Supporting Information

Inducing Local Charge Polarization by Constructing Isomeric Covalent Organic Frameworks with Different Orientation of Imine Bonds for Enhancing Photocatalytic Hydrogen Evolution

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1. Experimental section

1.1 Materials

All chemicals and reagents were of analytical grade materials and used as received without further purification. The *o*-DCB (1,2-Dichlorobenzene, 99%), anhydrous *n*-But (*n*-Butanol, 99.4%), Acetic acid (>99.0%), all monomers were purchased from Jilin Chinese Academy of Sciences-Yanshen technology Co. Ltd.

1.2 Characterization

1.2.1 Powder X-ray diffraction (PXRD) analysis

Powder X-ray diffraction data was conducted on a Rigaku and Smartlab diffractometer in reflection geometry operating with a Cu K α anode ($\lambda = 1.54178$ Å) operating at 40 kV and 40 mA. Samples were ground and mounted as loose powders onto a Si sample holder. PXRD patterns were collected from 1 to 30 20 degrees with a step size of 0.02 degrees and an exposure time of 2 seconds per step.

1.2.2 Fourier transform infrared spectroscopy (FTIR) analyses

Fourier transformed infrared (FTIR) spectra were tested on a Nicolet Avatar 6700 FT-IR spectrometer (Thermo Fisher, America).

1.2.3 Solid-state diffuse reflectance Ultraviolet-visible spectroscopy (UV-DRS) analysis

The UV-vis diffuse reflection spectra (UV-vis DRS) of the powders were carried out on a Shimadzu UV-2600 UV-vis-NIR spectrophotometer.

1.2.4 N₂ Physisorption measurements

 N_2 sorption measurements were performed on a volumetric sorption instrument (Autosorb-iQ-MP). Prior to the gas sorption studies of COFs, the samples were dried under a dynamic vacuum (<10⁻³ Torr) at room temperature (RT) followed by heating to 120 °C for 12 h. Using the N_2 adsorption isotherms, the surface areas were calculated over a pressure range 0.01-0.9 =P/P₀ using Brunauer-Emmett-Teller (BET).

1.2.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) data was carried out by a VG ESCALAB250 surface measurement system. The specific condition is that the excitation source: Al K α Ray (hv = 1486.6 eV), Beam spot: 400um, vacuum degree of the analysis chamber is better than 5.0 E-7 mBar, working voltage: 12 kV, filament current: 6 mA, full spectrum scanning: pass energy: 100 eV, step size: 1eV; Narrow spectrum scanning: the energy is 50 eV, and the step size is 0.1 eV. The narrow spectrum shall be subject to at least 5 times of cyclic signal accumulation (different scanning times for different elements), and the binding energy correction: charge correction shall be conducted with C 1s = 284.80eV binding energy as the energy standard.

1.2.6 High-resolution transmission electron microscopy (HRTEM) and Scanning electron microscopy (SEM)

Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 electron microscope. Scanning electron microscopy (SEM) was conducted on a Hitachi S-4800 field emission scanning electron microscope.

1.2.7 Electron spin resonance spectroscopy (ESR)

ESR measurements in X-band (microwave frequency ≈ 9.87 GHz) were performed at 293 K by a Bruker EMX CW micro spectrometer equipped with an ER 4119HS-WI high-sensitivity optical resonator with a grid in the front side. The samples were illuminated by a 300 W Xe lamp with 420 nm cut-off filter (LOT Oriel). All the samples were measured under the same conditions (microwave power: 6.74 mW, receiver gain: 2×104 , modulation frequency: 100 kHz, modulation amplitude: 3 G, Sweep time: 45 s). g values have been calculated from the resonance field B0 and the resonance frequency v using the resonance condition $hv = g\beta B0$.

