

## Supplementary Information

### Structure Control and Photocatalytic Performance of Porous Conjugated Polymers Based on Perylene Diimide

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### Contents

<b>1. Supplementary Methods</b>	<b>(Pages S2-S4)</b>
<b>2. Supplementary Tables and Figures</b>	<b>(Pages S5-S12)</b>
<b>4. Supplementary References</b>	<b>(Page S13)</b>

## Experimental Section

All chemicals obtained from commercial suppliers were used without further purification. All solvents were purified with a standard distillation procedure prior to use. Monomers  $M_1$ ,<sup>1</sup>  $M_2$ ,<sup>2</sup>  $M_3$ <sup>3</sup> and melem<sup>4</sup> were prepared according to literatures. <sup>1</sup>H-NMR spectra were recorded on a Bruker DRX-400 or DRX-500 spectrometer, with tetramethylsilane as an internal reference. Elemental analysis was performed by Midwest MicroLab. TGA measurement of the polymers was performed using a TA Q600 instrument over the temperature range 50 to 800 °C under N<sub>2</sub> with a heating rate of 15 °C/min. FTIR spectra were recorded on Nicolet™ iS™10 FTIR Spectrometer as KBr pellets. UV–vis absorption spectra were measured on a Shimadzu UV-3600 device. Diffuse reflectance accessory was used for the measurement of solid samples. SEM images were recorded on FEI NanoSEM. Surface areas were measured by nitrogen adsorption and desorption at 77.3 K from 0.005 to 1.0 bar. Powder samples were degassed at 100 °C for 12 hours under vacuum before measurement. Isotherms were recorded using Micromeritics ASAP 2020 (M+C). Surface areas were calculated in the relative pressure (P/P<sub>0</sub>) range from 0.005 to 0.20 of the adsorption branch. Metal content was determined by inductively coupled plasma mass spectrometry (ICP-MS), where the sample was first digested by H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (0.8 mL/0.2 mL) solvent at 60 °C for 24 h. The molecular geometries of the molecules were optimized, and their orbital energies and charge distributions calculated using the B3LYP DFT function with basis set 6-31G\* as implemented in Gaussian 09.

**General procedure for the synthesis of PCP1-x%PDI by Sonogashira coupling reaction.** All the polymerization reactions were carried out with a constant monomer concentration and a fixed reaction condition (80 °C, 24 h). The molar ratio of diethynyl monomer ( $M_1$ ) and the tetrabromo monomers ( $M_3$  and  $M_4$ ) was fixed at 2.0/1.0. The mole ratio of monomers  $M_3$  and  $M_4$  was varied ( $0 < x\% < 1.0$ ). A representative experimental procedure for PCP1-100%PDI is given as an example.

**PCP1-100%PDI:** Monomer  $M_1$  (80.8 mg, 0.400 mmol), Monomer  $M_3$  (180.0 mg, 0.200 mmol), tetrakis(triphenylphosphine)-palladium(0) (17.5 mg, 0.015 mmol), and copper(I) iodide (5.5 mg, 0.030 mmol) were dissolved in a mixture of anhydrous toluene (6.6 mL) and  $\text{Et}_3\text{N}$  (3.3 mL). The reaction mixture was heated to 80 °C and stirred for 24 hours under a nitrogen atmosphere. The mixture was cooled to room temperature. The insoluble precipitated polymer was filtered and washed with methanol and acetone. Further purification was carried out by Soxhlet extraction with tetrahydrofuran for 48 h. The product was dried in vacuum for 12 h at 60 °C to give PCP1-100%PDI.

**General procedure for the synthesis of PCP2-x%PDI by Sonogashira coupling reaction.** All the polymerization reactions were carried out with a constant monomer concentration and a fixed reaction condition (80 °C, 24 h). The molar ratio of diethynyl monomer ( $M_2$ ) and the tetrabromo monomers ( $M_3$  and  $M_4$ ) was fixed at 2.0/1.0. The mole ratio of monomers  $M_3$  and  $M_4$  was varied ( $0 < x\% < 1.0$ ). A representative experimental procedure for PCP1-100%PDI is given as an example.

**PCP2-100%PDI:** Monomer  $M_2$  (80.8 mg, 0.400 mmol), Monomer  $M_3$  (180.0 mg, 0.200 mmol), tetrakis(triphenylphosphine)-palladium(0) (17.5 mg, 0.015 mmol), and copper(I) iodide (5.5 mg, 0.030 mmol) were dissolved in a mixture of anhydrous toluene (6.6 mL) and  $\text{Et}_3\text{N}$  (3.3 mL). The reaction mixture was heated to 80 °C and stirred for 24 hours under a nitrogen atmosphere. The mixture was cooled to room temperature. The insoluble precipitated polymer was filtered and washed with methanol and acetone. Further purification was carried out by Soxhlet extraction with tetrahydrofuran for 48 h. The product was dried in vacuum for 12 h at 60 °C to give PCP2-100%PDI.

