

Supporting Information

Highly Stable Photomultiplication Type Organic Photodetectors with Single-Polymer Containing Intramolecular Traps as Active Layer

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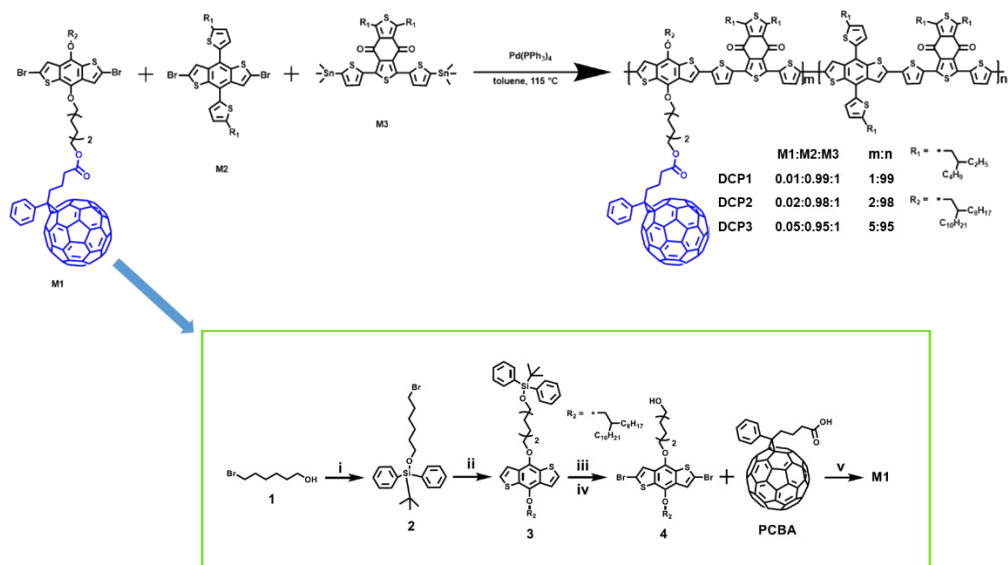
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Materials synthesis



Scheme 1. The synthetic procedures of DCP1-3. The green box shows the The synthetic routes of the monomer **M1**. (i) TBDPSCl, TEA, DMAP, CH₂Cl₂. (ii) 4,8-dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione, 9-(bromomethyl) nonadecane, TBAB, NaOH(aq). (iv) TBAF, THF, 0 °C. (v) PCBA, DMAP, EDCI, o-DCB.

The synthetic procedures of DCP1-3 are shown in **Scheme 1**. The monomers **M1**, **M2** and **M3** were dissolved in toluene at varied ratios. 0.03 equiv. of Pd(PPh₃)₄ was added into the mixtures after being flushed with argon for five minutes. The reactions were stirred at 115 °C for 48 h. The polymers were precipitated in methanol (100 mL) and filtrated through a Soxhlet thimbe. The polymers were extracted with acetone, hexane, dichloromethane and chloroform, and were collected by chloroform and then reprecipitated in acetone. The polymers were collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven for 24 h before use.

The structure of **M1** can be confirmed by ¹H and ¹³C nuclear magnetic resonance (NMR) spectra, mass spectrometry measurements, as shown in **Fig. S1-S3**. The experimental results can prove that the fullerene is coupled into **M1**.

