

SUPPORTING INFORMATION

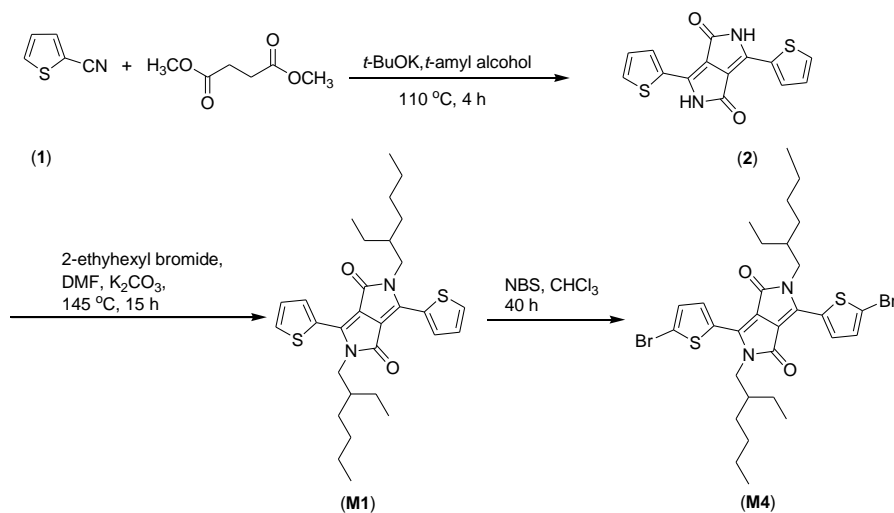
Impact of composition ratio of donor and acceptor moieties in conjugated polymer: optical and electrochemical properties

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Monomers synthesis



Scheme S1. Synthesis of monomers **M1** and **M4**

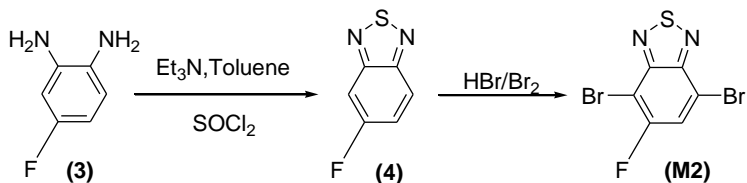
Synthesis of 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (2). 6.80 g (60.5 mmol) of potassium *t*-butoxide and 40 mL of *t*-amyl alcohol were put into a well-dried round flask under N_2 atmosphere. Then the reactant was heated with stirring for 1.5 h at 105 °C. At the same temperature, 4.71 mL of 2-thiophenecarbonitrile (**1**) (5.52 g, 50.6 mmol) was injected in one portion and stirred for 30 min. A solution of dimethyl succinate (3.52 g into 8 mL

of t-amyl alcohol) was dropped into the reaction mixture for 1.5 h. As the addition was completed, the reaction was kept at the same temperature for 1.0 h. To distil off the byproduct (methanol) the reaction was kept at the same temperature for another 2 h. After that, the reaction mixture was cooled to 65 °C, diluted with 50 mL of methanol, neutralized with acetic acid and again refluxed for 10 min. The resulting suspension was filtered, and the recovered black filter cake was washed with hot methanol and water twice each and dried in vacuum to get crude product **2**. The crude product was used directly for the next step without further purification.

