Supporting Information

Significant improvement of photocatalytic hydrogen evolution of diketopyrrolopyrrole-based donor-acceptor conjugated polymers through side-chain engineering

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Experimental Section

The synthesis of diketopyrrolopyrrole (DPP)

Firstly, the Sodium particles (4.0 g, 173.9 mmol) were added into 100 mL 2-methyl-2-butanol at 40 °C, and then warmed to 90 °C stirring until Sodium disappeared. After cooling down to 60 °C, 4-bromocyanobenzene was added into the solution under argon. Diisopropyl succinate was dissolved into 2-methyl-2-butanol, and dropwise added to the mixture. Subsequently, the solution was warmed to 90 °C and stirred for 12 h. Finally, the solution was cooled to room temperature, and poured into 200 mL methyl alcohol stirring intensely. PH was adjusted with hydrochloric acid, and color changed to bright red. The mixture was collected by filtration and dried at 45 °C in vacuum oven. Yield (15153 mg, 79 %).

The synthesis of DPP-C4

The preparation of monomer DPP-C4 was showed below. DPP (1.784 g, 4 mmol) and 20 mL N, N-dimethylformamide were added in flask, and then stirred for 1 h at indoor temperature. n-iodobutane (736 mg, 4 mmol) was added dropwise into the solution. The solution was heat to 100 °C and stirring overnight under Nitrogen. After cooling down to indoor temperature, the product was extracted from mixture with dichloromethane, and then DPP-C4 separated out by column chromatography. Yield (669 mg, 30 %). 1H NMR (400 MHz, Chloroform-d) δ 7.69 (d, J = 5.3 Hz, 8H), 3.76 -
3.71 (m, 4H), 1.26 (d, J = 7.4 Hz, 8H), 0.85 (t, J = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 162.45, 147.44, 132.25, 130.09, 126.93, 125.82, 109.94, 41.68, 31.54, 19.97, 13.60. HRMS (ESI-MS) m/z calcd. For C$_{34}$H$_{42}$N$_{2}$O$_{2}$Br$_{2}$: 579.0259. [M + H$^+$].

The synthesis of DPP-C8

The preparation of monomer DPP-C8 was showed below. DPP (1.784 g, 4 mmol) and 20 mL N, N-dimethylformamide were added in flask, and then stirred for 1 h at indoor temperature. 1-bromohexane (2.6 g, 10 mmol) was added dropwise into the solution. The solution was heat to 100 °C and stirring 12 h under Nitrogen. The product was extracted from mixture with dichloromethane, and then DPP-C8 separated out by column chromatography. Yield (759 mg, 28 %). $^{1}$H NMR (400 MHz, Chloroform-d) δ 7.68 (d, J = 1.9 Hz, 8H), 3.75 - 3.69 (m, 4H), 1.20 (s, 20H), 0.91 - 0.80 (m, 10H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 162.40, 147.43, 132.22, 130.09, 126.93, 125.81, 109.90, 41.84, 31.72, 29.39, 29.09, 28.98, 26.67, 22.61, 14.10. HRMS (ESI-MS) m/z calcd. For C$_{34}$H$_{42}$N$_{2}$O$_{2}$Br$_{2}$: 691.1511. [M + H$^+$]. Found: 691.1517.

The synthesis of DPP-O4

The preparation of monomer DPP-O4 was showed below. 2-methoxyethan-1-ol
(3.80 g, 50 mmol), Triethanolamine (5.5 g, mmol) and 50 mL dichloromethane were added in 250 mL three-necked flask at 0 °C. 4-toluene sulfonyl chloride was dissolved in 30 mL DCM, and then added into the solution drop by drop. The solution kept stirring for 30 min at 0 °C, and then stirring at room temperature overnight. The organic phase was extracted with dichloromethane/water and the mixture was purified by column chromatography on silica.

