

Electronic Supplementary Information

Side-chain-extended conjugation: a strategy for improving photocatalytic hydrogen production performance of a linear conjugated polymer

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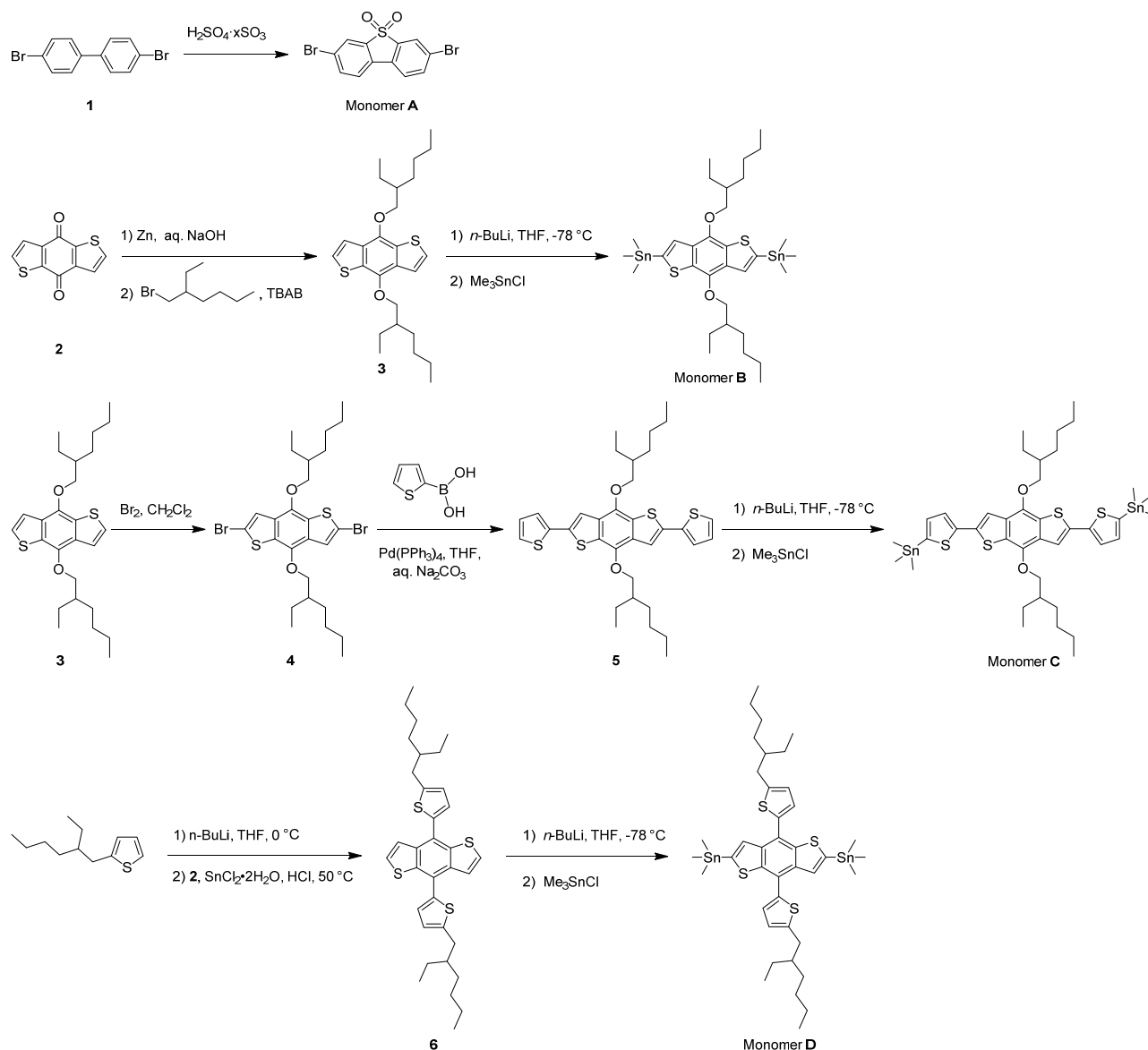
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1. Monomer Synthesis