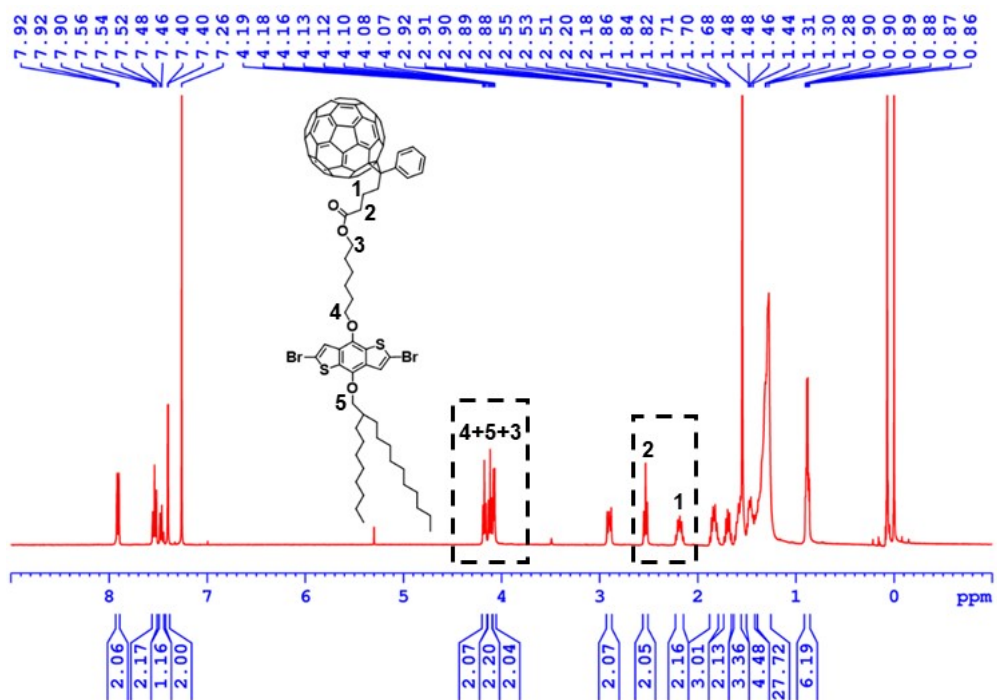


Fig. S1. ¹H NMR of M1 in chloroform-*d*.

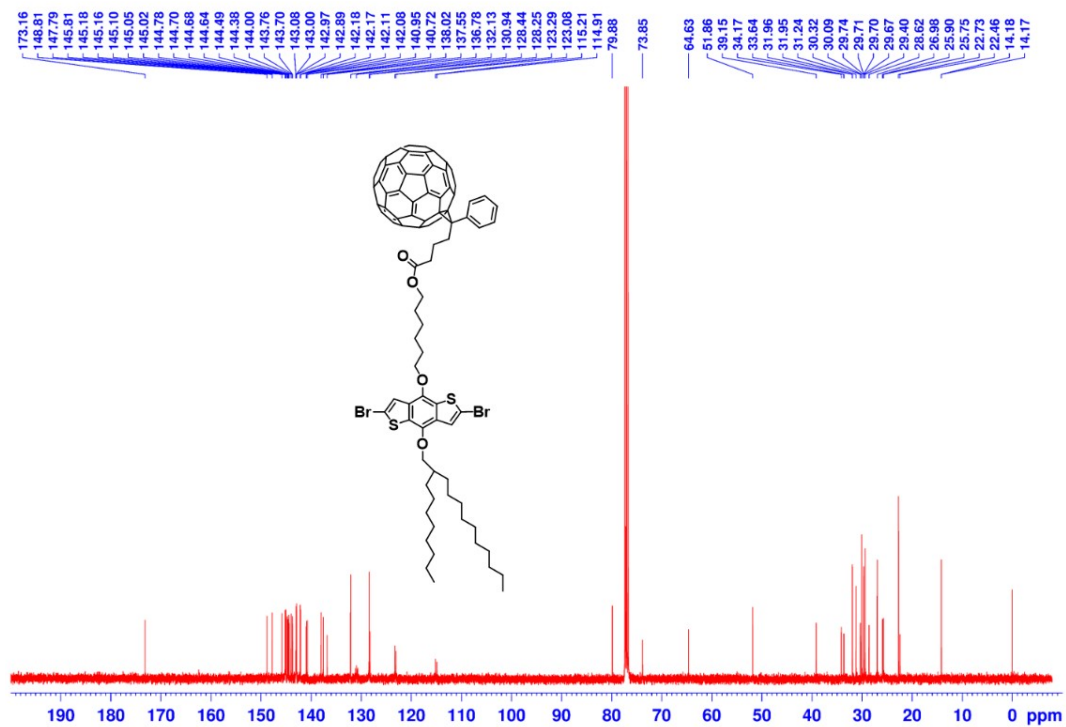


Fig. S2. ¹³C NMR of M1 in chloroform-*d*.

