# The competitive influence of intramolecular electric field and hydrophilic active sites of D-A conjugated porous polymers on photocatalytic hydrogen evolution performance

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# 1. Reagents

## 1.1 The source of the reagents

3,7-dibromodibenzothiophene-5,5-dioxide,

tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) were obtained from Zhengzhou Alfachem Co., Ltd. N-methypyrrolidone (NMP), ethanol, chloroform, N,N-1,1'dimethylformamide (DMF), bis(diphenylphosphino)ferrocenepalladium(II)dichloride dichloromethane complex (Pd(dppf)Cl<sub>2</sub>·DCM), acetonitrile (MeCN), potassium acetate (KOAc), potassium carbonate were bought from Aladdin Co., Ltd. All reactants were used directly without further purification. Besides the 3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2monomers including yl)dibenzo[b,d]thiophene-5,5-dioxide (M1),<sup>1,2</sup> 3,7-dibromo-10-(4-bromophenyl)-10Hphenothiazine 5,5-dioxide (M3) and 3,7-dibromo-10-methyl-10H-phenothiazine 5,5dioxide (M5)<sup>3, 4</sup> are prepared according to the previous reports. The detailed procedure are given as follows.

1.2 Synthesis of 3,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)dibenzo[b,d]thiophene-5,5-dioxide (M1)



Fig. S1 The synthesis routes of M1

Under argon atmosphere, 3,7-dibromodibenzothiophene-5,5-dioxide (2.70 mmol, 1.01 g), bis(pinacolato)diboron (5.88 mmol, 1.49 g), anhydrous KOAc (15.99 mmol, 1.57 g) and dry dioxane (50 mL) were added in a two-necked flask (100 mL). After degassed with argon for 15 min, Pd(dppf)Cl<sub>2</sub>·DCM (0.16 mmol, 131 mg) was added. Then the mixture was degassed for another 15 min. The mixture was heated at 100 °C for 32 h under argon atmosphere. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was diluted with water (50 mL). The aqueous solution was extracted twice with DCM ( $2 \times 50$  mL), washed twice with water

 $(2 \times 20 \text{ mL})$ , and dried with anhydrous MgSO<sub>4</sub>. The crude product was purified by silica gel chromatograph to afford white solid product (1.01 g, 85%).

# 1.3 Synthesis of 3,7-dibromo-10-(4-bromophenyl)-10H-phenothiazine 5,5-dioxide (M3)



Fig. S2 The synthesis routes of M3

3,7-dibromo-10-(4-bromophenyl)-10H-phenothiazine (1.95mmol, 1.0 g), H<sub>2</sub>O<sub>2</sub> (30%, 2ml), and 10 ml HAC were added to a 100 mL flask. Then the mixture was refluxed at 120°C for 12 hours. The product was filtered, washed by deionized water, and dried by vacuum oven to give a pale white solid. <sup>1</sup>HNMR (500 MHz, CDC1<sub>3</sub>)  $\delta$  8.25 (d, J=2.3 Hz, 2H), 7.88-7.82 (m, 2H), 7.49 (dd, J = 9.2. 2.4Hz, 2H), 7.27-7.22 (m, 2H, 6.51 (d, J= 9.1 Hz. 2H) (Fig. S2a). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  139.22, 137.14, 136.07, 135.05, 131.86, 126.05, 124.57, 123.91, 119.00, 115.08 (Fig. S2b)



**Fig. S3** (a) <sup>1</sup>H NMR spectrum and (b) <sup>13</sup>C NMR spectrum of M3 **1.4 Synthesis of 3,7-dibromo-10-methyl-10H-phenothiazine 5,5-dioxide (M5)** 



Fig. S4 The synthesis routes of M5

3,7-dibromo-10-methyl-10H-phenothiazine (2.69mmol, 1g),  $H_2O_2$  (30%, 1ml), and 10ml HAC were added to a 100 mL flask. Then the mixture was refluxed at 120°C for 12 hours. The product was filtered, washed by deionized water, and dried by vacuum oven to give a pale white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, J = 2.3 Hz, 2H), 7.71 (dd, J = 9.0, 2.3 Hz, 2H), 7.18 (s, 2H), 3.67 (s, 3H) (Fig. S4a). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  140.76, 136.29, 126.15, 125.53, 117.58, 114.70, 36.10 (Fig. S4b).