Synthesis of 2,5-diethylhexyl-3,6-dithiophen-2-ylpyrrolo[3,4-c]pyrrole-1,4-dione (M1). Compound **2** (2.0 g, 6.67 mmol) and anhydrous K₂CO₃ (3.64 g, 26.64 mmol) were charged in two necks round bottom flask along with 12 mL of anhydrous N,N-dimethylformamide (DMF) and heated to 145 °C with stirring under the N₂ protection until the K₂CO₃ dissolved. After that 2-ethylhexyl bromide (7.73 g, 40 mmol) was injected in one portion by syringe at the same temperature. Then the reaction was allowed to stir for 15 h at 150 °C followed by cooling the reaction up to room temperature. The resulting reaction mixture was poured into 30 mL of cold water, and filtered. The filter cake was washed with water and methanol several times. After drying in vacuum, the crude product was purified by silica gel chromatography using dichloromethane and hexane as eluent to obtain a purple-black sticky solid **M1**. The compound **M1** was characterised by ¹H NMR spectra. Yield: 22% (Two steps). ¹H NMR (CDCl₃, 500 MHz), δ 8.91 (d, 2H, J= 5.0 Hz), 7.64 (d, 2H, J = 5.0 Hz), 7.28 (d, 2H, J = 5.0 Hz), 4.06 (m, 4H), 1.68(m, 2H)1.38-1.27 (m, 16 H) and 0.93 (m, 12H).

Synthesis of 2,5-Diethylhexyl-3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione (M4): Compound **M1** (620 mg, 1.18 mmol) and CHCl₃ (10 mL) were taken into a round bottom flask and allowed to cool at 0 °C and stir for 30 min. After that N-bromosuccinimide (NBS, 525 mg, 2.9 mmol) was added into the reaction mixture in three fractions at the same temperature. After complete addition, the temperature was raised to room temperature and allowed to stir for 40 h at room temperature. The mixture was poured into 20 mL of methanol and filtered. The filter cake was washed with hot methanol. After drying in vacuum, the pure product **M4** was obtained as a purple-black solid. Yield: 49.5%. The monomer **M4** was

characterized by ^1H NMR spectra. ^1H NMR (CDCl_3 , 500 MHz), δ (ppm): 8.64 (d, 2H, $J = 5.1$ Hz), 7.20 (d, 2H, $J = 5.1$ Hz), 1.80 (m, 2H), 1.36-1.24 (m, 16H) and 0.84 (m, 12H).



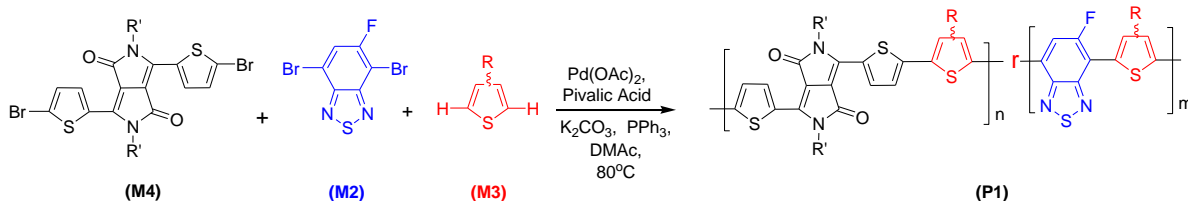
Scheme S2: Synthesis of compound **M2**.¹

Synthesis of 5-fluoro-2,1,3-benzothiadiazol (4): 4-Fluoro-1,2-phenylenediamine (**3**, 5.0 g, 40.0 mmol) and triethylamine (Et_3N) (24.0 ml, 168.0 mmol) along with 50 mL of toluene was charged into a well dried 250 mL round bottom flask. Thereafter thionylchloride (6.0 mL, 82.0 mmol) was added slowly. After complete addition, the reaction mixture was refluxed for 1 h. The reaction mixture was cooled down and poured into ice water and further diluted with toluene. The solid was filtered off and the remaining filtrate was washed with water several times and dried over anhydrous MgSO_4 . Toluene was evaporated under a vacuum and the crude product was further purified by column chromatography over silica gel with hexane/ethyl acetate as eluent. The resulting product **4** was obtained with 40% yield.