**General procedure for the synthesis of PCP3-x%bpy by Sonogashira coupling reaction.** All the polymerization reactions were carried out with a constant monomer concentration and a fixed reaction condition (80 °C, 24 h). The molar ratio of diethynyl monomer ( $M_1$  and  $M_2$ ) and the tetrabromo monomers ( $M_3$ ) was fixed at 2.0/1.0. The mole ratio of monomers  $M_1$  and  $M_2$  was varied ( $0 < x\% < 1.0$ ). A

representative experimental procedure for PCP3-100%bpy is given as an example.

**PCP3-100%bpy:** Monomer M<sub>2</sub> (80.8 mg, 0.400 mmol), Monomer M<sub>3</sub> (180.0 mg, 0.200 mmol), tetrakis(triphenylphosphine)-palladium(0) (17.5 mg, 0.015 mmol), and copper(I) iodide (5.5 mg, 0.030 mmol) were dissolved in a mixture of anhydrous toluene (6.6 mL) and Et<sub>3</sub>N (3.3 mL). The reaction mixture was heated to 80 °C and stirred for 24 hours under a nitrogen atmosphere. The mixture was cooled to room temperature. The insoluble precipitated polymer was filtered and washed with methanol and acetone. Further purification was carried out by Soxhlet extraction with tetrahydrofuran for 48 h. The product was dried in vacuum for 12 h at 60 °C to give PCP3-100%bpy.

**Photocatalytic hydrogen production:** In order to carry out the photocatalytic reaction in triethylamine/water solution, 3.5 mg of the PCP photocatalyst was suspended in a pre-degassed triethylamine/water mixture (3.5 mL, 2/8, v/v) and the vial was sealed and stirred vigorously in the dark for 12 h to furnish a uniform suspension. Then, the suspension was transferred into a home-made quartz cell (6.4 mL free volume), which was sealed with a gas-tight rubber cap. Nitrogen was bubbled for 3 min in the solution phase and 2 min in the gas phase inside the reactor to remove the oxygen. The reaction mixture was illuminated with a 150 W Xe light-source. Cooling fans were used to maintain the reaction temperature at room temperature. Gas samples were taken and analyzed by GC.

**Photocatalytic degradation of methylene blue (MB):** For MB degradation, 5.0 mg of PCP sample powders were suspended in 20 ml of MB methylene blue aqueous solution (50 µg/mL). The suspension was first kept in a dark condition for 60 min to minimize adsorption effect. The photoactivity of the photocatalyst was evaluated by monitoring the intensity of the strongest absorption peak of MB at 664 nm in the UV-vis spectra. The temperature during irradiation was controlled at room temperature by cooling fans to remove infrared radiation and heat. 0.5 ml aliquots were sampled and diluted at various time intervals. The solution was passed through a 0.45-µm PTFE filter before UV-vis measurement.

**Table 1. Relative molar ratio of monomers used in the copolymerization.**

PCPs	Relative molar ratio				PCPs	Relative molar ratio				PCPs	Relative molar ratio			
	M	M	M	M		M	M	M	M		M	M	M	M
PCP1-0%PDI	2.	0	<b>0</b>	1.	PCP2-0%PDI	0	2.	<b>0</b>	1.	PCP3-0%bpy <sup>a</sup>	2.	<b>0</b>	1.	0
PCP1-20%PDI	2.	0	<b>0.</b>	0.	PCP2-20%PDI	0	2.	<b>0.</b>	0.	PCP3-20%bpy	1.	<b>0.</b>	1.	0
PCP1-50%PDI	2.	0	<b>0.</b>	0.	PCP2-50%PDI	0	2.	<b>0.</b>	0.	PCP3-50%bpy	1.	<b>1.</b>	1.	0
PCP1-80%PDI	2.	0	<b>0.</b>	0.	PCP2-80%PDI	0	2.	<b>0.</b>	0.	PCP3-80%bpy	0.	<b>1.</b>	1.	0
PCP1-100%PD	2.	0	<b>1.</b>	0	PCP2-100%PD	0	2.	<b>1.</b>	0	PCP3-100%bp	0	<b>2.</b>	1.	0

<sup>a</sup> PCP1-100%PDI and PCP3-0%bpy represent the same sample.