1.2.8 Electrochemical analysis

The working electrodes was fabricated as follows: 5 mg photocatalyst powder was added into 4 mL ethanol solution containing 20 μ L 0.25% of Nafion under ultrasound for 1 h to obtain a slurry. Then, 0.5 mL of the slurry homogeneously dropped on a FTO glass (2 cm × 3.5 cm). After being calcined for 1 h in a tube furnace at 150 °C (N₂ carrier gas), an electrode was obtained. Electrochemical impedance spectra (EIS) and transient photocurrent experiments were conducted on a CHI-660e electrochemical workstation (Zahner Elektrik, Germany) with a standard three-electrode system, which employed as-fabricated electrodes as the working electrode, a platinum plate as the counter electrode and Ag/AgCl as the reference electrode. A Xe arc lamp (350 W) with a cut-off filter (λ > 420 nm) was used as the light source. 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. Mott-Schottky curves were measured in 0.1 M Na₂SO₄ in water, with a 1000, 1500 and 2000 Hz alternating current potential frequency.

1.2.9 Fluorescence spectrum

Steady-state PL, Temperature-dependent PL spectra and phosphorescence spectrum were acquired using Edinburgh Instruments, FLS980 spectrometer. The exciton binding energy could be calculated as follows:

$$I(T) = \frac{I_0}{1 + Ae^{-E_b/k_B T}}$$

1.3 Photocatalytic hydrogen evolution method and parameters

The photocatalytic water splitting reaction under visible-light irradiation was performed in a 250 mL Pyrex top-irradiation reaction vessel with a stationary temperature at 5 °C, which was connected to a glass closed gas system (Labsolar-6A, Perfect Light). In a typical process, 5 mg of photocatalyst was dispersed in a Pyrex reaction cell with 100 mL 0.1 M ascorbic acid aqueous solution and 3 wt% Pt. The reaction cell was sealed, and then irradiated with a 350 W Xe lamp (PLS-SXE300, Beijing Perfect Light Technology Co., Ltd, $\lambda > 420$ nm) under normal atmospheric pressure. During the photocatalytic reaction, the suspension was continuously stirred. The generated hydrogen was detected by GC-9500 online chromatograph.

1.4 Calculations Details and Discussions:

The geometry optimizations and characterization of the electronic structures of molecules were obtained at the B3LYP/6-311G* level (Gaussian 9.0 software package). The excited state energies and oscillator strengths from TD-DFT (TD-B3LYP/6-311G*) scrf calculations for the transient species. The implicit solvent model and dispersion correction are also used in the calculation. Multiwfn is used for electronic orbitals analysis and electrostatic potential¹⁻³. A hole-electron analysis was performed in the Multiwfn (version 3.8). Visualisation images of electronic orbitals were obtained from VMD software (version 1.9.3)⁴. A structural model of COFs was executed by using the Materials Visualizer module of Materials Studio software following the procedure: The space groups were obtained from the Reticular Chemistry Structure Resource (RCSR)^{5, 6}. P222 was chosen for PyAl-TpbAm-COF under sql topology symbol. The PyAl linker was first located at the position indicated by the vertices and edges information from RCSR. TpbAm linkers were then linked by PyAl building units. Upon completion of the structural model, an energetic minimization was performed using the universal force field implemented in the Forcite module. Pawley refinements of the PXRD patterns were done in the Reflex module. The integrated intensities were extracted using Pseudo-Voigt profile. The unit cell parameters a, b, c, FWHM parameters U, V, W, profile parameters NA, NB, and zero point were refined. The background was refined with 20th order polynomial. Simulated PXRD patterns were generated based on the optimized structures using Reflex module. The COF after imine bond torsion adopts the same method.

1.5 Synthetic procedures

PyAl-TpbAm-COF: A Pyrex tube was charged with PyAl (31.1 mg, 0.05 mmol), TpbAm (22.1 mg, 0.05 mmol), o-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone (200 mL). After freeze-drying, the product was obtained powder (41.3 mg, 78%).

PyAm-TpbAl-COF: A Pyrex tube was charged with PyAm (28.6 mg, 0.05 mmol), TpbAl (29.8 mg, 0.05 mmol), o-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone (200 mL). After freeze-drying, the product was obtained powder (47.6 mg, 82%).

