of CO₂

The photocatalytic CO₂ reduction was conducted in a 100 mL self-designed quartz reactor with a water bath for controlling the temperature. Before irradiation, the as-prepared photocatalyst (1 mg), [Ru(bpy)₃]Cl₂·6H₂O (5mg), and TEOA (1 mL) was dispersed in the mixture solution of CH₃CN and H₂O, and stirred by magnetic stirrer with a speed of 500 r/min in the reactor. Subsequently, the quartz reactor was sealed with a quartz glass top and purged and filled with a CO₂ (99.999%) source. A Xe lamp (PLS-SXE 300UV, Perfectlight, China) with a 420 nm cut filter was used as a light source. The temperature of the reaction solution was maintained at 25 °C. After irradiation, gas products were detected by FULI 9790II gas chromatography equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID), possible liquid products were detected by ¹H-NMR spectroscopy (BUXI-I NMR, 400MHz). For the isotopic labeling experiment, ¹³CO₂ gas (>99%) was employed to replace ¹²CO₂ gas as the carbon source with the same reaction, and the gas products were analyzed by gas chromatography-mass spectrometry (SHIMADZU GCMS-QP2010).

1.7 Determination of apparent quantum yield (AQY) for Photocatalytic CO₂RR

The AQY was measured under the same photocatalytic reaction condition determined by using

monochromatic light sources ($\lambda = 350, 420, 450, 475, 520$, and 600 nm) for irradiation for 2 h. The AQY value was calculated based on the following equation .The AQY was calculated as follow:

AQY(CO)% = 2 × [
$$({}^{n_{CO+}} {}^{n_{H_2}})$$
 × N_A × h × c)] / (I × S × t × λ) × 100%

Where, N_A is Avogadro constant (6.022 × 10²³ mol⁻¹), h is the Planck constant (6.626 × 10⁻³⁴ J·s), c is the speed of light (3 × 10⁸ m s⁻¹), S is the irradiation area (5.06 cm²), I is the intensity of irradiation light, t is the photoreaction time (7200 s).

1.8 Stability tests of BCz-Por(Co)-COF for Photocatalytic CO₂RR

The recycled experiments for Photocatalytic CO_2RR were performed under the same conditions to evaluate the stability and reusability of the catalyst in a long-term operation. After the reaction was completed, the catalyst was centrifuged and washed using acetonitrile, and then a fresh solution of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ as described above was injected to conduct the next cycle.

1.9 Photoelectrochemical measurements

All photoelectrochemical measurements were conducted by a CHI 760E electrochemical workstation via a standard three-electrode cell in 0.2 M Na₂SO₄ electrolyte solution. A saturated Ag/AgCl electrode was used as the reference electrode, and a Pt mesh was used as the counter electrode. The catalyst-coated F-doped SnO₂ (FTO) was used as working electrodes, which were prepared as per the following procedure: 2 mg sample was dispersed in dimethylformamide (480 μ L) containing 5% Nafion solution (20 μ L). The as-obtained mixture was ultrasonically dispersed for 30 min. Subsequently, 100 μ L of the mixture was taken out and dropped on 1 × 1 cm² FTO and dried at room temperature. The transient photocurrent responses were recorded over a sampling interval of 20 s using a 60W white LED lamp (PLS-LED 100C, Perfectlight, China). For EIS measurements, the samples were tested with a frequency range from 1×10⁶ Hz to 1×10² Hz. Mott-Schottky experimental plots were determined at

frequencies of 500, 1000, and 1500 Hz.

1.10 In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

In-situ DRIFTS spectra were collected on a Nicolet iS 10 Fourier transform infrared spectrometer equipped with a mercury cadmium telluride detector. The reaction chambers used kHVC-DRP-5 (HARRICK) equipped with two KBr windows and one quartz window. The sample along with a Cu holder was put into the reaction chamber. The *in-situ* DRIFTS tests were carried out with two parts: (1) Chemical adsorption of CO₂. Before the measurement, the sample was treated at 200 °C under N₂ (50 mL/min) to remove adsorbed contaminants on the catalysts. After the reaction chamber was cooled down to 298K, the catalyst was first collected as the background prior to CO₂ introduction. After continuous flow of 5% CO₂ gas (20 mL/min) into the reaction chamber for 0.5 h, the spectra were recorded to investigate the chemical adsorption of CO₂ at different temperatures (30-200 °C).