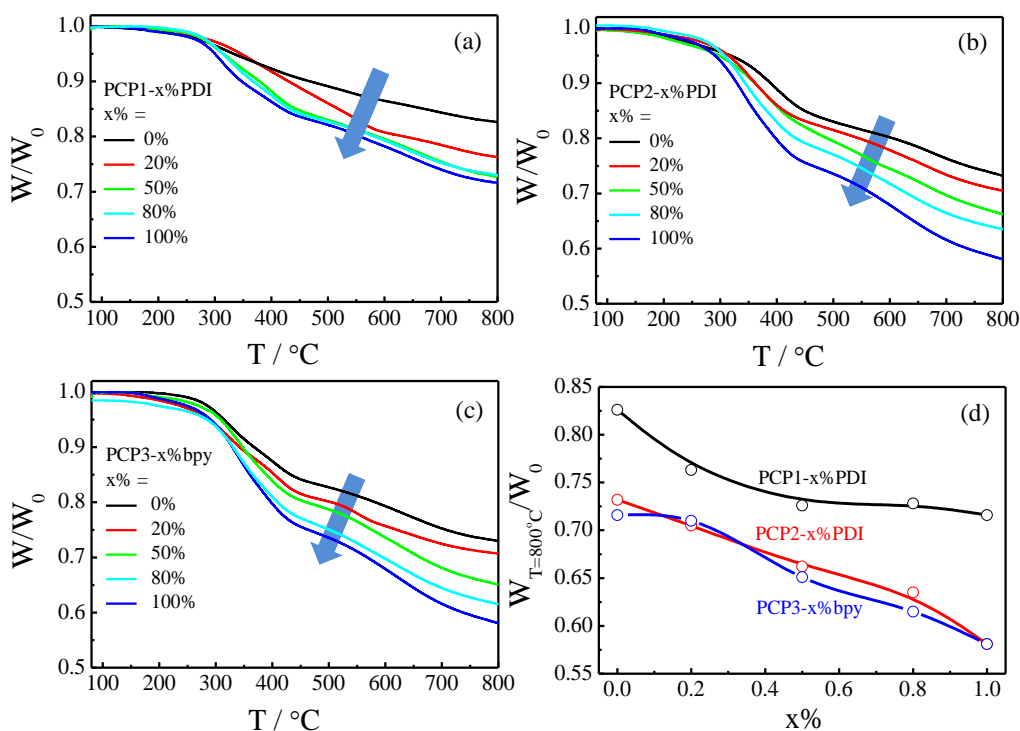
<sup>b</sup> PCP2-100%PDI and PCP3-100%bpy represent the same sample.

**Table S2. Elemental analysis results for the PCPs-0%PDI and PCPs-100%PDI.**

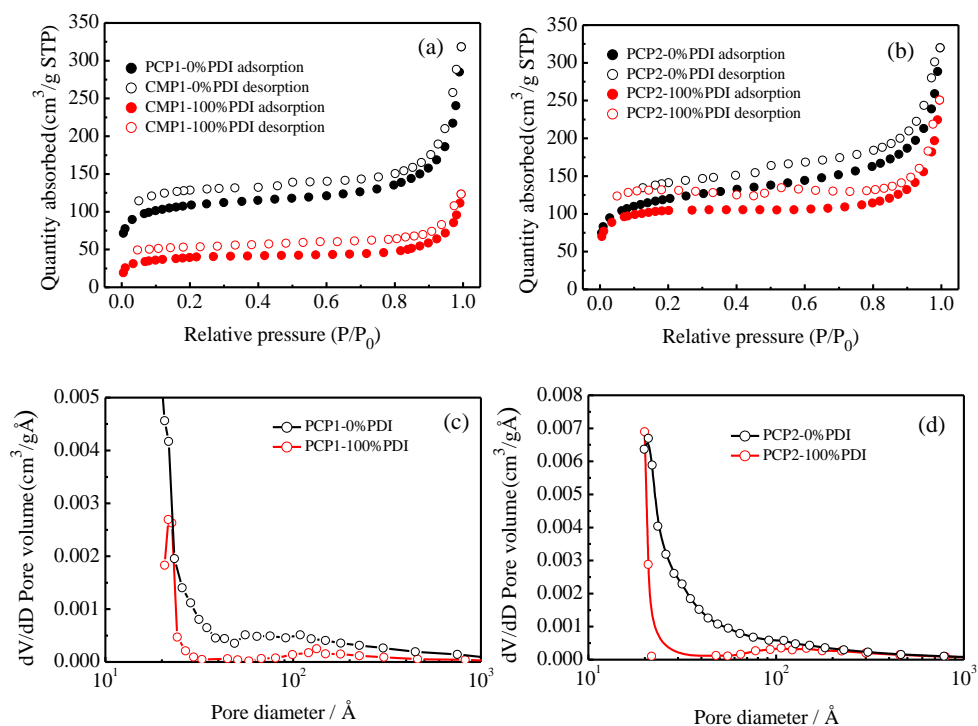
PCP	Chemical structure	Theoretical ratio			Experimental ratio		
		C	H	N	C	H	N
PCP1-0%PDI	C <sub>38</sub> H <sub>22</sub>	95.37	4.63	0	90.37	4.39	0
PCP1-100%PDI	C <sub>70</sub> H <sub>54</sub> N <sub>2</sub> O <sub>4</sub>	85.17	5.51	2.84	78.45	5.36	2.44
PCP2-0%PDI	C <sub>34</sub> H <sub>18</sub> N <sub>4</sub>	84.63	3.76	11.61	80.12	3.58	10.90
PCP2-100%PDI	C <sub>66</sub> H <sub>50</sub> N <sub>6</sub> O <sub>4</sub>	79.98	5.08	8.48	73.20	4.90	7.70

