

SUPPORTING INFORMATION

Dye-sensitized Photoelectrochemical Cells Constructed by Metal-free Perylene Diimide-based Oxygen Production Polymers and Calixarene Dyes

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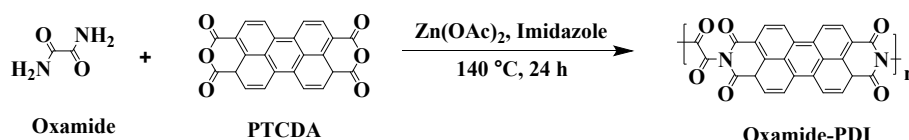
Experimental section

1. Synthesis of C4BTP and C4EOP

The synthesis route of calixarene dyes **C4BTP** and **C4EOP** referred to our previous literature [1,2].

2. Synthesis of oxygen producing polymers

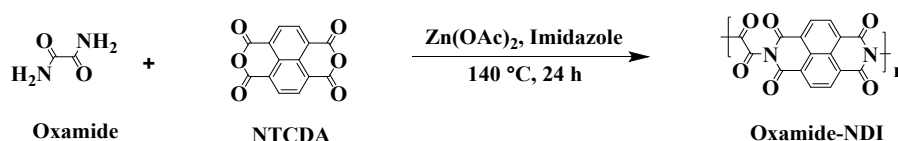
2.1 Synthesis of Oxamide-PDI



Scheme S1. Synthetic route of **Oxamide-PDI**.

PTCDA (784.6 mg, 2 mmol), Oxamide (176.1 mg, 2 mmol), and anhydrous zinc acetate (366.9 mg, 2 mmol) were mixed in a 250 mL double necked flask, followed by adding 7.8 g of imidazole. The mixture was stirred and heated to 140°C for 24 h under N₂ protection. Afterwards, the mixture was cooled to 90°C, added by 200 mL of 1 mol L⁻¹ hydrochloric acid solution and stirred for 20 minutes. The mixture was vacuum-filtered to obtain a dark red powder, and the solid was washed with a saturated solution of K₂CO₃ until no bubbles are formed. Then, the obtained powder was washed three times with deionized water, followed by washing with DMSO until colorless, and washing with deionized water again to remove residual DMSO. Finally, the product was dried in vacuum at 110 °C for 12 h to obtain purplish-red powder [3].

2.2 Synthesis of Oxamide-NDI

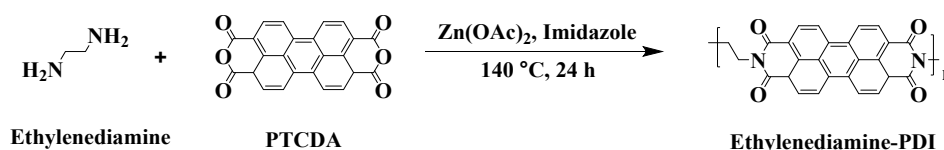


Scheme S2. Synthetic route of **Oxamide-NDI**.

NTCDA (536.4 mg, 2 mmol), Oxamide (176.1 mg, 2 mmol), and anhydrous zinc acetate (366.9 mg, 2 mmol) were mixed in a double necked flask, followed by adding 7.8 g of imidazole. The mixture was stirred and heated to 140°C for 24 h under N₂

protection. After cooled to 90°C, the mixture was added by 200 mL of 1 mol L⁻¹ hydrochloric acid solution and stirred for 20 minutes. After vacuum-filtering, the precipitate was rinsed with a K₂CO₃ saturated solution until no bubbles remained. The resultant powder was subsequently washed three times with deionized water, then washed with DMSO until colorless, and washed with deionized water again to remove residual DMSO. Finally, the solid was dried in vacuum at 110°C for 12 h to obtain a gray flocculent powder product was obtained [3].

2.3 Synthesis of Ethylenediamine-PDI



Scheme S3. Synthetic route of **Ethylenediamine-PDI**.

PTCDA (784.6 mg, 2 mmol), Ethylenediamine (120.2 mg, 2 mmol), and anhydrous zinc acetate (366.9 mg, 2 mmol) mixed in double necked flask, and 5.0 g of imidazole was added afterwards. The mixture was stirred and heated to 140°C for 24 h under N₂ protection. After cooled to room temperature, the mixture was added by 200 mL of 1 mol L⁻¹ hydrochloric acid solution and kept stirred until there was no further precipitate. After vacuum-filtering, the precipitate was rinsed with deionized water for three times, dried in vacuum at 65°C, washed with DMSO until colorless, and washed with deionized water again to remove residual DMSO. The solid powder was finally dried in vacuum at 110°C for 12 h to obtain black powder [3].

3. Preparation of FTO|TiO₂ Film Electrodes

3.1 Preparation of TiO₂ film electrode

The nano-crystalline P25-TiO₂ particles was screen-printed onto FTO glass using a prefabricated paste to produce 1 cm² films used for assembling DSPEC devices and 0.16 cm² films for other photoelectrochemical tests. Afterwards, the electrodes were placed in a muffle furnace for sintering at 500°C for 1 h.

3.2 Post processing of TiO₂ film electrodes

The re-prepared film electrodes were soaked in 40 mmol L⁻¹ TiCl₄ solution, and subsequently treated at a constant temperature of 70°C for 30 min [4]. And then the electrodes were washed twice with deionized water and ethanol. Afterwards, the electrodes were heated for 30 minutes at 500°C, and then cooled by air flow for 10 min.

4. Preparation of FTO|TiO₂|dye|WOC Film Electrodes

4.1 Dye sensitization of electrodes

C4BTP and C4EOP were respectively dissolved in dichloromethane to obtain a 0.3 mM solution of C4BTP and a 0.3 mM solution of C4EOP. The electrodes were immersed in a dye solution for a sensitization time of 1 hour. After sensitization, excess dye molecules on the electrode surface were rinsed with dichloromethane.

4.2 Loading of oxygen producing polymers

0.25 cm² square hole was drilled on 3M adhesive tape using a punch and the active area on TiO₂ film electrodes were covered by square hole. Three kinds of ethanol suspension were prepared (the concentration of oxygen producing polymer, including Oxamide-PDI, Oxamide-NDI and Ethylenediamine-PDI, was 5 mg mL⁻¹, and the concentration of Nafion was 0.05 wt%) [5]. 10 μL of mixed suspension was dropped into the square hole after ultrasound. And then complete photoanodes were obtained until the solvent was completely evaporated.

5. Characterizations

The infrared spectra (FT-IR) were measured via a Fourier transform infrared spectrometer (FT-IR, iS10, Thermo Fisher Nicolet), with a range from 1200 to 1800 cm⁻¹ and a resolution of 10 cm⁻¹ in total reflection mode. X-ray photoelectron spectroscopy (XPS) spectra were obtained on X-ray Photoelectron Spectroscopy (XPS, K-ALPHA, Thermo Fisher Scientific) using a monochromatic Al K α source as the X-ray source. Software named Avantage was utilized to analyze the test findings. X-ray diffraction (XRD) patterns were recorded by an X-ray diffractometer (XRD,

MiniFlex600, Rigaku) with a scanning range from 10 to 60° as well as a scanning step size of 0.02° under Cu-K α radiation.

