**Supporting Information**

Substituent regulation Improves photocatalytic hydrogen evolution of conjugated polyelectrolytes

Yichen Wu, Xi Zhang, Yetong Xing, Zhicheng Hu,* Haoran Tang, Wei Luo, Fei Huang,* Yong Cao
State Key Laboratory of Luminescent Materials and Devices, Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China
*Email: msfhuang@scut.edu.cn (F.H.); zchu@scici.cn (Z.H.).

Experiment Section

**Scheme S1** Synthetic Route for the Monomers and polymers. Reagents and conditions: (a) (Ph₃P)₂PdCl₂, Cul, trimethylsilylacetylene, chlorobenzene, trimethylamine, 6h, Ar, 70°C; (b) KOH, THF, MeOH, H₂O, 1h, Ar; (c) diethylamine, DMF, reflux, 12h, Ar; (d) Pd(PPh₃)₄, Cul, toluene, triethylamine, Ar, 70 °C, 24 h; (e) bromoethane, tetrahydrofuran, 50°C, 5 days.

Monomer FEN was synthesized according to the reported reference.¹

**Preparation of conjugated polymers:**
**PF-Ph:** FEN (105 mg, 0.2 mmol) and 1,4-diiodobenzene (66.0 mg, 0.2 mmol) were dissolved in a mixture of 4 mL of anhydrous chlorobenzene and 1 mL of anhydrous trimethylamine under the protection of argon. The mixture was deoxygenated with argon for 20 min before 2 mg of Pd(PPh₃)₄ and 1 mg of CuI were added. Then, the mixture was heated to 70°C with vigorous stirring overnight in argon atmosphere. After cooling to room temperature, the reaction mixture was poured into 200 mL of methanol. The precipitated material was obtained by filtration. Then, the polymer was redissolved in chloroform, precipitated in methanol and the process was repeated for several times. After dried in a vacuum oven overnight, PF-Ph was given as a light yellow solid (105 mg, 88%).

**1H-NMR** (500 M, CDCl₃, δ ppm): 7.78-7.48 (m, 10H), 3.25-2.85 (m, 16H), 1.42-1.19 (m, 18H), 0.51-0.44 (m, 10H). Mn = 22.0 kDa, Đ = 2.66. **13C NMR** (126 MHz, CDCl₃, δ ppm) 150.05, 139.85, 136.54, 132.04, 130.53, 129.84, 124.95, 122.12, 120.82, 119.09, 91.38, 88.63, 87.89, 54.22, 51.81, 45.84, 28.84, 26.28, 25.64, 22.66. Anal. calcd for C₄₃H₅₆N₂: C 85.94, H 9.39, N 4.66; found: C 84.64, H 10.42, N 4.43.

**PF-PhF:** PF-PhF was synthesized using the same method with that of PF-Ph. PF-PhF was obtained as a yellow solid (97 mg, 77%).

**1H-NMR** (500 M, d₆-DMSO, δ ppm): 8.47-6.91 (m, 8H), 3.19-2.75 (m, 16H), 1.48-0.42 (m, 28H). Mn = 16.6 kDa, Đ = 1.72. **13C NMR** (126 MHz, d₆-DMSO, δ ppm) 151.23, 140.72, 134.08, 132.15, 129.88, 128.62, 121.38, 116.97, 111.53, 103.18, 89.36, 85.47, 68.86, 53.27, 46.89, 29.90, 28.43, 26.76, 22.88. Anal. calcd for C₄₅H₅₈F₂N₂: C 81.28, H 8.79, F 5.71, N 4.21; found: C 79.63, H 9.61, N 5.98.

**PF-PhCN:** PF-PhCN was synthesized using the same method with that of PF-Ph. PF-PhCN was obtained as an orange solid (110 mg, 85%).

**1H-NMR** (500 M, CDCl₃, δ ppm): 8.02-7.92 (m, 2H), 7.82-7.49 (m, 6H), 2.90-2.23 (m, 12H), 1.44-0.33 (m, 8H). GPC (CHCl₃): Mn = 20.7 kDa, Đ = 2.88. **13C NMR** (126 MHz, CDCl₃, δ ppm) 151.50, 142.02, 135.92, 131.85, 129.75, 128.61, 126.43, 120.71, 118.74, 115.75, 101.37, 84.90, 83.94, 65.58, 52.67, 46.78, 40.14, 29.78, 27.27, 26.52, 23.74. Anal. calcd for C₄₅H₅₄N₄: C 83.03, H 8.36, N 8.61; found: C 82.29, H 9.69, N 9.06.