3,7-Dibromodibenzo[b,d]thiophene 5,5-dioxide (monomer A). Fuming sulfuric acid (5 mL) was put into a 25 mL flask at room temperature. Next, 4,4'-dibromo-1,1'-biphenyl (Compound 1, 1 g, 3.21 mmol) was added slowly in a stirred state. During the reaction, the color changed from green to white. Afterward, the reaction was stirred overnight. The reaction was neutralized by saturated NaHCO₃ solution. The resulted mixture was extracted with ethyl acetate. Organic layers were combined, dried over anhydrous MgSO₄, and concentrated under vacuum. The obtained solids was further dried to afford monomer A as white powder (0.53 g, yield 44%). EI-MS Calcd. for C₁₂H₆Br₂O₂S 374.046, Found 374 (M⁺). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.93 (d, *J* = 1.7 Hz, 2H), 7.79–7.75 (m, 2H), 7.66–7.62 (m, 2H).

4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (Compound 3). A mixture of benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (Compound 2, 4.4 g, 20 mmol), zinc powder (3.07 mg, 48 mmol), NaOH (12 g, 300 mmol) was put into a 250 mL flask under the protection of argon. After addition of 60

mL deionized water, the reaction mixture was heated to reflux for 1 h under vigorous stirring. During the reaction, the color changed from yellow, to dark red, and then to orange. Next, a catalytic amount of tetrabutylammonium bromide (TBAB) and 2-ethylhexyl bromide (11.523 g, 60 mmol) were added into the reaction mixture. After refluxing for additional 2 h, the reaction mixture was poured into cold water and extracted with dichloromethane. Organic layers were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The obtained crude product was finally purified by silica column chromatography using hexane as eluent to afford compound **3** as colorless oil (7.6 g, yield 85%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.46 (d, *J* = 5.6 Hz, 2H), 7.34 (d, *J* = 5.6 Hz, 2H), 4.16 (d, *J* = 4.5 Hz, 4H), 1.81–1.34 (m, 16H), 0.99 (t, *J* = 7.6 Hz, 6H), 0.92 (t, *J* = 7.2 Hz, 6H).

(4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (monomer B). Compound **3** (2.678 g, 6 mmol) was dissolved in 80 mL dry THF under the protection of argon. After the solution was cooled down to -78 °C using a dry ice-acetone bath, *n*-butyllithium (9.5 mL, 1.6 M in *n*-hexane, 15 mmol) was added dropwise. Then, the reaction mixture was slowly warmed up to room temperature, stirred for 2 h, cooled down to -78 °C again, and then added with trimethyltin chloride (18 mL, 1 M in *n*-hexane, 18 mmol) in one portion. Afterward, the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction was terminated by pour of cool water, and resulted mixture was extracted with diethyl ether. Organic layers were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The obtained crude product was recrystallized from isopropanol to afford monomer **B** as colorless needles (3.028 g, yield 65%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.51 (s, 2H), 4.18 (d, *J* = 6.8 Hz, 4H), 1.42–1.38 (m, 16H), 1.02 (t, *J* = 10.0 Hz, 6H), 0.94 (t, *J* = 8.0 Hz, 6H), 0.44 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm): 143.2, 140.4, 133.8, 132.9, 128.0, 75.6, 40.6, 30.5, 29.2, 23.9, 23.2, 14.2, 11.3.