The UV-vis spectra were measured using a UV-vis spectrophotometer (UV-vis, UV-2600, Shimadzu). The drop shape analysis instrument (CA, DSA100S, KRÜSS) was used in the contact angle testing experiment. 5 μ L of water was dropped onto the sample for measuring the contact angle of polymer solid tablets and dye sensitized electrodes. Scanning electron microscopy (SEM, SU8000, Hitachi) was used to observe the images of electrode multilayer structures

6. Determination of dye adsorption capacity

Three identical dye-sensitized electrodes were immersed in a 4 mL mixed solution of chloroform/acetic acid (1:1 v/v) (with additional 16 drops of water to encourage acetic acid hydrolysis) and heated at 60 °C for 48 hours, then the dye molecules on the electrodes desorbed from TiO₂ surface and dissolved in the solution. In order to draw a standard curve, two dyes were dissolved in mixed solutions with the same ratio separately to prepare a series of concentration standard solutions, and then the absorbance of each solution was measured. Next, the absorbance of the sample solution was measured after dilution by ten times. **Equation S1** and **S2** were used to determine the amount of dye molecules that have been adsorbed on the electrode. The results were displayed in **Table S1**.

$$A_{Smaple} = \varepsilon L c_{Smaple} \#(S1)$$

$$\Gamma = \frac{c_{Smaple} \times 10 \times 8 \text{ mL}}{3 \times 0.16 \text{ cm}^2} \#(S2)$$

Where, A_{Smaple} is the absorbance of sample solution, εL is a constant, and c_{Smaple} is the concentration of sample solution in **Equation S1**; Γ is the amount of dye molecules that are adsorbed onto the electrode in **Equation S2**.

7. Photoelectrochemical testing of electrodes

The electrochemical workstation (Chenhua, CHI 760E) was used to conduct the

electrochemical and photoelectrochemical (Mott Schottky test, linear sweep voltammetry, photocurrent-time curve, electrochemical impedance spectroscopy, voltage-time decay curve, and oxygen generation performance) tests of the electrodes. Unless otherwise noted, a three-electrode system was employed for all photoelectrochemical tests, among which the working electrode was the as-prepared photoelectrode, the counter electrode was graphite bar, and the reference electrode was Ag/AgCl. In the testing cell, 0.025 M phosphate buffer solution (PBS, pH = 6.8) was utilized as the electrolyte. A xenon lamp (CEL-HXF300E7, 300W; cutoff filter, $\lambda > 420$ nm) served as the source of light for the experiment.

The Mott Schottky test (MS) was conducted under the conditions of initial E =1 V, final E =-1 V, incremental E =0.05 V, and amplitude = 0.005 V. Three frequencies, including 500 Hz, 1000 Hz, and 1500 Hz, were applied to the Mott Schottky test of electrodes. The running time of the voltage-time (V-t) decay curve was 110 s, with the first 10 seconds under irradiation and the following 100 seconds under dark. The bias range of linear sweep voltammetry (LSV) experiment was between -0.6 and 0.6V, with a scanning speed of 0.005 V/s. Parameters in the electrochemical impedance spectroscopy (EIS) experiments were: bias = -0.6 V, high frequency = 10^6 Hz, low frequency =0.01 Hz, in the dark for testing charge recombination impedance; bias = 0.2 V, high frequency = 10^6 Hz, low frequency = 0.01 Hz, under irradiation for testing charge transfer impedance. In the photocurrent-time (i-t) curve test, a bias voltage of 0.2 V vs. RHE (=0 V vs. Ag/AgCl) was applied to the photoanode, while a bias voltage of 0 V vs. RHE was used for testing the performance of the photoanode only under light-driving.

8. Incident photon-to-electron conversion efficiency (IPCE)

Incident photon-to-electron conversion efficiency (IPCE) was defined as the ratio of the number of electrons flowing through a closed circuit to the number of photoelectrons of incident monochromatic light [6]. It was calculated by measuring the

photocurrent under the illumination of monochromatic LEDs with various wavelengths. To avoid light leakage during testing, the entire electrolytic cell was covered with tin foil. The LED lights used in the experiment had wavelengths of 365 nm (10 W/cm²), 405 nm (460 W/cm²), 425 nm (860 W/cm²), 450 nm (1100 W/cm²), 470 nm (1000 W/cm²), 515 nm (920 W/cm²), 550 nm (600 W/cm²), and 590 nm (550 W/cm²). The other testing conditions were consistent with the i-t curve test. The calculation for IPCE is shown in **Equation S3**:

$$IPCE = \frac{1240 \times (I_{light} - I_{dark})}{P_{light} \times \lambda_{max}} \times 100\% \#(S3)$$

Among these, I_{light} and I_{dark} corresponded to the photocurrent density under irradiation and in the dark, respectively. And P_{light} was the luminous flux, while λ_{max} was maximum absorption wavelength. The photocurrent density under illumination is taken as the photocurrent density at 200 s, and the photocurrent density under dark conditions is taken as the photocurrent density at 185 s.

9. Oxygen generation performance

The electrodes with active area of 1 cm² were used for the oxygen production performance test. The as-prepared electrode served as the photoanode, and the collection electrode was bare FTO glass. The two electrodes were insulated between each other with several layers of 3M adhesive tape, and the electrodes were fixed with clips to form a DSPEC device [7]. The test was conducted using an H-cell, and the counter electrode was substituted with a platinum plate. The remaining conditions were the same as those for the photoelectrochemical performance test of the photoanode.

The Faraday efficiency (η_F) of each combination of dyes and oxygen producing polymers can be calculated using **Equation S4**.

$$\text{Faradaic efficiency}(\eta_F) = \frac{Q_{col}}{Q_{gen} \times \eta_{col}} \#(S4)$$

Where was the amount of charge generated on the G-electrode within 900~1800s,

and Q_{col} was the amount of charge collected on the C-electrode from 900 to 2700 s

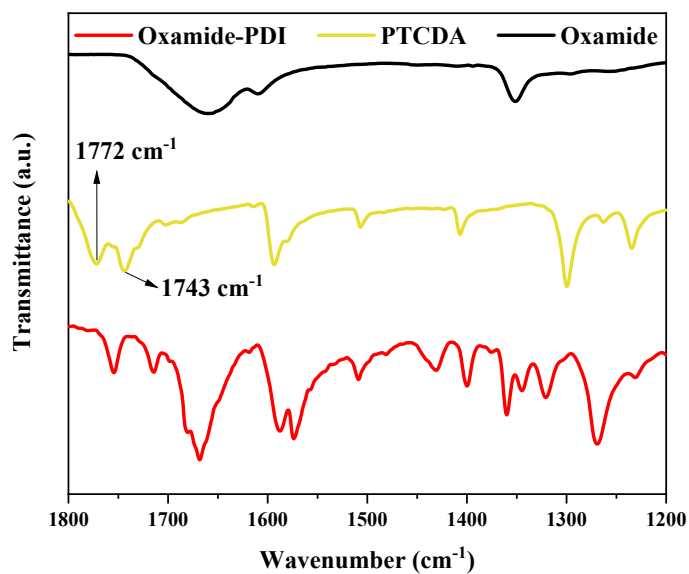


Figure S1. FT-IR spectra of Oxamide-PDI and its monomers

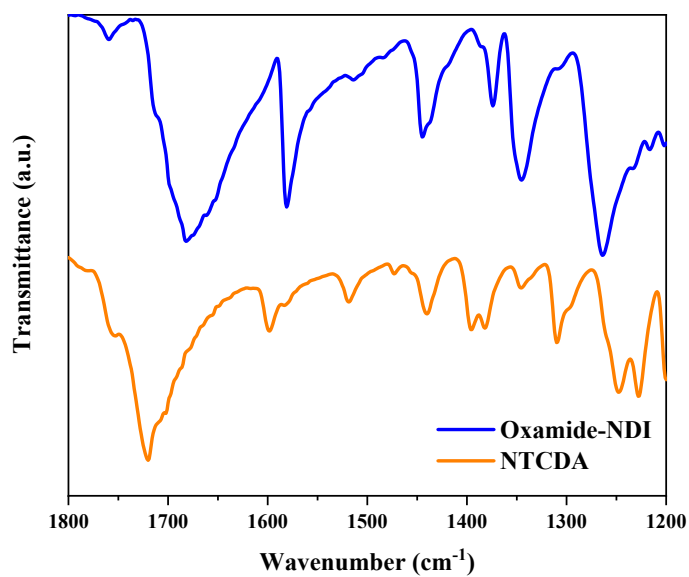


Figure S2. FT-IR spectra of Oxamide-NDI and its monomers.

