

Effects on Photovoltaic properties of copolymers with five-membered chalcogen- π -heterocycles bridges

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■ EXPERIMENTAL SECTION

Materials Synthesis. Reagents. Pd(PPh₃)₄ was purchased from Frontier Scientific Inc. All of the commercial available compounds and reagents were used without any further treatment.

Synthesis of PBDB-TF-S and PBDB-TF-Se. (1). Tributyl(furan-2-yl)stannane and (2). Tributyl(selenophen-2-yl)stannane. Furan (15g, 0.22 mol) or Selenophene (28.8g, 0.22 mol) was dissolved in 200 mL of tetrahydrofuran in a 500 mL of two-neck round bottom flask under argon protection. After cooling the mixed solution to -78 °C, BuLi (2.5M, 70 mL) was added into the flask dropwise in 1 hour. The reactant was then stirred at room temperature for 2 hours. Tri-n-butyltin chloride (57g, 0.175 mol) was added into the flask while the reactant solution was cooled down to -78 °C and the mixture was stirred at room temperature overnight. The solution was then poured into 200 mL of water and extracted by ether (200mL×3), the organic phase was collected and dried by using sodium sulphate. After concentrating by rotary evaporator, the product (1) and (2) was used into next step without any further purification.

(4). 1,3-bis(2-ethylhexyl)-5,7-di(furan-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione. Compound 3 (1.5 g, 2.5 mmol), compound 1 (3.6g, 10 mmol) and the catalyst (50 mg), Pd(PPh₃)₄, was mixed into 15 mL of toluene under argon protection. The reaction was stirred at 110 °C for 16 hours and then the solvent was removed by rotary evaporator. The product (4) was purified by silica gel chromatographic column by using hexane as eluent. (1.1g, yield=76%)

¹HNMR (CDCl₃, 300 MHz): 8.14-8.13 (d, *J*=3.3Hz, 2H), 7.53 (d, 2H), 6.61-6.60 (t, *J*=1.6Hz, 2H), 3.33-3.31 (m, *J*=6.9Hz, 4H), 1.81 (m, 2H), 1.39 (m, 16H), 0.96 (m, 12 H).

(5).1,3-bis(2-ethylhexyl)-5,7-di(selenophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione. The synthetic method for compound 5 is the same as compound 4.

¹HNMR (CDCl₃, 300 MHz): 8.29-8.27 (d, *J*=5.7Hz, 2H), 7.97-7.96 (d, *J*=3.9Hz, 2H), 7.41-7.38 (t, 2H), 3.33-3.30 (m, 4H), 1.81 (m, 2H), 1.38 (m, 16H), 0.96 (m, 12 H).

(6).1,3-bis(5-bromofuran-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione. Compound 4 (1 g, 1.74 mmol) was dissolved into 15 mL of chloroform at room temperature, and N-Bromosuccinimide (0.65 g, 3.65 mmol) was added into the flask in several portions. After the completion of the reaction, the resultant solution was poured into 50 mL water and extracted by ether. The raw product was obtained by concentrating the collected organic phase and compound 6 was then purified by silica gel chromatographic column by using hexane as eluent. (0.96 g, yield=75%)

¹HNMR (CDCl₃, 400 MHz): 8.11-8.10 (d, *J*=3.6Hz, 2H), 6.53-6.52 (d, *J*=3.6Hz, 2H), 3.30-3.28 (m, 4H), 1.78 (m, 2H), 1.35 (m, 16H), 0.95 (m, 12 H).

(7).1,3-bis(5-bromoselenophen-2-yl)-5,7-bis(2-ethylhexyl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione. The synthetic method for compound 7 is the same as compound 6.

¹HNMR (CDCl₃, 300 MHz): 8.26-8.24 (d, *J*=5.6Hz, 2H), 7.33-7.30 (t, *J*=4Hz, 2H), 3.30-3.28 (m, 4H), 1.78 (m, 2H), 1.36 (m, 16H), 0.96 (m, 12 H).

Polymerization (PBDB-TF-O, PBDB-TF-S and PBDB-TF-Se): The BDD monomer with furan, thiophene or selenophene as the π -bridge (as shown in **Scheme 1**, 0.5 mmol) and compound 8 (the BDT monomer part, 0.5 mmol) was dissolved into 10 mL of toluene. The mixture was purged by argon for 5 min and then Pd(PPh₃)₄ was added into the solution in one portion. The reactant was purged by argon for another 15 min and stirred at 110 °C for ~16 hours. The polymer solution was precipitated from 100 mL of methanol and the raw product was then filtered, dried, and further purified by silica gel chromatographic column by using hot toluene as eluent. The yields of the polymers are over 60%.