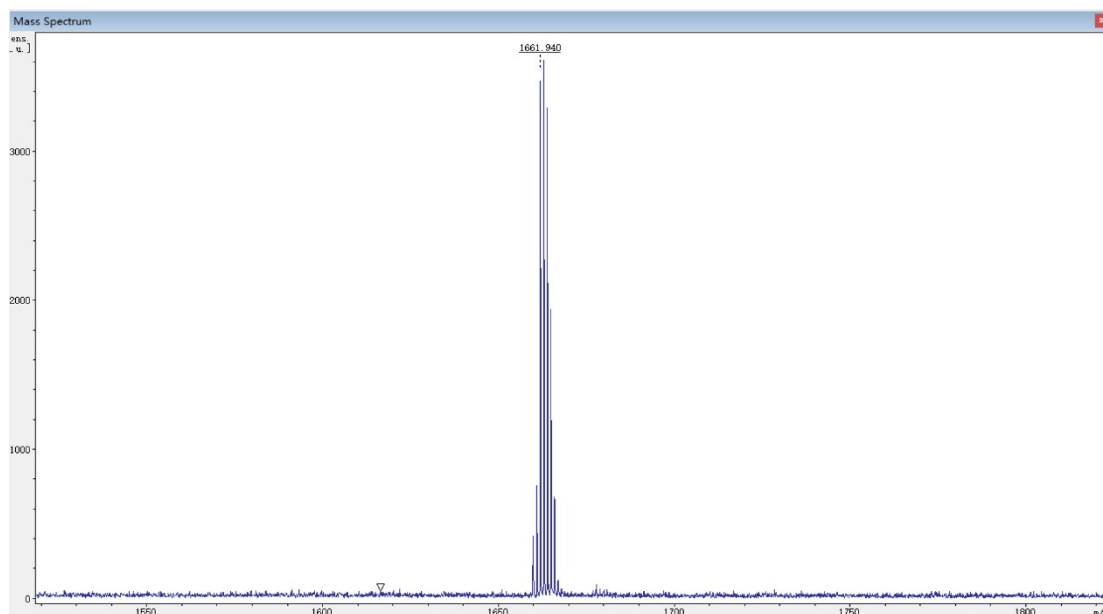


Fig. S3. The low resolution mass spectrometry of **M1**.

It is very difficult to confirm the fullerene content in DCP1-3 by NMR spectra due to the rather less fullerene and the complexity of proton signals in these polymers. To further confirm the fullerene attached to the polymer backbone, NMR spectra were carried out on the polymers attached more fullerene, as shown in **Fig. S4**. The denoted *H* proton 1-5 in the NMR spectra is assigned from the monomer **M1** with fullerene pendant. The peak intensity of 1-5 can be markedly enhanced along with the increasing the content ratio of **M1** during Stille polymerization, suggesting the enhancement of fullerene content in the polymer P1-P4. The experimental results confirm that fullerene can be attached to the polymer backbone by using FP method. The rather less fullerene attached to polymer backbone will form intramolecular electron traps to realize hole tunneling injection from external circuit and PM effect.

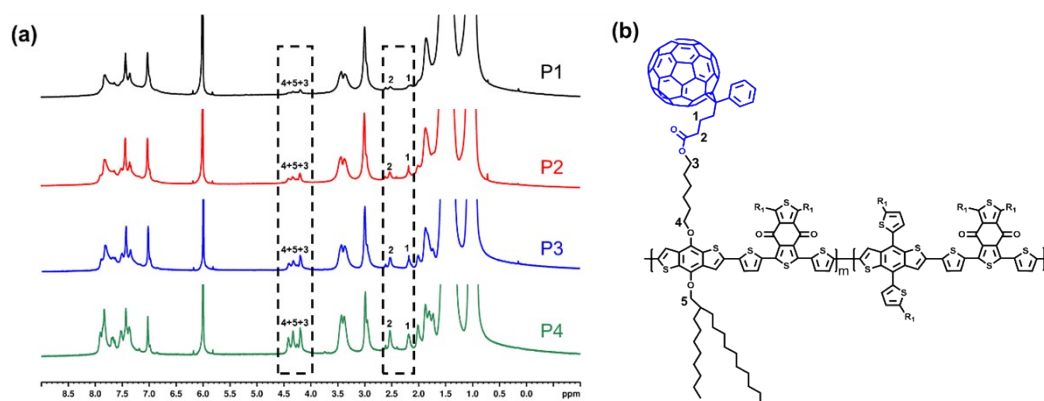


Fig. S4. (a) ¹H NMR spectra of the polymers P1-P4 recorded at 100 °C with 1,1,2,2-

tetrachloroethane-d₂ as the solvent. (b) Chemical structures of the polymers, 1-5 are positions of H. The feed ratios of **M1:M2:M3** for P1-P4 are 0.1:0.9:1, 0.2:0.8:1, 0.3:0.7:1 and 0.5:0.5:1. The proton peaks from fullerene-contained monomer M1 can be clearly observed in H-NMR spectra, indicating the presence of fullerene side units in the conjugated polymers DCP1-3.