Synthesis of compound M2. Compound **4** (3.0 g, 20.25 mmol) and 15 mL of HBr were added in a well-dried 100 mL round bottom flask. After that 4.0 mL of Br_2 was added dropwise. The reaction mixture was stirred for 48 h at 90°C and further continued for 48 h at room temperature. The reaction mixture was put in water and the solid was filtered off, washed several times with water and dried. The product was recrystallized from MeOH . The resulting product **M2** as a white solid was obtained (Yield 30 %) and confirmed by ^1H NMR. ^1H NMR (CDCl_3 , 500 MHz), δ (ppm): 7.80 (d, 1H, $J = 10.0$ Hz).

Synthesis of polymers P1-5 by direct heteroarylation polymerization.

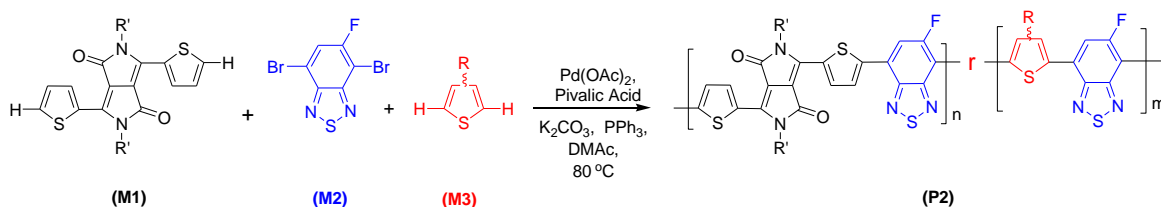
Synthesis of polymer P1: Compound **M3** (130 mg 0.773 mmol) was charged into a well dried 25 mL round bottom flask along with **M2** (120 mg, 0.39 mmol) and **M4** (262 mg, 0.39 mmol) as shown in Scheme S3. Then anhydrous *N,N*-dimethylacetamide (DMAc; 4.0 mL) was added as a solvent, followed by K_2CO_3 (200 mg, 1.515 mmol) and Piv(OH) (30 mg) under an inert atmosphere at room temperature. The reaction mixture was flushed twice by purging the nitrogen gas and PPh_3 (25 mg, 16% mol) as a ligand along with a pinch of $Pd(OAc)_2$ as a catalyst was added. The reaction mixture was allowed to stir at 80 °C for 12 h. Initially, the reaction mixture's colour was dark red then turned red-vine to purple-red and ultimately became dark bluish-green as the reaction proceeded. After 12 h, the reaction mixture was cooled down to room temperature and poured in methanol (10 mL). The resulting dark green-blue precipitate was a dark green-blue color solid polymer and dried under vacuum for 1 day to get the final product. The resulting polymer is soluble in CH_2Cl_2 , $CHCl_3$ and chlorinated aromatic solvents. Yield: 40% (157.0 mg).



Where R' is 2-ethylhexyl and R is hexyl chain

Scheme S3: Synthesis of polymer P1

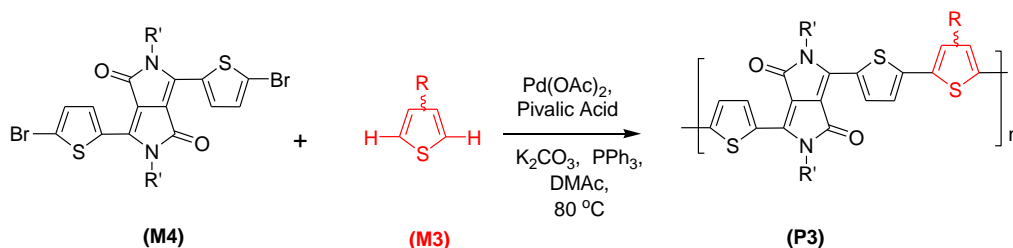
Synthesis of polymer P2: Polymer **P2** was obtained by direct heteroarylation polymerization among monomers **M1**, **M2** and **M3** as shown in Scheme S4, according to the procedure adopted for polymer **P1**. Yield: 64 % (185 mg).