Elemental analysis. Calculated for PBDB-TF-O: C 69.04, H 6.79; found: C 68.91, H 6.79. Calculated for PBDB-TF-S: C 67.27, H 6.61; found: C 66.23, H 6.28. Calculated for PBDB-TF-Se: C 62.57, H 6.15; found: C 61.88, H 5.92.

Instruments and Measurements. UV-vis absorption spectra were performed through a Hitachi UH4150 spectrophotometer. Photoluminescence spectra were detected using a steady state fluorescence spectrometer (FLS 980). Thermogravimetric analysis (TGA) was carried out with a heating rate of 10 °C min⁻¹ under an inert atmosphere on TGA-2050 from TA Instruments, Inc. The cyclic voltammetry curves were measured by a CHI650D electrochemical workstation, where the tetrabutylammonium hexafluorophosphate acetonitrile solution was used as the electrolyte with the 100 mV s⁻¹ scan rate. TEM images were recorded using a JEOL 2200FS instrument (bright-field mode, accelerating voltage, 160 kV). AFM height and phase images were obtained by a Nanoscope V AFM microscope (Bruker) using the soft tapping mode. J-V characteristics of the OSCs were measured by using a AAA solar simulator (XES-70S1, SAN-EI Electric Co., Ltd.) under standard AM 1.5G (100 mW cm⁻²), calibrated with a standard Si solar cell (made by Enli Technology Co., Ltd., Taiwan, calibrated by the NMI). The EQE spectra were measured by the Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd., Taiwan). The wavelength dependent refractive index and extinction coefficient measured a Germany SENpro spectroscopic ellipsometry. The light intensity was calibrated by a standard single-crystal Si photovoltaic cell. EQE_{EL} measurements were carried out by applying external voltage/current sources through the devices (ELCT-3010, Enlitech). The photo-CELIV measurements were carried out by the all-in-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland.

Fabrication of OSCs. All devices were fabricated with the conventional structure of glass/ITO/PEDOT:PSS/active layers/PFN-Br/Al. Firstly, the diluted PEDOT:PSS (with the same volume of water) was spin coated on the precleaned ITO substrates and annealed for 20 min at 150 °C. All active layer solutions were dissolved in CB at a polymer concentration of 10 mg mL⁻¹, polymers and BTP-4Cl were mixed at a ratio of 1:1. After the active layer materials were fully dissolved (the solution was stirred for at least 2 h), 0.5% volume of 1,8-diiodooctane (DIO) was added to the above solutions. The active layer was then spin coated on the PEDOT:PSS and heated for 10 min at 100 °C. Then PFN-Br dissolved in methanol (0.5 mg mL⁻¹) was spin-coated on the top of the active layers. Finally, the cathode Al layer was thermally evaporated under high vacuum (3 × 10⁻⁴ Pa). The operating area of solar cell devices are all 0.037 cm².

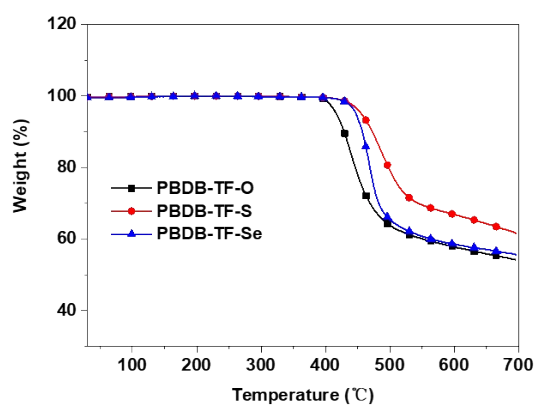


Fig. S1. Thermogravimetric analysis plots of the three polymers.