Device fabrication

The patterned indium tin oxide (ITO) glass coated substrates (sheet resistance 15 Ω/\square) were consecutively cleaned in ultrasonic baths containing detergent, de-ionized water and ethanol, respectively. The cleaned ITO substrates were blow-dried by high pure nitrogen gas and then treated by oxygen plasma for 1 min to improve its work function and clearance. The ITO substrates were then moved into high-purity nitrogen-filled glove box to fabricate PFN-Br interfacial layer. The PFN-Br (purchased from Solarmer Materials Inc and used as received) was dissolved in methanol (adding 0.3 vol% acetic acid to accelerate dissolution) to prepare 5 mg/ml solution. The concentrated solution was further dilute into 0.2 mg/ml, 0.3 mg/ml, 0.5 mg/ml and 0.7 mg/ml solution. The PFN-Br solution was spin-coated at 5000 RPM for 35 s to prepare PFN-Br thin films, and then annealed at 100 °C for 5 mins. Polymers PBDB-T (Purchased from Organtec Ltd.), DCP1-3 were dissolved in chlorobenzene with concentration of 20 mg/ml, 15 mg/ml, 30mg/ml and 35 mg/ml, respectively. The active layers were fabricated by spin coating PBDB-T, DCP1-3 solution on PFN-Br/ITO substrates at 800 RPM for 35 s and then annealed at 100 °C for 10 mins to prepare active layer with a thickness of ~350 nm. The thickness of active layer was measured by Ambios Technology XP-2 stylus Profiler. The MoO₃/Ag (10 nm/100 nm) films were deposited by thermal evaporation with a shadow mask under 10⁻⁴ Pa and the thickness was monitored by a quartz crystal microbalance. The active area is about 3.8 mm², which is defined by the vertical overlap of ITO and Ag.

Film and Device Characterization

The ultraviolet-visible (UV-Vis) absorption spectra of films were obtained using a Shimadzu UV-3101 PC spectrometer. Photoluminescence (PL) spectra of films were measured by a HORIBA Fluorolog®-3 spectrofluorometer system. Cyclic voltammetry

was performed under an inert atmosphere at a scan rate of 0.1 V s⁻¹ and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. The current-voltage (*I-V*) curves of all PM-OPDs were measured in a high-purity nitrogen-filled glove box using a Keithley 2400 source meter. The capacitance versus voltage (*C-V*) curves were measured by a KEYSIGHT E4990A impedance analyzer. The electrochemical impedance spectroscopy (EIS) was performed by Zahner Electrochemical Workstation. A monochromatic light can be obtained by the combination of a 150 W xenon lamp with a monochromator. The monochromatic light intensity spectrum was measured by utilizing a Thorlabs S120VC power meter. The LDR of the PM-OPDs was measured under monochromatic light of 532 nm generated by a laser. The incident light intensity was manipulated by utilizing different neutral density filters. Transient photocurrent of PM-OPDs was measured through a 532 nm light source modulated through an electronic shutter with a period of 1 s. GIWAXS measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.

Space charge-limited current (SCLC) device fabrication:

The structure of electron-only devices is ITO/ZnO/active layer/PDIN/Al and the structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Ag. The *J-V* curves of hole-only and electron-only devices were measured in dark to calculate hole mobility (μ_h) and electron mobility (μ_e) according to the following formula:

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \mu \frac{V^2}{d^3} \exp \left[0.89 \gamma \sqrt{\frac{V}{d}} \right] \quad (S1)$$

Where, ϵ_r is dielectric constant of used materials (~ 3), ϵ_0 is the vacuum permittivity (8.854×10^{-12} CF m⁻¹), μ represents charge mobility, V represents the applied voltage and d represents active layer thickness (~ 100 nm). The equation (S1) can be described as:

$$\ln \left(\frac{Jd^3}{V^2} \right) = 0.89 \gamma \sqrt{\frac{V}{d}} + \ln \left(\frac{9}{8} \epsilon_r \epsilon_0 \mu \right) \quad (S2)$$

