# **Supporting Information**

# Molecular engineering of donor-acceptor sp<sup>2</sup>-carbon-linked covalent organic frameworks for enhancing photocatalytic hydrogen production

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#### 1. Materials and Methods

### **1.1 Materials**

All reactions and manipulations are carried out under an  $N_2$  atmosphere by using standard Schlenk techniques or an inter-atmosphere glovebox. All reagents were used without further purification unless otherwise stated.

## 1.2 Methods

# 1.2.1 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde

(TFPB)



Under N<sub>2</sub>, the (4-formylphenyl)boronic acid (900.3 mg, 6.0 mmol) was reacted with 1,3,5-tribromobenzene (311.8 mg, 1.0 mmol) by Suzuki reaction using Pd(PPh<sub>3</sub>)<sub>4</sub> (57.8 mg, 0.05 mmol) and K<sub>2</sub>CO<sub>3</sub> aqueous solution (2.0 M, 2.0 mL) as catalysts in THF (60 mL) at 85°C for 12 h. After the mixture were cooled to room temperature, water was added. The solution was extracted with  $CH_2Cl_2$  again and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and crude product was purified by column chromatography on silica gel ( $CH_2Cl_2$ : petroleum ether = 3:1) to give pure product (232.0 mg, yield 59%). <sup>1</sup>H NMR (500 MHz, DMSOd<sub>6</sub>,  $\delta$  ppm): 10.11 (s, 3H), 8.21-8.07 (m, 9H), 8.07-8.05 (m, 6H). Unfortunately, the <sup>13</sup>C NMR spectra is not obtained due to poor solubility. The corresponding <sup>1</sup>H NMR was shown in Fig. S1.



Fig. S1. The <sup>1</sup>H NMR of 5'-(4-formylphenyl)-[1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde (TFPB).

# 1.2.2 Synthesis of 5,5',5''-(benzene-1,3,5-triyl)tris(thiophene-2-carbaldehyde)

(TFTB).



Under N2, the (5-formylthiophen-2-yl)boronic acid (936.0 mg, 6.0 mmol) was

reacted with 1,3,5-tribromobenzene (311.8 mg, 1.0 mmol) by Suzuki reaction using Pd(PPh<sub>3</sub>)<sub>4</sub> (57.8 mg, 0.05 mmol) and K<sub>2</sub>CO<sub>3</sub> aqueous solution (2.0 M, 2.0 mL) as catalysts in THF (60 mL) at 85°C for 12 h. After the mixture were cooled to room temperature, water was added. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> again and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by rotary evaporation and crude product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>: petroleum ether = 3:1) to give pure product (253.0 mg, yield 62%). <sup>1</sup>H NMR (500 MHz, CF<sub>3</sub>CO<sub>2</sub>D,  $\delta$  ppm): 9.78 (s, 3H), 8.04 (m, 3H), 8.03-8.02 (m, 3H), 7.64-7.62 (m, 3H). Unfortunately, the <sup>13</sup>C NMR spectra are not obtained due to poor solubility. The corresponding <sup>1</sup>H NMR was shown in Fig. S2.



Fig. S2. The <sup>1</sup>H NMR of 5,5',5"-(benzene-1,3,5-triyl)tris(thiophene-2-carbaldehyde) (TFTB).

# 1.2.3 Synthesis of benzo[1,2-b:3,4-b':5,6-b'']trithiophene-2,5,8-tricarbaldehyde (BTT)



The product was prepared according to a modified literature method<sup>1</sup>. To a mixture of 2,4,6-trichlorobenzene-1,3,5-tricarbaldehyde (320 mg, 1.2 mmol), pdithiane-2,5-diol (274 mg, 1.8 mmol) and anhydrous DMF (5.0 mL) was added triethylamine (1.0 mL, 7.2 mmol) dropwise in the ice bath. Then the mixture was stirred at 40 °C overnight. It was poured into ice water and centrifuged after returning to RT, washed with water and THF repeatedly. Finally, a pale brown solid was obtained with 72.8% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub> and CF<sub>3</sub>CO<sub>2</sub>D,  $\delta$  ppm): 10.19 (s, 3H), 8.67-8.65 (m, 3H). Unfortunately, the <sup>13</sup>C NMR spectra are not obtained due to poor solubility. The corresponding <sup>1</sup>H NMR was shown in Fig. S3.