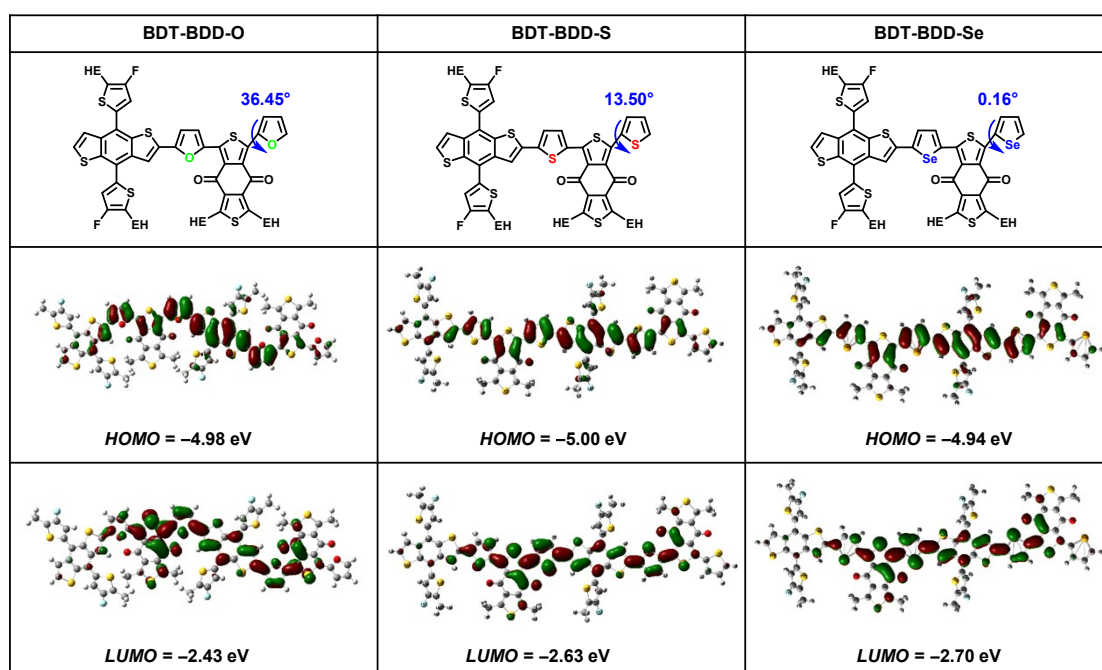


Fig. S2. Theoretical calculations of the BDT unit connected with BDD unit with furan, thiophene and selenophene, respectively, along with energy levels calculated by density functional theory (DFT) at the B3LYP/6-31G (d, p) level.

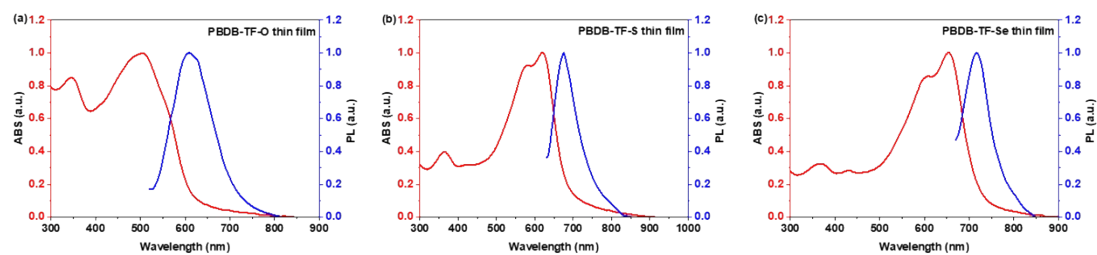


Fig. S3. Steady-state UV-visible absorption and PL spectra of (a) PBDB-TF-O, (b) PBDB-TF-S, and (c) PBDB-TF-Se films.

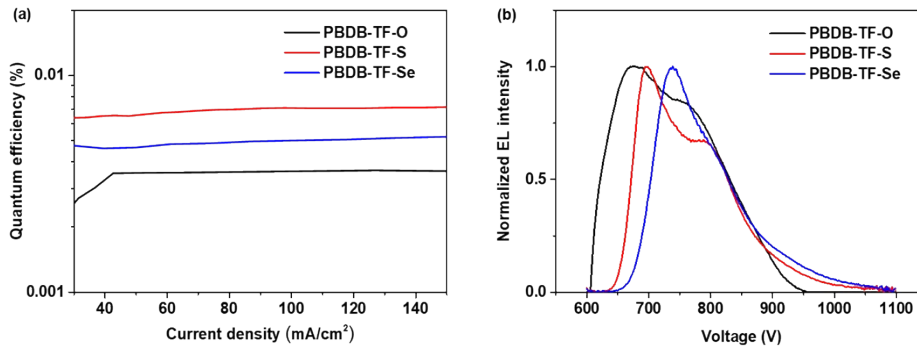


Fig. S4. (a) EL quantum efficiencies of the devices based on pure polymers of PBDB-TF-O, PBDB-TF-S, and PBDB-TF-Se at various injected current densities, along with (b) the corresponding normalized EL curves of PBDB-TF-O, PBDB-TF-S, and PBDB-TF-Se.

