## **Supporting Information**

# Rapid Metal-Free Syntheiss of Pyridyl-Functionalized Conjugated Microporous Polymers for Visible-Light- Driven Water Splitting

Zhonghua Cheng, <sup>§a</sup> Lei Wang, <sup>§b</sup> Yan He, <sup>§a</sup> Xingjia Chen, <sup>b</sup> Xiaojun Wu, <sup>b</sup> Hangxun Xu, <sup>\*b</sup> Yaozu Liao, <sup>\*a</sup> and Meifang Zhu<sup>a</sup>

a. State Key Laboratory for Modification of Chemical Fibers and Polymer Materials & College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

b. Hefei National Laboratory for Physical Sciences at the Microscale and CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China

§ These authors equally contributed to this work

#### **Corresponding Author**

\* yzliao@dhu.edu.cn; hxu@ustc.edu.cn

### **Table of Contents**

- **S1. Experimental Section**
- S1.1. Chemicals
- S1.2. Synthesis of a model molecular analogue 1,3,5-tris(2,6-diphenylpyridin-4-

yl)benzene(tris-DPPB)

S1.3. Synthesis of PCMPs

- **S2.** Characterization and Measurements
- S2.1. Structure and morphology characterization
- S2.2. Synchrotron radiation photoemission spectroscopy (SRPES) measurements
- S2.3. Deposition of platinum (Pt) on PCMPs
- S2.4. Deposition of Cobalt(Co) on PCMPs
- *S2.5. Photocatalysis experiments*
- S2.6. The apparent quantum efficiency (AQE) measurements
- S2.7. Photocurrents and photoelectrochemical measurements
- **S3.** Supplementary Tables and Figures
- **S4. Supplementary References**

#### **S1. Experimental Section**

*S1.1. Chemicals.* 1,4-Diacetylbenzene (DAB, 99%), terephthalaldehyde (TPA, 98%), and 1,3,5triacetylbenzene (TAB, 98%) were purchased from Tokyo Chemical Industry Co. Ltd. 1,3,5triformylbenzene (TFB, 96%) was purchased from Bide Pharmatech Ltd. Ammonium acetate (98%) and acetophenone (98%) was purchased from Sinopharm Chemical Reagent Co. Ltd. Acetic acid (99.5%) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd. All chemicals were used as received.

S1.2. Synthesis of a model molecular analogue 1,3,5-tris(2,6-diphenylpyridin-4-yl)benzene (tris-DPPB). A 50 mL round-bottom flask was charged with acetophenone (0.35 mL, 3 mmol), TFB (162 mg, 1 mmol), and ammonium acetate (3 g, 39 mmol). Anhydrous acetic acid (35 mL) was added and the reaction mixture was heated to 120 °C under stirring. After refluxed 2 h, cold water was added for the precipitation of sample. The crude sample was filtered and purified by chromatography on silica gel using hexanes/ethyl acetate as eluent to remove byproducts including 1-(2,6-diphenylpyridin-4-yl)benzene and 1,3-di(2,6-diphenylpyridin-4-yl)benzene. The remained solids were dried in a vacuum oven for 72 h to afford a light yellow tris-DPPB product (37% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>-d, 25°C):  $\delta$ =7.57 (t, 12H), 7.60(s, 3H), 7.66 (t, 6H), 7.68 (s, 6H), 7.93 (d, 12H) ppm; *IR* (neat): 1661, 1593, 1445, 1286, 1213, 1015, 1026, 849, 773, 681 cm<sup>-1</sup>; MALDI/TOF MS Found (M-1): 765.31.