2,6-Dibromo-4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (compound 4). Compound **3** (893.4 mg, 2 mmol) was put into a 100 mL flask under the protection of argon in an ice bath. Br₂ (0.21 mL, 4 mmol) was dissolved in 20 mL dichloromethane and was added dropwise. The reaction was terminated by adding saturated NaHSO₃ solution, and resulted mixture was extracted with methylene chloride. Organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum. The obtained crude product was finally purified by silica column chromatography using petroleum ether as eluent to afford compound **4** as yellow oil (0.743 g, yield 61%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.41 (s, 2H), 4.09 (d, *J* = 5.6 Hz, 4H), 1.77 (dt, *J* = 12.2, 5.9 Hz, 2H), 1.69–1.58 (m, 4H), 1.56–1.49 (m, 4H), 1.38 (td, *J* = 7.3, 3.6 Hz, 8H), 1.00 (t, *J* = 7.4 Hz, 6H), 0.94 (dd, *J* = 8.7, 5.3 Hz, 6H).

4,8-Bis((2-ethylhexyl)oxy)-2,6-di(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (compound 5). A mixture of compound **4** (624 mg, 1.03 mmol), thiophen-2-yl-boronic acid (528.4 mg, 4.13 mmol), THF (18 mL), K₂CO₃ (2.14 g, 15.48 mmol), Pd(PPh₃)₄ (59.64 mg, 0.0516 mmol) was put into a 250 mL

flask under the protection of argon. The mixture was then subjected to thorough degassing with three freeze–pump–thaw cycles and backfilled with Ar. After stirring at 80 °C for 36 h, the resulted mixture was extracted with methylene chloride. Organic layers were combined, washed with brine, dried over anhydrous Na₂SO₄, and concentrated under vacuum. The obtained crude product was finally purified by silica column chromatography using petroleum ether as eluent to afford compound **4** as dark yellow powder (628.8 mg, yield 88%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.48 (d, *J* = 9.3 Hz, 2H), 7.39–7.27 (m, 4H), 7.13–7.04 (m, 2H), 4.19 (d, *J* = 5.2 Hz, 4H), 1.88–1.79 (m, 2H), 1.76–1.64 (m, 4H), 1.55 (d, *J* = 6.9 Hz, 4H), 1.43 (s, 8H), 1.05 (t, *J* = 7.3 Hz, 6H), 0.97 (s, 6H).

((4,8-Bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(thiophene-5,2- diyl)bis(trimethylstannane) (Monomer C). Monomer **C** was obtained as colorless oil (358 mg, yield 73%) following the same method for monomer **B** using compound **5** (320 mg, 0.524 mmol) in place of compound **3**. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.48 (s, 2H), 7.42 (d, *J* = 3.4 Hz, 2H), 7.14 (d, *J* = 3.4 Hz, 2H), 4.18 (d, *J* = 5.4 Hz, 4H), 1.82 (dd, *J* = 11.9, 5.9 Hz, 2H), 1.70 (td, *J* = 13.9, 7.0 Hz, 4H), 1.54 (d, *J* = 6.1 Hz, 4H), 1.42 (d, *J* = 3.6 Hz, 8H), 1.04 (t, *J* = 7.4 Hz, 6H), 0.97 (t, *J* = 7.0 Hz, 6H), 0.50–0.33 (m, 18H).

4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (Compound 6). 2-(2-ethylhexyl)thiophene (1.227 g, 6.25 mmol) was put into a 100 mL flask under the protection of argon. After the solution was cooled down to 0 °C, 45 mL dry THF was added. The reaction was slowly warm to room temperature and then then added with compound **2** (550 mg, 2.5 mmol) quickly. Afterward SnCl₂·2H₂O (4.5 g, 20 mmol) and HCl (10 mL, 10%) were added. The reaction was terminated by pour of cool water, and resulted mixture was extracted with methylene chloride. Organic layers were combined, washed with brine, dried over anhydrous MgSO₄, and concentrated under vacuum. The crude product was finally purified by silica column chromatography using hexane/dichloromethane (2:1) as eluent to afford compound **6** as yellow oil (1.44 g, yield 95%). ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.64 (d, *J* = 5.6 Hz, 2H), 7.45 (d, *J* = 5.6 Hz, 2H), 7.29 (d, *J* = 3.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 2H), 2.86 (d, *J* = 5.6 Hz, 4H), 1.71–1.65 (m, 2H), 1.45–1.32 (m, 16H), 0.90–0.86 (m, 12H).