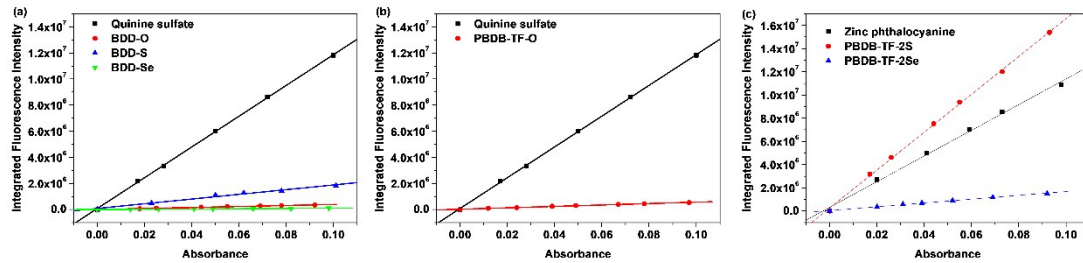


Fig. S5. The linear plots for two standards and three monomers and polymers. (a) BDD-O, BDD-S, BDD-Se, and PBDB-TF-O in CB with quinine sulfate as the standard in 0.1 mol/L H_2SO_4 . (b) PBDB-TF-S, PBDB-TF-Se in CB and zinc phthalocyanine as the standard in toluene with 1% pyridine. (According to the main range of PL for the monomers and polymers, we picked quinine sulfate as the standard for BDD-O, BDD-S, BDD-Se, and PBDB-TF-O, and zinc phthalocyanine as the standard for PBDB-TF-S, and PBDB-TF-Se. The maximum value of the recorded absorbance was controlled less than 0.1 to make sure the accuracy of measurement (optical path lengths, 10 mm).)The solvents used are all spectroscopic grade. The photoluminescence quantum efficiency could be

$$\Phi_x = \Phi_s \left(\frac{Grad_x}{Grad_s} \right) \left(\frac{\eta_x^2}{\eta_s^2} \right)^{1-2}$$

calculated according to the following equation:

Where Φ presents photoluminescence quantum. Grad is the gradient obtained from the plots of integrated fluorescence intensity vs. absorbance. η denotes the refractive index of the solvent. The subscripts of x and s present the test sample and standard respectively.)

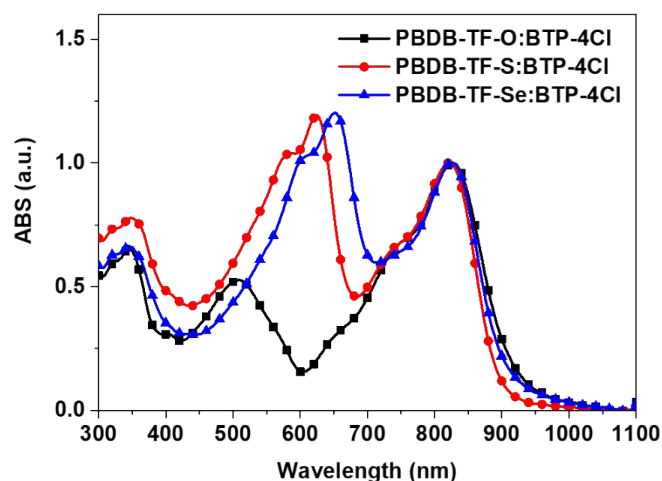


Fig. S6. (a) The absorption spectra of the PBDB-TF-O:BTP-4Cl, PBDB-TF-S:BTP-4Cl and PBDB-TF-Se:BTP-4Cl blend films (normalized by the absorbance of the second peaks).

Table S1. The Contact Angle and Surface Tension of Water and Glycerol on The Polymer Films.