Where R' is 2-ethylhexyl and R is hexyl chain

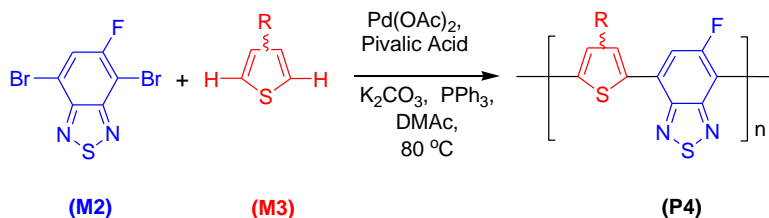
Scheme S4: Synthesis of polymer P2.

Synthesis of polymer P3: Polymer **P3** was obtained by direct heteroarylation polymerization between **M3** and **M4** according to the procedure adopted for polymer **P1**. Yield: 56% (57.0 mg).



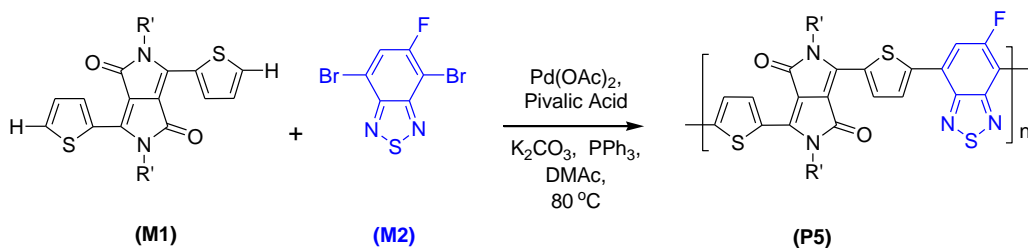
Scheme S5: Synthesis of polymer **P3**, where R' is 2-ethylhexyl and R is hexyl chain.

Synthesis of polymer P4: Polymer **P4** was prepared by direct heteroarylation polymerization between **M2** and **M3** following the procedure for polymer **P1**. Yield: 90% (96.0 mg).



Scheme S6: Synthesis of copolymer **P4**, where R is the hexyl chain

Synthesis of polymer P5: The polymer was prepared by direct heteroarylation polymerization between **M1** and **M2** following the procedure as used for polymer **P1**. Yield: 74% (77.0 mg)



Scheme S7: Synthesis of polymer **P5**, where R' is the 2-ethylhexyl chain.