**Scheme S1** Chichibabin pyridine synthesis between 1,3,5-triformylbenzene and acetophenone.

**S1.3.** *Synthesis of PCMPs.* For PCMP-1 synthesis, a 50mL round-bottom flask was charged with TPA (134 mg, 1 mmol), DAB (324 mg, 2 mmol), and ammonium acetate (2.3 g, 30mmol). Anhydrous acetic acid (35 mL) was added and the reaction mixture was heated to 120 °C under stirring. After refluxed 1 h, the heater was removed and solvents were then removed by filtration. The remaining solids were washed by 1% aqueous ammonia, hot water and methanol (200 mL, 24 h each), and then dried in a vacuum oven 3 days to afforded a yellow powder with a yield of 75%. *Anal. Found*: C, 80.39%; H, 5.00%; N, 3.62%. By replacing TPA and DAB with TFB (162 mg, 1 mmol) and TAB (408 mg, 2 mmol), respectively, following the synthetic procedure of PCMP-1 gave yellow PCMP-2 powder with a yield of 83%. *Anal. Found*: C, 77.01%; H, 4.95%; N, 4.56%.

#### S2. Characterization and Measurements

**S2.1.** Structure and morphology characterization. The <sup>1</sup>H NMR spectra were recorded on a Bruker Advance III HD 600MHz using  $CDCl_3$ -*d* as a solvent. The elemental analyses were carried out using an Elamentar VarioEL III Elemental Analyzer. The solid-state UV-vis spectra were recorded on a Shimadzu UV-3600 Spectrometer. The <sup>13</sup>C CP/MAS NMR spectra were taken at a

Bruker Advance 400 (400 MHz) spectrometer. The FT-IR spectra were taken on a Thermo Scientific Nicolet iS5 spectrometer. The XRD patterns were obtained on Arigaku D Max 2550 VB PC (18 KW) using Cu K $\alpha$  radiation ( $2\theta$  = 3-90°). The SEM images were obtained on a Hitachi SU8010 microscope. The TEM images were obtained on a FEI Talos F200S microscope. The TGA analyses were carried out on a Netzsch TG 209 F1 Libra® apparatus in a nitrogen atmosphere (flow rate 30 mL/min) in a temperature range of 40-1000 °C (heating rate 10 °C/min. Nitrogen adsorption/desorption measurements at 77.4 K were performed after degassing the samples under high vacuum at 120 °C for 20 h using a Micromeritics ASAP2460 machine. X-ray photoelectron spectroscopy (XPS) measurements were performed on an X-ray photoelectron spectrometer (Thermo ESCALAB 250). Photoluminescence spectra were recorded on a HORIBA FluoroMax-4 fluorometer with an excitation wavelength of 320 nm.

**S2.2.** Synchrotron radiation photoemission spectroscopy (SRPES) measurements. SRPES measurements were conducted to determine the valence band (VB) positions of both polymers. To obtain the secondary electron cutoff, an excitation of 168.8 eV was utilized. The binding energy (BE) was calibrated and referenced to the  $E_f$  of a gold foil. The work function (WF) of samples was determined according to the equation  $\Phi = hv - \Delta E$ , where  $\Delta E$  is the spectrum width, *i.e.* the energy difference between the secondary electron cutoff and the sample Fermi level. In order to obtain the secondary electron swith higher kinetic energy (KE) to overcome the WF of the analyzer.

**S2.3.** Deposition of platinum (Pt) on PCMPs. The Pt co-catalyst was loaded on the PCMPs surface by in situ photo-deposition method reported previously.<sup>S1</sup> In a typical synthesis,50 mg PCMP photocatalyst powder was dispersed in deionized water (50 mL) contained 10% vol (5 mL) methanol (MeOH) as the sacrificial agent. A certain amount of H<sub>2</sub>PtCl<sub>6</sub> (3 wt%, based on Pt atoms) were added to the solution. After 1 hour photo-deposition using full arc irradiation with a 300 W lamp, the photocatalyst was filtration and washed with deionized water several times. Then the photocatalyst was dried at 60 °C overnight.

**S2.4. Deposition of Cobalt (Co) on PCMPs.** The Co co-catalyst was loaded on the PCMPs surface by was obtained by an immersion method reported previously.<sup>S2</sup> In a typical synthesis, 50 mg of the PCMPs was immersed into the aqueous solutions containing 5 mg of Co(NO<sub>3</sub>)<sub>2</sub> hexahydrate compound. Subsequently, the mixture was sonicated for 15 min to achieve a homogenous suspension. Then 0.5 mL ammonia was added dropwise into the above solution. Then the obtained product was washed with water. The final hybrid photocatalyst was obtained after drying under an oven at 80 °C for 12 h.