**PFBr-Ph:** To a solution of PF-Ph (100 mg, 0.17 mmol) in 20 mL of chloroform and 1 mL of DMF, 2 mL of bromoethane was added, and the reaction mixture was stirred at 50 °C. 2 mL of methanol was added every 12 hours. After stirred at 50 °C for 5 days, the reaction was evaporated under reduced pressure and precipitated into ethyl acetate. The polymer was collected, re-dissolved in methanol, and precipitated in ethyl acetate two more times. After dried in a vacuum oven overnight, PFBr-Ph was obtained as a yellow solid (119 mg, 86%).

**1H-NMR** (500 M, d₆-DMSO, δ ppm): 8.22-7.50 (m, 10H), 3.10-2.80 (m, 12H), 2.58-2.52 (m, 14H). Mn = 34.7 kDa, Đ = 1.82. **13C NMR** (126 MHz, d₆-DMSO, δ ppm) 151.26, 138.18, 133.61, 132.25, 56.31, 55.48, 52.44, 50.99, 46.61, 31.53, 30.50, 28.98, 26.12, 23.15, 21.17, 8.90. Anal. calcd for C₄₇H₆₆Br₂N₂: C 68.94, H 8.12, Br 19.52, N 3.42; found: C 67.98, H 9.61, N 3.71.

**PFBr-PhF:** PFBr-PhF was synthesized using the same method with that of PFBr-Ph. PFBr-PhF was obtained as a yellow solid (116 mg, 85%).

**1H-NMR** (500 M, d₆-DMSO, δ ppm): 8.48-6.97 (m, 8H), 3.24-2.52 (m, 26H). Mn = 35.7 kDa, Đ = 1.82. **13C NMR** (126 MHz, d₆-DMSO, δ ppm) 154.39, 150.77, 125.43, 118.41, 104.25, 60.27, 55.53, 21.22, 49.01, 46.66, 32.58, 31.54, 30.51, 28.44, 25.39, 21.30, 18.08, 14.56, 8.90. Anal. calcd for C₄₉H₆₈Br₂F₂N₂: C 66.66, H 7.76, Br 18.10, F 4.30, N 3.17;
PFBr-PhCN: PFBr-PhCN was synthesized using the same method with that of PFBr-Ph. PFBr-PhCN was obtained as a dark yellow solid (117 mg, 90%). H-NMR (500 M, d_6-DMSO, δ ppm): 8.68-7.55 (m, 8H), 3.22-2.83 (m, 12H), 2.62-2.52 (m, 14H), 1.57-0.33 (m, 28H). C NMR (126 MHz, d_6-DMSO, δ ppm): 152.39, 151.87, 144.95, 126.75, 118.47, 116.45, 56.35, 52.53, 51.00, 46.74, 30.57, 28.50, 25.71, 23.199, 21.12, 18.14. Anal. calcd for C49H64Br2N4: C 67.73, H 7.42, Br 18.39, N 6.45; found: C 64.98, H 9.24, N 5.98.

Photocatalytic Experimental: CPEs were dissolved into 0.5 mL methanol with a concentration of 5 mg/mL. With slow stirring, the 0.5 mL of each CPE solution was dispersed into 50 mL containing 0.2 M ascorbic acid (AA) solution (pH = 4, adjusted by 1.0 M NaOH solution). The mixed solution was ultrasonicated for 15 minutes and vacuumed to remove methanol. The photocatalytic experiments were performed on a Labsolar-IIIAG photocatalytic system (PerfectLight) equipped with a 50-mL reactor. 3 wt% Pt (from H2PtCl6) of each CPE was added and illuminated for 0.5 h as cocatalyst. The reaction unit was sealed with a quartz septum and the resulted reaction mixture was degassed by vacuuming before illumination. A Xe lamp (300W, Ceaulight) was used as the light source. The luminous power reaching the surface of the reaction solution was calibrated to be 150 mW cm⁻² by a power meter. Hydrogen was detected using a gas chromatography (GC7900II, using Ar as carrier gas). The sensor was standardized by injecting different volumes of hydrogen with the experiment condition. The sensor was polarized at +36 mV until reaching a stable value before every measurement. The oxygen evolution was conducted using AgNO₃ as sacrificial agent and La₂O₃ as buffer agent (0.01M AgNO₃ and 100 mg La₂O₃).