(4,8-Bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6- diyl)bis(trimethylstannane) (Monomer D). Monomer **D** was obtained as colorless oil (1.16 g, yield 64%) following the same method for monomer **B** using compound **6** (1160 mg, 2 mmol) in place of compound **3**. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 7.64 (s, 2H), 7.30 (d, *J* = 3.6 Hz, 2H), 6.88 (d, *J* = 3.6 Hz, 2H), 2.85 (d, *J* = 6.8 Hz, 4H), 1.70–1.66 (m, 2H), 1.45–1.34 (m, 16H), 0.90–0.84 (m, 12H), 0.37 (s, 18H).

2. Supporting figures and table:

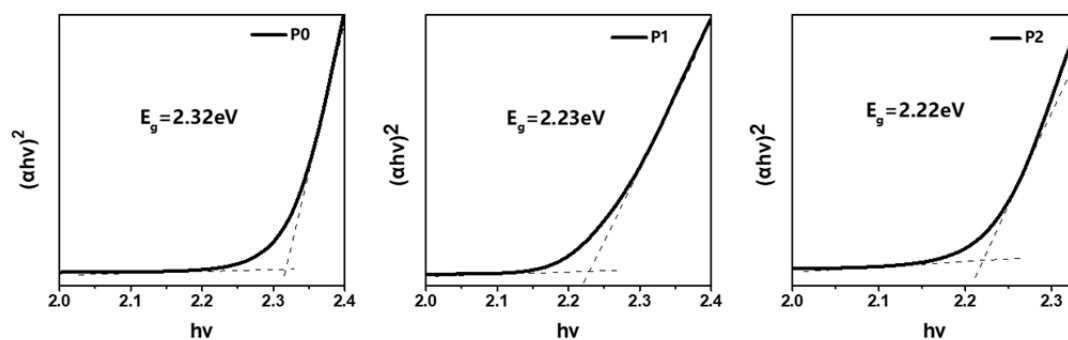


Fig. S1 Tauc plots of polymer **P0**, **P1**, and **P2**.