**S2.5.** Photocatalysis experiments. 10 mg photocatalyst and 50 mL H<sub>2</sub>O containing 10 vol % triethanolamine as an electron donor were put in a hermetic device mainly composed of a quartz tube and sealing components. Prior to the photocatalytic test, the device was purged with Ar flow to remove air. A 300W Xe lamp (Perfect Light PLS-SXE 300) was used as the light source. A cutoff filter (Kenko L-42) was used to achieve light irradiation ( $\lambda$ >420 nm). The amount of H<sub>2</sub> evolved was determined using gas chromatography (SHIMADZU GC-2014, thermal conductivity detector (TCD), Ar carrier, Agilent). Cycling photocatalytic tests were

performed using the same way after the samples were collected and washed with water. For water photo-oxidation, in a typical experiment, 10 mg photocatalyst suspended in 50 mL water with 0.01 M AgNO<sub>3</sub> as the sacrificial electron acceptors and La<sub>2</sub>O<sub>3</sub> (0.1 g) as a pH buffer agent was subjected to photoirradiation (Xe lamp, Perfect Light PLS-SXE 300, using  $\lambda$ >420 nm cutoff filters). The suspension was sonicated for 15 min for a better dispersion then purged with argon gas for at least 120 min to expel the dissolved O<sub>2</sub>. The amount of O<sub>2</sub> evolved was determined using gas chromatography (SHIMADZU GC-2014, thermal conductivity detector (TCD), Ar carrier, Agilent) and NeoFox Sport Oxygen Sensor (Ocean Optics).

**S2.6.** The apparent quantum efficiency (AQE) measurements. AQE measurements for hydrogen or oxygen evolution were measured under the illumination of a 300 W Xe lamp with different band pass filters ( $\lambda_0 \pm 20$  nm) for 8 hours. For these tests, 50 mg of photocatalyst was used. The apparent quantum efficiency was calculated using the following formula:

AQE (%)= 
$$\frac{a \times \text{amount of gas molecules evolved}}{\text{Total photons incident}} \times 100\%$$

where a=2 for the H<sub>2</sub> evolution reaction and a=4 for the O<sub>2</sub> evolution reaction.

**S2.7.** Photocurrents and photoelectrochemical measurements. The measurements were conducted on a Metrohm Autolab PGSTAT302N potentiostat/galvanostat in a three-electrode cell system under ambient conditions under irradiation of a 300 W Xe lamp (Perfect Light PLS-SXE 300). Visible light ( $\lambda$ >420 nm) with a power density of 100 mW·cm<sup>-2</sup> was used as the illumination source. The FTO glass (1×2 cm<sup>2</sup>) coated materials (2 mg photocatalyst) as the photoelectrode, a Pt foil as the counter electrode, and a Ag/AgCl electrode as the reference

electrode. The three electrodes were inserted in a quartz cell filled with 0.5 M  $Na_2SO_4$ electrolyte. The  $Na_2SO_4$  electrolyte was purged with Ar for 1 h prior to the measurements.

#### **S3.** Supporting Figures and Tables



Figure S1 SEM images of (a) PCMP-1 and (b) PCMP-2.



Figure S2 (a)  $N_2$  adsorption/desorption isotherms and (b) corresponding DFT pore size distributions of PCMPs.



Figure S3 Powder XRD patterns of PCMP-1 and PCMP-2.



Figure S4 C 1s core-level XPS spectra of (a) PCMP-1 and (b) PCMP-2.



Figure S5 TGA curves of PCMPs.



Figure S6 FT-IR spectra of (a) PCMP-1 and (b) PCMP-2 synthesized under different reflux durations.



**Figure S7** PXRD patterns of (a) PCMP-1 and (b) PCMP-2 synthesized under different reflux durations.



Scheme S2 Polymerization mechanism of PCMP-1.



Figure S8 Calculated partial density of states (PDOS) of FCMPs.



Figure S9 The measured Mott-Schottky plots of (a) PCMP-1 and (b) PCMP-2.