PaAm-TabAl-COF: A Pyrex tube was charged with PaAm (0.15 mmol), TabAl (0.1 mmol), *o*-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone (200 mL). After freeze-drying, the product was obtained powder.



PaAl-TpbAm-COF: A Pyrex tube was charged with PaAl (0.15 mmol), TpbAl (0.1 mmol), *o*-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone (200 mL). After freeze-drying, the product was obtained powder.



TabAl-TapbAm-COF: A Pyrex tube was charged with TabAl (0.1 mmol), TapbAm (0.1 mmol), o-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone (200 mL). After freeze-drying, the product was obtained powder.



TabAm-TapbAl-COF: A Pyrex tube was charged with TabAm (0.1 mmol), TapbAl (0.1 mmol), o-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone (200 mL). After freeze-drying, the product was obtained powder.



TpbAl-BdAm-COF: A Pyrex tube was charged with TpbAl (0.1 mmol), BdAm (0.2 mmol), *o*-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone

(200 mL). After freeze-drying, the product was obtained powder.



TpbAm-BdAl-COF: A Pyrex tube was charged with TpbAl (0.1 mmol), BdAm (0.2 mmol), *o*-1,2-Dichlorobenzene (1 mL), n-Butanol (1 mL), and 6 M Acetic acid (0.1 mL). This mixture was homogenized by sonication for 10 minutes and the tube was then flash frozen at 77 K (liquid N_2 bath) and degassed by three freeze-pump-thaw cycles and evacuated to an internal pressure of 100 m Torr. The tube was sealed off and then heated at 120 °C for 3 days. The brown precipitate was collected by centrifugation and washed with Tetrahydrofuran (100 mL) and anhydrous acetone (200 mL). After freeze-drying, the product was obtained powder.



TpbAm

BdAl

2. Results and discussion



Figure S1. (A) C 1s and (B) N 1s XPS spectrum of PyAl-TpbAm-COF.



Figure S2. (A) C 1s and (B) N 1s XPS spectrum of PyAm-TpbAl-COF.



(B)



Figure S3. SEM images of PyAl-TpbAm-COF and PyAm-TpbAl-COF.



Figure S4. Bandgap of PyAl-TpbAm-COF and PyAm-TpbAl-COF.



Figure S5. Mott–Schottky plots of PyAm-TpbAl-COF.



Figure S6. Mott-Schottky plots of PyAl-TpbAm-COF.



Figure S7. EPR spectra TEMPO h⁺ PyAl-TpbAm-COF and PyAm-TpbAl-COF under

dark.



Figure S8: (A) Frontier molecular orbitals and HOMO-LUMO energies of the smallest model unit of PyAl-TpbAm-COF. (B) Frontier molecular orbitals and HOMO-LUMO energies of the smallest model unit of PyAm-TpbAl-COF.



Fig. S9 Fragment UV-visible spectrum calculated of (A) ultraviolet-visible area and (B) visible area, respectively.



Fig. S10 Hydrogen production activity and XRD of COFs with other three different imine bond orientations



Fig. S11 HOMO and LUMO energy level diagram for the monomers.



Fig. S12 PL spectra of PyAl-TpbAm-COF and PyAm-TpbAl-COF.



Fig. S13 crystal lattice spacing of (A) PyAl-TpbAm-COF and (B) PyAm-TpbAl-COF.



Fig. S14 (A) Fs-TA spectra of PyAl-TpbAm-COF, (B) 2D mapping TA spectra of PyAl-TpbAm-COF, (C)Transient absorption traces for PyAl-TpbAm-COF normalized to the 720 nm exciton bands, (D) Fs-TA spectra of PyAm-TpbAl-COF, (E) 2D mapping TA spectra of PyAm-TpbAl-COF, (F)Transient absorption traces for PyAm-TpbAl-COF normalized to the 720 nm exciton bands



Fig. S15 The D-A interface and linking band co-planes (A) PyAl-TpbAm-COF, (B) PyAm-TpbAl-COF

Table S1. Atomistic coordinates of the simulated PyAl-TpbAm-COF and PyAm-TpbAl-COF.