Fig. S3. The <sup>1</sup>H NMR of benzo[1,2-b:3,4-b':5,6-b"]trithiophene-2,5,8-tricarbaldehyde (BTT)

# 1.2.4 Synthesis of Ph-COF



The Ph-COF was synthesized similar to previously reported method with some modification [2]. A pyrex tube was charged with 1,3,5-tris(4-formylphenyl)benzene (39.05 mg, 0.10 mmol), *p*-phenylenediacetonitrile (23.42 mg, 0.15 mmol),  $Cs_2CO_3$  (96.6 mg, 0.27 mmol), and *o*-dichlorobenzene/1-butanol (2.5 mL, 1/4 by V:V). The mixture was degassed by freezepump-thaw technique for three times and sealed under vacuum, and then heated under 120 °C for 3 days. After being cooled to RT, the precipitate was isolated by filtration and Soxhlet extracted by water, THF and ethanol. The solid was freeze-dried for 48 h to obtain the final product in 92% isolated yield.

# 1.2.5 Synthesis of Th-COF



A pyrex tube was charged with 5,5',5"-(benzene-1,3,5-triyl)tris(thiophene-2carbaldehyde) (40.80 mg, 0.10 mmol), *p*-phenylenediacetonitrile (23.42 mg, 0.15 mmol), Cs<sub>2</sub>CO<sub>3</sub> (96.6 mg, 0.27 mmol), and *o*-dichlorobenzene/1-butanol (2.5 mL, 3/2 by V:V). The mixture was degassed by freezepump-thaw technique for three times and sealed under vacuum, and then heated under 120 °C for 3 days. After being cooled to RT, the precipitate was isolated by filtration and Soxhlet extracted by water, THF and ethanol. The solid was freeze-dried for 48 h to obtain the final product in 84% isolated yield.

#### 1.2.6 Synthesis of TTh-COF



A pyrex tube was charged with benzo[1,2-b:3,4-b':5,6-b"]trithiophene-2,5,8tricarbaldehyde (33.0 mg, 0.10 mmol), *p*-phenylenediacetonitrile (23.42 mg, 0.15 mmol),  $Cs_2CO_3$  (96.6 mg, 0.27 mmol), and *o*-dichlorobenzene/1-butanol (2.5 mL, 3/2 by V:V). The mixture was degassed by freezepump-thaw technique for three times and sealed under vacuum, and then heated under 120 °C for 3 days. After being cooled to RT, the precipitate was isolated by filtration and Soxhlet extracted by water, THF and ethanol. The solid was freeze-dried for 48 h to obtain the final product in 89% isolated yield.



**Fig. S4**. The experimental and simulated PXRD patterns of (a) Ph-COF; (b) Th-COF; (c) TTh-COF; and the chemical structure in AA stacking model, (d) top view for Ph-COF; (e) top view for Th-COF; (f) top view for TTh-COF; (g) side view for Ph-COF; (h) side view for Th-COF; (i) side view for TTh-COF.

#### 2、 Electrochemical measurements

Electrochemical impedance spectra (EIS) measurements were carried out using a CHI650E electrochemical workstation with a three-electrode system: prepared membrane electrode, Pt plate, and Ag/AgCl as the working electrode, counter electrode, and reference electrode, respectively. A solution of 0.5 M Na2SO4 was used as the supporting electrolyte, and a 300 W Xe-lamp (CEL-HXF 300) with a cut-off filter (420 nm $\leq\lambda\leq$ 780 nm) served as the light source. EIS was determined in the frequency range of 102 to 106 Hz, and the AC amplitude under the open circuit voltage at room temperature was 10 mV.

## 3、The AQY measurement

The apparent quantum yield (AQY) for  $H_2$  production under monochromatic light irradiation ( $\lambda$ =420, 450, 500, 550, 600, 630 nm) was estimated as the following equation.

$$AQY = \frac{2 \times number \ of \ evolved \ H_2 \ molecules}{number \ of \ incident \ photons} \times 100\% = \frac{2 \times C \times N_A}{S \times P \times t \times \frac{\lambda}{h \times c}} \times 100\%$$
(1)

where C is the H<sub>2</sub> production amount (mmol) per hour; N<sub>A</sub> is the Avogadro constant  $(6.02 \times 10^{23} \text{ mol}^{-1})$ ; S is the irradiation area (12.56 cm<sup>2</sup>); P is the monochromatic light intensity (W cm<sup>-2</sup>) (P is detected by optical power meter); t is the light exposure time (1 h);  $\lambda$  is the monochromatic light wavelength (nm); h is the Planck constant (6.626 × 10<sup>-34</sup> J s); c is the speed of light (3 × 10<sup>8</sup> m s<sup>-1</sup>). The light intensity of  $\lambda$  = 420, 450, 500, 550, 600, 630 nm are 1.96, 2.03, 2.46, 2.41, 2.19 and 2.12 mW cm<sup>-2</sup>, respectively.



