

Supporting information for
Efficient Organic Self-Powered Photoelectrochemical
Photodetectors Based on Conjugated Polymer/Fullerene
Heterojunction

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EXPERIMENTAL SECTION

Materials

Monomer distannylated-DTBT and dibromo-Qx were synthesized according to the previous reported procedures ^[1,2]. Reagents used in the experiment such as petroleum ether, dichloromethane, ethyl acetate, n-hexane, tetrahydrofuran, diethyl ether, toluene, chlorobenzene, N,N-dimethylformamide, methanol, ethanol, ethylene glycol, acetonitrile, glacial acetic acid, chloroform, etc., as well as the commonly used drugs for the experiment, anhydrous magnesium sulfate, sodium hydroxide, sodium hydrogen sulfite, etc. were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd., and the ultra-dry chlorobenzene used in the polymerization was from Anheji Chemical Technology Co., Ltd. Purchase, use directly. The column chromatography silica gel powder is used in the specification of 200-300 mesh and purchased from

Qingdao Ocean Chemical Co., Ltd. All chemicals used in the experiment were obtained from formal commercial sources and used without further purification unless stated otherwise.

Synthesis of PDTBT-Qx

Monomer DTBT (0.25 mmol, 156.5 mg), monomer Qx (0.25 mmol, 277.8 mg), Pd₂(dba)₃ (5 mg) and P(o-tolyl)₃ (10 mg) were successively added in 25 mL flask and deoxygenated with nitrogen. Then, the extra dry chlorobenzene (5 mL) was added. The mixture solution was further evacuated and refilled with nitrogen three times and then was heated to reflux for 48 h. Then, 2-(tributylstannyl)thiophene (0.2 mL) was added to the solution and reacted for 12 h. Subsequently, 2-bromothiophene (0.2 mL) was added and stirred for 12 h to complete the end-capping reaction. After cooling to room temperature, the reaction solution was poured into methanol to precipitate the product. Then, the product collected by filtration was further precipitated in acetone and hexane to remove the unreacted monomers and oligomers. The final product was collected and dried in vacuum drying oven to give the black solid with a decent yield of 81%.

Fabrication of PDTBT-Qx/PC₇₁BM OPEC PDs

OPEC PDs were fabricated with a simple structure of FTO/PDTBT-Qx/PC₇₁BM/electrolyte/Pt/FTO. PDTBT-Qx and PC₇₁BM were dissolved in chlorobenzene and stirred to obtain the blend solution with a total concentration of 14 mg/mL. The blend solution was spin-coated on the top of FTO substrate at 1500 rpm for 40 s in the air to manufacture the photoanode of OPEC PDs. To avoid the contribution from the region out of the heterojunction area^[3], the PDTBT-Qx/PC₇₁BM

thin film was used as the photoanode of the photodetector after a circular area with a diameter of 6 mm was retained. Then, the photoanode was combined with the Pt-coated counter electrode (Pt/FTO) by a 30- μm heat-sealing film under a hot-pressing condition. Finally, the iodine electrolyte was injected into the space between photoanode and counter electrode by vacuum back filling system.

Measurement of device

The device performance was recorded by the semiconductor Characterization and the light sources were provided by LED. In detail, the negative electrode is connected to the Pt electrode, and the positive electrode is connected to the photoanode. Meantime a shutter is used to control the on and off of the incident light. Besides, the whole process of measurement was operated in the dark to avoid the influence of indoor light, and the tinfoil was used to block areas other than the photoactive area to mitigate the influence out of the heterojunction area. Moreover, the incident light focus only on the photoactive(0.2827 cm^2) instead of the whole substrate, and the LED light spot size is larger than photoactive area to ensure the uniformity of light intensity.

Characterizations

The spectral absorption spectrum of as-synthesized polymers were measured by UV-vis-NIR spectrophotometer (Varian Gary 5000). The mutual accumulation of molecular chains was characterized by X-ray diffractometer (PANalytical). The morphology of the polymer film was observed by tapping mode atomic force microscopy (NanoMan VS microscope) and transmission electron microscopy (Tecnai G2 F30). The current density-voltage (J-V) characteristics curves and time dependent

photocurrent response curves (J-t) were recorded by a semiconductor Characterization system (Keithley Instruments). The Metrohm electrochemical workstation (Autolab-PGSTAT302N) was used to measure electrochemical impedance spectroscopy (EIS). The UV or visible light sources were provided by LED (365nm, 650nm).

