

## Supporting information

### **New wide bandgap D-A polymer based on Benzothiadiazole-pyrrolo[3,4-b]dithieno[2,3-f:3',2'-h]quinoxalindione and thiazole functionalized benzo[1,2-b:4,5-b']dithiophene units for high performance ternary organic solar cells with over 16% efficiency**

M. L. Keshtov, I.O. Konstantinov, S. A. Kuklin, N.K. Davydova, V.G. Alekseev, Zh. Xie, Anupam Agarwal, Ganesh D. Sharma

#### **Experimental Section**

##### **Instruments and characterization methods**

<sup>1</sup>H NMR spectra were collected on a Bruker AVANCE 500 spectrometer VHz (CDCl<sub>3</sub> as solvent). The elemental analysis was carried out on “Elemental Vario EL III” element analyzer. The average molecular weight and polydispersity index of the polymers was determined using “Water 1515” Gel permeation chromatography (GPC) measurement with *o*-dichlorobenzene as eluent at 50°C and polystyrene as reference standard. Thermogravimetric analysis (TGA) measurement was conducted under a dry nitrogen at a heating rate of 10°C/min on Netzsch STA 449C. Ultraviolet visible-near (UV-vis-NIR) spectra were recorded using a Hitachi U-4100 spectrophotometer. Cyclic voltammetry (CV) measurement was carried out on a “Autolab” voltametric analyzer by using 0.1M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte in acetonitrile solution at a scan rate of 100mVs<sup>-1</sup>. The potentials were measured against a Ag/Ag<sup>+</sup> reference electrode. Fe/Fe<sup>+</sup> was used as the internal standard (0.37 V).

##### **4.2. Materials and Synthesis**

Pd(PPh<sub>3</sub>)<sub>4</sub> were purchased from Sigma-Aldrich or Acros. All solvents used for synthesis were purified and dried according to standard methods. Toluene was dried and distilled over sodium/benzophenone. CHCl<sub>3</sub> and AcCN were dried with CaH<sub>2</sub> and distilled prior to use. All chemicals were reagent grade and purchased from Sigma-Aldrich and used without further purification. All chromatographic separations were carried out on silica gel (200-300 mesh). The monomers 2,2'-(2,6-bis-(trimethylstannanyl) benzo [1,2-b: 4,5-b'] dithiophene-4,8-diyl) bis-(4,5-diundecylthiazole) (M1) [1], 5,6-Dichloropyrazine-2,3-dicarboxylic acid anhydride (5) [2], 5,6-Dichloropyrazine-2,3-dicarboxylic acid N-(2-octyldodecyl)amide (6) [3] were prepared according to the reported procedures.

## Synthesis monomer M2

### **6-(2-Octyldodecyl)-2,3-di(thiophen-2-yl)- 5H-pyrrolo[3,4-*b*]pyrazine-5,7(6H)-dione (7).**

The mixture of 2,3-dichloro-6-(2-octyldodecyl)-5H-pyrrolo[3,4-*b*]pyrazine-5,7(6H)-dione (6) (8.91 g, 17.86 mmol), 3-(tributylstannyl)thiophene (16 g, 42.86 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (1g, 0.865 mmol) in dry THF (400 ml) was refluxed for 65 h under argon. After cooling the mixture was evaporated and dried. Title compound was obtained by column chromatography on SiO<sub>2</sub> (hexane-toluene = 1:1). Yield is 8.0 g (75%) of yellow solid. Elem. Anal. Calcd for (C<sub>34</sub>H<sub>47</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>): C, 68.76; H, 7.98; N, 7.08; S, 10.80. Found: C, 68.48; H, 7.82; N, 6.89; S, 10.57%. <sup>1</sup>H NMR (400.13 MHz; CDCl<sub>3</sub>; δ, ppm): 7.60 (m, 2H); 7.50 (m, 2H); 7.07 (m, 2H); 3.73 (d, 2H); 1.4-1.2 (m, 33H); 0.89 (t, 6H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; δ, ppm): 164.37; 150.59; 143.14; 139.69; 131.21; 130.70; 127.94; 42.83; 37.11; 31.92; 31.90; 29.97; 29.65; 29.64; 29.62; 29.36; 29.31; 26.25; 22.70; 14.14 (Figure S1 and S2).