**Table S3. Physical and chemical properties and hydrogen production rates of the PCP photocatalysts.**

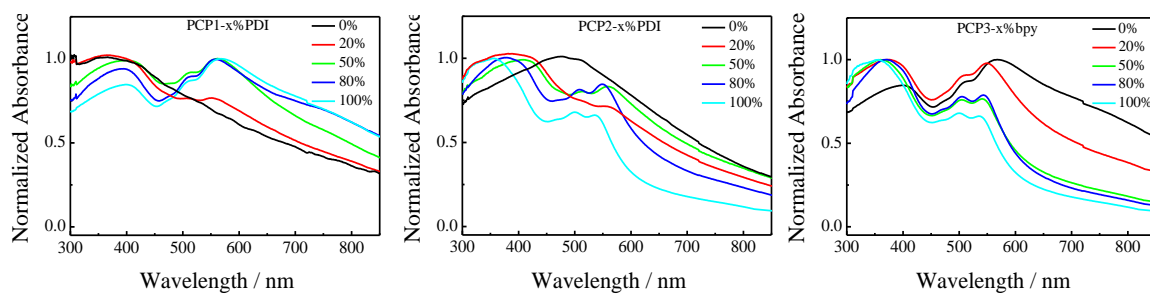
PCPs	Relative molar ratio				E <sub>g</sub> (eV)	Pd <sup>d</sup> (wt%)	Cu <sup>d</sup> (wt%)	H <sub>2</sub> (μmol/h)
	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>4</sub>				
PCP1-0%PDI	1.0	0	<b>0</b>	1.0	2.06	0.41	0.43	3.4
PCP1-20%PDI	1.0	0	<b>0.2</b>	0.8	1.91	0.23	0.23	2.4
PCP1-50%PDI	1.0	0	<b>0.5</b>	0.5	1.87	0.41	0.349	2.5
PCP1-80%PDI	1.0	0	<b>0.8</b>	0.2	1.55	0.32	0.12	2.3
PCP1-100%PDI	1.0	0	<b>1.0</b>	0	1.54	0.36	0.21	1.2
PCP2-0%PDI	0	1.0	<b>0</b>	1.0	2.25	0.19	1.12	2.7
PCP2-20%PDI	0	1.0	<b>0.2</b>	0.8	2.01	0.35	0.87	4.6
PCP2-50%PDI	0	1.0	<b>0.5</b>	0.5	1.97	0.32	0.72	6.9
PCP2-80%PDI	0	1.0	<b>0.8</b>	0.2	2.03	0.19	0.66	7.2
PCP2-100%PDI	0	1.0	<b>1.0</b>	0	2.05	0.25	0.57	7.6
PCP3-0%PDI	1.0	<b>0</b>	1.0	0	1.55	0.36	0.21	1.2
PCP3-20%PDI	0.8	<b>0.2</b>	1.0	0	1.94	0.42	0.29	3.9
PCP3-50%PDI	0.5	<b>0.5</b>	1.0	0	2.01	0.36	0.55	6.3
PCP3-80%PDI	0.2	<b>0.8</b>	1.0	0	2.01	0.23	0.65	6.4
PCP3-100%PDI	0	<b>1.0</b>	1.0	0	2.03	0.25	0.57	7.6



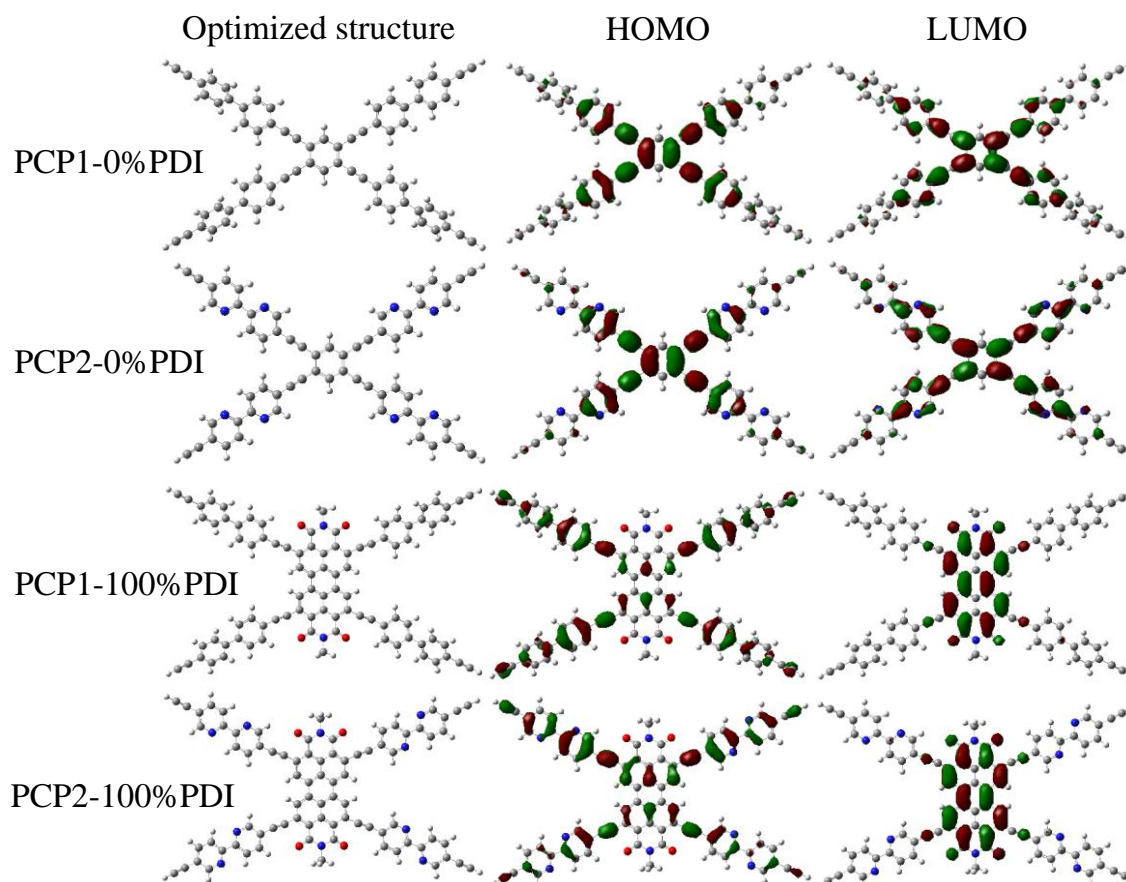
**Figure S1.** (a)-(c) TGA spectra of the PCPs in air. (d) Retention ratio of residual mass ( $W_{T=800^\circ\text{C}}$ ) and initial mass ( $W_0$ ) of PCP networks as a function of the monomer composition.