Characterizations: The H-NMR spectra of these CPEs were characterized with a Bruker-600 spectrometer operating at 600 MHz in deuterated chloroform solution at 298 K. Chemical shifts were recorded as δ values (ppm) with the internal standard of tetramethylsilane. The number-average (Mn) and weight-average (Mw) molecular weights of neutral conjugated polymers were determined by a Waters GPC 2410 in DMF using a calibration curve of polystyrene standards. The UV-vis absorption conjugated polymers micelles were recorded on a HP 8453 spectrophotometer. Photoluminescent spectra of conjugated polymers and their blends were recorded on a JobinYvon Fluorolog-3 spectrophotometer. The electrochemical cyclic voltammetry was conducted on a CHI600D Electrochemical Workstation, in a 0.1 M Bu₄NPF₆ in CH₃CN at a potential scan rate of 50 mV s⁻¹ with an SCE reference electrode and a platinum wire counter electrode. The ferrocene/ferrocenium (Fc/Fc⁺) reference was used as an internal standard, which was assigned an absolute energy of ~4.8 eV vs vacuum level. Under the same experimental conditions, the onset potential of Fc/Fc⁺ was measured to be 0.27 V with respect to the saturated calomel electrode reference electrode. The lowest unoccupied molecular orbital (LUMO) energy levels and the highest occupied molecular orbital (HOMO) energy levels of conjugated copolymers were calculated as E_LUMO = −(E_re+4.53) (eV) and E_HOMO = −(E_ox+4.53) (eV) respectively, where E_re and E_ox are the onset of the reduction and oxidation) potential vs the saturated calomel electrode reference electrode. Water contact angle measurements of these CPEs were performed on a VCA15 surface contact angle analyzer (Dataphysics). The high resolution transmission electron microscope (HR-TEM) images of the dispersed CPEs was obtained from TF20, Joel 2100F Microscope. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). The residual Pd
content was obtained by PerkinElmer ICP 2100. The $E_F$ was calculated from the equation \( \frac{1}{c^2} = \frac{2(E - E_F - \frac{k_B T}{e})}{\varepsilon \varepsilon_0 \hbar^2 N_D} \) from the Mott-Schottky plots. A straight tangent line can be drawn from the plot of $1/c^2$ vs $E$, of which the intercept with $E$ axis can be determined as $E_F$. The AQY was measured at selected wavelengths using band pass filters (380, 420, 450, 500 and 550 nm). The AQY can be calculated from the equation: 

\[
N_0 = \frac{E\lambda T\%}{h c}, \quad N = \frac{V \times 6.02 \times 10^{23}}{22.4 t}, \quad AQY = \frac{2N}{N_0},
\]

$N_0$ represent the number of incident photons, $N$ represents the number of collected $H_2$ molecules, $E$ represents the energy of incident light at a selected wavelength determined by a calibrated power meter, $\lambda$ represents the wavelength of the incident light, $V$ represents the volume of generated $H_2$ in a certain period of time($t$), detected by GC, $T\%$ represents the transmittance of the quartz cell.

Figure S1. GPC analysis of the synthesized polymers. (a) PFBr-Ph (b) PFBr-PhF (c) PFBr-PhCN.
Figure S2. UV-vis absorption of (a) PF-PhF, PF-PhCN and (b) PFBr-PhF, PFBr-PhCN in films and solution (chloroform for PF-PhF and PF-PhCN; methanol for PFBr-PhF and PFBr-PhCN)

Figure S3. Water contact angles of CPE thin films

Figure S4. Size distributions of CPEs in H₂O from dynamic light scattering (DLS) experiments.
**Figure S5.** Mott–Schottky plots of PFBr-Ph, PFBr-PhF and PFBr-PhCN in 200Hz, 500Hz and 1000Hz.

**Figure S6.** Temperature dependent UV-vis absorption spectra of (a) PFBr-PhCN in DMF; and (b) PF-PhCN in chlorobenzene.

**Figure S7.** Absorption spectrum of PFBr-PhCN and apparent quantum yield (AQY) values as a function of light wavelength.
Figure S8. Hydrogen evolution of PFBr-PhCN with over 20-h illumination.

Figure S9. UV-vis spectra, FT-IR and $^{13}$C NMR of PFBr-PhCN before and after 20-h testing. (the FT-IR spectrum of PFBr-PhCN after testing is a mixture of the spectra from AA and PFBr-PhCN)
**Figure S10.** UV-vis spectra and FT-IR of PFBr-Ph and PFBr-PhF before and after testing. (the FT-IR spectrum of CPEs after testing is a mixture of the spectra from AA and CPEs)

**Figure S11.** Produced H₂ of PFBr-PhCN as a function of time in AA solution (pH=4, pH=6) or with TEOA as sacrificial reagent.
Figure S12. Time course for photocatalytic oxygen evolution of PFBr-PhCN.

Table S1 Pd content of the CPEs measured by ICP.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Pd Content (wt%)</th>
<th>HER(μmol/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBr-PhCN</td>
<td>1.32%</td>
<td>38.3</td>
</tr>
<tr>
<td>PFBr-PhF</td>
<td>2.59%</td>
<td>8.8</td>
</tr>
<tr>
<td>PFBr-Ph</td>
<td>1.87%</td>
<td>3</td>
</tr>
</tbody>
</table>

Reference