### **2,3-bis(5-bromothiophen-3-yl)-6-(2-octyldodecyl)-5H-pyrrolo[3,4-*b*]pyrazine-5,7(6H)-dione (8)**

To the solution of 6-(2-Octyldodecyl)-2,3-di(thiophen-2-yl)- 5H-pyrrolo[3,4-*b*]pyrazine-5,7(6H)-dione (7) (8.154 g, 13.75 mmol) in CHCl<sub>3</sub> (100 ml) and AcOH (100 ml) NBS (5.34 g; 30 mmol) was added and the mixture was stirred at r. t. for 48 h. Water was added (400 ml), mixture was neutralized with NaHCO<sub>3</sub> and extracted with CHCl<sub>3</sub>. Combined organic phase was dried with MgSO<sub>4</sub> and evaporated. Residue was crystallized from CH<sub>2</sub>Cl<sub>2</sub>-hexane to give 8.3 g (80%) of the title compound. Elem. Anal. Calcd for (C<sub>34</sub>H<sub>45</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>): C, 54.33; H, 6.03; Br<sub>2</sub>, 21.26; N, 5.59; S, 8.53. Found: C, 54.15; H, 5.89; N, 5.38; S, 8.24%. <sup>1</sup>H NMR (400.13 MHz; CDCl<sub>3</sub>; δ, ppm): 7.38 (d, 2H); 7.06 (d, 2H); 3.72 (d, 2H); 1.8 (m, 1H); 1.4-1.2 (m, 32H); 0.89 (t, 6H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; δ, ppm): 173.06; 163.97; 148.85; 143.19; 140.77; 131.05; 130.98; 119.55; 42.91; 37.10; 31.91; 31.38; 29.55; 29.95; 29.63; 29.35; 29.30; 28.70; 26.21; 22.68; 14.13 (Figure S3 and S4).

### **2,5-Dibromo-9-(2-octyldodecyl)-8H-pyrrolo[3,4-*b*]bisthieno[2,3-*f*:3',2'-*h*]quinoxaline-**

**8,10(9H)-dione (M2).** The mixture of 6-(2-octyldodecyl)-2,3-bis(5-bromothiophen-2-yl)-5H-pyrrolo[3,4-*b*]pyrazine-5,7(6H)-dione (8) (1 g, 1.33 mmol), iodine (169 mg, 0.665 mmol) in dry toluene (250 ml) was irradiated with medium pressure mercury lamp for 10 h. When reaction mixture was evaporated, residue was washed with acetone, dried and purified by column chromatography on SiO<sub>2</sub> (toluene as eluent) to give 0.69 g (69%) M2. Elem. Anal. Calcd for (C<sub>34</sub>H<sub>43</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>): C, 54.47; H, 5.78; Br<sub>2</sub>, 21.32; N, 5.61; S, 8.55. Found: C, 54.30; H, 5.71; N, 5.47; S, 8.21%. <sup>1</sup>H NMR (400.13 MHz; CDCl<sub>3</sub>; δ, ppm): 8.44 (s, 2H); 3.86 (s, 2H); 2.03 (m, 1H); 1.4-1.1 (m, 32H); 0.89 (t, 6H). <sup>13</sup>C NMR (125 MHz; CDCl<sub>3</sub>; δ, ppm): 164.51;

143.75; 138.82; 137.81; 135.06; 127.46; 115.51; 43.02; 36.80; 31.90; 31.52; 29.98; 29.64;  
29.58; 29.35; 29.32; 26.27; 22.68; 14.11 (Figure S5 and S6).