Polymer	ϑ_{water} (deg)	ϑ_{GL} (deg)	Surface tension (mN m^{-1})
PBDB-TF-O	99.9	93.5	19.6
PBDB-TF-S	104.4	99.8	16.8
PBDB-TF-Se	105.4	100.3	16.6

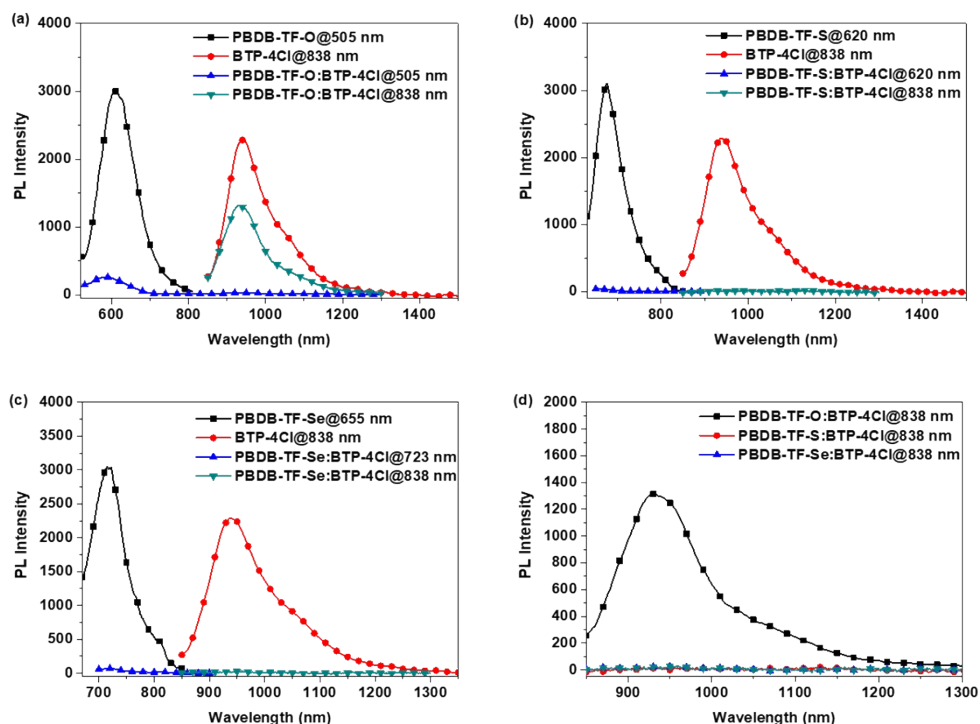


Fig. S7. (a) Photoluminescence spectra of PBDB-TF-O, BTP-4Cl, PBDB-TF-O:BTP-4Cl films. (b) Photoluminescence spectra of PBDB-TF-S, BTP-4Cl, PBDB-TF-S:BTP-4Cl films. (c) Photoluminescence spectra of PBDB-TF-Se, BTP-4Cl, PBDB-TF-Se:BTP-4Cl films. (d) Comparison of the quenching condition under the same excitation wavelength for the three blend films.

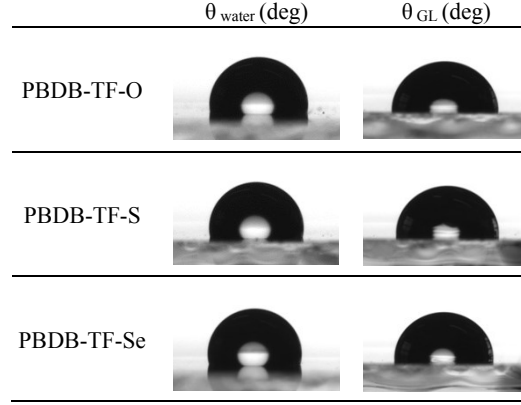


Fig. S8. The contact angle of water and glycerol on the polymer films. The surface tension could be calculated

using the Wu model.³

$$\gamma_{water}(1 + \cos \theta_{water}) = \frac{4\gamma_{water}^d \gamma^d}{\gamma_{water}^d + \gamma^d} + \frac{4\gamma_{water}^p \gamma^p}{\gamma_{water}^p + \gamma^p},$$

$$\gamma_{GL}(1 + \cos \theta_{water}) = \frac{4\gamma_{GL}^d \gamma^d}{\gamma_{GL}^d + \gamma^d} + \frac{4\gamma_{GL}^p \gamma^p}{\gamma_{GL}^p + \gamma^p},$$

and $\gamma^{total} = \gamma^d + \gamma^p$. where ϑ is the droplet of water/glycerol (GL) contact angle on the pure polymer film. γ^{total} is the total surface tension of pure polymer. γ^d and γ^p are the dispersion and polar components of γ^{total} . γ_{water} and γ_{GL} are the total surface tension of the water and glycerol.