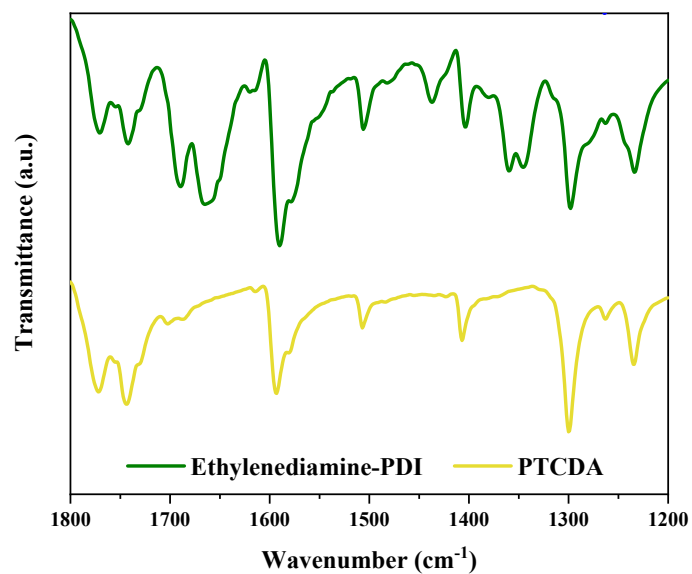


Figure S3. FT-IR spectra of Ethylenediamine-PDI and its monomers.

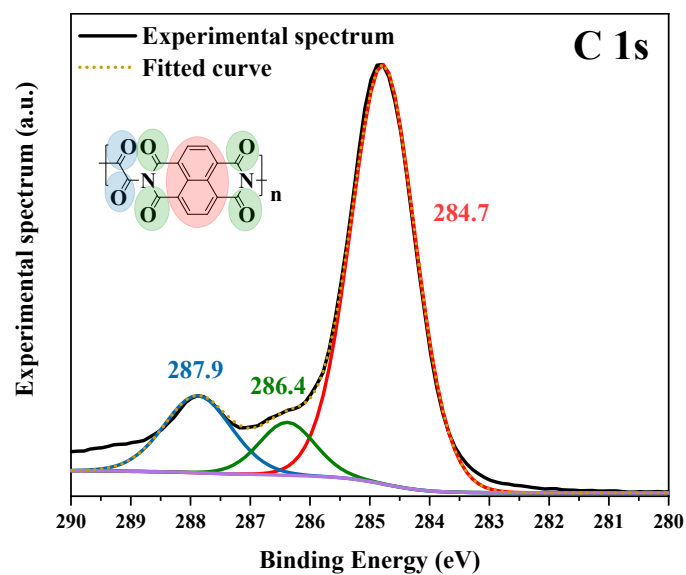


Figure S4. C1s XPS spectrum of Oxamide-NDI.

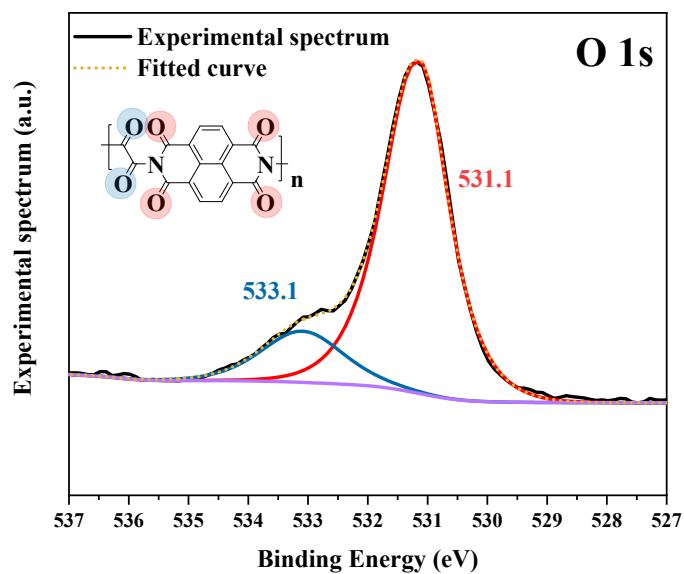


Figure S5. O1s XPS spectrum of Oxamide-NDI.

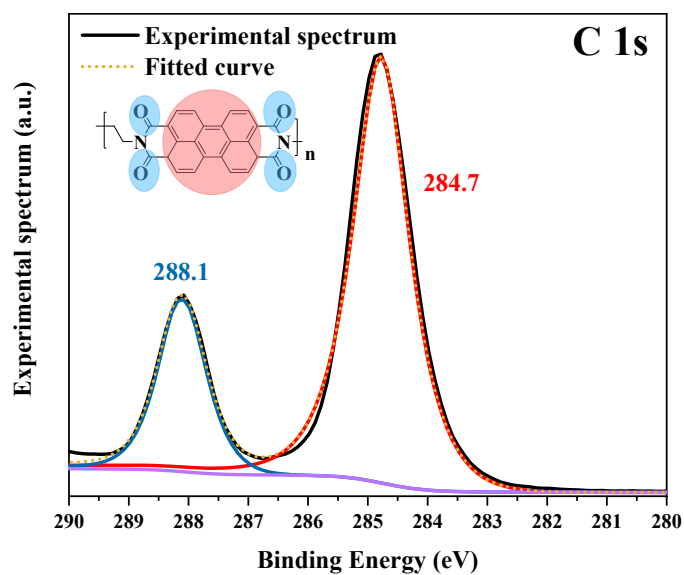


Figure S6. C1s XPS spectrum of Ethylenediamine-PDI.

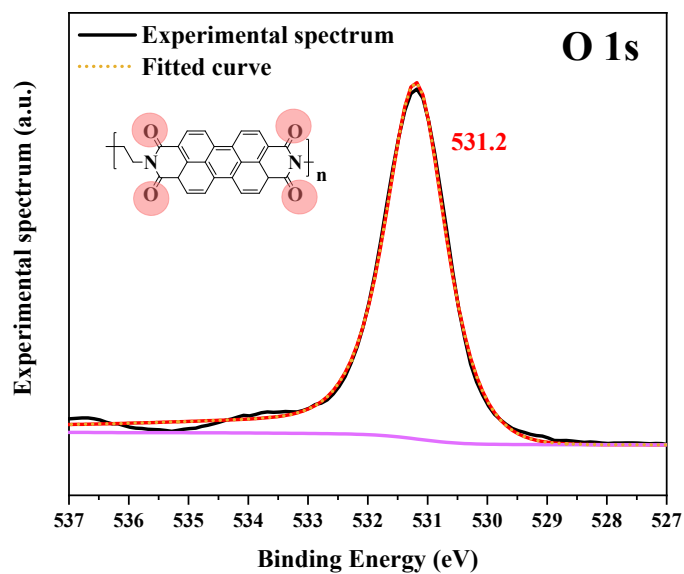


Figure S7. O1s XPS spectrum of Ethylenediamine-PDI.