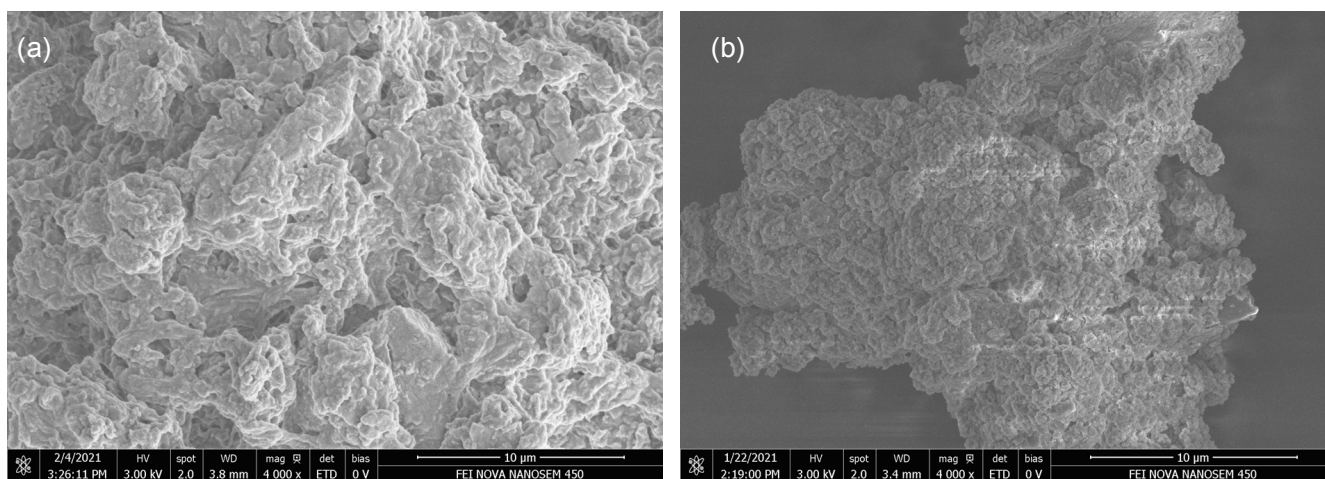


Fig. S2. SEM images of **P2** (a) after sonication in $\text{H}_2\text{O}/\text{MeOH}/\text{DMF}/\text{TEA}$ (v/v/v/v: 8/2/1/5) but before photo-reaction, and (b) after photoreaction.

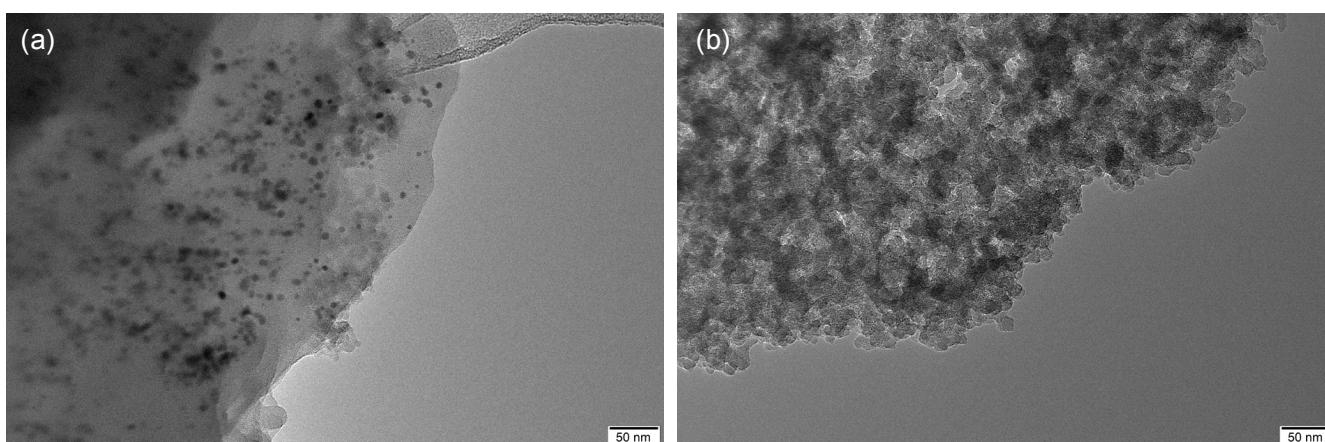


Fig. S3. TEM images of **P2** (a) before and (b) photo-reaction.

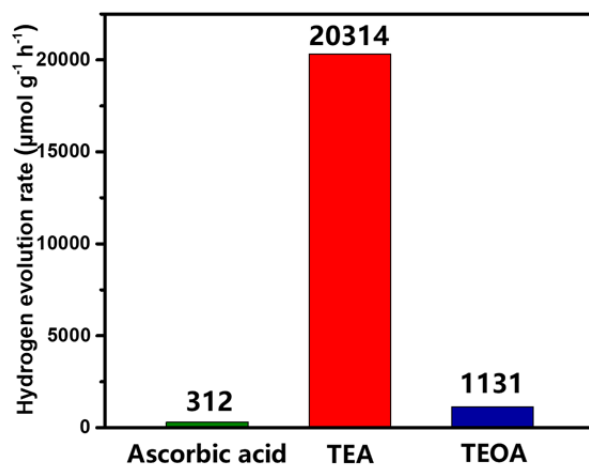


Fig. S4 Hydrogen evolution rates of **P2** by using different sacrificial agents (SA). Conditions: 3.5 mg **P2**, 16 mL $\text{H}_2\text{O}/\text{MeOH}/\text{SA}/\text{DMF}$ (v/v/v/v: 8/2/5/1) mixture, 3% wt Pt added, exposed to a 300 W Xe lamp.

