

Electronic Supplementary Information (ESI)

Regioregular Donor–Acceptor Copolymer Allowing High Gain–Bandwidth Product in Photomultiplication-Type Organic Photodiode

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Experimental Section

Materials

All starting materials and reagents were purchased from commercial supplies unless otherwise specified and used without further purification. In particular, 2,6-bis(trimethyltin)-4,8-bis(5-(2-hexyldecyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene was purchased from Solarmer Materials Inc. 2,2'-[[6,6,12,12-tetrakis(4-hexylphenyl)-6,12-dihydrodithieno[2,3-*d*:2',3'-*d'*]-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,8-diyl]bis[methyldiyne(3-oxo-1H-indene-2,1(3H)-diylidene)]bis[propanedinitrile] (ITIC) were purchased from 1-Material and poly(3-hexylthiophene-2,5-diyl) (P3HT) was obtained from RIEKE METALS. [6,6]-phenyl-C71-butyric acid methyl ester (PCBM) was bought from Nano-C and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Clevious P VP.AI 4083) aqueous solution was supplied by Heraeus Holding GmbH. Mucosol, acetone, isopropanol, 1,2-dichlorobenzene (DCB) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification processes.

Synthesis of Compound M1

Compound 1 (0.76 g, 0.68 mmol) and NBS (0.28 g, 1.57 mmol) were dissolved into 40 mL of tetrahydrofuran in a round flask under nitrogen protection. The solution was protected from light and stirred at room temperature for 24 h, then poured into 100 mL of water and extracted with methylene chloride. Solvent was evaporated under vacuum and the crude product was purified by chromatography on silica gel with hexane to chloroform gradually to obtain a red solid (0.51 g, 66% yield). ¹H NMR (CDCl₃, 500 MHz, [ppm]): δ 8.017 (d, 2H, J=3.5 Hz), 7.899 (s, 2H), 7.695 (d, 2H, J=13 Hz), 7.321 (d, 2H, J=3.5 Hz), 2.572 (d, 4H, J=7 Hz), 1.748 (br, 2H), 1.318 (m, 36H), 0.919 (m, 12H); MALDI-TOF: m/z 1126.2, calcd 1126.13.

PDBD-FBT Polymerization

M1 (0.248 g, 0.22 mmol) and 2,6-bis(trimethyltin)-4,8-bis(5-(2-hexyldecyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (M2, 0.248 g, 0.22 mmol), 12 mL of toluene, and 3 mL of DMF were charged into a 100 mL flask in a nitrogen atmosphere to give a uniform solution. The obtained solution was bubbled with nitrogen for 30 min and then mixed with Pd(pph₃)₄ (5.8 mg, 0.005 mmol). The mixed solution was stirred at 100 °C for 48 h. After polymerization, the resultant solution was cooled to room temperature. Afterward, the mixture was poured into 200 mL of methanol + 30 mL of 2M HCl. The precipitated polymer was collected by filtration. The collected polymer was subjected to Soxhlet extraction in a sequence of methanol, acetone, hexane, dichloromethane, and chlorobenzene. The chlorobenzene extraction was concentrated and then poured into methanol to cause the polymer to precipitate. The precipitated polymer was collected again by filtration and dried under vacuum overnight. A 391 mg mass of purified polymer with a purple-black shine was yielded. Yield: 88%, Mn = 11.9 kDa, PDI = 3.04.

Device Fabrication

For the fabrication of PM-OPDs, ITO-patterned glass substrates were cleaned through sequential sonication in Mucosol solution, distilled water, acetone, and isopropanol. The cleaned substrates were treated with UV ozone for 30 minutes. The PEDOT:PSS aqueous solution was spin-coated on top of the ITO substrates at 4000 rpm, followed by the thermal treatment at 120 °C for evaporating the residual solvent. The PDBD-FBT:ITIC (100:1 w/w) blend was dissolved in DCB with the concentration of 28 mg mL⁻¹ for active layer thickness of 200 nm. In the case of P3HT:PCBM reference device, P3HT:PCBM (100:1 w/w) blend was dissolved in DCB with the concentration of 50 mg mL⁻¹ for the same active layer thickness. The solutions were stirred at 80 °C for 24h, then spin-coated at 1000 rpm on top of the PEDOT:PSS layers, and were thermally annealed at 150 °C for 10 minutes inside a nitrogen-filled glove box. For various cathode deposition, Al, Ag, Au electrodes were deposited on top of the active layer with thermal evaporation under high vacuum.

