Supporting Information

Enhanced protonation ability of covalent organic frameworks via

N,O-bidentate chelation for photocatalytic H₂ evolution

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1. General information

1.1 Chemicals

Unless otherwise stated, all the chemicals were purchased in analytical purity from commercial suppliers and used as received. 1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPy), benzo[c][1,2,5]thiadiazole-4,7-diyl)dianiline (BT), and difluorobenzo[c][1,2,5]thiadiazole-4,7-diyl)dianiline (FBT) were prepared according to the reported procedures^{1,2}.

1.2 Characterization methods

¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 600 MHz spectrometer at ambient temperature, and chemical shifts (δ) were reported in ppm relative to the residual solvent peaks. Peaks are reported as follows: s = singlet, d = doublet, with coupling constants in Hz. Powder X-ray diffraction (PXRD) analysis was executed on a Bruker D8 Advance with Cu K α radiation (2 θ range: 2-40°; Scan step size: 0.02°; Time per step: 1 s). Fourier transform infrared (FT-IR) measurements were carried out on a Nicolet 6700 spectrometer (Thermo Scientific, USA) equipped with an ATR cell. High resolution transmission electron microscopy (HRTEM) images were collected on JEM-2100F and JEM-ARM200F. The solid-state UV-Vis diffuse reflectance spectra (UV/Vis DRS) were collected on a Perkin-Elmer LAMBDA 650S spectrometer with BaSO₄ as the reference. The specific Brunauer-Emmett-Teller (BET) surface area and pore size distribution were measured using a Micrometrics ASAP 2040 instrument. Thermal stability was investigated on a DSC 200 PC (NETZSCH) thermogravimetric analyzer with temperature ranging from 303 to 1073 K under N₂ atmosphere at a heating rate of 5 K min⁻¹. Steady-state photoluminescence spectra were recorded on an RF-5301 PC spectrofluorometer with the excitation wavelength at 400 nm. Time-correlated single photon counting (TCSPC) measurements were conducted on an FLS1000 photoluminescence spectrometer (Edinburgh Instruments, UK).

1.3 Electrochemical measurements

The electrochemical measurements were performed on the CHI660E workstation

(Chenhua Instruments, China) with a standard three-electrode system, which included a counter electrode (platinum plate), a reference electrode (Ag/AgCl electrode), and a working electrode. The working electrode was prepared as follows: 15 mg of sample was thoroughly mixed with 200 μ L isopropanol containing 5% Nafion; The resulting suspension was carefully loaded on an ITO glass ($10 \times 2.5 \times 1.1$ mm), which was then dried at 60 °C under vacuum for 1 h. 0.1 M Na₂SO₄ aqueous solution was served as the electrolyte for the photocurrent test while the aqueous solution of 0.1 M KCl + 0.005 M K₃[Fe(CN)₆] was employed as the electrolyte for the electrochemical impedance spectroscopy (EIS) measurement. For Mott-Schottky tests, the perturbation was 5 mV with frequencies of 1000, 2000, and 3000 Hz.

1.4 Computational details

Geometries were determined with 6-31G(d) basis set while energies were determined by single point calculations with 6-311+G(d,p) basis set on optimized structures. All calculations were performed using the Gaussian09 package.³ Frequency analysis was used to verify the nature of stationary points.

1.5 Photocatalytic H₂ production procedure

A flask was charged with COFs (15 mg) and 0.1 M aqueous ascorbic acid solution, and the mixture was ultrasonicated for 5 min to afford a well-dispersed suspension, following addition of H₂PtCl₆ (10 μ l, 1.0 wt% Pt of aqueous solution). The suspension was transferred to a Pyrex top-irradiation reaction vessel connected to a closed gas system (PerfectLight, Labsolar-IIIAG). After being evacuated for 10 min by oil pump to exclude the dissolved air, the suspension was irradiated with the Xe lamp equipped with a UV cut-off ($\lambda > 420$ nm) filter, and the temperature was kept at 5 °C by circulating cooling EtOH. The hydrogen evolution rate was calculated using an online gas chromatography (SP7820, 5 Å molecular sieve columns, Ar carrier, and TCD detector).