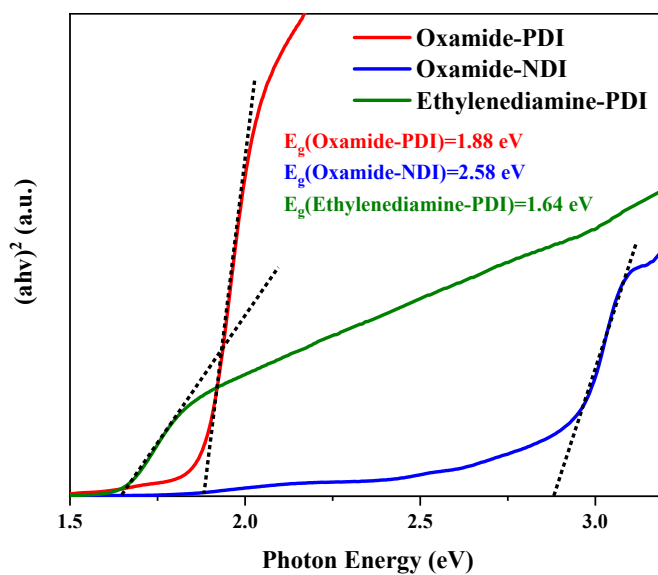


Figure S8. Tauc plots for three polymers transformed from the solid-state UV-vis spectra in Figure 1E.

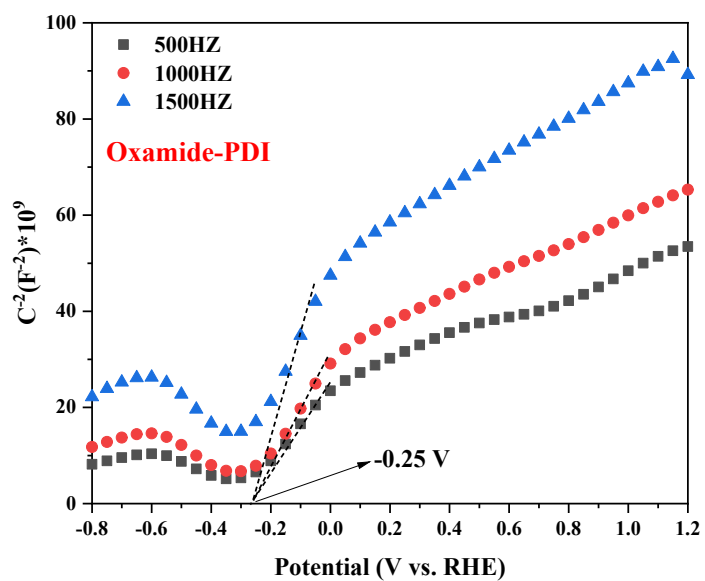


Figure S9. Mott-Schottky plots of Oxamide-PDI at frequencies of 500 Hz, 1000 Hz and 1500 Hz.

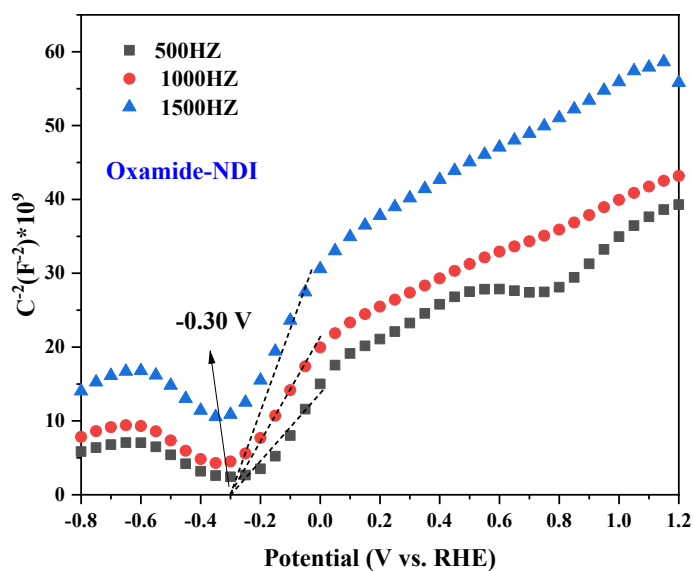


Figure S10. Mott-Schottky plots of Oxamide-NDI at frequencies of 500 Hz, 1000 Hz and 1500 Hz.

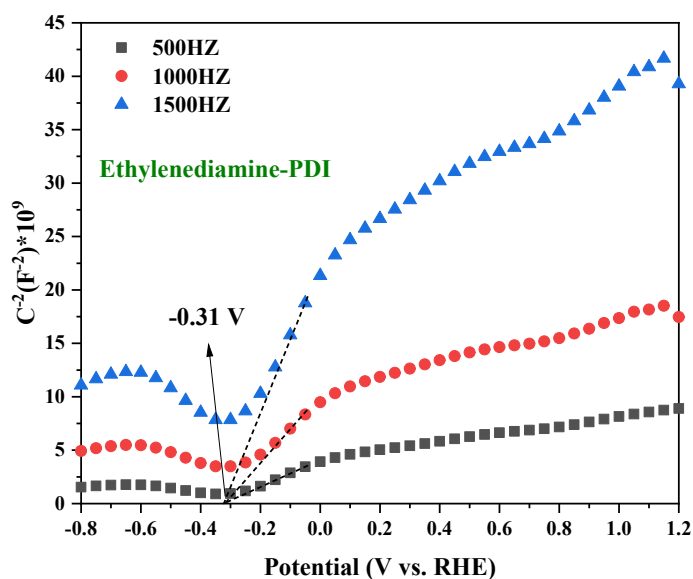


Figure S11. Mott-Schottky plots of Ethylenediamine-PDI at frequencies of 500 Hz, 1000 Hz and 1500 Hz.

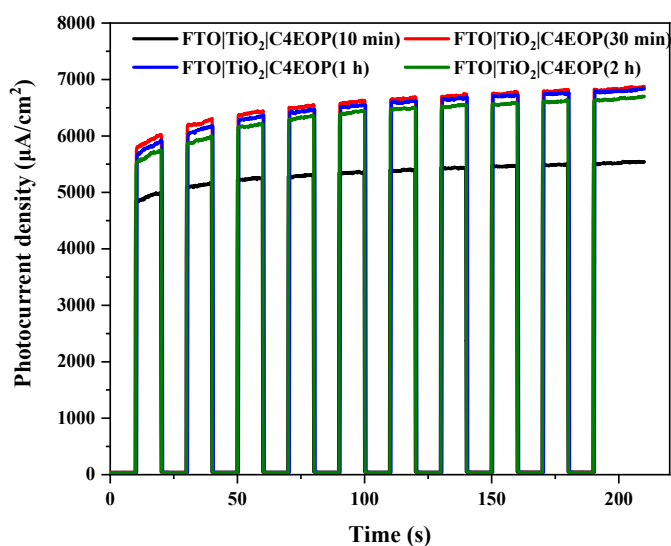


Figure S12. I-t curves of sensitized electrodes under different soaking times using dichloromethane as solvent and 0.3 M ascorbic acid (AA) as sacrificial agent.