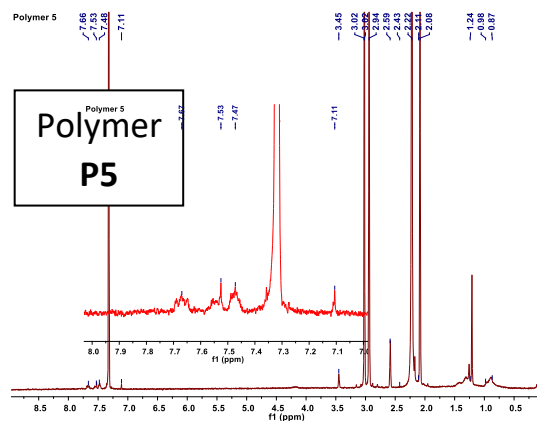
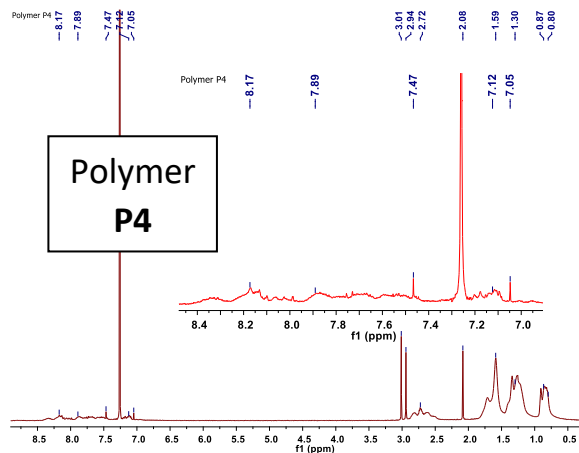
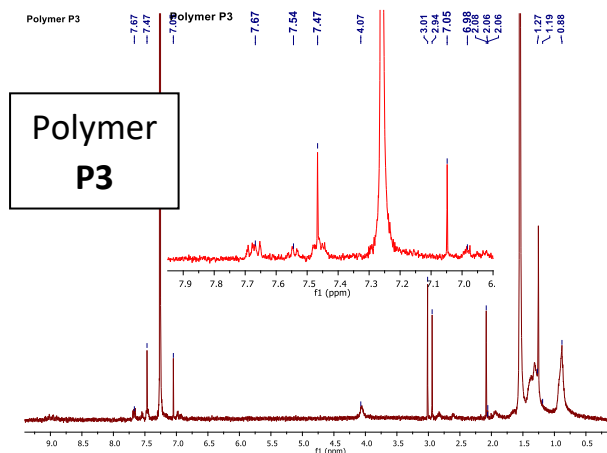
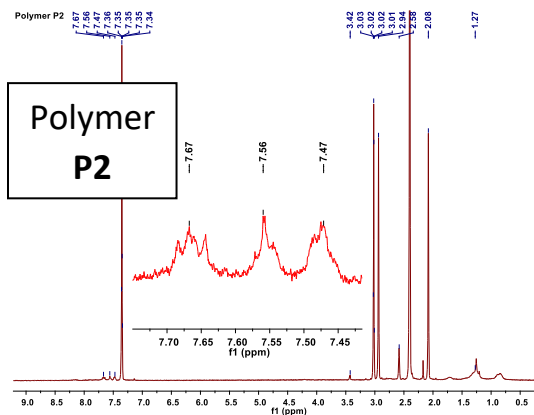
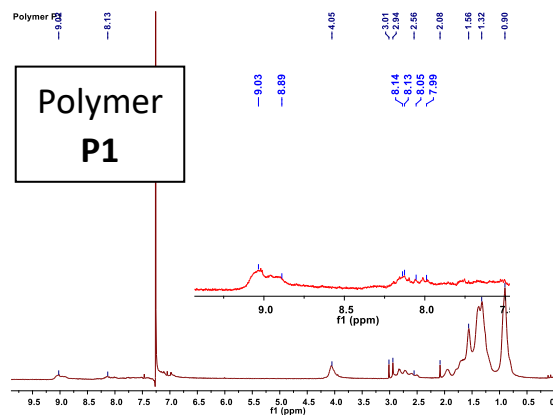