Calculation of performance parameters: The external quantum efficiency (EQE) of

PM-OPDs can be calculated according to the ratio of the number of holes collected by electrode to the number of incident photons. Responsivity (R) is defined as the ratio of the photo-induced current density to the incident light intensity. The EQE and R can be calculated according to

$$EQE = \frac{(J_L - J_D) / e}{I_{in} / h\nu} \quad (S3)$$

$$R = \frac{EQE \cdot e}{h\nu} \quad (S4)$$

in which J_L is the current density under light illumination, J_D is the current density in dark condition, e is elementary electron charge (1.6×10^{-19} C), I_{in} is incident light intensity, h is the Plank constant, ν is photon frequency.

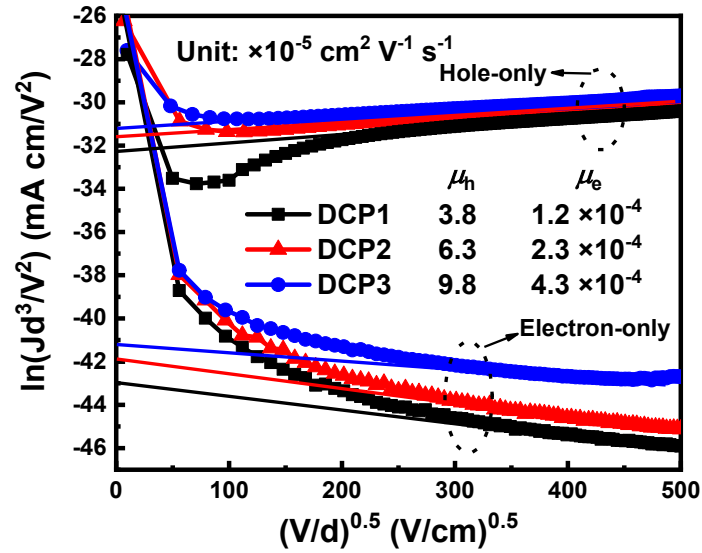


Fig. S5. The $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ curves of hole-only and electron-only devices with DCP1, DCP2 or DCP3 as active layers.