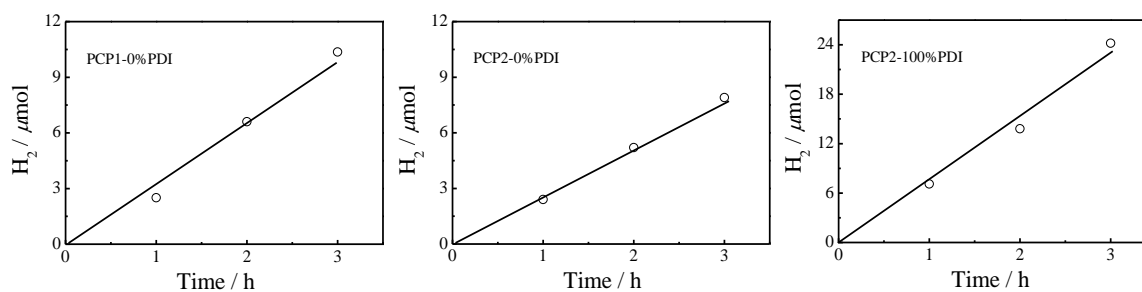
**Figure S2.** (a) and (b) Nitrogen sorption isotherms for PCP networks measured at 77.3 K from 0.005 to 1 bar. (c) and (d) Pore size distribution based on Barrett–Joyner–Halenda (BJH) adsorption mode.



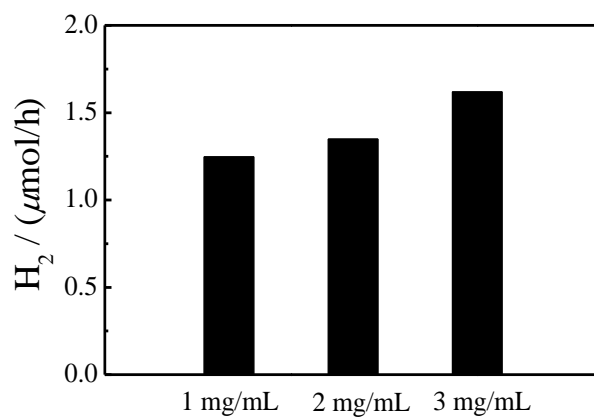
**Figure S3.** UV-Vis spectra of polymer networks in PEG-300 suspension.



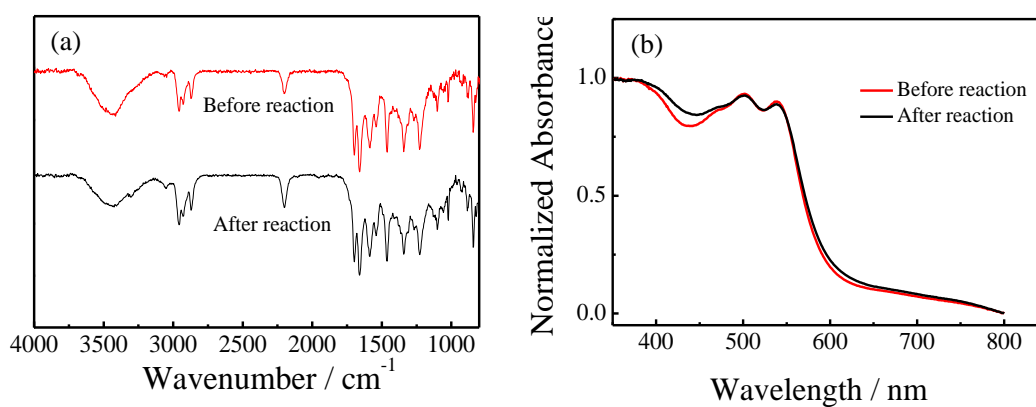
**Figure S4.** Molecular orbital diagrams of PCP1-x%PDI and PCP2-x%PDI networks.