Diketopyrrolopyrrole (1.78 g, 4 mmol) and 20 mL N, N-dimethylformamide were added in flask, and then stirred for 1 h at indoor temperature. 2-methoxyethyl-4-methylbenzenesulfonate (2.30 g, 10 mmol) was added dropwise into the solution. The solution was heat to 100 °C and stirring for 12 h under Nitrogen. The product was extracted from mixture with dichloromethane, and then DPP-O4 separated out by column chromatography. Yield (562 mg, 25 %). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.89 (d, \(J = 8.6\) Hz, 4H), 7.68 - 7.64 (m, 4H), 3.89 (t, \(J = 5.4\) Hz, 4H), 3.64 (t, \(J = 5.3\) Hz, 4H), 3.28 (s, 6H). \(^13\)C NMR (101 MHz, Chloroform-d) \(\delta\) 162.77, 148.13, 132.17, 130.82, 126.74, 125.94, 109.75, 70.18, 58.98, 42.20. HRMS (ESI-MS) m/z calcd. For C\(_{34}\)H\(_{42}\)N\(_2\)O\(_2\)Br\(_2\): 582.9844. [M + H\(^+\)]. Found: 582.9846.

The synthesis of DPP-O8

The preparation of monomer DPP-O8 was showed below. 2-(2-ethoxyethoxy)ethan-1-ol (6.0 g, 50 mmol), Triethanolamine (5.5 g, mmol) and 50 mL DCM were added in 250 mL three-necked flask at 0 °C. 4-toluene sulfonyl chloride was dissolved in 30 mL DCM, and then added into the solution drop by drop. The solution kept stirring for 30 min at 0 °C. Next, the solution was stirred overnight. The organic phase was extracted with dichloromethane/water and the mixture was purified by
column chromatography on silica.

DPP (1.784 g, 4 mmol) and 20 mL N, N-dimethylformamide were added in flask, and then stirred for 1 h at indoor temperature. 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (2.6 g, 10 mmol) was added dropwise into the solution. The solution was heat to 100 °C and stirring 12 h under Nitrogen. After cooling down to indoor temperature, the product was extracted from mixture with dichloromethane, and then DPP-O8 separated out by column chromatography. Yield (678 mg, 25 %).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.92 (dd, $J = 8.8, 2.4$ Hz, 4H), 7.64 (s, 4H), 3.94 (dt, $J = 27.6, 5.3$ Hz, 4H), 3.78 (dt, $J = 19.8, 5.3$ Hz, 4H), 3.58 - 3.53 (m, 4H), 3.53 - 3.49 (m, 4H), 3.46 (t, $J = 7.0$ Hz, 4H), 1.18 (td, $J = 7.0, 3.0$ Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 162.78 , 148.22 , 132.09 , 130.95 , 126.76 , 125.89 , 109.73 , 70.68 , 69.68 , 68.86 , 66.69 , 42.35 , 15.17 . HRMS (ESI-MS) m/z calcd. For C$_{30}$H$_{34}$N$_2$O$_6$Br$_2$: 699.0681. [M + H$^+$]. Found: 699.0691.

Characterization

$^1$H and $^{13}$C NMR spectra were obtained in deuterated solvents on Bruker AM-400 MHz using tetramethylsilane (TMS) as an internal standard. High-resolution mass spectra (HRMS) measurements were performed using a Waters LCT Premier XE spectrometer. UV-vis diffuse reflectance absorption spectra (DRS) were recorded at room temperature on a Varian Cary 500 spectrophotometer. Photoluminescence (PL) spectrum was obtained on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Time-resolved fluorescence spectra (TRFS) were obtained on an Edinburgh FES 920 with an excitation wavelength of 377 nm and emission wavelength as detection wavelength. The FTIR spectra were recorded on NICOLET 380 spectrometer using a standard KBr pellet technique in the frequency range of 4000 - 400 cm$^{-1}$. Powder XRD patterns was obtained on a RigakuD/MAX 2550 diffract meter (Cu K radiation, $\lambda = 1.5406$ Å), operated at 40 kV and 100 mA. The morphologies were characterized by Scanning Electron Microscope (SEM). Thermal gravimetric analysis (TGA) was conducted on a thermal analysis instrument (WRT-3P) under a nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. Dynamic light scattering (DLS)
was conducted on Malvern ZETASIZER (ZSE). The residual palladium of polymers have been detected by ICP-OES (Varian 710 ES). Molecular weight of polymers were measured via Gel Permeation Chromatography (THF/ Waters1515).