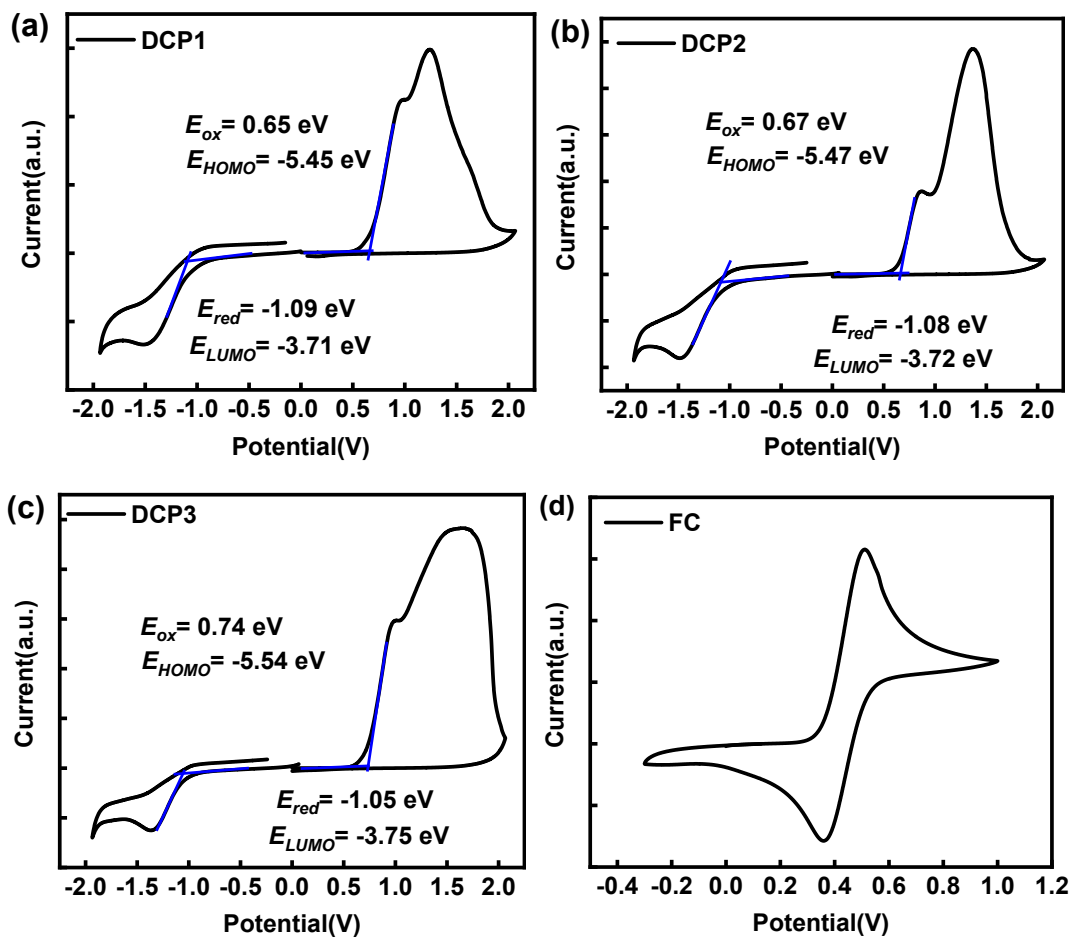


Fig. S6. Cyclic voltammograms of DCP1-3 in thin films.

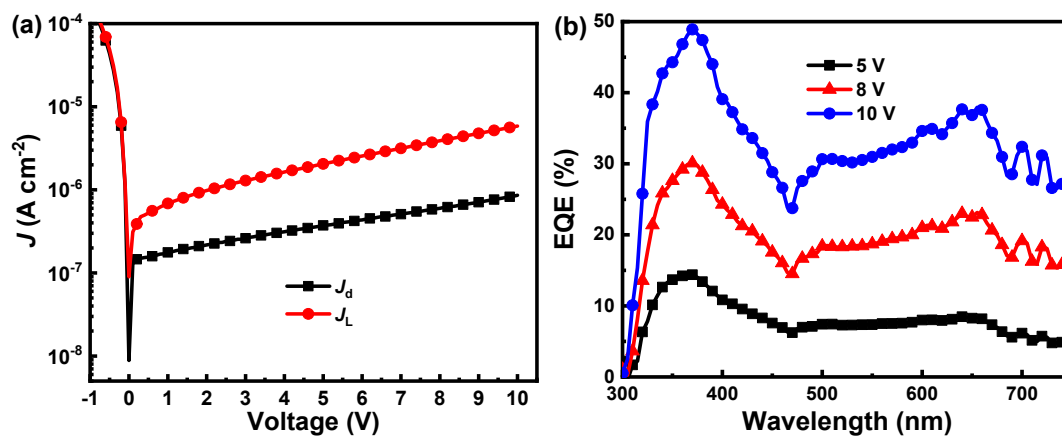


Fig. S7. J - V curves (a) and EQE spectra (b) of pure PBDB-T based device.