Device Characterization

UV-vis absorption spectra were measured using Cary 5000 spectrophotometer. Dark and illuminated *J-V* characteristics, EQE and specific detectivity spectra were obtained from the combination of an Oriel Cornerstone 130 1/8 m monochromator and Keithley 2450 SourceMeter, in control of home-made LabView programs. Noise currents were measured with a Stanford Research SR830 DSP lock-in amplifier in connection with the same SourceMeter. The LDR can be calculated using the equation of $LDR=20\log J_{max}/J_{NEP}$, where J_{max} is the maximum value of the measurable photocurrent density and J_{NEP} is the photocurrent density extracted from noise equivalent power. Two different light sources were used for LDR measurement: A monochromatic light (520 nm) from 300 W Xe arc lamp of the above-mentioned monochromator for light intensities below 1.16 mW cm⁻² and a laser diode (520 nm) modulated by AFG310 arbitrary function generator (Tektronix) for light intensities up to 18.7 mW cm⁻². -3 dB frequency was measured at various light source frequencies using a Tektronix TDS5052 digital phosphor oscilloscope and an optical filtered laser diode in connection with a Tektronix AFG310 arbitrary function generator. Space-charge-

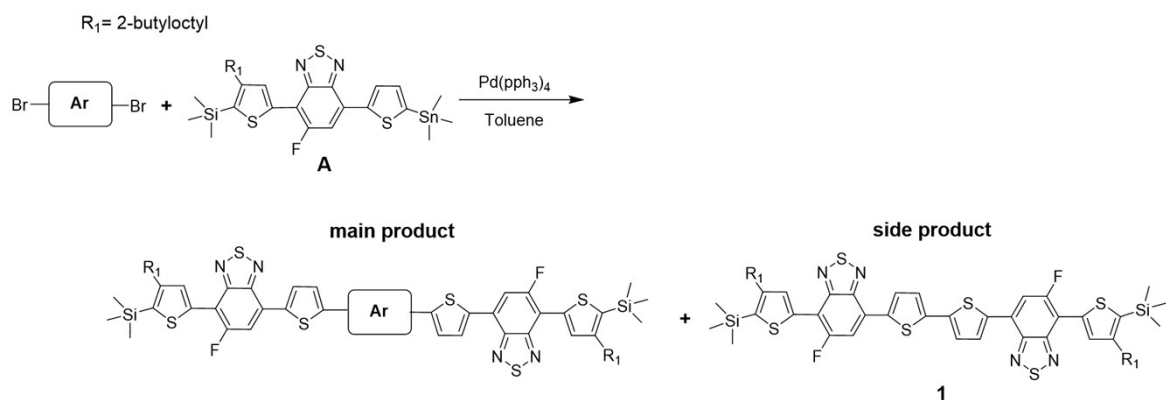
limited current method were performed with the geometry of ITO/PEDOT:PSS/PDBD-FBT:ITIC (100:1 w/w)/MoO₃/Ag for hole-only device. The theoretical fitting is provided with the space charge limited current (J) equation of $J=9\varepsilon\varepsilon_0\mu(V-V_{bi})^2/8d^3$, where ε is the relative permittivity of the thin film (assumed to be 3), ε_0 is the permittivity of free space, μ is the charge carrier mobility, and d is the thickness of the thin film. The trap density of states distribution $N_T(E)$ can be calculated by

$$N_T(E_\omega) = \frac{\beta V_{bi}\omega d C}{q A d k T \omega},$$

where β is the correction factor, A is the device area, d is the thickness, V_{bi} is the built-in potential, C is the capacitance and ω is the frequency. Also, trap energy E_ω corresponding to a measurement frequency is given by

$$E_\omega = k T \ln\left(\frac{\omega_0}{\omega}\right),$$

where ω_0 is the rate prefactor for thermal excitation from the trap commonly considered as 10^{12} Hz.