The apparent quantum yield (AQY) for hydrogen evolution was measured by a similar process for photocatalytic H₂ production except the replacement of cut-off (λ > 420 nm) filter by band-pass filter (λ = 420, 450 nm, etc.) so as to achieve

monochromatic light. The AQY was calculated via the following equation:



2. Synthesis of the building blocks

Scheme S1. Synthesis of TFPPy(OMe)

1,3,6,8-Tetrakis (4-formyl-3-methyloxyphenyl)pyrene (TFPPy(OMe)): A round-bottom flask was charged with 1,3,6,8-tetrabromopyrene (S1, 2.05 g, 4.0 mmol), 4-(4-formyl-3-methoxyphenyl)boronic acid (S2, 4.32 g, 24 mmol), Pd(PPh₃)₄ (0.12 g, 0.10 mmol), and K₂CO₃ (2.07 g, 15.0 mmol) in a mixed solvent of 1,4-dioxane (100 mL)/H₂O (10 mL). Subsequently, the mixture was degassed with Ar for 10 min and then stirred at 110 °C under Ar atmosphere for 3 days. Upon cooling down, MeOH (200 mL) was added to quench the reaction and the suspension was filtered to afford the raw product, which was further purified by Soxhlet extraction with MeOH for 24 hours. The final product (2.39 g, 97%) was obtained as a yellow powder after being dried under vacuum at 60 °C overnight. ¹H NMR (CDCl₃, 600 MHz) δ 10.59 (s, 4H), 8.20 (s, 4H), 8.03 (d, *J* = 2.1 Hz, 4H), 8.02 (s, 2H), 7.34 (d, *J* = 7.9 Hz, 4H), 7.27 (d, *J* = 1.1 Hz, 4H), 4.00 (s, 12H).



Scheme S2. Synthesis of TFPPy(OH)

1,3,6,8-Tetrakis (4-formyl-3-hydroxylphenyl)pyrene (TFPPy(OH)): A roundbottom flask was charged with TFPPy(OMe) (738 mg, 1.0 mmol) in CH₂Cl₂ (150 mL) with Ar as the protecting atmosphere. After being cooled to -78 °C, BBr₃ (10 mmol) was added dropwise. To drive the reaction, the temperature was then raised to 25 °C and the mixture was stirred at this temperature for another 24 hours. To purify the as-obtained product, CH₂Cl₂ was removed under vacuum and MeOH was then added to the residual. The resulting suspension was sonicated vigorously, and the solid was collected by filtration. This procedure was repeated three times, and the final product was afforded as a yellow powder (580 mg, 85%) after being dried under vacuum at 60 °C overnight. ¹H NMR (CDCl₃, 600 MHz) δ 11.21 (s, 4H), 10.04 (s, 4H), 8.22 (s, 4H), 8.02 (s, 2H), 7.75 (d, *J* = 7.8 Hz, 4H), 7.33 (d, *J* = 7.8 Hz, 4H), 7.31 (s, 4H).

3. Synthesis of COFs

Taking synthesis of $\text{COF}_{\text{TFPPy}(\text{OMe})-\text{BZ}}$ as an example, a Pyrex glass tube (10 mL) was charged with TFPPy(OMe) (36.5 mg, 0.05 mmol), 4,4'-benzidine (18.4 mg, 0.1 mmol), N,N-Dimethylacetamide (0.7 mL), mesitylene (0.7 mL), 1,4-dioxane (0.4 mL), and 6 M acetic acid aqueous solution (0.1 mL). This tube was sonicated for 10 minutes, degassed by three freeze-pump-thaw cycles (liquid nitrogen), and sealed under vacuum, which was then heated in an oven at 120 °C for 3 days. Upon cooling to room temperature, the suspension was centrifuged to separate the solid, which was repeatedly washed by tetrahydrofuran and water until the solvent was colourless. $\text{COF}_{\text{TFPPy}(\text{OMe})-\text{BZ}}$ was finally obtained as a yellow powder after being dried under vacuum at 120 °C. Other TFPPy-based COFs were synthesized following a similar synthetic procedure of $\text{COF}_{\text{TFPPy}(\text{OMe})-\text{BZ}}$.