Fig. S5. (a) TGA traces of polymers Ph-COF, Th-COF and TTh-COF; XPS valence band spectrum

#### of Ph-COF (b), Th-COF(c), TTh-COF (d).



Fig. S6. The Mulliken charge analysis for Ph-COF, Th-COF and TTh-COF at the level of CAM-



B3LYP/6-31G(d)

**Fig. S7**. PXRD of (a) Ph-COF; (b) Th-COF; (c) TTh-COF after treatment in different conditions for 72 h; FTIR spectra of (d) Ph-COF; (e) Th-COF (f) TTh-COF after treatment in different conditions for 72 h.

COFs	Band gap (eV)	Sacrificial agent	Co-catalyst	AQY	HER mmol g <sup>-1</sup> h <sup>-1</sup>	Ref
TTh-COF	2.06	AA (0.1 M)	Pt (1%wt)	14.7% (λ=420 nm)	22.22	This work
Th-COF	2.13	AA (0.1 M)	Pt (1%wt)	10.3% (λ=420 nm)	15.58	This work
Ph-COF	2.53	AA (0.1 M)	Pt (1%wt)	6.2% (λ=420 nm)	3.48	This work
BTT-Hz-1	2.14	AA (0.1 M)	Pt (3%wt)	8.6% (λ=400 nm)	17.27	2
TFPT-COF	2.8	TEOA (10 vol%)	Pt (2.2%wt)	2.2% (λ=400 nm)	1.97	3
PyTz-COF	2.2	AA (0.1 M)	Pt (3%wt)	-	2.0724	4
TpPa-1-COF	1.97	AA (0.1 M)	Pt-PVP (6%wt)	0.4% (λ=475 nm)	8.42	5
H-COF	2.8	TEOA (20 vol%)	Pt (4.2%wt)	-	0.609	6
ODA-COF	2.0	TEOA (20 vol%)	Pt (4.2%wt)	0.42% (λ=420 nm)	2.615	6
NKCOF-108	1.82	AA (0.1 M)	Pt (5%wt)	2.96% (λ=520 nm)	12	7

BTT-Bpy-COF (BTT-based)	2.16	AA (0.1 M)	Pt (5%wt)	3.72% (λ=500 nm)	15.8	8
BTH-3 (BTT-based)	1.42	AA (0.1 M)	Pt (15.2%wt)	1.256% (λ=500 nm)	15.1	9
COF-3 (BTT-based)	2.18	AA (0.1 M)	Pt (8%wt)	-	20.2	10
BTT-NDA (BTT-based)	1.90	AA (0.1 M)	Pt (3%wt)	5.42% (λ=470 nm)	5.22	11
COF-DFB	2.39	AA (0.1 M)	Pt (2.5%wt)	0.7% (λ=435 nm)	3.23	12
COF-BPDA	2.16	AA (0.1 M)	Pt (2.5%wt)	2.1% (λ=435 nm)	2.10	12
N <sub>3</sub> -COF	2.6-2.7	TEOA (1 vol %)	Pt (3.8%wt)	0.44% (λ=450 nm)	1.703	13
TFPT–DETH	2.77	SA (0.1 M)	Pt (7.5%wt)	1.11% (λ=420 nm)	2.301	14
sp <sup>2</sup> c-COF	2.05	TEOA (10 vol%)	Pt (3%wt)	-	1.36	15
sp <sup>2</sup> c-COF- ERDN	2.00	TEOA (10 vol%)	Pt (3%wt)	0.48% (λ=495 nm)	2.12	15
FS-COF	1.85	AA (0.1 M)	Pt (3.8%wt)	3.2% (λ=420 nm)	10.1	16
F-COF	-	AA (0.1 M)	Pt (3.8%wt)	-	4.4	16

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