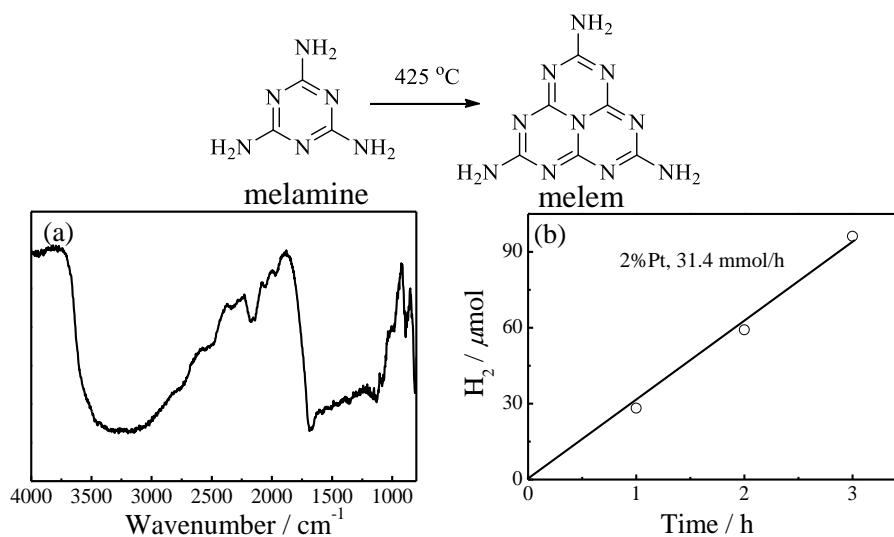
**Figure S5.** Time course of  $H_2$  production from water for PCP1-0%PDI, PCP2-0%PDI and PCP2-100%PDI under-arc illumination.



**Figure S6.** Photocatalyst concentration dependent hydrogen production rate by using PCP1-100%PDI as photocatalyst.

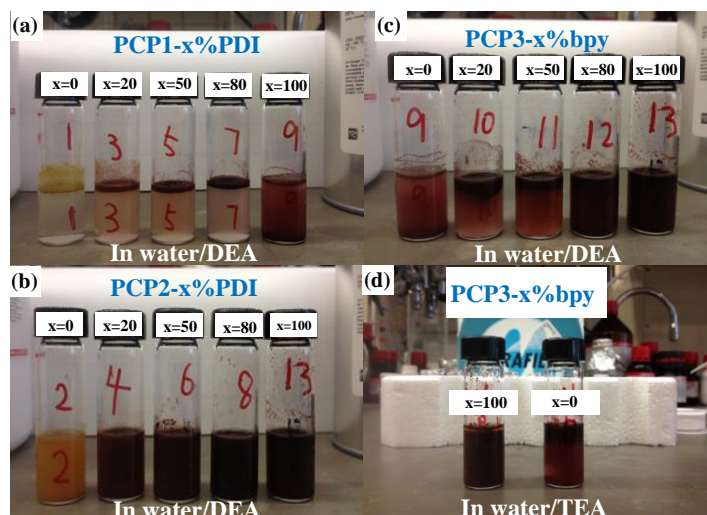


**Figure S7.** (a) FTIR spectra and (b) UV-vis spectra of PCP2-100%PDI photocatalyst before and after reaction.

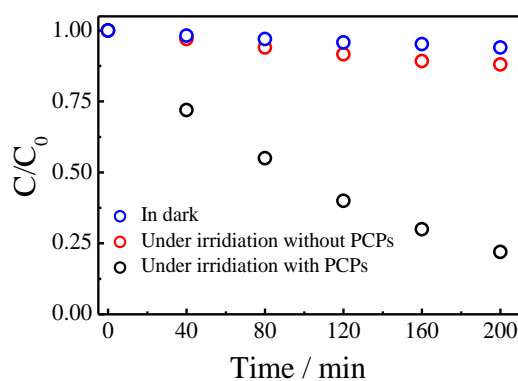


**Figure S8.** (a) FTIR spectrum of the prepared melem. (b) Time course of H<sub>2</sub> production from water for melem loaded with 2%wt of Pt cocatalyst under-arc illumination.