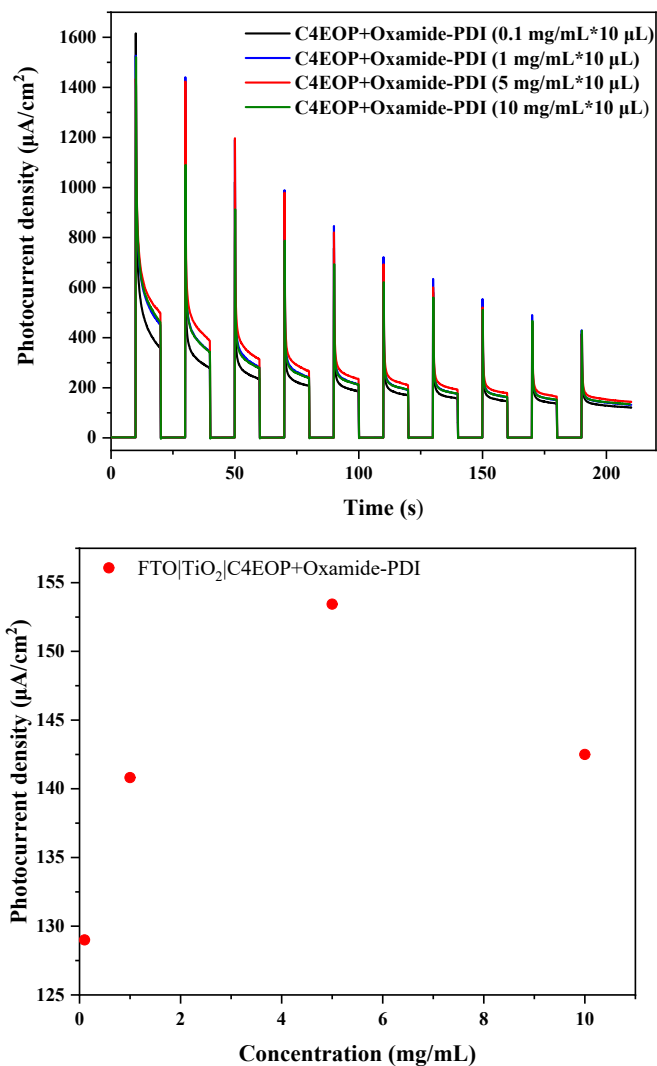


Figure S13. I-t curves of FTO|TiO₂|C4EOP+Oxamide-PDI electrodes with different OPP loading amounts (above) and their photocurrent density after exposed to chopping light for 200 s (below).

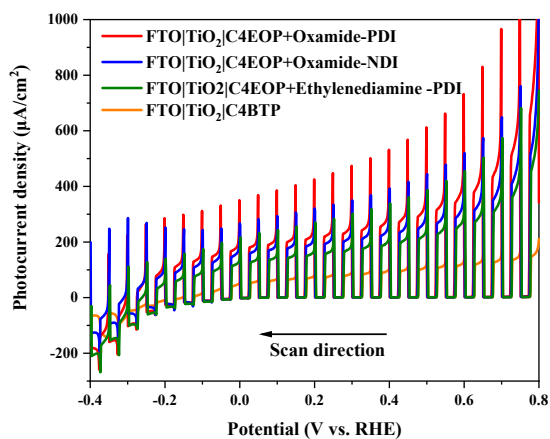
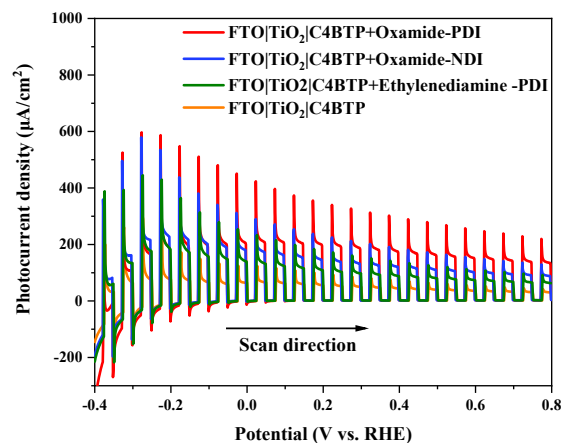


Figure S14. LSV curves of the C4BTP-sensitized electrodes corresponding to the three OPPs under positive scan direction (above) and negative scan direction (below).

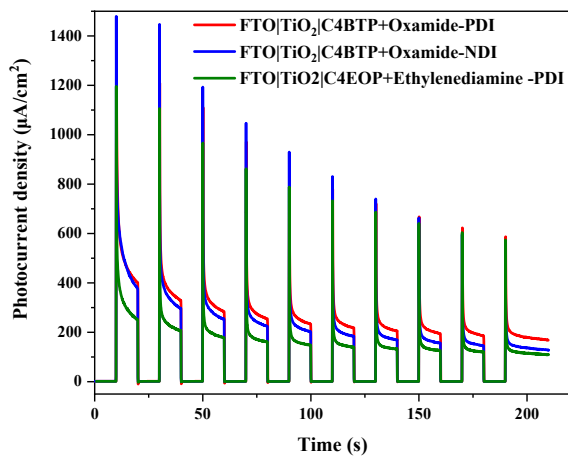


Figure S15. I-t curves of C4BTP-sensitized electrodes loaded with different OPPs with a bias of 0.2 V vs RHE.

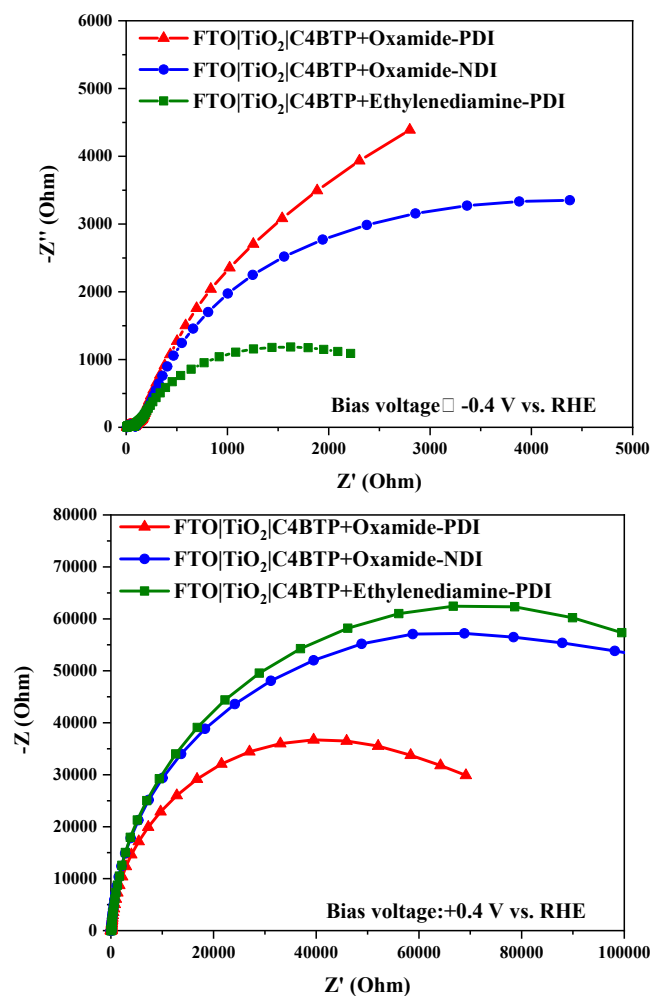


Figure S16. EIS Nyquist plots of C4BTP-sensitized electrodes loaded with different OPPs with a bias of -0.4 V vs. RHE in the dark (above) and with a bias of 0.4 V vs. RHE under irradiation (below).