Fig. S5 (a)  $^{1}$ H NMR spectrum and (b)  $^{13}$ C NMR spectrum of M5





**Fig. S7** The elemental mapping images of PPTBT (a), PPTOBT (b), PTBT (c) and PTOBT (d), respectively.



**Fig. S8** SEM images of the CMP after catalysis. (a) PPTBT, (b) PPTOBT, (c) PTBT and (d) PTOBT; TEM images of (e) PPTBT, (f) PPTOBT, (g) PTBT and (h) PTOBT.



**Fig. S9** High-resolution XPS spectra of the CMP after catalysis. (a) C1s region; (b) N1s region; (c) O1s region; (d) S 2p region.



Fig. S10 The simulated UV-vis of PTBT, PTOBT, PPTBT and PPTOBT.

Element	Normalized quality(%)	Atom	1 1	Element	Normalized quality(%)	Aton
		(%)				(%)
С	7 <b>8.1</b> 7	86.22		С	75.99	84.
S	11.28	4.66		S	11.98	5.00
0	7.24	6.00		0	10.32	8.64
N	3.31	3.13		Ν	1.71	1.64
ГВТ			PTOF	ЗТ		
TBT Elem ent	Normalized quality(%)	Atom	PTOF	BT Element	Normalized anality(%)	Atom
FBT Elem ent	Normalized quality(%)	Atom (%)	PTOF	BT Element	Normalized quality(%)	Aton (%)
ГВТ Element С	Normalized quality(%) 69.23	Atom (%) 76.82	PTOF	BT Element C	Normalized quality(%) 65.11	Aton (%) 75.8
FBT Element C S	Normalized quality(%) 69.23 16.71	Atom (%) 76.82 8.30	PTOF	BT Element C S	Normalized quality(%) 65.11 17.59	Atom (%) 75.8 7.6
BT Element C S O	Normalized quality(%) 69.23 16.71 10.36	Atom (%) 76.82 8.30 10.12	PTOF	BT Element C S O	Normalized quality(%) 65.11 17.59 11.34	Aton (%) 75.8( 7.67 11.32

Table. S1 Quantitative analysis of various elements from EDS

Table. S2 Photocatalytic hydrogen evolution performance of the reported organic Photocatalysts

Photocatalyst	Cocatalyst	Sacrificial agent	HER (mmol $g^{-1} h^{-1}$ )	Refs
P1	NO	TEOA	$0.05(\lambda \ge 420 \text{ nm})$	7
S-CMP3	NO	TEA	$6.076(\lambda > 295 \text{ nm})$	21
TAPB	NO	AA	20.2	46
En <sub>tapt-tdoeb</sub>	Pt	AA	2.396	47
PFC-1@Pt	Pt	AA	2.2025	48
B-BTDO-DT	Pt	TEOA	0.259	49
РРТВТ	NO	AA	63.96	This work

#### 2. Characterization methods

#### 2.1 Instrumental information

The structural identification of polymers was fulfilled by instrumental methods including Nicolet Avatar 360 FT-IR spectrometer, Bruker Avance III HD 500 MHz NMR spectrometer. ESCALAB 250Xi spectrometer was used to get the elements and their valence states. Scanning electron microscope (SEM) (Thermo Fisher Scientific FIB-SEM GX4) was coupled with an Energy dispersive X-ray spectrometry (SEM-EDS) to examine the morphology and the elemental distribution of the polymers. The transmission electron microscopy (TEM) was also taken to investigate the structural characterization using JEM-2100F TEM. Nitrogen isotherm adsorption desorption was conducted at 77.3 K using ASAP 2460-3 (Micromeritics) volumetric adsorption analyzer. The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was conducted on an Agilent Carry 5000 spectrophotometer (CA, USA). Photoluminescence (PL) spectra were collected on an F-7000 FL spectrophotometer. Time-resolved PL spectra were measured using a time-correlated single-photon counting system (FLS1000). The Electron paramagnetic resonance spectroscopy was measured using a China instru & Quantumtech (Hefei) EPR200-Plus with continuous-wave X band frequency.