**Photoelectrochemical measurement**

Cyclic voltammetry (CV) curves were measured by a CHI650E electrochemical workstation in a normal three-electrode cell which using glassy carbon as the working electrode, Pt wire as counter electrode and Ag/AgCl electrode as the reference electrode. The experiments were carried out in DCM solutions with 0.1 m tetra-n-butylammonium hexafluorophosphate (TBAPF 6) as the supporting electrolyte at a scan rate of 100 mV s$^{-1}$. The ferrocenium/ferrocene (Fc/Fc$^+$) redox couple was used as an external potential reference. Fc/Fc$^+$ redox potential (0.41 V vs Ag/AgCl in the present study) was measured at the end of each experiment in order to calibrate the pseudo reference electrode. The HOMO levels were determined as follows: HOMO (eV) = $-4.8 - (E_{ox\_onset} - 0.41)$. The LUMO levels were then calculated from the equation of LUMO = HOMO + $E_g$. The transient photocurrent responses (I–t) and electrochemical impedance spectra (EIS) of composite photocatalyst samples were investigated on a CHI650E electrochemical workstation with a three-electrode (glassy carbon electrode, Pt wire, and Ag/AgCl as working, counter, and reference electrode, respectively) system. An aqueous solution of 0.5 M Na$_2$SO$_4$ was used as the supporting electrolyte and a 350 W Xe-lamp served as the light source. The films electrodes were prepared as follows: 25 mg of the as-synthesized photocatalysts was separately ground with 10 µL of a Nafion (5%) aqueous solution and 50 µL of ethanol to make slurry. The slurry was then coated onto FTO glass electrodes with an active area of 0.25 cm$^2$, and these electrolytes were dried at 120 °C for 1 h to evaporate the solvent in muffle furnace. The photocurrent intensity of as-prepared electrodes was measured at 0 V versus Ag/AgCl with the light on and off. EIS was determined over the frequency range of $10^2$–$10^6$ Hz with an ac amplitude of 10 mV at the open circuit voltage under room-light illumination.

**Measurement of photocatalytic activity and AQY**

The photocatalyst (25mg) was dispersed in the mixture of deionized
water/methanol (3:1). 240 μl H\textsubscript{2}PtCl\textsubscript{6}·6H\textsubscript{2}O aqueous solution (10 g/L) was dropped into the solution. After 5 hour of light, 3% Pt loaded photocatalyst was obtained by centrifugation and dried on under vacuum. Then 3% Pt loaded photocatalyst (25mg) was dispersed in the solution of deionized water (50 mL) and TEOA (10 mL). The mixture was stirring in a glass gas-closed-circulation system (CEL-SPH2N) under illumination with 300 W xenon lamp (CEL-HXF 300). The yield of hydrogen was detected by an online gas chromatograph (GC 2060 and TCD detector), and argon was used as the carrier gas.

In addition, a 300 W xenon lamp with monochromatic light (λ = 420 nm, 450 nm, 475 nm, 500 nm, 550 nm, 578 nm, 600 nm and 630 nm) was used as the light source. AQY for hydrogen evolution was calculated according to the following equation:

\[
\text{AQY (\%) } = \frac{2 \times \text{Number of evolved H}_2 \text{ molecules}}{\text{Number of incident photons}} \times 100 \% = \frac{2 \times C \times \mathcal{N}_A}{S \times P \times t \times \frac{\lambda}{h \times c}} \times 100 \%
\]

where, \(C\) is the hydrogen evolution amount (μmol) per hour; \(\mathcal{N}_A\) is the Avogadro constant \((6.022 \times 10^{23} \text{ mol}^{-1})\); \(S\) is the illumination area \((12.56 \text{ cm}^2)\); \(P\) is the light intensity \((20.62 \text{ W cm}^{-2})\); \(t\) is the illumination time \((3600 \text{ s})\); \(\lambda\) is the wavelength of the monochromatic light \((\text{m})\); \(h\) is the Plank constant \((6.626 \times 10^{-34} \text{ J s})\); \(c\) is the speed of light \((3 \times 10^8 \text{ m s}^{-1})\).
Fig. S1. TGA curves of PDPP3B-C4, PDPP3B-C8, PDPP3B-O4 and PDPP3B-O8.