Scheme S1 The synthesis route of compound 1.

Materials

Compound A was purchased from Solarmer Materials Inc.^{S1}

Synthesis of compound 1

Dibromo-compound (1.81 mmol), compound A (2.96 g, 4.1 mmol), and toluene (50 ml) were mixed in a flask, then tetrakis(triphenylphosphine)palladium (58 mg, 0.05 mmol) was added, and the mixture was heated to 100 °C for 48 h. After cooling, the reaction mixture was poured into methanol and filtered. The filtered compound was dissolved in dichloromethane and washed with water. The solvent was removed via rotary evaporation, and the residue was purified with column chromatography on silica gel with hexane:dichloromethane=9.5:0.5 as eluent to give a main product (Yield: 1.81 g, 63% yield) and side product (766 mg). ¹H NMR (CDCl₃, 500 MHz, [ppm]): δ 8.148 (s, 2H), 8.080 (d, 2H, J=4 Hz), 7.791 (d, 2H, J=12.5 Hz), 7.404 (d, 2H, J=4 Hz), 2.695 (d, 4H, J=7 Hz), 1.796 (br, 2H), 1.334 (m, 36H), 0.893 (m, 12H), 0.421 (s, 18H); MALDI-TOF: m/z 1114.3, calcd 1114.39.

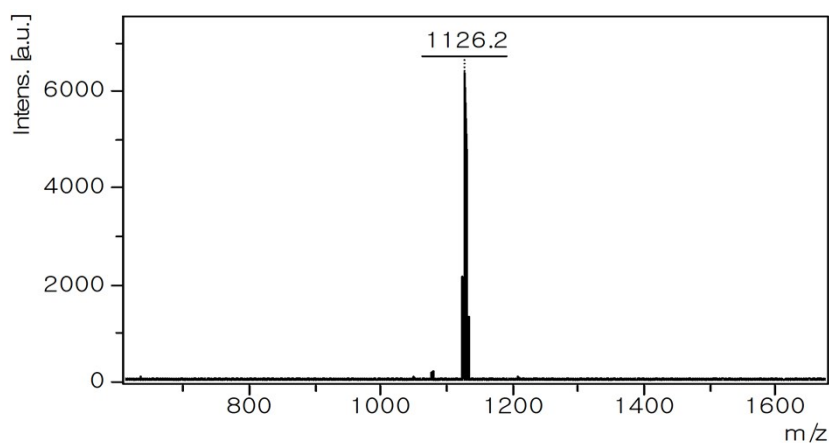


Fig. S1 MALDI-TOF spectrum for compound M1.

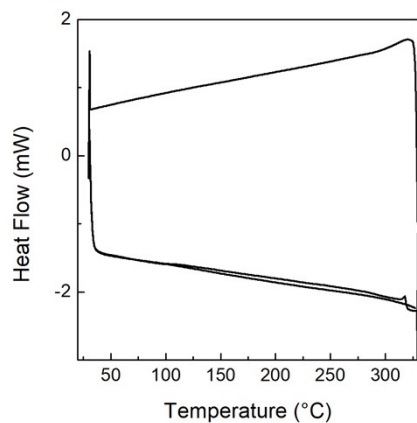


Fig. S2 Differential scanning calorimetry measurement of PDBD-FBT.