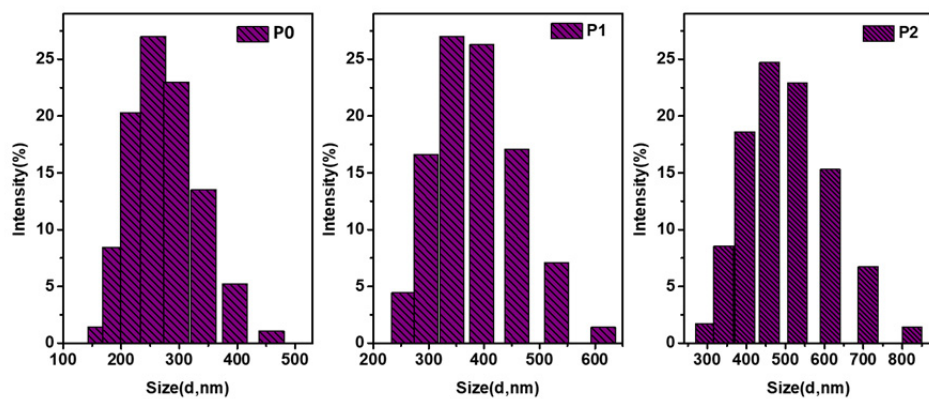


Fig. S5 Particle size distribution of **P0**, **P1**, and **P2** in $\text{H}_2\text{O}/\text{MeOH}/\text{DMF}$ (v/v/v: 8/2/0.5) mixture.

Table S1 Performances of some reported organic photocatalysts.

| Photocatalyst | Conditions | HER ($\mu\text{mol g}^{-1} \text{h}^{-1}$) | AQY | Reference ^c |
|---|---|---|--|---|
| P7 | 25 mg photocatalyst, 22.5 mL H ₂ O/MeOH/TEA (v/v/v: 1/1/1), reaction temperature: not specified, 300 W Xe-lamp, no additional cocatalyst added. | 5800 ($\lambda > 295 \text{ nm}$), 3680 ($\lambda > 420 \text{ nm}$) | 2.3% @420 nm | [13] Angew. Chem., Int. Ed. 55 (2016) 1792– 1796. |
| P7-E | 30 mg photocatalyst, 30 mL H ₂ O/TEOA (v/v: 9/1), reaction temperature: not specified, 300 W Xe-lamp, 3% Pt added as cocatalyst. | 8677 ($\lambda > 420 \text{ nm}$, 260.3 $\mu\text{mol h}^{-1}$) ^a | 7.2% @420 nm | [44] J. Catal. 350 (2017) 64–71. |
| P10 | 25 mg photocatalyst, 22.5 mL H ₂ O/MeOH/TEA (v/v/v: 1/1/1), reaction temperature: not specified, 300 W Xe-lamp, no additional cocatalyst added. | 3260 ($\lambda > 420 \text{ nm}$) | 11.6% @420 nm | [32] Nat. Commun. 9 (2018) 4968. |
| PDBTSO (P10) | 10 mg photocatalyst, 100 mL aqueous solution containing 20 vol% TEOA, 2 mmol K ₂ HPO ₄ , reaction temperature: 10 \pm 0.5 $^{\circ}\text{C}$ 300 W Xe-lamp, 3% Pt added as cocataly | 44200 ($\lambda > 420 \text{ nm}$) | 8.5% @420 nm, ^b 7.1% @450 nm, ^b 2.7% @500 nm ^b | [28] Appl. Catal. B: Environ. 261 (2020) 118230. |
| P10-e (polymer dot prepared by mini-emulsion polymerization) | 325 μg photocatalyst, 25 mL H ₂ O/toluene/MeOH/TEA (v/v/v/v 9/1/10/10), 10 mg mL ⁻¹ SDS, 3.5 mg mL ⁻¹ Na ₂ CO ₃ , reaction temperature: not specified, 300 W Xe-lamp, no additional cocatalyst added. | 60600 ($\lambda > 420 \text{ nm}$) | 5.8% @420 nm | [53] J. Mater. Chem. A 7 (2019) 2490–2496. |
| B-BT-1,4-E | 30 mg photocatalyst, 30 mL H ₂ O/TEOA (v/v: 9/1), reaction temperature: not specified, 300 W Xe-lamp, 3% Pt added as cocatalyst. | 11820 ($\lambda > 420 \text{ nm}$, 354.6 $\mu\text{mol h}^{-1}$) ^a | 3.7% @420 nm | [44] J. Catal. 350 (2017) 64–71. |
| N-PDBT-O | 30 mg photocatalyst, 30 mL H ₂ O/TEOA (v/v: 9/1), reaction temperature: ambient, 300 W Xe-lamp, no additional cocatalyst added. | 12200 ($\lambda > 420 \text{ nm}$, 366 $\mu\text{mol h}^{-1}$) ^a | 3.7% @420 nm, 1.5% @500 nm, ^b 1.55% @550 nm, ^b 0.9% @600 nm ^b | [52] Macromol. Rapid Commun. 40 (2019) 1800494 |
| P-FSO | 50 mg photocatalyst, 110 mL H ₂ O/TEOA (v/v: 10/1), reaction temperature: 12 $^{\circ}\text{C}$, 300 W Xe-lamp, | 8000 ($\lambda > 420 \text{ nm}$, 400 $\mu\text{mol h}^{-1}$) ^a | 8.5% @ 420 nm, 8.2% @450 nm, ^b 2.8% @520 nm, ^b 0.25% @575 nm ^b | [51] Appl. Catal. B: Environ. 245 (2019) 596–603. |