Fig. S2. Cyclic voltammetry measurements of Fe/Fe⁺.
Fig. S3. FT-IR of PDPP3B-C4, PDPP3B-C8, PDPP3B-O4 and PDPP3B-O8 after reaction.

Fig. S4. XRD of PDPP3B-C4, PDPP3B-C8, PDPP3B-O4 and PDPP3B-O8 after reaction.
**Fig. S5.** DRS of PDPP3B-C4, PDPP3B-C8, PDPP3B-O4 and PDPP3B-O8 after reaction.

**Fig. S6.** The apparent quantum yields (AQY) of PDPP3B-C4 and PDPP3B-O8.
Fig. S7. Hydrogen generation of PDPP3B-O4 produced from different batches with 1 wt % Pt under visible light ($\lambda > 400$ nm).

Fig. S8. The control experiment of PDPP3B-C4, PDPP3B-C8, PDPP3B-O4 and PDPP3B-O8.
Fig. S9. The absorption spectrum and fluorescence spectra of PDPP3B-C4, PDPP3B-C8, PDPP3B-O4 and PDPP3B-O8 in DCM solution.

Fig. S10. The images of PDPP3B-C4, PDPP3B-C8, PDPP3B-O4 and PDPP3B-O8 dispersing in solution (water/TEOA/MeOH=5:1:1).

\[
D^{[3,2]} = \frac{\sum_{1}^{n} D_{iv_i}^3}{\sum_{1}^{n} D_{iv_i}^2}
\]

Sauter mean diameter, D[3,2], gives the diameter of a sphere that has the same volume : surface area ratio as the entire distribution.
Table S1. Recent representative photocatalytic H\textsubscript{2} evolution activities of D-A conjugated polymer-based photocatalysts.