(2) Photocatalytic CO_2 Reduction. After the reaction chamber was cooled down to 298K and the 5% CO_2 gas (20 mL/min) was put through H₂O vapor before sending into the reaction chamber. The reactor was illuminated (0-20 min) with a 60W white LED lamp to investigate the conversion of CO_2

1.11 DFT Calculation Methods.

The DFT calculations of DOS and free energy were performed in the Vienna *ab initio* simulation (VASP5.4.1) code.^[3] The exchange-correlation is simulated with PBE functional and the ion-electron interactions were described by the PAW method.^[4,5] The vdWs interaction was included by using the empirical DFT-D3 method.^[6] The Monkhorst-Pack-grid-mesh-based Brillouin zone k-points are set as $1 \times 1 \times 1$ for all periodic structure with the cutoff energy of 450 eV. The convergence criteria are set as 0.05 eV A^{-1} and 10^{-5} eV in force and energy, respectively. A 20 Å vacuum layer along the *z* direction is employed to avoid interlayer interference. The charge distributions of monolayer and bilayer

configurations were calculated by Materials Studio with the same parameters, where a double Numerical plus polarization basis set with polarization functions was applied. The excited state charge density was calculated by time-dependent DFT (TDDFT) method and the key details about using TDDFT to calculate excited-state charge density are the same as before.

The free energy calculation of species adsorption (ΔG) is based on Nørskov *et. al*'s hydrogen electrode model.

$$\Delta G = \Delta E + \Delta E_{\rm ZPE} - T \Delta S \tag{2}$$

Herein ΔE , ΔE_{ZPE} , and ΔS respectively represent the changes of electronic energy, zero-point energy, and entropy that are caused by the adsorption of intermediate. The entropy of H⁺+e⁻ pair is approximately regarded as half of H₂ entropy in standard condition.

Section 2. Supplement Figures and Tables



Figure S1. FTIR spectra of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c) BCz-Por(Ni)-COF.



Figure S2. Solid-state ¹³C NMR spectra of (a) BCz-Por(H₂)-COF and (b) BCz-Por(Co)-COF.



Figure S3. Thermogravimetric analysis of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c)

BCz-Por(Ni)-COF.



Figure S4. Nitrogen sorption isotherms of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c)

BCz-Por(Ni)-COF.



Figure S5. Pore size distribution profiles of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c)

BCz-Por(Ni)-COF.



Figure S6. SEM images of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c) BCz-Por(Ni)-COF.



Figure S7. Element mappings of (a) BCz-Por(Co)-COF and (b) BCz-Por(Ni)-COF.



Figure S8. XPS full spectra of BCz-Por(H₂)-COF, BCz-Por(Co)-COF, and BCz-Por(Ni)-COF.



Figure S9. Mott-Schottky curves of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c) BCz-

Por(Ni)-COF.



Figure S10. GC spectra of gaseous sample during the photocatalytic CO_2 reduction.



Figure S11. (a) ¹H and (b) ¹³C NMR spectrum using D_2O for the liquid phase of the photocatalytic

experiments.



Figure S12. Production rates of photocatalytic reduction with different (a) sacrificial agents, amounts of (b) Ru(bpy)₃Cl₂ and (c) catalyst.



Figure S13. (a) N₂ sorption isotherms of fresh and reused BCz-Por(Co)-COF, Pore size distribution profiles of (b) fresh and (c) reused BCz-Por(Co)-COF.



Figure S14. FT-IR spectra of fresh and reused BCz-Por(Co)-COF.



Figure S15. PXRD patterns of fresh and reused BCz-Por(Co)-COF.



Figure S16. Co 2p XPS spectra of reused BCz-Por(Co)-COF.



Figure S17. The PDOS of Co and Ni 3d orbitals in BCz-Por(Co)-COF or BCz-Por(Ni)-COF.



Figure S18. Top and side views for the monolayer charge density difference isosurfaces of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c) BCz-Por(Ni)-COF in the ground state. The purple and

blue regions denote electron accumulation and depletion, respectively.