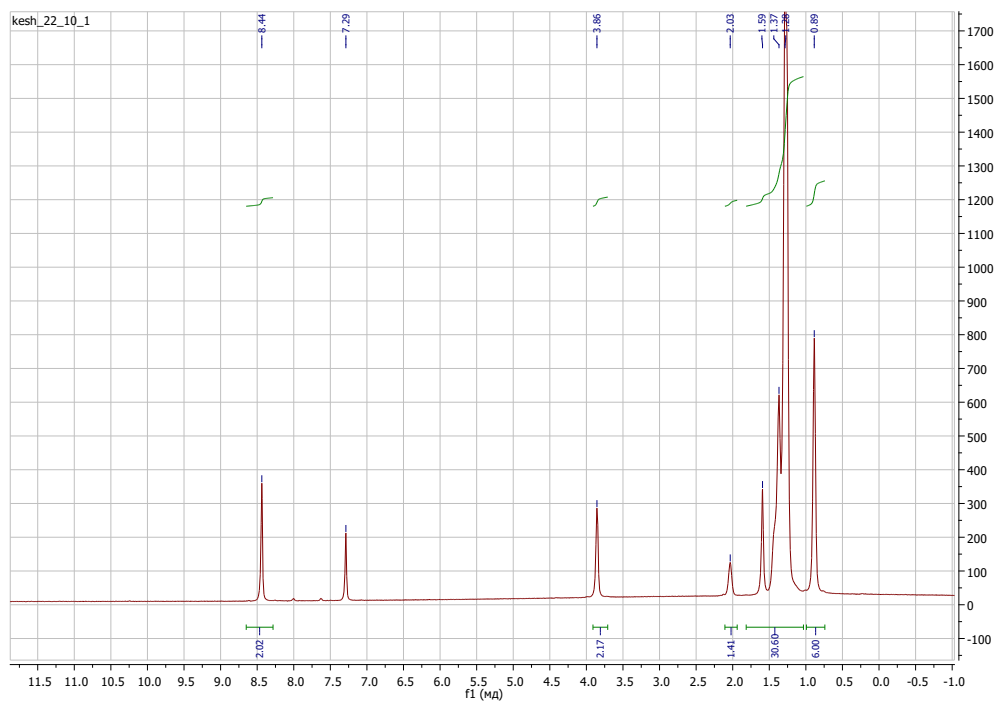


Figure S1. <sup>1</sup>H NMR spectrum(2,5-dibromo-9-(2-octyldodecyl)-8H-pyrrolo [3,4-b]dithieno[2,3-f:3',2'h] quinoxaline-8,10 (9H)-dione M2