Polymer	Optical gap (eV)	HER λ> 420 nm (μmol h-1 g-1)	Reference	
PCMP-1	2.83	100	This work	
PCMP-2	2.96	20		
P11	2.48	258		
P12	2.42	420		
P13	2.29	250	62	
P14	2.20	175	53	
P15	2.12	78		
P16	2.06	72		
CTP1	2.98	150		
CTP2	2.66	500	S4	
CTP3	2.36	50		
PrCMP-3	1.53	65	S5	
P7	2.70	1492	56	
S-CMP3	2.56	3106	50	
P10	2.58	6130	S7	
L-PDBT-O	1.95	11200	S8	

**Table S1** Optical properties and photocatalytic  $H_2$  evolution properties of the polymeric photocatalysts.

#### Acronyms

P11-16: benzene/thiophene-based conjugated polymers

CTP1-3: conjugated triazine-based polymers

PrCMP-3: pyrene-containing conjugated microporous polymer

P7: 1,4-benzene-linked dibenzo[b,d]-thiophene sulfone copolymer;

S-CMP3: 9,9'-spirobifluorene material

P10: dibenzothiophene sulfone conjugated polymer

L-PDBT-O: linear dibenzothiophene sulfone/pyrene-based conjugated polymer



**Figure S10** J–V curves of (a) PCMP-1 and (b) PCMP-2 under light irradiation ( $\lambda$ >420nm).



Figure S11 The transient photocurrents of PCMPs under visible light irradation.



Figure S12 Photoluminescence emission spectra of PCMP-1 and PCMP-2 ( $\lambda_{ex}$ =320 nm).



Figure S13 (a) UV-vis spectra and (b) Tauc plots of PCMPs.

Aldelyde	Br Co	но	OCH3 H3CO	
Ketone	) } { }	° ↓ ↓ ¢	$\mathbf{x} \in \mathbf{x}$	
Polymer	Br Br Br Br Br Br Br Br Br Br Br Br Br B	HO HO N N N N N N N N N N N N N N N N N	H <sub>3</sub> CO +U +U +U +U +U +U +U +U +U +U +U +U +U	
Photo				
Aldelyde	ر مراح کی از م			
Ketone	<u>}~{}~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~</u>			
Polymer	PCMP-6	PCMP-7		
Photo				

 Table S2 A series of PCMPs synthesized via aminative cyclization between different aryl

 aldehydes and ketones.

#### References

- S1 L. Lin, C. Wang, W. Ren, H. Ou, Y. Zhang, X. Wang, Chem. Sci. 2017, 8, 5506-5511.
- S2 L. Wang, Y. Wan, Y. Ding, Y. Niu, Y. Xiong, X. Wu, H. Xu, Nanoscale 2017, 9, 4090-4096.
- S3 R. S. Sprick, C. M. Aitchison, E. Berardo, L. Turcani, L. Wilbraham, B. M. Alston, K. E. Jelfs, M. A. Zwijnenburg and A. I. Cooper, *J. Mater. Chem. A*, 2018, **6**, 11994-12003.
- S4 Z.-A. Lan, Y. Fang, Y. Zhang and X. Wang, Angew. Chem. Int. Ed., 2018, 57, 470-474.
- S5 Y. Xu, N. Mao, S. Feng, C. Zhang, F. Wang, Y. Chen, J. Zeng and J.-X. Jiang, *Macromol. Chem. Phys.*, 2017, **218**, 1700049-1700049.
- S6 R. S. Sprick, Y. Bai, A. A. Guilbert, M. Zbiri, C. M. Aitchison, L. Wilbraham, Y. Yan, D. J. Woods,M. A. Zwijnenburg and A. I. Cooper, *Chem. Mater.*, 2018, **31**, 305-313.
- S7 C. M. Aitchison, R. S. Sprick and A. I. Cooper, J. Mater. Chem. A, 2019, 7, 2490-2496.
- S8 X. Wang, B. Chen, W. Dong, X. Zhang, Z. Li, Y. Xiang and H. Chen, *Macromol. Rapid Commun.*, 2019, **40**, 1800494- 1800494.