Figure S19. Top and side views for the bilayer charge density difference isosurfaces of (a) BCz-Por(H₂)-COF, (b) BCz-Por(Co)-COF, and (c) BCz-Por(Ni)-COF in the ground state. The purple and blue regions denote electron accumulation and depletion, respectively.

	BCz-Por(H ₂)-COF space group :P2										
$a = 4.04$ Å, $b = 30.98$ Å, $c = 24.99$ Å, $\alpha = \beta = \gamma = 90^{\circ}$											
Atom	Atom x y z Atom x y										
C1	0.54788	-0.04841	1.0454	C43	0.06009	0.19079	0.87773				
C2	0.47306	-0.09205	0.97147	C44	0.02474	0.13852	0.80612				
C3	0.45315	-0.12536	0.93426	C45	0.00639	0.14783	0.86104				
C4	0.41055	-0.11597	0.87981	C46	0.4157	0.35117	1.47633				
C5	0.38332	-0.07233	0.86408	C47	0.29031	0.40894	1.40725				
C6	0.40473	-0.03842	0.90042	C48	0.3861	0.39611	1.45983				
C7	0.3184	-0.49004	1.33244	H1	0.48431	-0.15868	0.94746				
C8	0.37671	-0.47543	1.38604	H2	0.39221	-0.00535	0.88628				
C9	0.41231	-0.3987	1.36083	Н3	0.34371	-0.06472	0.82185				
C10	0.21731	-0.36136	1.36672	H4	0.3044	-0.46959	1.29738				
C11	0.60142	-0.40228	1.31422	Н5	0.04514	-0.35962	1.39975				
C12	0.23464	-0.32749	1.33071	H6	0.75853	-0.43049	1.30898				
C13	0.6076	-0.36936	1.27658	H7	0.07697	-0.2993	1.33592				
C14	0.43954	-0.33047	1.2858	H8	0.76322	-0.37163	1.24146				
C15	0.46751	-0.25749	1.26621	H9	0.40764	-0.24945	1.30814				
C16	0.51977	-0.22121	1.23058	H10	0.75298	-0.25935	1.16991				
C17	0.66622	-0.22716	1.18039	H11	0.30645	-0.17487	1.28461				
C18	0.42065	-0.17961	1.24571	H12	0.82336	-0.1973	1.10776				
C19	0.70094	-0.1926	1.14592	H13	0.35208	-0.11361	1.22151				
C20	0.44931	-0.14518	1.21047	H14	0.50991	-0.34606	0.55284				
C21	0.58517	-0.15117	1.15958	H15	0.34409	0.15813	1.04824				
C22	0.50763	-0.37418	0.52712	H16	0.0713	0.00377	1.0869				
C23	0.57805	-0.43242	0.59725	H17	0.85471	0.06228	1.14402				

Table S1.	Fractional	atomic	coordinates	for the	unit ce	ll of BC	z-Por(H ₂)	-COF.

C24	0.52703	-0.41922	0.54359	H18	0.74434	0.44507	0.70088
C25	0.67001	0.04825	0.96415	H19	0.44652	0.32804	0.61214
C26	0.39734	0.09197	1.02332	H20	0.19	0.41645	0.66964
C27	0.27798	0.12463	1.05608	H21	0.62491	0.27546	0.67902
C28	0.09099	0.11412	1.10101	H22	0.31861	0.36705	0.74449
C29	0.01509	0.07031	1.11075	H23	0.08558	0.23691	0.70359
C30	0.13165	0.0372	1.07869	H24	0.13638	0.25705	0.85363
C31	0.71194	0.46593	0.66649	H25	0.07389	0.16387	0.72642
C32	0.68709	0.45187	0.61184	H26	0.05927	0.19837	0.92037
C33	0.81356	0.37628	0.63298	H27	0.98082	0.10564	0.79216
C34	0.66103	0.33555	0.63715	H28	0.32472	0.32302	1.45523
C35	0.05579	0.38615	0.67249	H57	0.40887	0.48879	1.45868
C36	0.75671	0.30602	0.676	N1	0.49192	-0.29679	1.24995
C37	0.13178	0.35838	0.71443	N2	0.07211	0.28854	0.75711
C38	0.99125	0.31698	0.7159	N9	0.3728	0.48841	1.41812
C39	0.09428	0.24809	0.74572	N5	0.5	-0.02224	1
C40	0.10479	0.21431	0.78585	N6	0.5	0.02215	1
C41	0.10677	0.22356	0.84098	N7	0.5	-0.44598	1.5
C42	0.07465	0.17121	0.76918	N8	0.5	0.42285	1.5