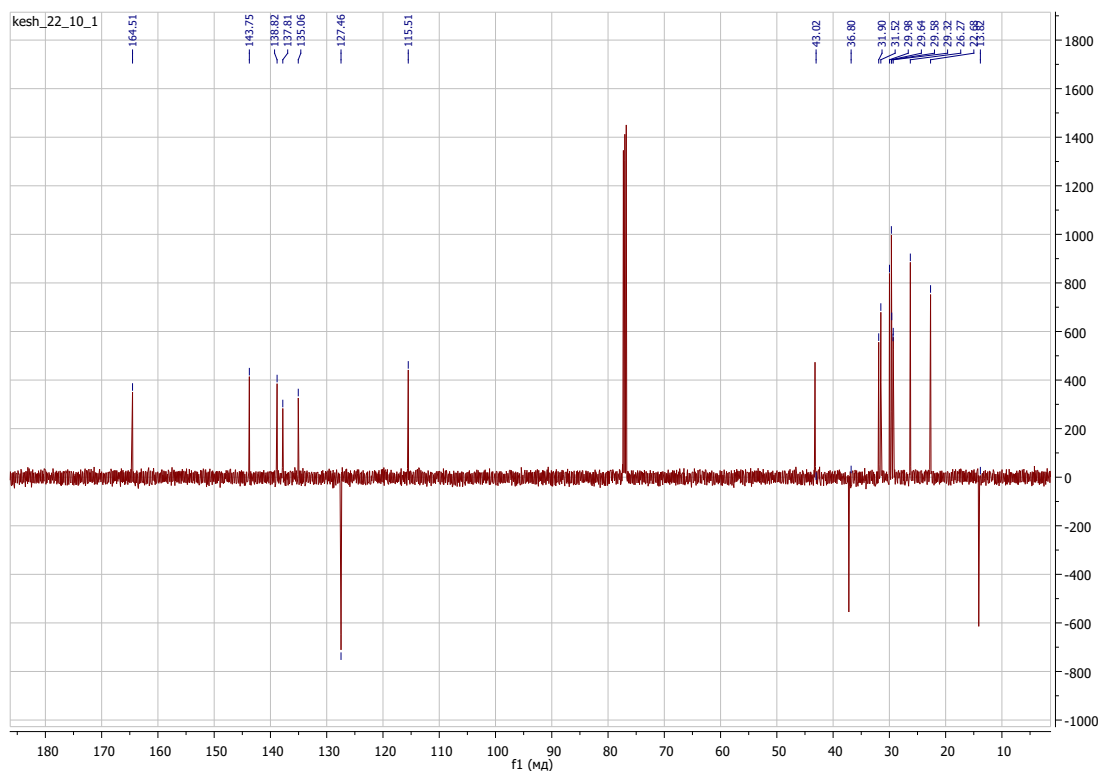


Figure S2.  $^{13}\text{C}$  NMR spectrum(2,5-dibromo-9-(2-octyldodecyl)-8H-pyrrolo [3,4-b]dithieno[2,3-f:3',2'h] quinoxaline-8,10 (9H)-dione M2

### Synthesis of copolymer P125

The polymerization was performed by a Stille coupling reaction. Monomers M1 (0.6497, 0.5mmol) and M2 (0.3748g, 0.5mmol) were dissolved in 14ml of toluene and the solution was flushed with argon for 20min,  $\text{Pd}(\text{Ph}_3\text{P})_4$  (27 mg, 0.023mmol) was added under argon into the solution and the mixture was flushed with argon for 20min. Then reaction mixture was heated to reflux for 48h. After cooling to room temperature, the mixture was slowly poured into methanol (400mL). Polymer was collected by filtration and then purified via Soxhlet extraction by washing consequentially with methanol, hexane and chloroform for 20 hours. Polymers were obtained from chloroform fraction by rotary evaporation to yield final polymer P125 as dark solid, with a yield 0.63g, (81%). Elem. Anal. Calcd for ( $\text{C}_{94}\text{H}_{137}\text{N}_5\text{O}_2\text{S}_6$ ): C, 72.30; H, 8.84; N, 4.48; S, 12.32. Found: C, 71.88; H, 8.77; N, 4.25; S, 11.94%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $\delta$  / ppm): 8.81-7.80(4H), 4.41-3.75(4H), 3.58-2.85(8H), 2.75-0.25(121H)