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|-----------------------------|---|---|---|--|
| | no additional cocatalyst added. | | | |
| DBTD-CMP1 | 50 mg photocatalyst, 100 mL H ₂ O/TEOA (v/v: 4/1), reaction temperature: 10 °C, 300 W Xe-lamp, 3% Pt added as cocatalys | 9200 ($\lambda > 300$ nm), 4600 ($\lambda > 420$ nm) | 3.3% @400 nm, 1.6% @450 nm, 0.2% @500 nm | [50] ACS Catal. 8 (2018) 8590–8596. |
| PCP4e | 3.5 mg photocatalyst, 3.5 mL H ₂ O/Et ₃ N (v/v: 8/2), reaction temperature: ambient, 150 W Xe-lamp, no additional cocatalyst added. | 9430 (full-arc, 33.0 $\mu\text{mol h}^{-1}$), ^a 1900 ($\lambda > 400$ nm), 6.65 $\mu\text{mol h}^{-1}$) ^a | 0.34% @ 350 nm | [15] J. Am. Chem. Soc. 138 (2016) 7681–7686. |
| CTF-BT/Th-1 | 50 mg photocatalyst, 110 mL H ₂ O/TEOA (v/v: 10/1), reaction temperature: 25 °C, 300 W Xe-lamp, 3% Pt added as cocataly. | 6600 ($\lambda > 420$ nm) | 7.3% @420 nm, 5.2% @450 nm, 2.5% @500 nm | [45] Angew. Chem., Int. Ed. 58 (2019) 8676– 8680. |
| FS-COF | 5 mg photocatalyst, 25 mL ascorbic acid aqueous solution (0.1 M), reaction temperature: not specified, 300 W Xe-lamp, 8% Pt added as cocataly. | 10100 ($\lambda > 420$ nm) | 3.2% @420 nm, 0.6% @600 nm | [27] Nat. Chem. 10 (2018) 1180– 1189. |
| FS-COF + WSSF | 5 mg photocatalyst, 5 mg dye, 25 mL ascorbic acid aqueous solution (0.1 M), reaction temperature: not specified, 300 W Xe-lamp, 8% Pt added as cocataly. | 16300 ($\lambda > 420$ nm) | 7.4% @420 nm ^b 2.2% @600 nm, 0.7% @700 nm | [27] Nat. Chem. 10 (2018) 1180– 1189. |
| Triazine-Th- CPP | 9 mg photocatalyst, 22 mL H ₂ O/TEOA/ (v/v: 15/7), 300 W Xe-lamp, reaction temperature: 5 °C, no additional cocatalyst added. | 16287 (full-arc), 3502 ($\lambda > 420$ nm) | 61.5% @365 nm, 7.5% @420 nm, ^b 3% @450 nm, ^b 0.5% @500 nm ^b | [29] Chem. Commun. 56 (2020) 1601– 1604. |
| B-FOBT-1,4E | 30 mg photocatalyst, 30 mL H ₂ O/TEOA/ (v/v: 9/1), reaction temperature: not specified, 300 W Xe-lamp, no additional cocatalyst added. | 13300 ($\lambda > 420$ nm) | 5.7% @420 nm, 2.3% @450 nm, ^b 1.3% @500 nm, 0.7% @550 nm, ^b 0.2% @600 nm, ^b 0.1% @ 650 nm, ^b 0.08% @700 nm ^b | [42] ACS Energy Lett. 3 (2018) 2544–2549 |
| FSO-FS | 50 mg photocatalyst, 110 mL H ₂ O/TEOA/ (v/v: 10/1), reaction temperature: room temperature, 300 W Xe-lamp, no additional cocatalyst added | 3400 ($\lambda > 420$ nm), 170 $\mu\text{mol h}^{-1}$) ^a | 6.8% @420 nm, 6.0% @450 nm, ^b 3.2% @470 nm, ^b 1.5% @490 nm ^b | [46] Angew. Chem. Int. Ed. 58 (2019) 10236– 10240. |