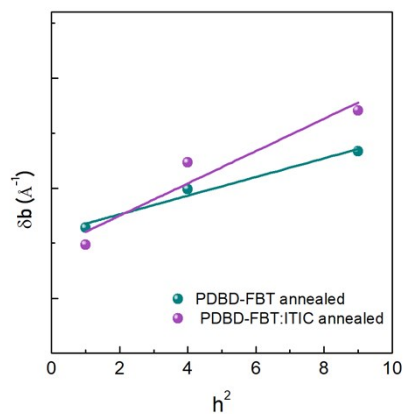


Fig. S3 The δb - h^2 plot of annealed films extracted from out-of-plane intensity profiles of respective films.

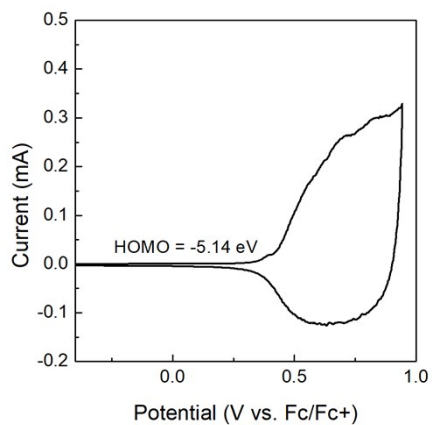


Fig. S4 Cyclic voltammetry of PDBD-FBT.

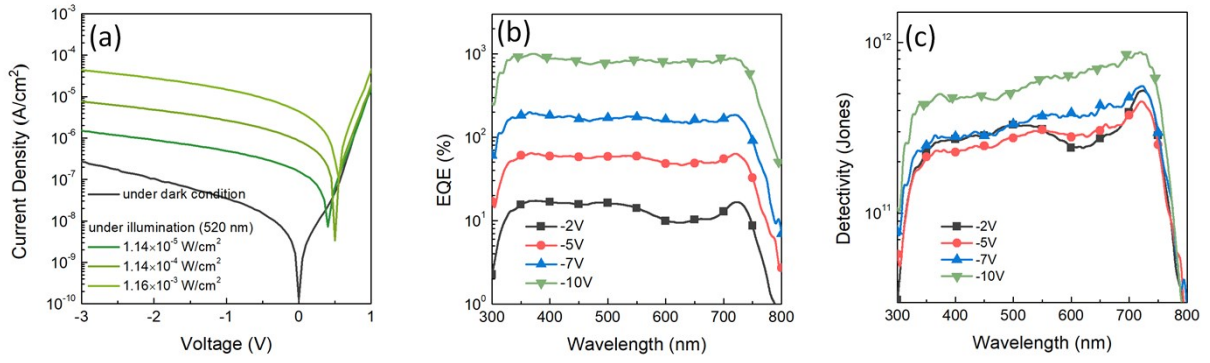


Fig. S5 Performances of PM-OPDs based on PDBD-FBT with Al cathode. (a) *J-V* characteristics. (b) EQE spectra. (c) Detectivity spectra.

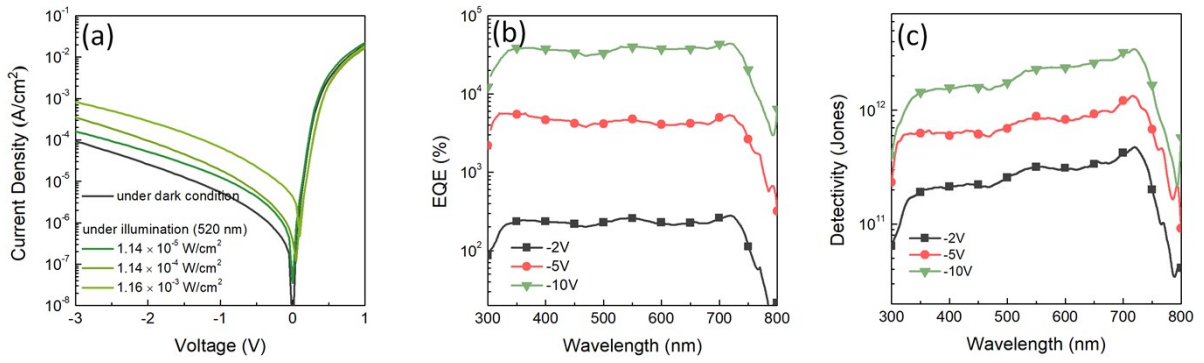


Fig. S6 Performances of PM-OPDs based on PDBD-FBT with Au cathode. (a) *J-V* characteristics. (b) EQE spectra. (c) Detectivity spectra.