	BCz-Por(Co)-COF space group :P2										
	$a = 4.04$ Å, $b = 30.98$ Å, $c = 24.99$ Å, $\alpha = \beta = \gamma = 90^{\circ}$										
Atom	om x y z Atom x y										
C1	0.54788	0.95159	0.0454	C43	1.06009	0.19079	0.87773				
C2	0.47306	0.90795	0.97147	C44	1.02474	0.13852	0.80612				
C3	0.45315	0.87464	0.93426	C45	1.00639	0.14783	0.86104				
C4	0.41055	0.88403	0.87981	C46	0.4157	0.35117	0.47633				
C5	0.38332	0.92767	0.86408	C47	0.29031	0.40894	0.40725				
C6	0.40473	0.96158	0.90042	C48	0.3861	0.39611	0.45983				
C7 C8 C9	0.3184	0.50996	0.33244	H1	0.48431	0.84132	0.94746				
	0.37671	0.52457	0.38604	H2	0.39221	0.99465	0.88628				
	0.41231	0.6013	0.36083	Н3	0.34371	0.93528	0.82185				
C10	0.21731	0.63864	0.36672	H4	0.3044	0.53041	0.29738				
C11	0.60142	0.59772	0.31422	Н5	0.04514	0.64038	0.39975				
C12	0.23464	0.67251	0.33071	H6	0.75853	0.56951	0.30898				
C13	0.6076	0.63064	0.27658	H7	0.07697	0.7007	0.33592				
C14	0.43954	0.66953	0.2858	H8	0.76322	0.62837	0.24146				
C15	0.46751	0.74251	0.26621	H9	0.40764	0.75055	0.30814				
C16	0.51977	0.77879	0.23058	H10	0.75298	0.74065	0.16991				
C17	0.66622	0.77284	0.18039	H11	0.30645	0.82513	0.28461				
C18	0.42065	0.82039	0.24571	H12	0.82336	0.8027	0.10776				
C19	0.70094	0.8074	0.14592	H13	0.35208	0.88639	0.22151				
C20	0.44931	0.85482	0.21047	H14	0.50991	0.65394	0.55284				
C21	0.58517	0.84883	0.15958	H15	0.34409	0.15813	0.04824				
C22	0.50763	0.62582	0.52712	H16	0.0713	0.00377	0.0869				
C23	0.57805	0.56758	0.59725	H17	-0.14529	0.06228	0.14402				

Table S2. Fractional atomic coordinates for the unit cell of BCz-Por(Co)-COF
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C24	0.52703	0.58078	0.54359	H18	0.74434	0.44507	0.70088
C25	0.67001	0.04825	0.96415	H19	0.44652	0.32804	0.61214
C26	0.39734	0.09197	0.02332	H20	1.19	0.41645	0.66964
C27	0.27798	0.12463	0.05608	H21	0.62491	0.27546	0.67902
C28	0.09099	0.11412	0.10101	H22	1.31861	0.36705	0.74449
C29	0.01509	0.07031	0.11075	H23	1.08558	0.23691	0.70359
C30	0.13165	0.0372	0.07869	H24	1.13638	0.25705	0.85363
C31	0.71194	0.46593	0.66649	H25	1.07389	0.16387	0.72642
C32	0.68709	0.45187	0.61184	H26	1.05927	0.19837	0.92037
C33	0.81356	0.37628	0.63298	H27	0.98082	0.10564	0.79216
C34	0.66103	0.33555	0.63715	H28	0.32472	0.32302	0.45523
C35	1.05579	0.38615	0.67249	N1	0.49192	0.70321	0.24995
C36	0.75671	0.30602	0.676	N2	1.07211	0.28854	0.75711
C37	1.13178	0.35838	0.71443	N9	0.3728	0.48841	0.41812
C38	0.99125	0.31698	0.7159	N5	0.5	0.97776	0
C39	1.09428	0.24809	0.74572	N6	0.5	0.02215	0
C40	1.10479	0.21431	0.78585	N7	0.5	0.55402	0.5
C41	1.10677	0.22356	0.84098	N8	0.5	0.42285	0.5
C42	1.07465	0.17121	0.76918	Со	0.5	0.48675	0.5