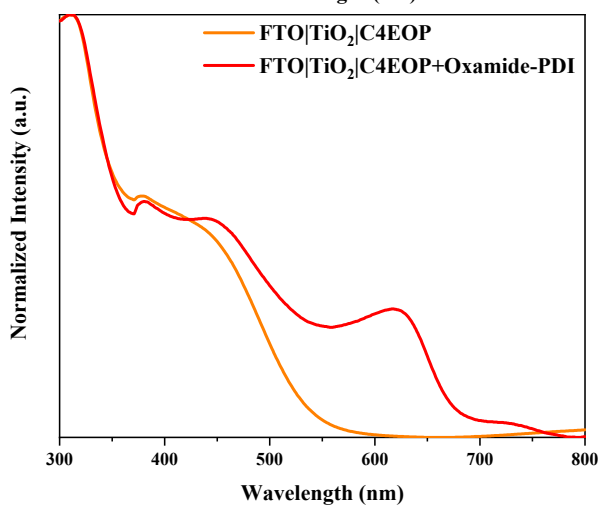
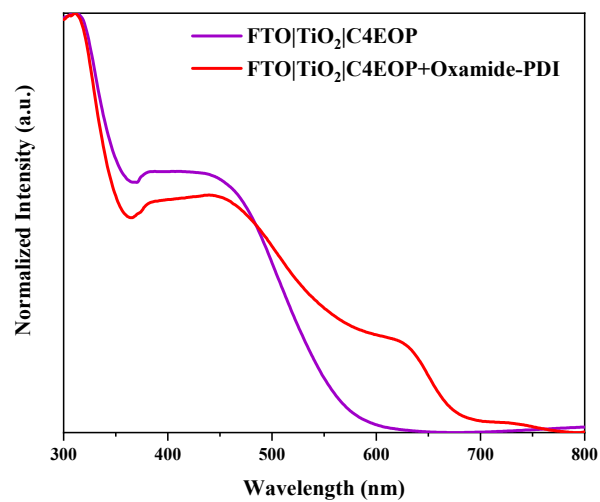


Figure S17. Solid-state UV-vis spectra of FTO|TiO₂|C4EOP and FTO|TiO₂|C4EOP+Oxamide-PDI (above), and FTO|TiO₂|C4BTP and FTO|TiO₂|C4BTP+Oxamide-PDI (below)

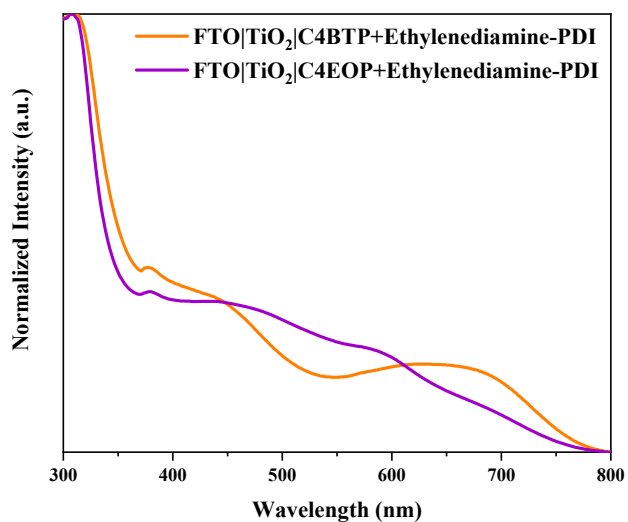


Figure S18. Solid-state UV-vis spectra of FTO|TiO₂|C4EOP+Ethylenediamine-PDI and FTO|TiO₂|C4BTP+Ethylenediamine-PDI.

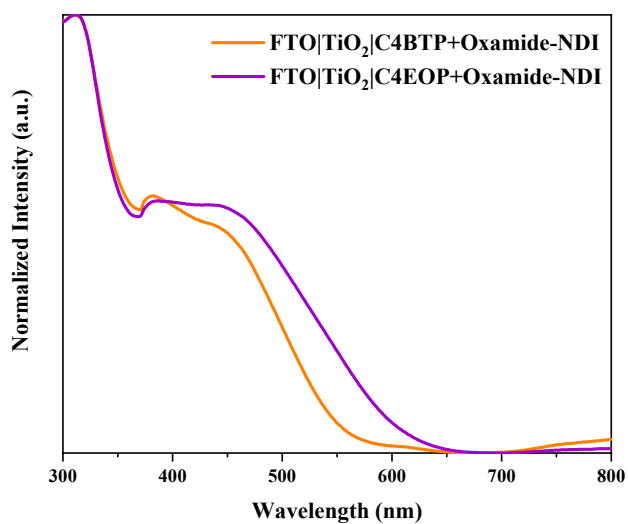


Figure S19. Solid-state UV-vis spectra of FTO|TiO₂|C4EOP+Oxamide-NDI and FTO|TiO₂|C4BTP+Oxamide-NDI.

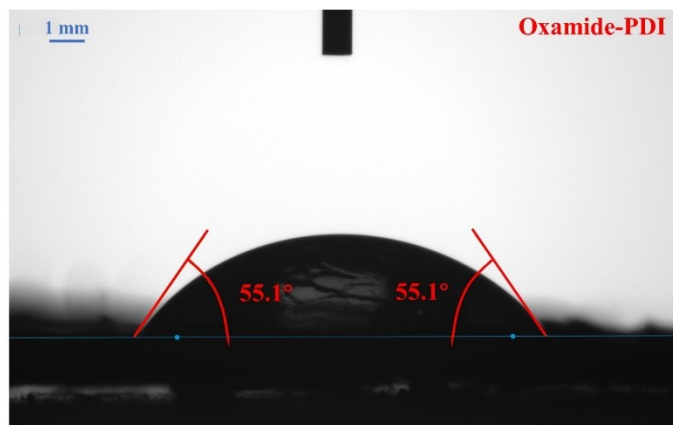


Figure S20. Contact angle of water on Oxamide-PDI tablet sample.

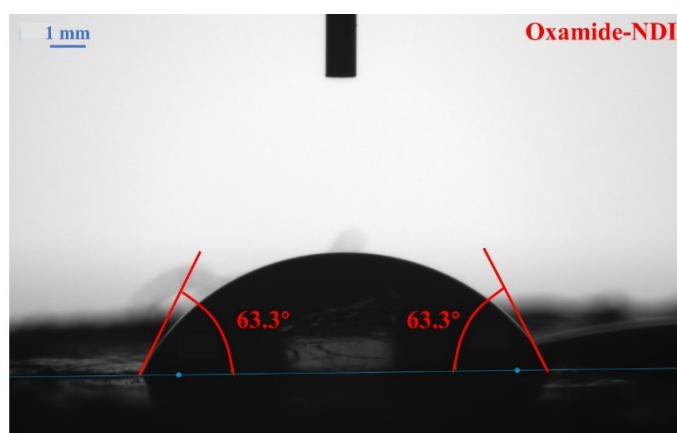


Figure S21. Contact angle of water on Oxamide-NDI tablet sample.