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|--------------------|--|--|--|---|
| P64 | 25 mg photocatalyst, 25 mL water/methanol/trimethylamine (v/v/v 1/1/1), reaction temperature: not specified, AM1.5G solar simulator , 1% Pt added as cocataly | 6038.5 | 20.7% @420 nm | [54] J. Am. Chem. Soc. 141 (2019) 9063–9071. |
| PyDF | 25 mg photocatalyst, 100 mL water/TEOA (v/v 4/1), reaction temperature: 20 °C, 300 W Xe-lamp, 3% Pt added as cocataly. | 18930 (full-arc), 13470 ($\lambda > 420$ nm) | 4.5% @400 nm, 4.2% @420 nm, ^b 3.8% @450 nm, ^b 1.2% @500 nm, ^b 0.8% @550 nm ^b | [43] J. Mater. Chem. A 8 (2020) 2404–2411. |
| DPP-bdy-TPA | 3.5 mg photocatalyst, 12 mL H ₂ O/MeOH/TEOA/ (v/v/v: 7/3/2), reaction temperature: 5 °C 300 W Xe-lamp, no additional cocatalyst added. | 6918 (full-arc) 2780 ($\lambda > 440$ nm) | 9.60% @420 nm, 8.56% @450 nm, 7.32% @500 nm, 2.30% @550 nm, 0.31% @600 nm | [34] Macromolecules 53 (2020) 2454– 2463 |
| P2 | 3.5 mg photocatalyst, 16 mL H ₂ O/MeOH/DMF/TEA/ (v/v/v/v: 8/2/1/5), reaction temperature: 5 °C, 300 W Xe-lamp, 3% Pt added as cocataly. | 20314 (full-arc) | 2.13% @420 nm, 2.49% @450 nm, 7.04% @500 nm, 5.06% @550 nm, 0.96% @600 nm | This work |

^a calculated from the reported HER value in a unit of $\mu\text{mol h}^{-1}$ and the used amount of photocatalyst in a unit of g.

^b estimated from the report figure.

^c The reference numbers in the main text are provided in square brackets.