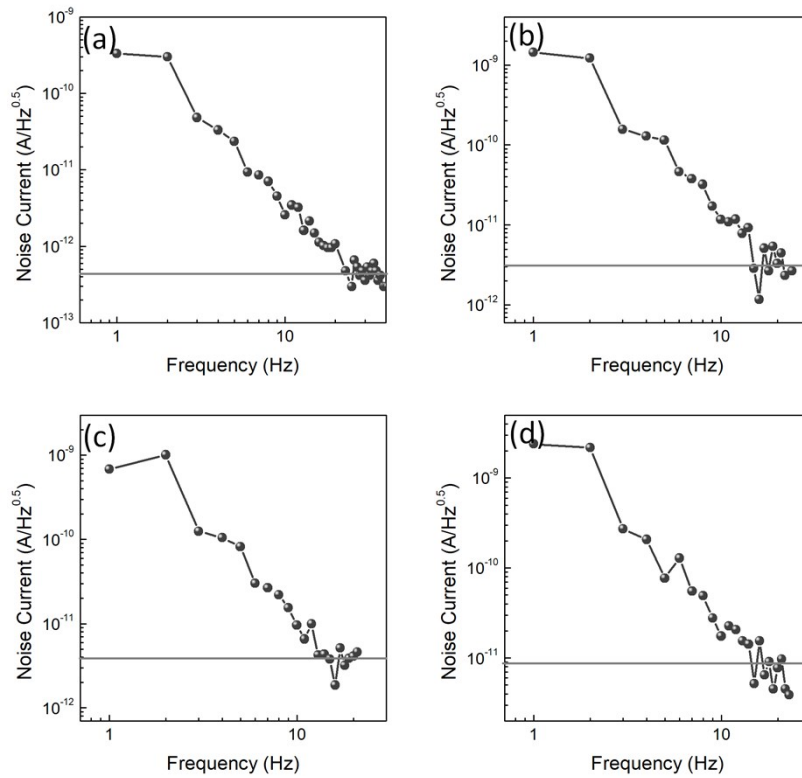


Fig. S7 Noise current spectra under (a) -2 V, (b) -5 V, (c) -7 V and (d) -10 V.

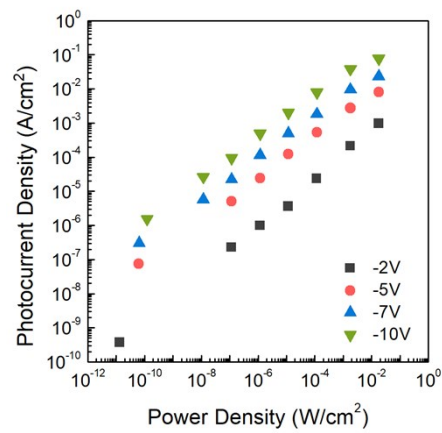


Fig. S8 Linear dynamic range for the optimized device under various biases.

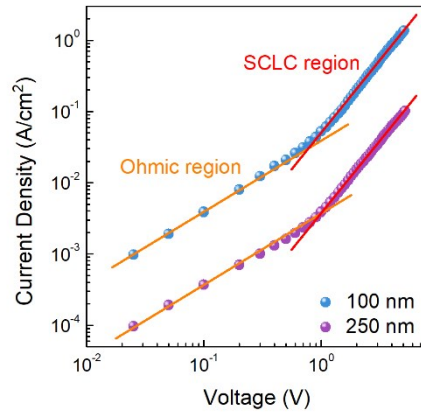


Fig. S9 Space-charge-limited current plot of hole-only device to extract hole mobility for 100 nm and 250 nm thicknesses of the active layer. Both SCLC devices yielded similar mobility values of $\sim 1.8 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, implying the reliability of the measurement..