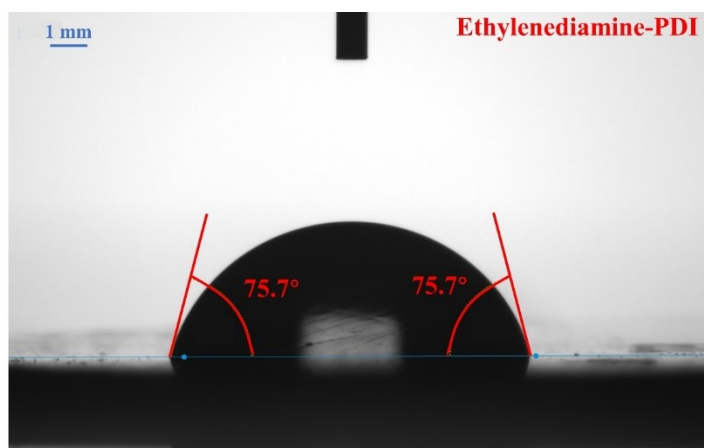


Figure S22. Contact angle of water on Ethylenediamine-PDI tablet sample.

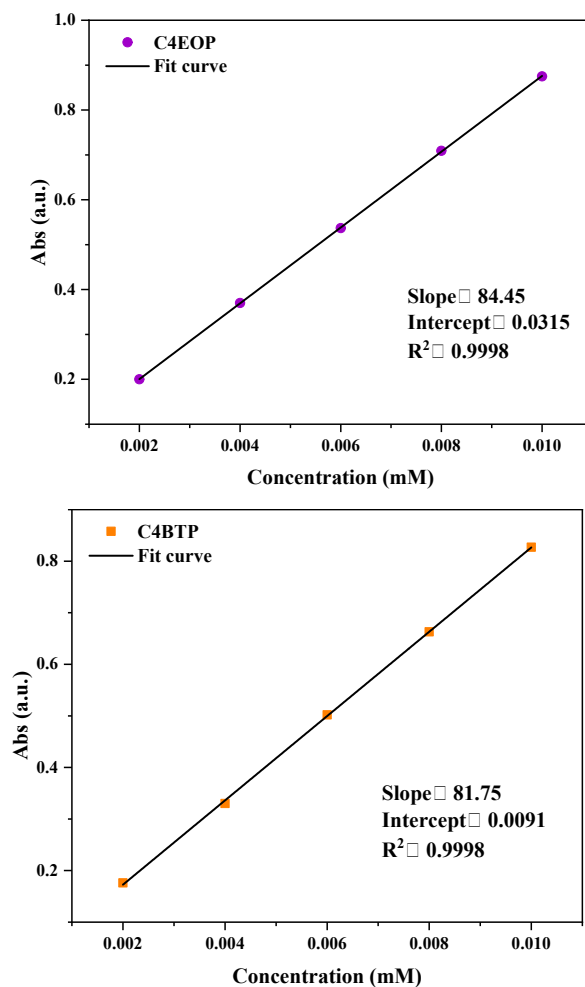


Figure S23. The absorbance-concentration standard curves of C4EOP (above) and C4BTP (below) in a mixed solution of chloroform/acetic acid (1:1 v/v) (with 8 drops of water added in every 2 mL) obtained through UV-vis absorption spectra. The standard formula for C4EOP was $\text{Abs} = 84.45 \times \text{concentration (mM)} + 0.0315$, while the standard formula for C4BTP was $\text{Abs} = 81.75 \times \text{Concentration (mM)} + 0.0091$

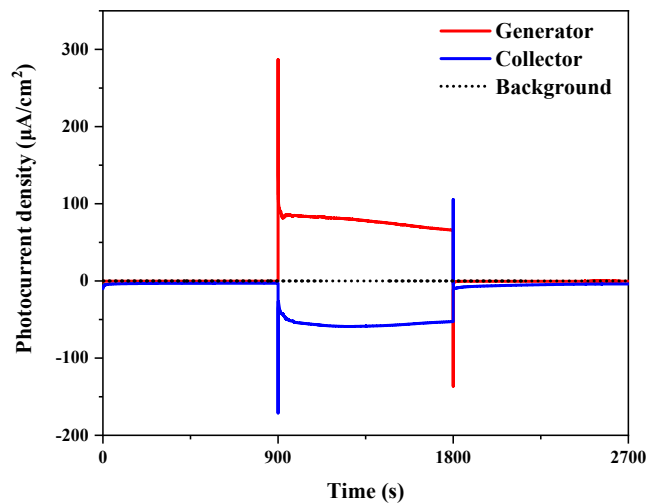


Figure S24. Calibration result of collection efficiency of DSPEC molecular devices for O_2 production.

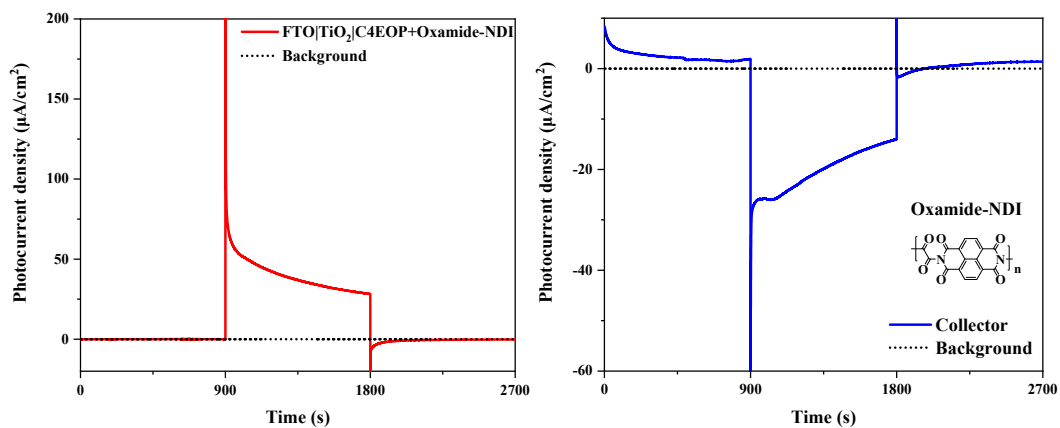


Figure S25. Faraday efficiency test curve of generator (left) and collector (right) in C4EOP-sensitized DSPEC devices loaded with Oxamide-NDI.

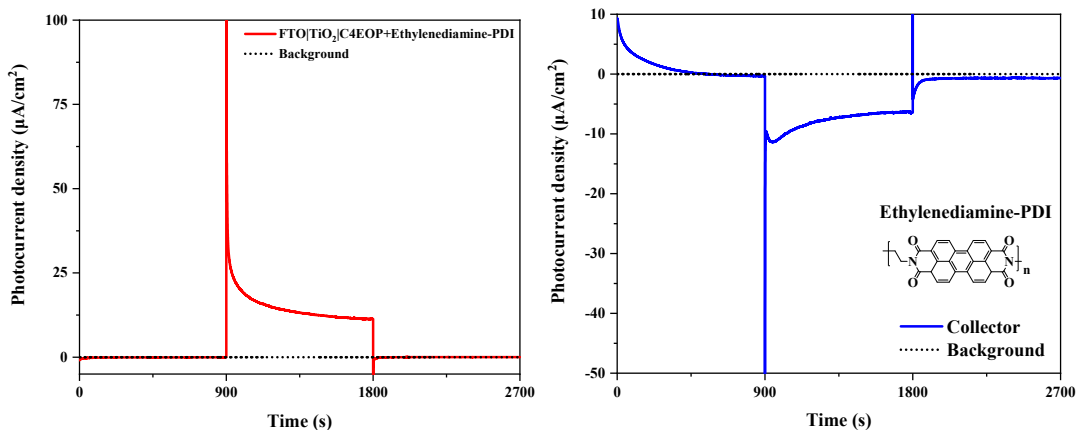


Figure S26. Faraday efficiency test curve of generator (left) and collector (right) in C4EOP-sensitized DSPEC devices loaded with Ethylenediamine-PDI.