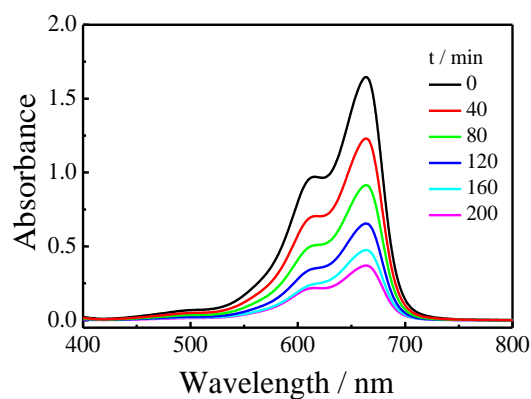




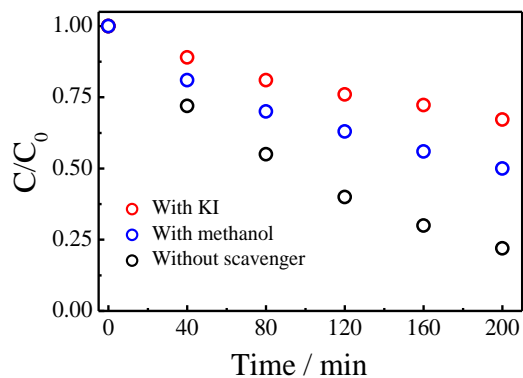
**Figure S9.** Photographs of (a) PCP1-x%PDI, (b) PCP2-x%PDI and (c) PCP3-x%bpy in water/DEA (8/2, v/v) solution after stopping stirring for 30 min. (d) Photographs of PCP3-x%bpy in water/TEA solution after stopping stirring for 30 min.



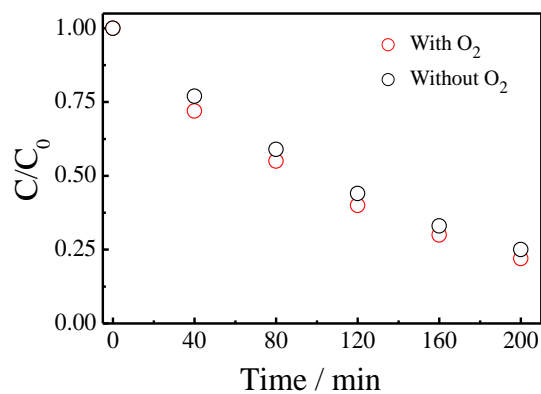
**Figure S10.** Reaction-time dependence of retention concentration ( $C/C_0$ ) of methylene blue under different conditions.



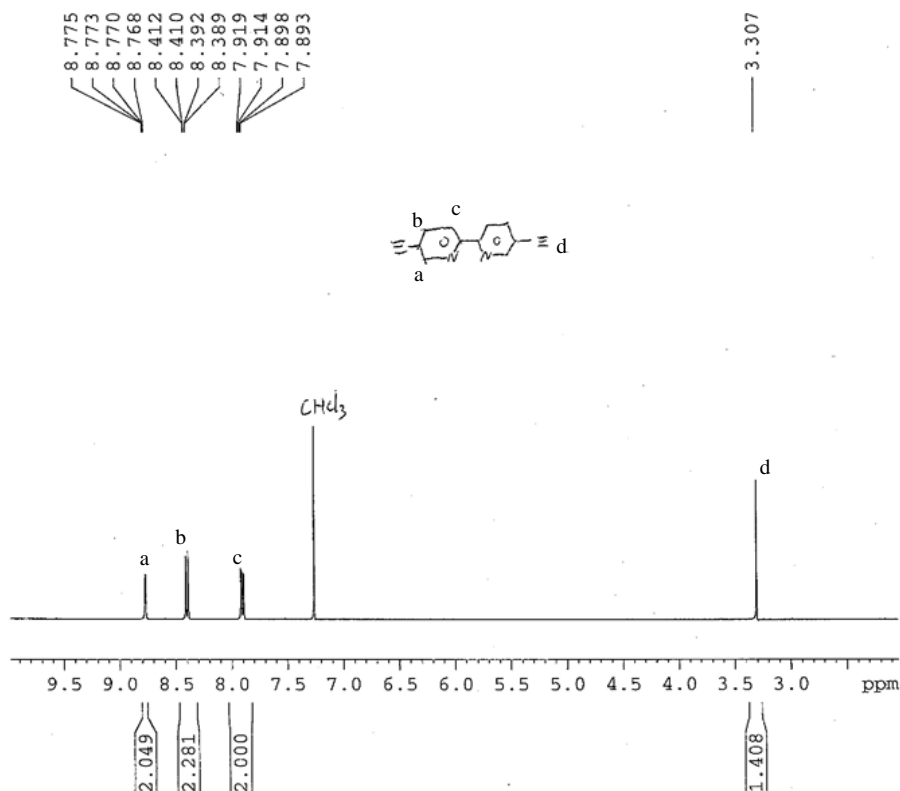
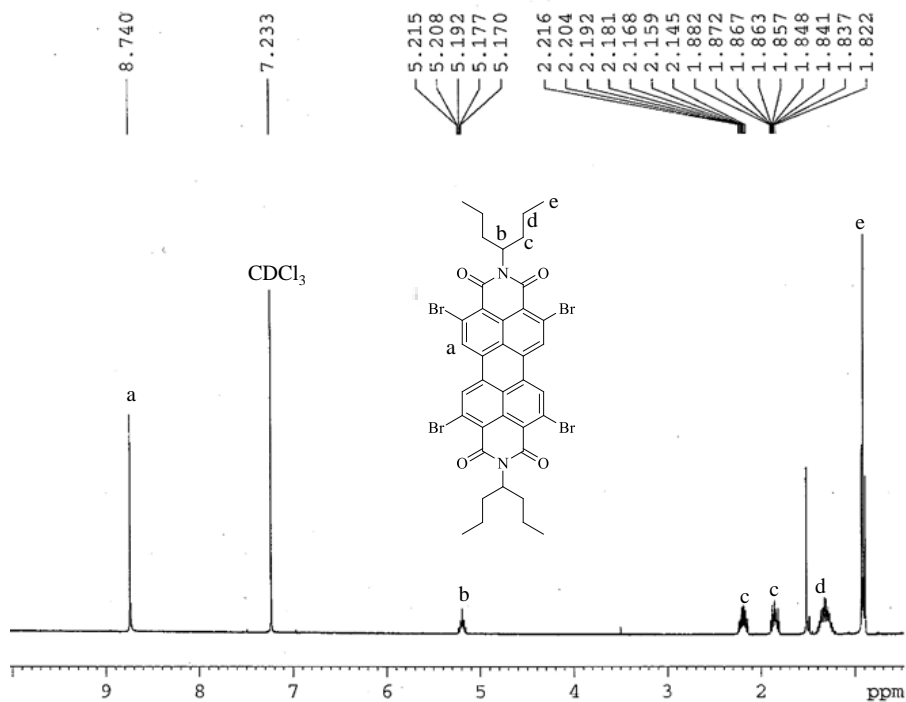
**Figure S11.** UV-vis spectra of methylene blue in reaction solution as a function of reaction time, where PCP2-100%PDI was used as photocatalyst.