4. Characterization of 2D COFs



Fig. S1 Solvothermal condensation of pyrene tetrabenzaldehyde derivatives (TFPPy(R)) and *p*-phenylenediamine (PA), 4.4'-benzidine (BZ), and 4,4'-diamino-p-terphenyl (TP) for the synthesis of $COF_{TFPPy(R)-PA}$, $COF_{TFPPy(R)-BZ}$, and $COF_{TFPPy(R)-TP}$, followed by protonation with addition of ascorbic acid. Depiction of iminium formation with and without intramolecular hydrogen bonds.

	R _{wp}	R _p	а	Ь	С	α	β	γ
COF _{TFPPy-PA}	3.76%	2.89%	23.8540 Å	24.5681 Å	3.8570 Å	90°	90°	90°
COF _{TFPPy(OMe)-PA}	1.41%	0.81%	24.6951 Å	24.1296 Å	3.9017 Å	90°	90°	90°
COF _{TFPPy(OH)-PA}	3.05%	1.92%	23.3510 Å	24.3828 Å	3.8667 Å	90°	90°	90°
COF _{TFPPy-BZ}	3.08%	1.54%	28.7600Å	28.2127 Å	3.5549 Å	90°	90°	90°
COF _{TFPPy(OMe)-BZ}	0.38%	0.23%	28.0741 Å	28.7247 Å	3.8879 Å	90°	90°	90°
COF _{TFPPy(OH)-BZ}	1.32%	0.73%	28.7107 Å	28.2977 Å	3.8120 Å	90°	90°	90°
COF _{TFPPy-TP}	1.38%	0.71%	32.7574 Å	33.1555 Å	3.5692 Å	90°	90°	90°
COF _{TFPPy(OMe)-TP}	1.50%	1.08%	32.3796 Å	33.0819 Å	3.9391 Å	90°	90°	90°
COF _{TFPPy(OH)-TP}	0.99%	0.52%	32.8869Å	32.7640 Å	3.7849 Å	90°	90°	90°

Table S1. Values of R_{wp} and R_p , and unit cell parameters of 2D COFs obtained by Pawley refinement



Fig. S2 PXRD patterns of $\text{COF}_{\text{TFPPy-PA}}$ (a), $\text{COF}_{\text{TFPPy(OMe)-PA}}$ (b), and $\text{COF}_{\text{TFPPy(OH)-PA}}$ (c): experimental data (black), Pawley refined profile (red), difference (orange), and Bragg positions (blue). Top and side views of the AA packing model of $\text{COF}_{\text{TFPPy-PA}}$ (d), $\text{COF}_{\text{TFPPy(OMe)-PA}}$ (e), and $\text{COF}_{\text{TFPPy(OH)-PA}}$ (f).



Fig. S3 PXRD patterns of $\text{COF}_{\text{TFPPy-TP}}$ (a), $\text{COF}_{\text{TFPPy(OMe)-TP}}$ (b), and $\text{COF}_{\text{TFPPy(OH)-TP}}$ (c): experimental data (black), Pawley refined profile (red), difference (orange), and Bragg positions (blue). Top and side views of the AA packing model of $\text{COF}_{\text{TFPPy-TP}}$ (d), $\text{COF}_{\text{TFPPy(OMe)-TP}}$ (e), and $\text{COF}_{\text{TFPPy(OH)-TP}}$ (f).