Figure S1. ^1H NMR (500 MHz) spectra of polymers **P1-5**

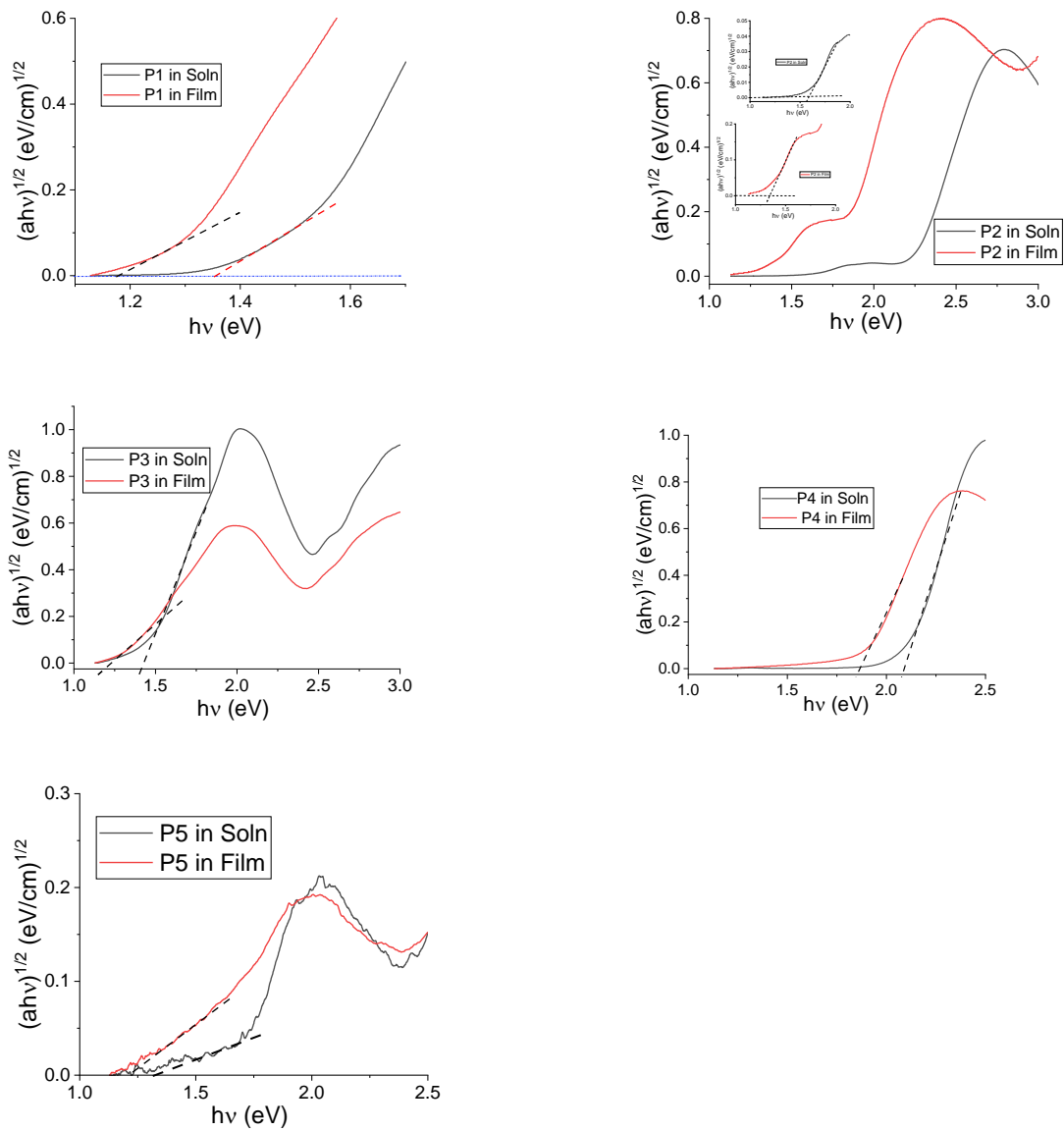


Figure S2. Optical band gaps were extracted from Tauc plots of polymer **P1-5**.

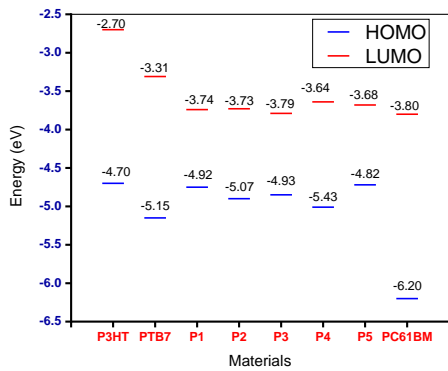


Figure S3. Orbital energetics comparison of polymers **P1-5** and PC₆₁BM with donors P3HT and PTB7.