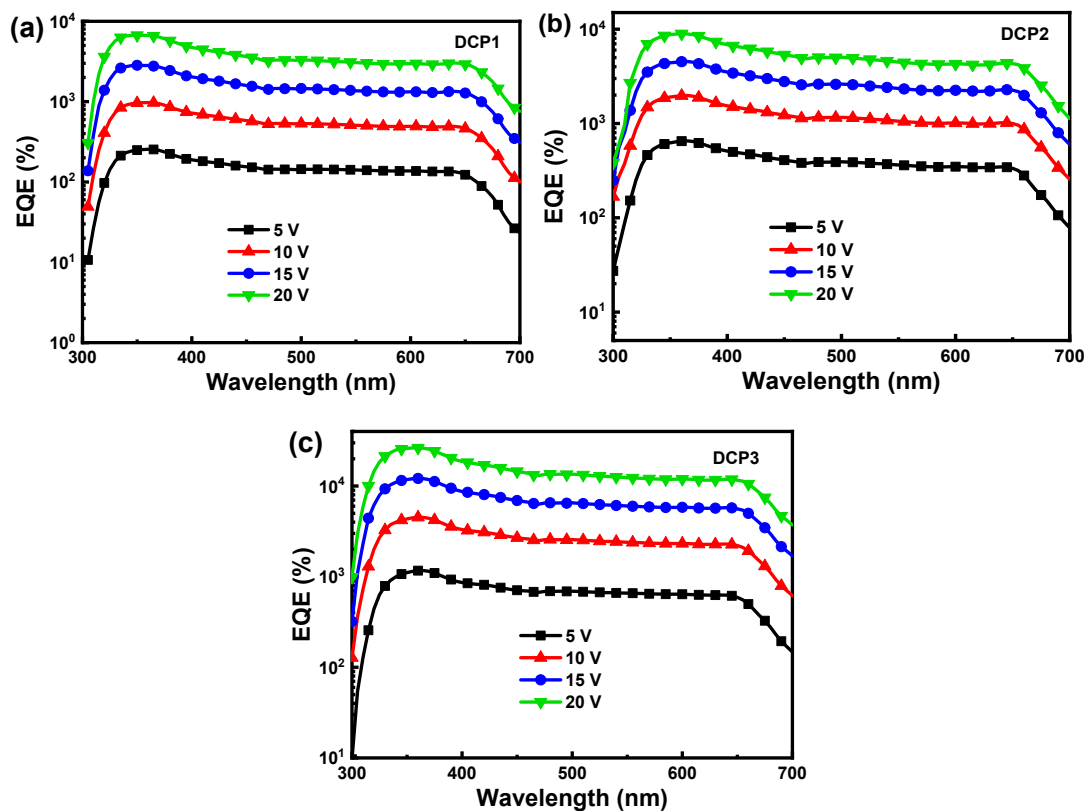


Fig. S8. EQE spectra of the PM-OPDs with different polymers under varied applied bias.

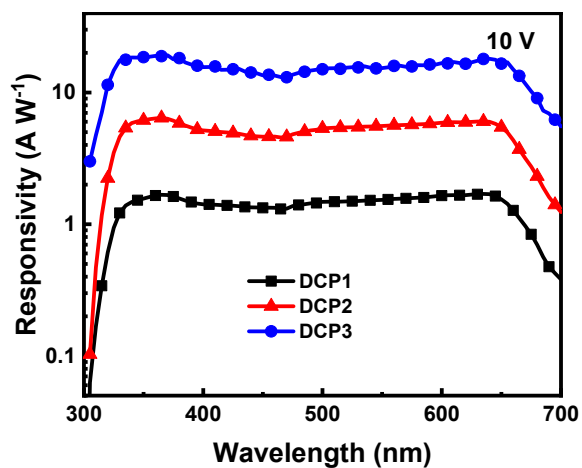


Fig. S9. The responsivity of PM-OPDs based on different active layers under 10 V bias.

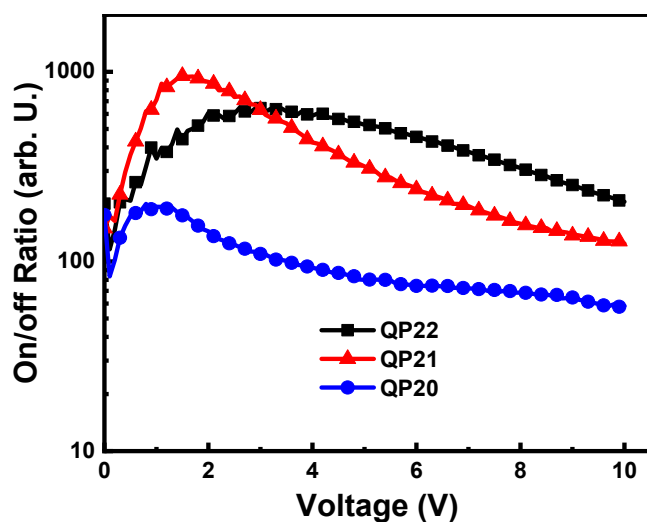


Fig. S10. The on/off ratio of PM-OPDs with different active layers.