	BCz-Por(Ni)-COF space group :P2										
	$a = 4.04$ Å, $b = 30.98$ Å, $c = 24.99$ Å, $\alpha = \beta = \gamma = 90^{\circ}$										
Atom	tom x y z Atom x y										
C1	0.54788	0.95159	0.0454	C43	1.06009	0.19079	0.87773				
C2	0.47306	0.90795	0.97147	C44	1.02474	0.13852	0.80612				
C3	0.45315	0.87464	0.93426	C45	1.00639	0.14783	0.86104				
C4	0.41055	0.88403	0.87981	C46	0.4157	0.35117	0.47633				
C5	0.38332	0.92767	0.86408	C47	0.29031	0.40894	0.40725				
C6	0.40473	0.96158	0.90042	C48	0.3861	0.39611	0.45983				
C7	0.3184	0.50996	0.33244	H1	0.48431	0.84132	0.94746				
C8	0.37671	0.52457	0.38604	H2	0.39221	0.99465	0.88628				
C9	0.41231	0.6013	0.36083	Н3	0.34371	0.93528	0.82185				
C10	0.21731	0.63864	0.36672	H4	0.3044	0.53041	0.29738				
C11	0.60142	0.59772	0.31422	Н5	0.04514	0.64038	0.39975				
C12	0.23464	0.67251	0.33071	H6	0.75853	0.56951	0.30898				
C13	0.6076	0.63064	0.27658	H7	0.07697	0.7007	0.33592				
C14	0.43954	0.66953	0.2858	H8	0.76322	0.62837	0.24146				
C15	0.46751	0.74251	0.26621	Н9	0.40764	0.75055	0.30814				
C16	0.51977	0.77879	0.23058	H10	0.75298	0.74065	0.16991				
C17	0.66622	0.77284	0.18039	H11	0.30645	0.82513	0.28461				
C18	0.42065	0.82039	0.24571	H12	0.82336	0.8027	0.10776				
C19	0.70094	0.8074	0.14592	H13	0.35208	0.88639	0.22151				
C20	0.44931	0.85482	0.21047	H14	0.50991	0.65394	0.55284				
C21	0.58517	0.84883	0.15958	H15	0.34409	0.15813	0.04824				
C22	0.50763	0.62582	0.52712	H16	0.0713	0.00377	0.0869				
C23	0.57805	0.56758	0.59725	H17	-0.14529	0.06228	0.14402				

Table S3. Fractional atomic coordinates for the unit cell of BCz-Por(N1)-COF.

C24	0.52703	0.58078	0.54359	H18	0.74434	0.44507	0.70088
C25	0.67001	0.04825	0.96415	H19	0.44652	0.32804	0.61214
C26	0.39734	0.09197	0.02332	H20	1.19	0.41645	0.66964
C27	0.27798	0.12463	0.05608	H21	0.62491	0.27546	0.67902
C28	0.09099	0.11412	0.10101	H22	1.31861	0.36705	0.74449
C29	0.01509	0.07031	0.11075	H23	1.08558	0.23691	0.70359
C30	0.13165	0.0372	0.07869	H24	1.13638	0.25705	0.85363
C31	0.71194	0.46593	0.66649	H25	1.07389	0.16387	0.72642
C32	0.68709	0.45187	0.61184	H26	1.05927	0.19837	0.92037
C33	0.81356	0.37628	0.63298	H27	0.98082	0.10564	0.79216
C34	0.66103	0.33555	0.63715	H28	0.32472	0.32302	0.45523
C35	1.05579	0.38615	0.67249	N1	0.49192	0.70321	0.24995
C36	0.75671	0.30602	0.676	N2	1.07211	0.28854	0.75711
C37	1.13178	0.35838	0.71443	N9	0.3728	0.48841	0.41812
C38	0.99125	0.31698	0.7159	N5	0.5	0.97776	0
C39	1.09428	0.24809	0.74572	N6	0.5	0.02215	0
C40	1.10479	0.21431	0.78585	N7	0.5	0.55402	0.5
C41	1.10677	0.22356	0.84098	N8	0.5	0.42285	0.5
C42	1.07465	0.17121	0.76918	Ni	0.5	0.48675	0.5