<table>
<thead>
<tr>
<th>Materials</th>
<th>light source</th>
<th>Cocatalyst</th>
<th>H\textsubscript{2} Production (mmol g\textsuperscript{-1} h\textsuperscript{-1})</th>
<th>AQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COP-TP\textsubscript{3:1}</td>
<td>&gt; 400 nm</td>
<td>3 wt% Pt</td>
<td>4.2</td>
<td>1.5 (400 nm)</td>
</tr>
<tr>
<td>DBTD-CMP1\textsuperscript{2}</td>
<td>&gt; 420 nm</td>
<td>3 wt% Pt</td>
<td>4.6</td>
<td>3.3 (400 nm)</td>
</tr>
<tr>
<td>B-BT-1,4\textsuperscript{3}</td>
<td>&gt; 420 nm</td>
<td>3 wt% Pt</td>
<td>0.116</td>
<td>4.01 (420 nm)</td>
</tr>
<tr>
<td>SNP-BTT1\textsuperscript{4}</td>
<td>&gt; 395 nm</td>
<td>3 wt% Pt</td>
<td>0.632</td>
<td>4.5 (420 nm)</td>
</tr>
<tr>
<td>PyBT-2\textsuperscript{5}</td>
<td>&gt; 420 nm</td>
<td>3 wt% Pt</td>
<td>0.03</td>
<td>unknown</td>
</tr>
<tr>
<td>PyDOBT-2\textsuperscript{6}</td>
<td>&gt; 420 nm</td>
<td>3 wt% Pt</td>
<td>8.523</td>
<td>6.1 (400 nm)</td>
</tr>
<tr>
<td>SP-CMP\textsuperscript{7}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>0.12</td>
<td>0.23 (420 nm)</td>
</tr>
<tr>
<td>F\textsubscript{0.5} CMP\textsuperscript{8}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>0.659</td>
<td>5.8 (400 nm)</td>
</tr>
<tr>
<td>S-CMP\textsuperscript{9}</td>
<td>&gt; 420 nm</td>
<td>2.1 wt% Pt</td>
<td>3.1</td>
<td>13.2 (420 nm)</td>
</tr>
<tr>
<td>HMP-3 _2:3\textsuperscript{10}</td>
<td>&gt; 395 nm</td>
<td>5 wt% Pt</td>
<td>1.6</td>
<td>unknown</td>
</tr>
<tr>
<td>CP-CMP10\textsuperscript{11}</td>
<td>&gt; 420 nm</td>
<td>3 wt% Pt</td>
<td>0.174</td>
<td>unknown</td>
</tr>
<tr>
<td>L-PyBT\textsuperscript{12}</td>
<td>&gt; 420 nm</td>
<td>3 wt% Pt</td>
<td>1.674</td>
<td>unknown</td>
</tr>
<tr>
<td>B-FOBT-1,4-E\textsuperscript{13}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>13.2</td>
<td>5.7 (420 nm)</td>
</tr>
<tr>
<td>P8-i\textsuperscript{14}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>0.86</td>
<td>0.56 (420 nm)</td>
</tr>
<tr>
<td>P7\textsuperscript{15}</td>
<td>&gt; 420 nm</td>
<td>3 wt% Pt</td>
<td>3.68</td>
<td>2.3 (420 nm)</td>
</tr>
<tr>
<td>P28\textsuperscript{16}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>0.96</td>
<td>6.7 (420 nm)</td>
</tr>
<tr>
<td>P12\textsuperscript{17}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>0.42</td>
<td>1.4 (420 nm)</td>
</tr>
<tr>
<td>P7-E\textsuperscript{18}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>5.963</td>
<td>4.2 (420 nm)</td>
</tr>
<tr>
<td>P10\textsuperscript{19}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>3.26</td>
<td>11.6 (420 nm)</td>
</tr>
<tr>
<td>FSO-FS\textsuperscript{20}</td>
<td>&gt; 420 nm</td>
<td>no Pt</td>
<td>3.4</td>
<td>6.8 (420 nm)</td>
</tr>
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</table>
Flu-SO_{21} > 420 \text{ nm} \quad \text{no Pt} \quad 5.04 \quad 2.13 (420 \text{ nm})

Fig. S11. $^1H$ NMR spectrum of DPP-C4 in CDCl$_3$. 

S14
Fig. S12. $^1$H NMR spectrum of DPP-C8 in CDCl$_3$.

![Fig. S12](image1)

Fig. S13. $^1$H NMR spectrum of DPP-O4 in CDCl$_3$.

![Fig. S13](image2)

Fig. S14. $^1$H NMR spectrum of DPP-O8 in CDCl$_3$.

![Fig. S14](image3)
Fig. S15. $^{13}$C NMR spectrum of DPP-C4 in CDCl$_3$.

Fig. S16. $^{13}$C NMR spectrum of DPP-C8 in CDCl$_3$. 
Fig. S17. $^{13}$C NMR spectrum of DPP-O4 in CDCl$_3$.

Fig. S18. $^{13}$C NMR spectrum of DPP-O8 in CDCl$_3$. 
Fig. S19. $^1$H NMR spectrum of PDPP3B-C4 in CDCl$_3$.

Fig. S20. $^1$H NMR spectrum of PDPP3D-C8 in CDCl$_3$. 
Fig. S21. $^1$H NMR spectrum of PDPP3B-O4 in CDCl$_3$.

Fig. S22. $^1$H NMR spectrum of PDPP3B-O8 in CDCl$_3$. 
Reference


(9) Sprick, R. S.; Bai, Y.; Guilbert, A. A. Y.; Zbiri, M.; Aitchison, C. M.; Wilbraham,


(17) Sprick, R. S.; Aitchison, Catherine M.; Berardo, E.; Turcani, L.; Wilbraham, L.;