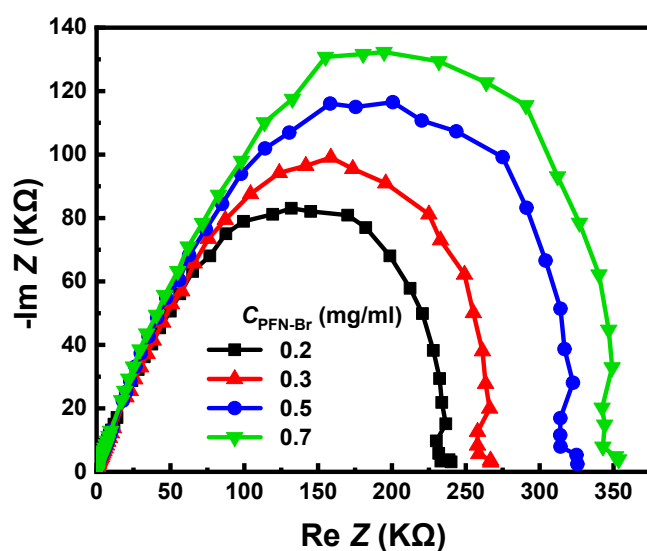


Fig. S11. The EIS measurements of the DCP3 based PM-OPDs with different $C_{\text{PFN-Br}}$ under dark condition.

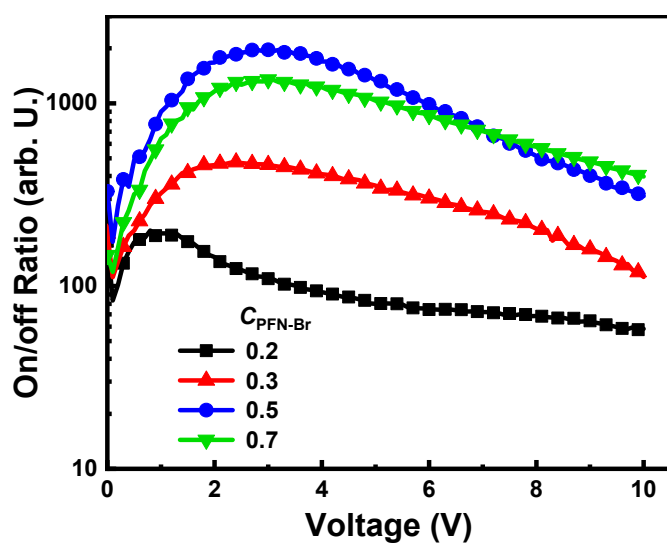


Fig. S12. The on-off ratio of the DCP3 based PM-OPDs with different $C_{\text{PFN-Br}}$.

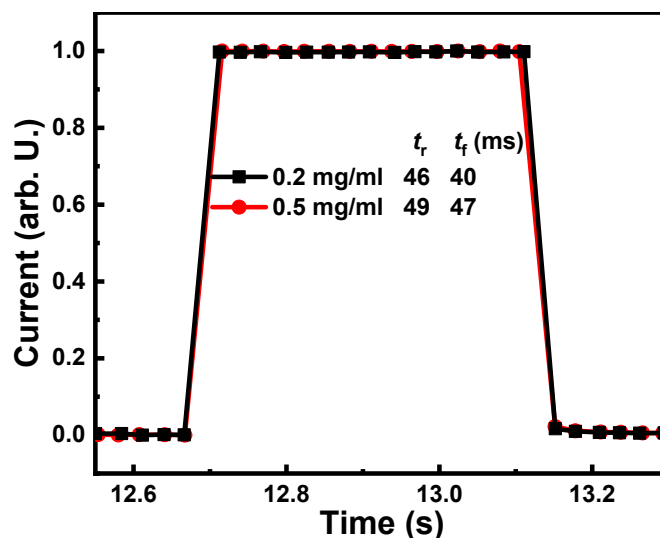


Fig. S13. The transient current of the DCP3 based PM-OPDs with $C_{\text{PFN-Br}}$ of 0.2 and 0.5 mg/ml.

The detailed description of the PM-OPDs monitoring the heart rate.

Heart rate of human can be obtained from photoplethysmography (PPG). PPG is a noninvasive optical measurement technique, which is used to detect blood volume changes in the microvascular bed of tissue by using a light source and a photodetector placed on the skin. PPG signal can be measured by the PM-OPDs due to their high sensitivity on slight change in light intensity. The heart rate of human can be obtained from the time difference between peaks of the PPG signal, as shown in **Fig. S14**.

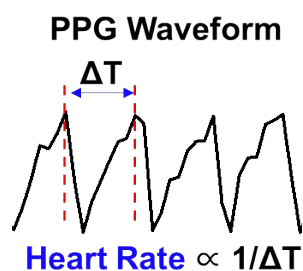


Fig. S14. Heart rate extracted from the PPG Signal.