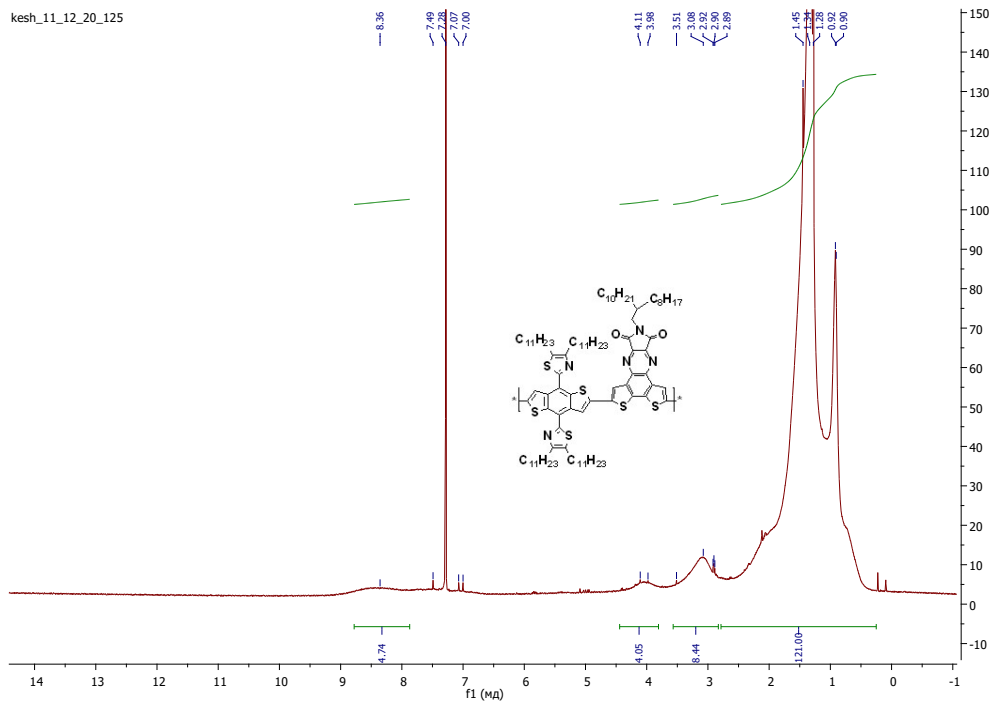


Figure S3.  $^1H$  NMR spectra of **P125**

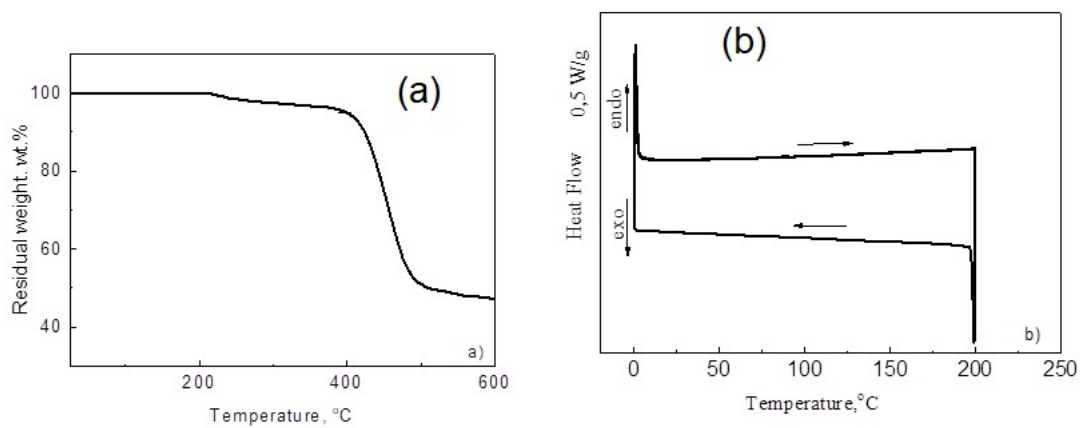


Figure S4. (a) TGA and (b) DSC curve of **P125** at a heating rate of  $10^\circ C min^{-1}$  under a nitrogen atmosphere