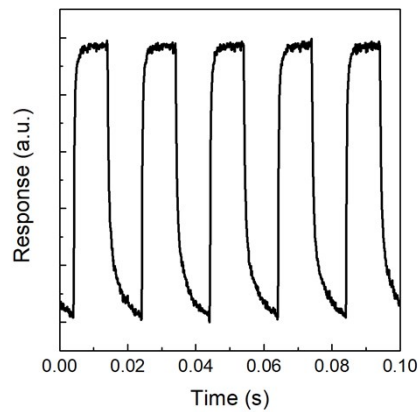


Fig. S10 Transient photoresponse of the optimized PM-OPD under -10 V.

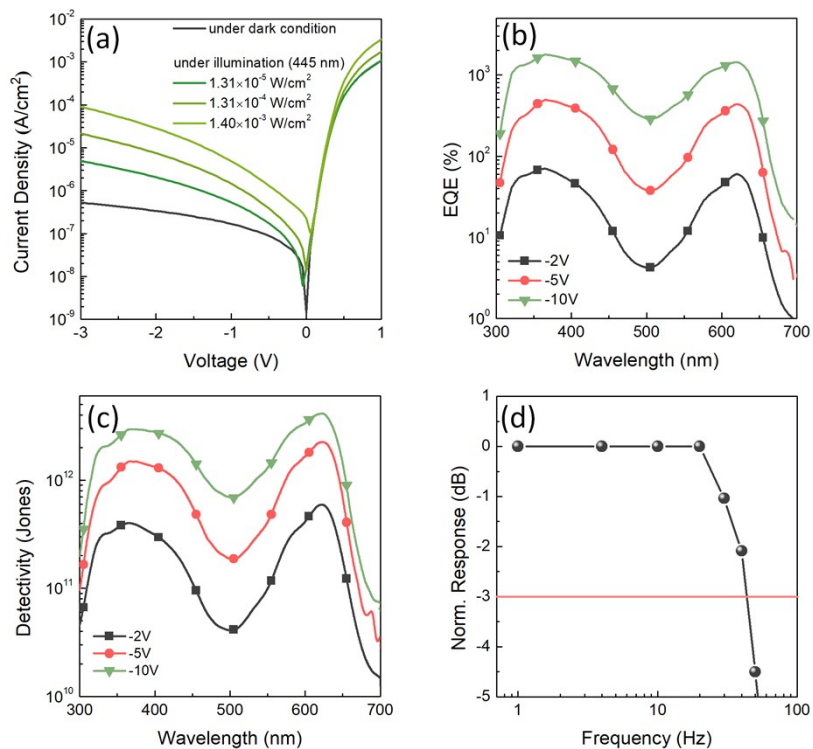


Fig. S11 Performances of P3HT:PCBM reference PM-OPD. (a) *J-V* characteristics. (b) EQE spectra. (c) Detectivity spectra. (d) Bode plot.

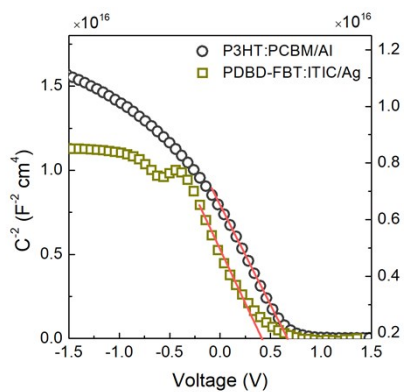


Fig. S12 Mott-Schottky plot of the devices based on PDBD-FBT and reference P3HT for characterizing the effective built-in potential (V_{bi}).

Reference

S1. B. Lim, D. X. Long, S.-Y. Han, Y.-C. Nah and Y.-Y. Noh, *J. Mater. Chem. C*, 2018, **6**, 5662.