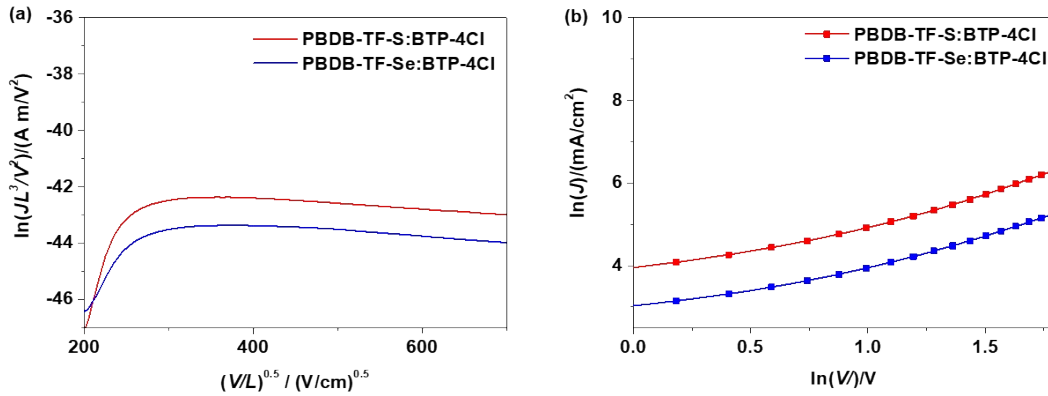


Fig. S9. (a) Plots for the hole mobilities of PBDB-TF-S:BTP-4Cl and PBDB-TF-Se:BTP-4Cl films obtained from the hole-only devices (ITO/PEDOT:PSS/active layer/Au). (b) Plots for the electron mobilities of PBDB-TF-S: BTP-4Cl and PBDB-TF-Se:BTP-4Cl films obtained from the electron-only devices (ITO/ZnO/active layer/Al). The film thicknesses of the devices are 100-110 nm.

Table S2. The Electron/Hole Mobilities of Devices for PBDB-TF-S:BTP-4Cl and PBDB-TF-Se:BTP-4Cl Blend Films, along with The Photo-CELIV Mobilities.

Active layer	Hole mobility μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Electron mobility μ_e ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_h/μ_e	Photo-CELIV mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
PBDB-TF-S:BTP-4Cl	2.30×10^{-4}	2.25×10^{-4}	1.02	1.79×10^{-4}

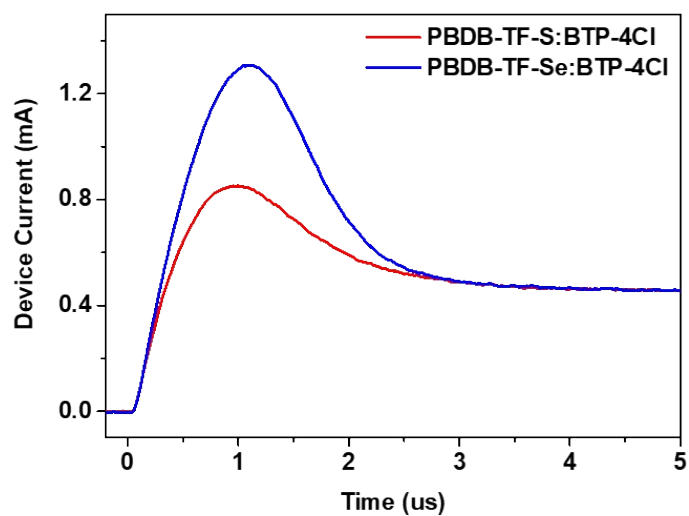


Fig. S10. The photo-CELIV plots of PBDB-TF-S:BTP-4Cl and PBDB-TF-Se:BTP-4Cl based devices.

Notes and references

- 1 T. R. Williams, S. A. Winfield and J. N. Miller, *Analyst*, 1983, **108**, 1067–1071.
- 2 S. Dhami, A. J. Mello, G. Rumbles, S. M. Bishop, D. Phillips and A. Beeby, *Photochem. Photobiol.* 1995, **61**, 341–346.
- 3 J. Comyn, *Int. J. Adhes. Adhes.* 1992, **12**, 145–149.