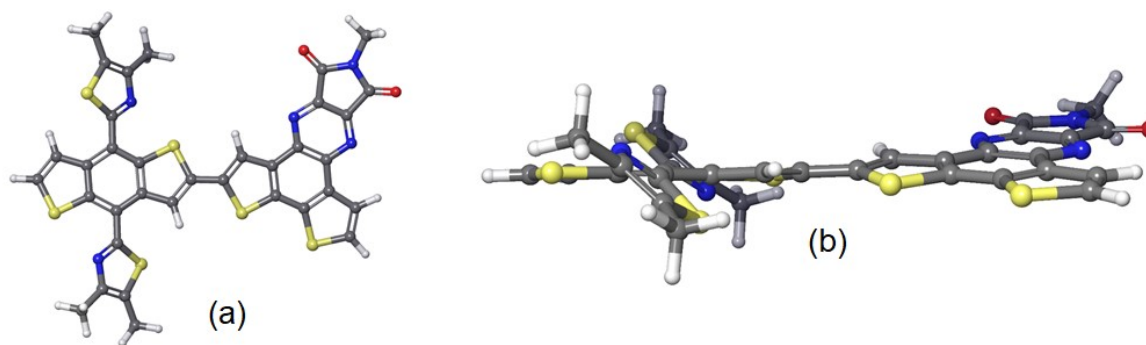


Figure S5 (a) Front view and (b) side view equilibrium geometry of **P125**

### Device fabrication and characterization methods

We have fabricated the PSC using a conventional structure of ITO/PEDOT:PSS/active layer/PFN/Al. The ITO glass was cleaned by ultrasonication using detergent, deionized water and iso-propyl alcohol, sequentially and then dried in vacuum oven for overnight. After cleaning and drying, a thin film of PEDOT:PSS was spin coated in ambient condition and annealed at 120°C to form the HTL of 40 nm. The prepared active solution of different donor to acceptor weight ratio of donor **P125** and acceptors DBTBT-IC or Y6 were prepared with total concentration of 16 mg/mL and then spin coated onto the top of PEDOT:PSS layer and then dried at room temperature for 30 min. For the solvent vapor annealing (SVA) treatment, the optimized active layer was placed in THF environment for 40s. The thickness of the active layers is  $90 \pm 5$  nm. The thin film of PFN (30 nm) was spin coated on the top of active layer from methanol solution to form the ETL. Finally, aluminum (Al) electrode was deposited on the top of PFN film through thermal evaporation with high vacuum chamber (under  $1 \times 10^{-5}$  torr). The active area of the devices is  $16 \text{ mm}^2$ . For the preparation of the ternary PSCs, we have varied the weight ratio between two acceptors i.e., DBTBT-IC and Y6 keeping the concentration of **P122** or **P123** constant with total concentration 16 mg/mL.

The current -voltage (J-V) characteristics of the fabricated PSCs were measured by Keithely 2400 source meter and solar simulator (AM1.5G,  $100 \text{ mW/cm}^2$ ). Incident photon to current conversion efficiency (IPCE) was recorded using Bentham IPCE system. The hole and electron mobilities were estimated using the space charge limited current (SCLC) model with fabricating the hole (ITO/PEDOT:PSS/active layer/Au) and electron (ITO/Al/active layer/Al) only devices, respectively.

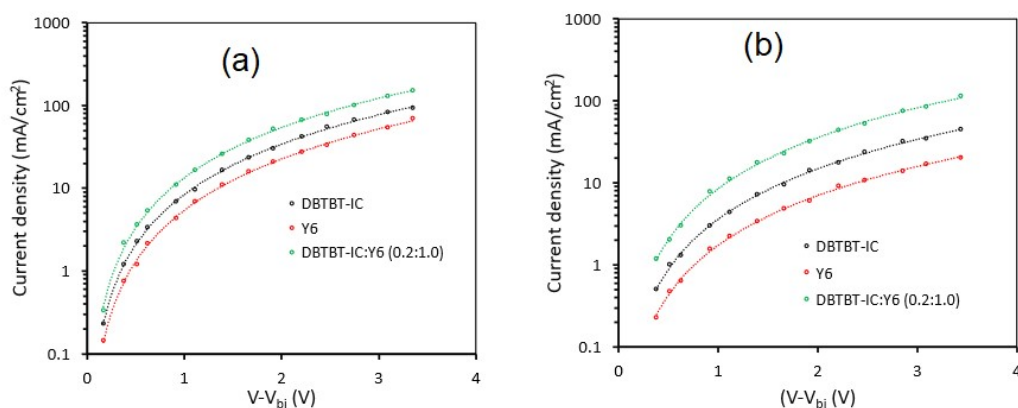


Figure S6 Dark J-V characteristics for (a) hole and (b) electron only devices using optimized **P125**:DBTBT-IC (1:1.2), **P125**:Y6 (1:1.2) and **P125**:DBTBT-IC:Y6 (1:0.2:1.0) films and fitted by SCLC model