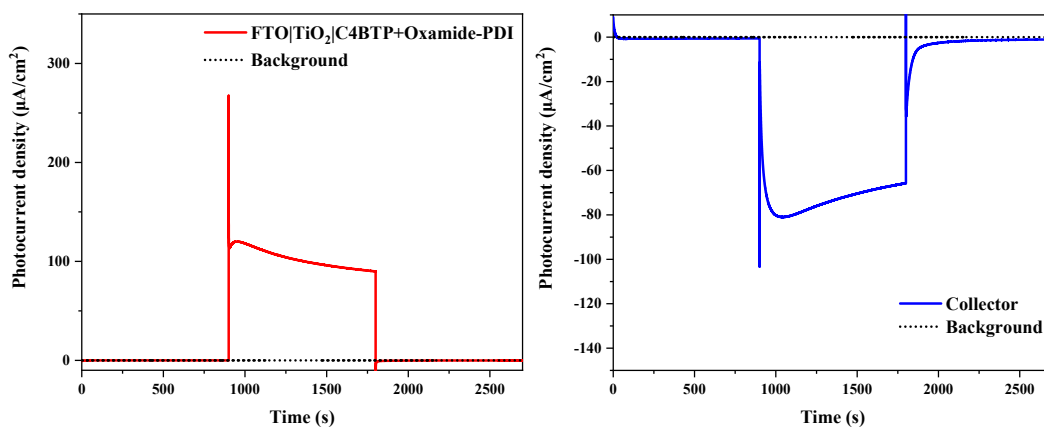


Figure S27. Faraday efficiency test curve of generator (left) and collector (right) in C4BTP-sensitized DSPEC devices loaded with Oxamide-PDI.

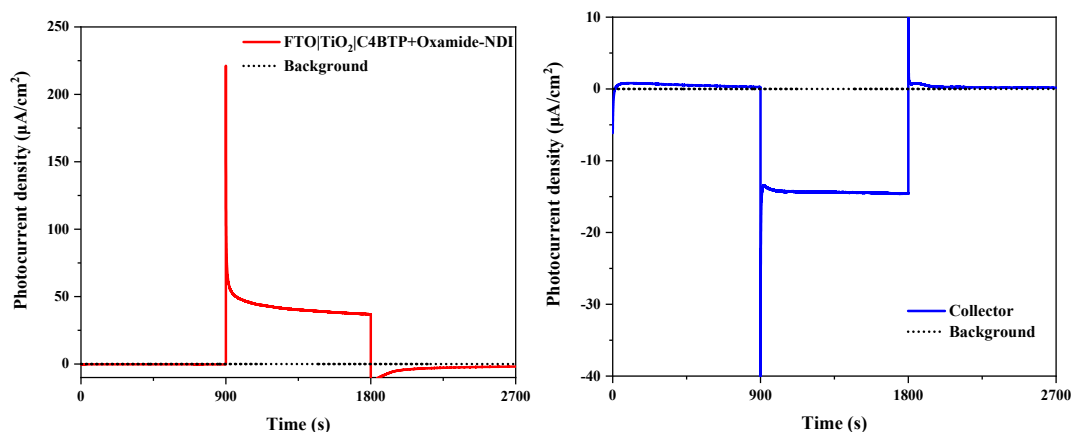


Figure S28. Faraday efficiency test curve of generator (left) and collector (right) in S24

C4BTP-sensitized DSPEC devices loaded with Oxamide-NDI.

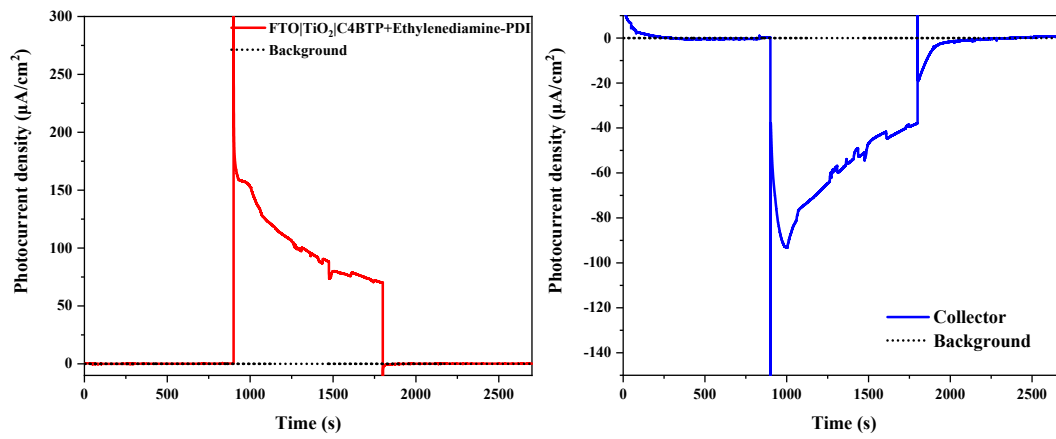


Figure S29. Faraday efficiency test curve of generator (left) and collector (right) in C4BTP-sensitized DSPEC devices loaded with Ethylenediamine-PDI.

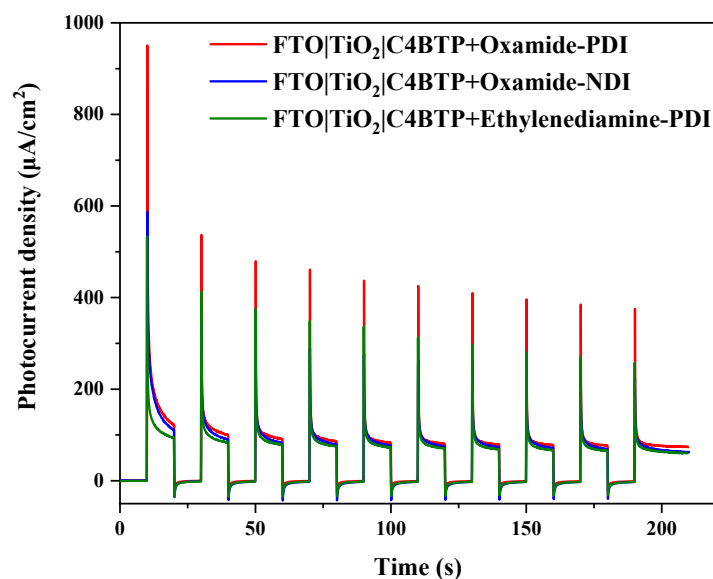


Figure S30. I-t curves of C4BTP- sensitized electrodes loaded with different OPPs with bias voltage of 0 V vs. RHE.

Table S1. Calculation of C4EOP and C4BTP loading amounts on electrodes

	C4EOP	C4BTP
Abs (Sample 1)	0.291	0.259
Abs (Sample 2)	0.296	0.256
Abs (Average value)	0.294	0.258
Concentration	0.0031 mM	0.0030 mM
Adsorption capacity	25.8 nmol cm ⁻²	25.0 nmol cm ⁻²

Table S2. Calculation of OPPs loading amounts on electrodes

	Oxamide-PDI	Oxamide-NDI	Ethylenediamine-PDI
Loading mass	50 μg	50 μg	50 μg
Loading capacity	700.1 nmol cm ⁻²	969.8 nmol cm ⁻²	746.9 nmol cm ⁻²
Ratio (= dye/ oxygen producing polymer)	1:27	1:38	1:29

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