Fig. S4 (a) Nitrogen adsorption and desorption isotherms for $\text{COF}_{\text{TFPPy-BZ}}$, $\text{COF}_{\text{TFPPy(OMe)-BZ}}$, and $\text{COF}_{\text{TFPPy(OH)-BZ}}$ measured at 77 K; (b) Pore size distribution of $\text{COF}_{\text{TFPPy-BZ}}$, $\text{COF}_{\text{TFPPy(OMe)-BZ}}$, and $\text{COF}_{\text{TFPPy(OH)-BZ}}$ calculated from nonlocal density functional theory (NLDFT) fitting curves.



Fig. S5 TGA profiles of $\text{COF}_{\text{TFPPy-BZ}}$, $\text{COF}_{\text{TFPPy(OMe)-BZ}}$, and $\text{COF}_{\text{TFPPy(OH)-BZ}}$.



Fig. S6 XRD patterns of P-COF_{TFPPy(OMe)-BZ} and P-COF_{TFPPy(OH)-BZ}.



Fig. S7 Tauc plots for (a) $COF_{TFPPy-BZ}$, (b) $COF_{TFPPy(OMe)-BZ}$, and (c) $COF_{TFPPy(OH)-BZ}$ before and after AA treatment.



Fig. S8 Simulated HOMO and LUMO energies of segments from $\text{COF}_{\text{TFPPy(OMe)-BZ}}$ and P-COF_{TFPPy(OMe)-BZ}



Fig. S9 UV/vis DRS spectra of (a) COF_{TFPPy-PA}, (b) COF_{TFPPy(OMe)-PA}, (c) COF_{TFPPy(OH)-PA}, (d) COF_{TFPPy-} TP, (e) COF_{TFPPy(OMe)-TP}, and (f) COF_{TFPPy(OH)-TP} before and after AA treatment.



Fig. S10 Tauc plots for (a) $COF_{TFPPy-PA}$, (b) $COF_{TFPPy(OMe)-PA}$, (c) $COF_{TFPPy(OH)-PA}$, (d) $COF_{TFPPy-TP}$, (e) $COF_{TFPPy(OMe)-TP}$, and (f) $COF_{TFPPy(OH)-TP}$ before and after AA treatment.



Fig. S11 Mott–Schottky plots of (a) $COF_{TFPPy-BZ}$, (b) $COF_{TFPPy(OMe)-BZ}$, (c) $COF_{TFPPy(OH)-BZ}$, (d) P- $COF_{TFPPy-BZ}$, (e) P- $COF_{TFPPy(OMe)-BZ}$, and (f) P- $COF_{TFPPy(OH)-BZ}$ at different frequencies.



Fig. S12 FT-IR spectra of $\text{COF}_{\text{TFPPy(OMe)-BZ}}$ and P-COF_{TFPPy(OMe)-BZ}.



Fig. S13 Pore size distribution of P-COF_{TFPPy(OMe)-BZ}.



Fig. S14 UV/vis DRS spectra of $COF_{TFPPy-BZ}$, $COF_{TFPPy(OMe)-BZ}$, and $COF_{TFPPy(OH)-BZ}$ after pure water treatment.



Fig. S15 Zeta potentials of P-COF_{TFPPy-BZ}, P-COF_{TFPPy(OMe)-BZ}, and P-COF_{TFPPy(OH)-BZ}.



Fig. S16 PXRD patterns of $COF_{TFPPy-BT}$ (a) and $COF_{TFPPy-FBT}$ (b): experimental data (black), Pawley refined profile (red), difference (orange), and Bragg positions (blue).



Fig. S17 Wavelength-dependent AQY of photocatalytic H_2 evolution with $COF_{TFPPy(OMe)-BZ}$ as the

photocatalyst.



Fig. S18 (a) Steady-state PL spectra (excitation at 400 nm), (b) transient photocurrent responses, (c) EIS Nyquist plots, and (d) TCSPC measurements (excitation at 400 nm) of $COF_{TFPPy(OMe)-BZ}$ and P-COF_{TFPPy(OMe)-BZ}. N.D. = not detected.

5. Copies of ¹H NMR spectra



Fig. S19 ¹H NMR of TFPPy(OMe)



Fig. S20 ¹H NMR of TFPPy(OH)

6. Reference

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