Catalyst	Photosensitizer	Sacrificial agent	CO generation rate (mmol g ⁻¹ h ⁻ ¹)	Ref.
USTB-37-kgm	[Ru(bpy) ₃]Cl ₂	TEOA	7.6	7
Co/Cu ₃ -TPA-COF	[Ru(bpy) ₃]Cl ₂	TEOA	13.0	8
Ni-PCD@TD-COF	[Ru(bpy) ₃]Cl ₂	TEOA	0.5	9
Fe SAS/Tr-COFs	[Ru(bpy) ₃]Cl ₂	TEOA	1.0	10
TFBD-COF-Co-SA	[Ru(bpy) ₃]Cl ₂	TEOA	1.5	11
Ni@TPHH-COF	[Ru(bpy) ₃]Cl ₂	TEOA	3.3	12
JUC-640-Co	[Ru(bpy) ₃]Cl ₂	BIH	15.1	13
COF-367-Co NS	[Ru(bpy) ₃]Cl ₂	TEOA	10.1	14
DQTP-COF-Co	[Ru(bpy) ₃]Cl ₂	AA	1.0	15
Ni-TP-CON	[Ru(bpy) ₃]Cl ₂	TEOA	4.4	16
CoP-TPE-COF	[Ru(bpy) ₃]Cl ₂	TEOA	2.4	17
Co@COF-TVBT-Bp	[Ru(bpy) ₃]Cl ₂	TEOA	1.1	18
CoPor-DPP-COF	[Ru(bpy) ₃]Cl ₂	TIPA	10.2	19
JNM-2	[Ru(bpy) ₃]Cl ₂	TEOA	0.8	20
CoNi-COF-3	[Ru(bpy) ₃]Cl ₂	TEOA	2.6	21
Ni-TpBpy	[Ru(bpy) ₃]Cl ₂	TEOA	0.8	22
Co-FPy-CoN	(Ir[dF(CF ₃)ppy] ₂ (dtbpy))PF ₆	TEOA	1.7	23
H-COF-Ni	$[Ru(bpy)_3]Cl_2$	TEOA	5.7	24
BCz-Por(Co)-COF	[Ru(bpy) ₃]Cl ₂	TEOA	15.4	This work

Table S4. The performance comparison of COFs-based photocatalysts for photocatalytic CO₂-to-CO conversion.

	Sample		$S_{BET}[m^2 \ g^{1}]^{a)}$		V _{Tot} [cm ³ g ⁻¹]	b)	V _{micro} [cm ³ g ⁻¹]	c)
	Fresh BCz-Por(Co)-COF		654.4		0.639		0.223	
Reused BCz-Por(Co)-COF		60	8.7	0.6	533	0.2	212	

Table S5. N₂ physisorption results of fresh and reused BCz-Por(Co)-COF.

^{a)} Specific surface area measured by BET model; ^{b)} The total pore volume measured at $P/P_0 = 0.99$; ^{c)} The microporous volume analyzed by NL-DFT method.

Table S6. Exciton binding energies fitting parameters based on the Arrhenius equation.

Cat.	BCz-Por(H ₂)-COF	BCz-Por(Ni)-COF	BCz-Por(Co)-COF
Equation	$y = A/(1 + B^* \exp(-K^*x))^a$		
А	6.55	6.67	4.62
В	325.77	5.73	1.28
K	1633.45	667.54	338.91
E _b	140.75	57.52	27.7
R ²	0.99	0.99	0.99

^a K = E_b/k_B (k_B is Boltzmann constant, 8.617*10⁻⁵ eV)

Section 3. Reference

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