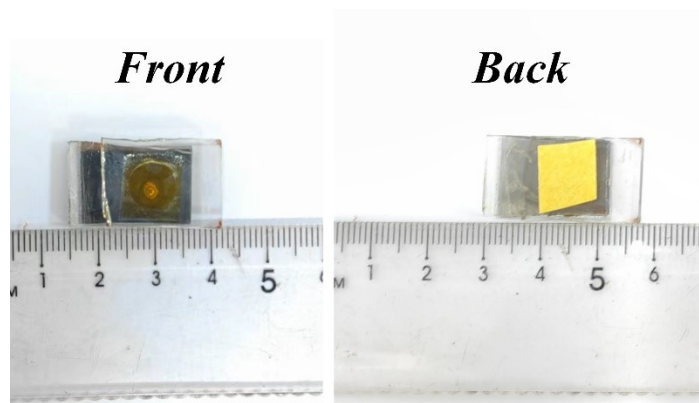


Figure S1 The real picture of OPEC PDs.

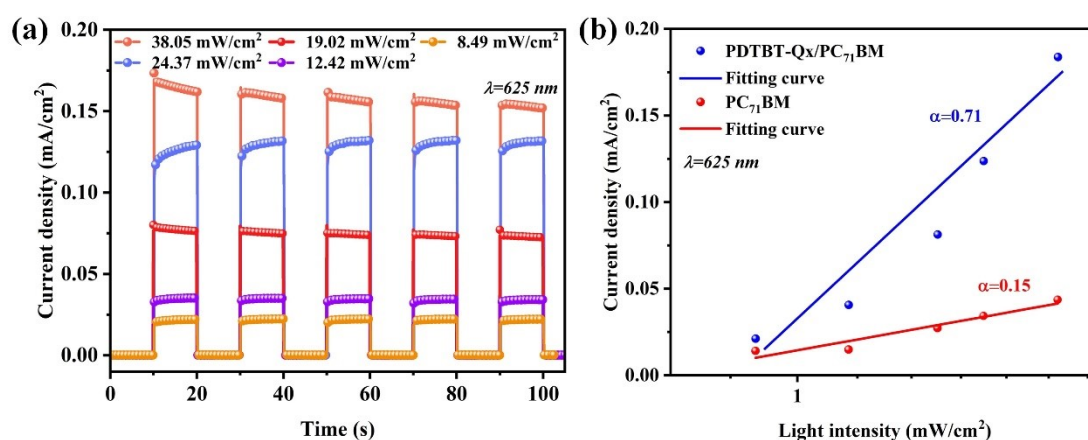


Figure S2 (a) The J-t curves of PDTBT-Qx/PC₇₁BM OPEC PDs under 625 nm light illumination with different intensities; (b) Light intensity dependent J_{SC} of PDTBT-Qx/PC₇₁BM and PC₇₁BM OPEC PDs under 625 nm light illumination.

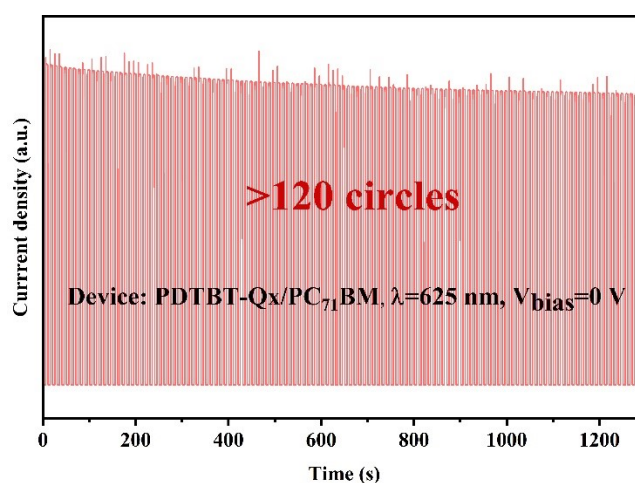


Figure S3 The repeatability of PDTBT-Qx/PC₇₁BM OPEC PDs under illumination of 625 nm light.

Table S1 Performance parameters comparison of current photoelectrochemical photodetectors heterojunction structure.

Materials	Spectral range (nm)	Responsivity (mA/W)	Electrolyte	Bias (V)	Ref.
PDTBT-Qx/PC ₇₁ BM	365-625	19.25	I ⁻ /I ₃ ⁻		This work
p-Te/n-Bi ₂ Te ₃	365-850	12.07	S ²⁻ /S _n ²⁻		[4]
Se/InSe	365-850	22.5	I ⁻ /I ₃ ⁻		[5]
Te/Se	365-980	4.04×10 ⁻³	KOH	0	[6]
ZnO/CdS	355-470	35.2	Na ₂ SO ₄		[7]
ZrO ₂ /TiO ₂	365-625	158.67	I ⁻ /I ₃ ⁻		[8]
ZnO/TiO ₂	365	17.85	I ⁻ /I ₃ ⁻		[9]

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