PyAl-TpbAm-COF								
<i>a</i> =18.2834 Å <i>b</i> = 21.3144 Å, <i>c</i> = 5.9711 Å,								
$\alpha = \beta = \gamma = 90^{\circ}$								
Atom	X	Y	Z	Atom	X	Y	Z	
C1	0.56321	0.03261	0.48588	C18	0.75871	0.22514	-0.14306	
N2	0.72956	0.17216	-0.10829	H19	0.66164	0.22419	0.28100	
C3	0.66454	0.17085	0.27010	H20	0.76215	0.05442	0.01655	
C4	0.70986	0.14217	0.10992	H21	0.68217	0.98961	0.27000	
C5	0.71878	0.07865	0.12304	H22	0.58702	0.15900	0.55094	
C6	0.67546	0.04277	0.26537	H23	0.82041	0.44322	0.46903	
C7	0.62355	0.07006	0.40397	H24	0.89651	0.25325	0.54115	
C8	0.62227	0.13506	0.41867	H25	0.81699	0.18567	0.28007	
С9	0.93742	0.43510	0.47606	H26	0.77816	0.34582	-0.16982	
C10	0.93929	0.37050	0.44393	H27	0.86119	0.41188	0.08124	
C11	0.87534	0.46809	0.48543	H28	0.75743	0.24400	-0.32167	
C12	0.88329	0.33537	0.32430	C29	0.50000	0.06318	0.50000	
C13	0.87114	0.27328	0.38210	H30	0.50000	0.11666	0.50000	
C14	0.82745	0.23720	0.24016	C31	0.00000	0.53249	0.50000	
C15	0.79409	0.26292	0.04000	C32	0.00000	0.66080	0.50000	
C16	0.80525	0.32510	-0.01460	H33	0.00000	0.71428	0.50000	
C17	0.84974	0.36067	0.12359					

PyAm-TpbAl-COF								
a = 18.2834 Å $b = 21.3144$ Å, $c = 5.9711$ Å,								
$\alpha = \beta = \gamma = 90^{\circ}$								
Atom	Χ	Y	Z	Atom	Χ	Y	Z	
C1	0.56752	0.03311	0.48310	N18	0.77577	0.21768	-0.15141	
C2	0.74371	0.16352	-0.13731	H19	0.73607	0.13719	-0.29016	
C3	0.66921	0.16857	0.21593	H20	0.66071	0.21852	0.19543	
C4	0.71520	0.13563	0.07086	H21	0.76956	0.04942	0.01166	
C5	0.72840	0.07249	0.11081	H22	0.69054	0.98862	0.26798	
C6	0.68519	0.03892	0.26236	H23	0.59734	0.16400	0.49331	
C7	0.63132	0.06964	0.38916	H24	0.81510	0.44334	0.47555	
C8	0.63068	0.13625	0.38179	H25	0.88169	0.25204	0.53769	
С9	0.93337	0.43428	0.47797	H26	0.82249	0.18422	0.27093	
C10	0.93543	0.36887	0.44808	H27	0.79577	0.33954	-0.18525	
C11	0.86707	0.46758	0.48505	H28	0.86465	0.40621	0.07124	
C12	0.87733	0.33457	0.32688	C29	0.50000	0.06433	0.50000	
C13	0.86119	0.27229	0.38372	H30	0.50000	0.11425	0.50000	

C14	0.82553	0.23355	0.23160	C31	0.00000	0.53290	0.50000
C15	0.80086	0.25761	0.02546	C32	0.00000	0.66333	0.50000
C16	0.81237	0.32087	-0.02436	H33	0.00000	0.71404	0.50000
C17	0.85082	0.35904	0.12377				

Supporting References

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