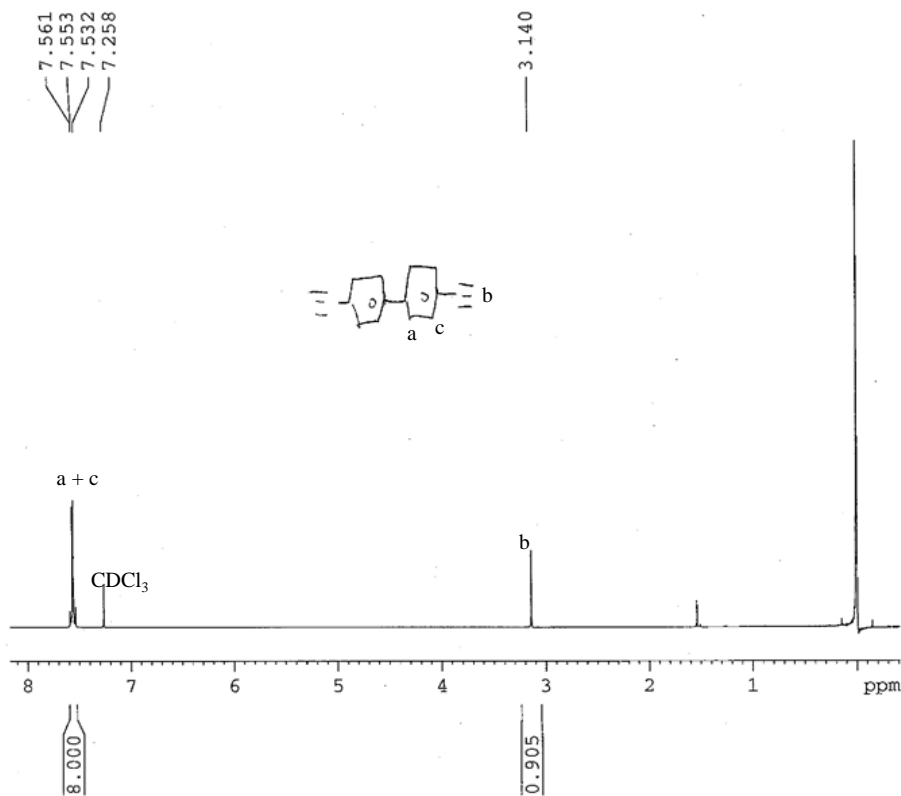


**Figure S12.** Reaction-time dependence of retention concentration ( $C/C_0$ ) of methylene blue in different reaction solution, where PCP2-100%PDI was used as photocatalyst. [methanol] = 5% (vol/vol), [KI] = 50 mg/mL.



**Figure S13.** Reaction-time dependence of retention concentration ( $C/C_0$ ) of methylene blue in solutions with and without oxygen.

Supplementary <sup>1</sup>H-NMR spectra



Current Data Parameters  
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EXPNO 1  
PROCNO 1

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F2 - Processing parameters  
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WDW EM  
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LB 0.00 Hz  
GB 0  
PC 1.00

**Supplementary References.**

1. Gerstel P; Klumpp S; Hennrich F; Poschlad A; Meded V; Blasco E; Wenzel W; Kappes MM; Barner-Kowollik C *ACS Macro Letters* **2014**, *3*, 10.
2. Kokil A; Yao P; Weder C *Macromolecules* **2005**, *38*, 3800.
3. Battagliarin G; Zhao Y; Li C; Müllen K *Organic Letters* **2011**, *13*, 3399.
4. Chu S; Wang C; Feng J; Wang Y; Zou Z *International Journal of Hydrogen Energy* **2014**, *39*, 13519.