#### 2.2 Transient photocurrent measurements

The transient photocurrent responses (I-t) were also measured on CHI660E (Chenhua, Shanghai) electrochemical workstation in a standard three-electrode system,

including a Pt sheet as the counter electrode (1 cm  $\times$  1 cm), an Ag/AgCl electrode as the reference electrode, and a photocatalyst-modified indium tin oxide (ITO) electrode as the working electrode. The Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M) was used as an electrolyte. The catalyst slurry was prepared by adding 10 mg of catalyst to a mixture solution with 1 mL isopropyl alcohol and 30 µL Nafion (5%), and the slurry was fully dispersed in an ultrasonic cleaner for 30 min before use. To prepare the ITO electrode, 20 µL of the above polymer slurry was coated on the ITO/glass electrode with a surface area of 1 cm  $\times$  1 cm and dried under an infrared lamp, then the photocurrent was analyzed under the irradiation of xenon lamp light source (The applied voltage on the working electrode is 1 V).

#### 2.3 Electrochemical measurements

Electrochemical impedance spectra (EIS) were measured on a CHI660E (Chenhua, Shanghai) electrochemical workstation in a standard three electrode system. The sample modified Pt-disk electrode with a diameter of 3 mm was used as the working electrode, and Pt flake and Ag/AgCl as the counter and reference electrodes, respectively. The mixture slurry containing polymer photocatalysts (10 mg), isopropyl alcohol (1 mL), and nafion (30  $\mu$ L), which was dispersed by ultrasound for 30 min. The mixture slurry (10  $\mu$ L) was dropped on the platinum plate electrode and dried under an infrared lamp before the measurements, which was used as the working electrode. EIS experiments were performed in a frequency range from 0.01 Hz to 100 kHz at 0.2 V, and Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.5 M, pH=6.8) was used as the electrolyte.

#### 2.4 AQY measurements

The apparent quantum yield (AQY) of the photocatalysts was measured with a monochromatic light obtained by using bandpass filters of 405, 475, 500, 550 and 600 nm with energy intensities of 35.8, 40.20, 45.70, 50.4, and 52.10 mW·cm<sup>-2</sup>, respectively. The AQY at a given wavelength was calculated by the following equation:<sup>5</sup>

$$AQY = 2\frac{N_0}{N_P} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where M is the amount of H<sub>2</sub> (mol) produced, N<sub>A</sub> is Avogadro constant ( $6.02 \times 10^{23}$ 

mol<sup>-1</sup>), h is the Planck constant ( $6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ ), c is the speed of light in vacuum (3  $\times 10^8 \text{ m/s}$ ), S is the irradiation area (19.6 cm<sup>2</sup> in this experiment), P is the intensity of irradiation light (W/cm<sup>2</sup>), t is the irradiation time (s),  $\lambda$  is the wavelength of the monochromatic light (nm).

## References

- F. Lan, Q. Wang, H. Chen, Y. Chen, Y. Zhang, B. Huang, H. Liu, J. Liu and R. Li, ACS Catalysis, 2020, 10, 12976-12986.
- 2. Z. Wang, X. Yang, T. Yang, Y. Zhao, F. Wang, Y. Chen, J. H. Zeng, C. Yan, F. Huang and J.-X. Jiang, ACS Catalysis, 2018, **8**, 8590-8596.
- 3. M.-X. Zhang, X. Yang, F. Tan, H. Zhang, G. Zeng, Z. Xu and S. H. Liu, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2023, **292**, 122427.
- 4. R. Hojo, K. Bergmann, S. A. Elgadi, D. M. Mayder, M. A. Emmanuel, M. S. Oderinde and Z. M. Hudson, *Journal of the American Chemical Society*, 2023, **145**, 18366-18381.
- 5. X. Han, F. Zhao, Q. Shang, J. Zhao, X. Zhong and J. Zhang, *ChemSusChem*, 2022, **15**, e202200828.