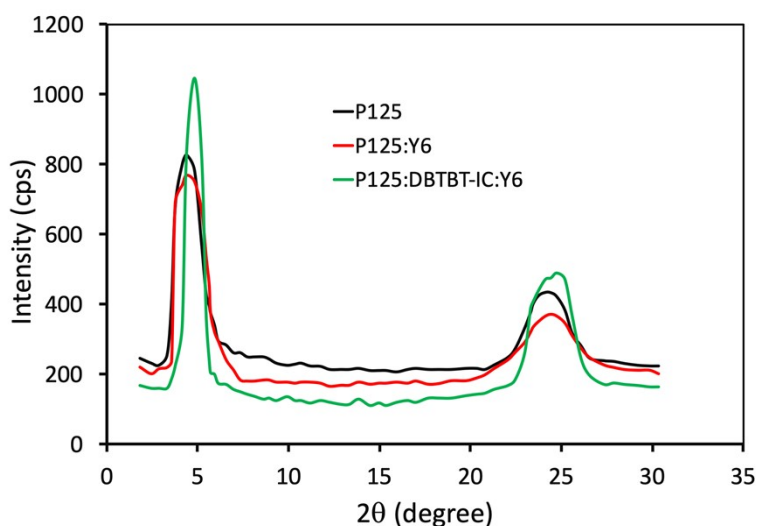


Figure S7 X-Ray diffraction patterns for pristine SVA treated **P125**, **P125**:Y6 (1:12) and **P125**:DBTBT-IC:Y6 (1:10.2:1.0) films

Table S1 (a) Photovoltaic parameters for the using **P125**:DBTBT-IC with different weight ratios processed with chloroform

Weight ratio <b>P125</b> :DBTBT-IC	$J_{SC}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF	PCE (%)
1:.0.4	12.02	1.05	0.53	6.69
1:0.8	12.64	1.04	0.56	7.36
1:1.2	13.56	1.06	0.58	8.34
1:1.4	13.08	1.06	0.55	7.62

Table S1 (b) Photovoltaic parameters for the using **P125**:Y6 with different weight ratios processed with chloroform

Weight ratio <b>P125:Y6</b>	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>OC</sub> (V)	FF	PCE (%)
1:0.4	16.43	0.92	0.49	7.41
1:0.8	17.21	0.92	0.50	7.92
1:1.2	17.97	0.91	0.54	8.83
1:1.4	17.24	0.91	0.51	8.00

Table S2 Photovoltaic parameters for the using **P125:DBTBT-IC:Y6** with different weight ratios between two acceptors i.e., DBTBT-IC and Y6 processed with chloroform

Weight ratio <b>P125:DBTBT-IC:Y6</b>	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>OC</sub> (V)	FF	PCE (%)
1:.0.1:1.1	18.23	0.97	0.59	10.43
1:0.2:1.0	19.08	0.95	0.60	10.87
1:0.3:0.9	18.21	0.935	0.62	10.56
1:0.5:0.7	17.42	0.92	0.61	9.78

## References

1. M. L. Keshtov, I. O. Konstantinov, I. E. Ostapov, A. R. Khokhlov, V. G. Alekseev, Zh. Xie, Hemraj Dahiya and Ganesh D. Sharma, New dithiazole side chain-benzodithiophene containing D-A copolymers for highly efficient non-fullerene solar cells, *Macromol. Chem. Phys.* 2021, 222, 2100053
2. M. L. Keshtov, S. A. Kuklin, F. C. Chen, A. R. Khokhlov, Rajnish Kurchania, G. D. Sharma, A New D–A Conjugated Polymer P(PTQD-BDT) with PTQD Acceptor and BDT Donor Units for BHJ Polymer Solar Cells Application, *J. Polym. Sci. Polym. Chem.* 2015. 53. 2390-2398