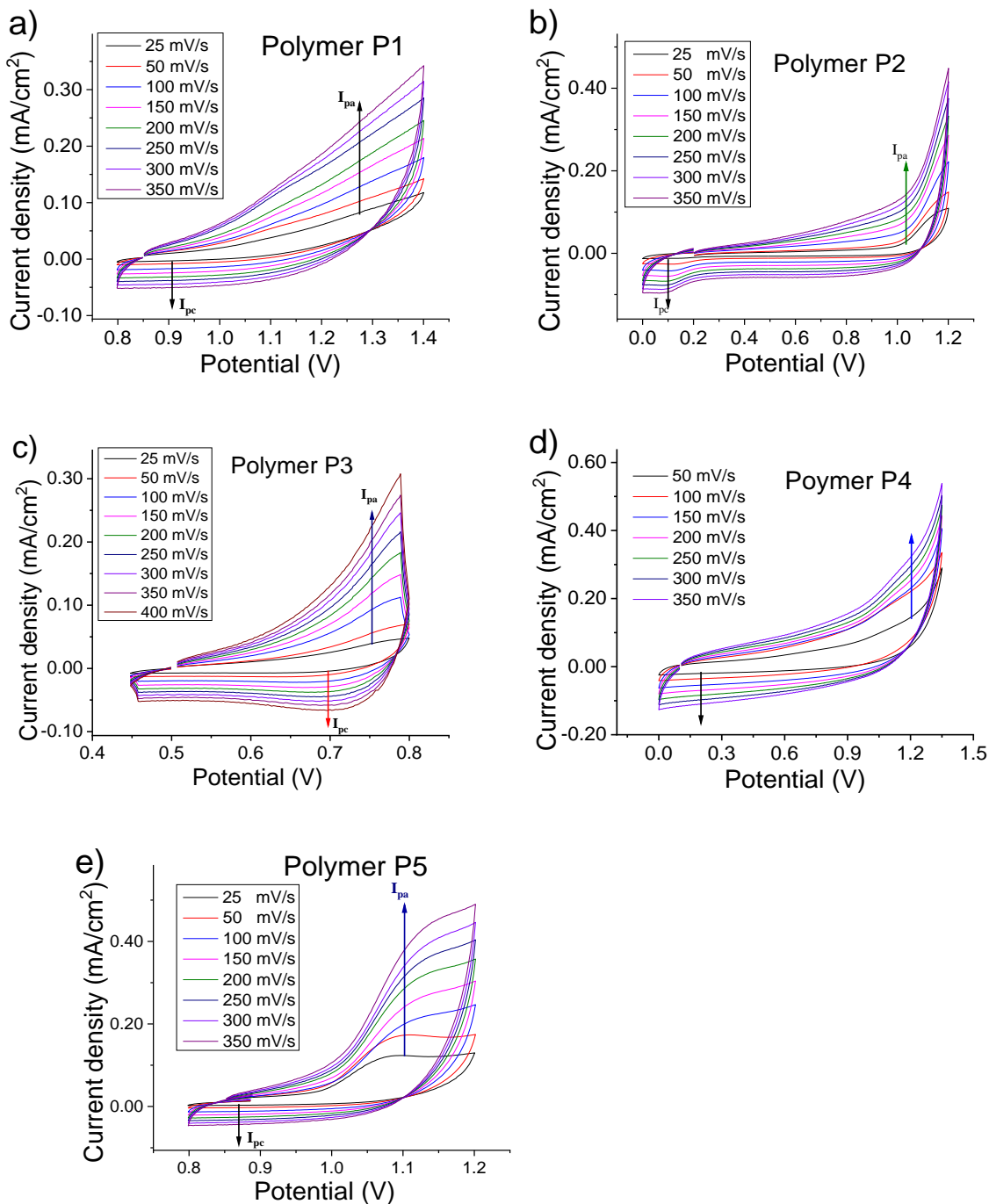


Figure S4. Scan rate-dependent cyclic voltammograms of polymer films on glassy carbon electrode using 0.1 M TBClO₄/MeCN at different scan rates.

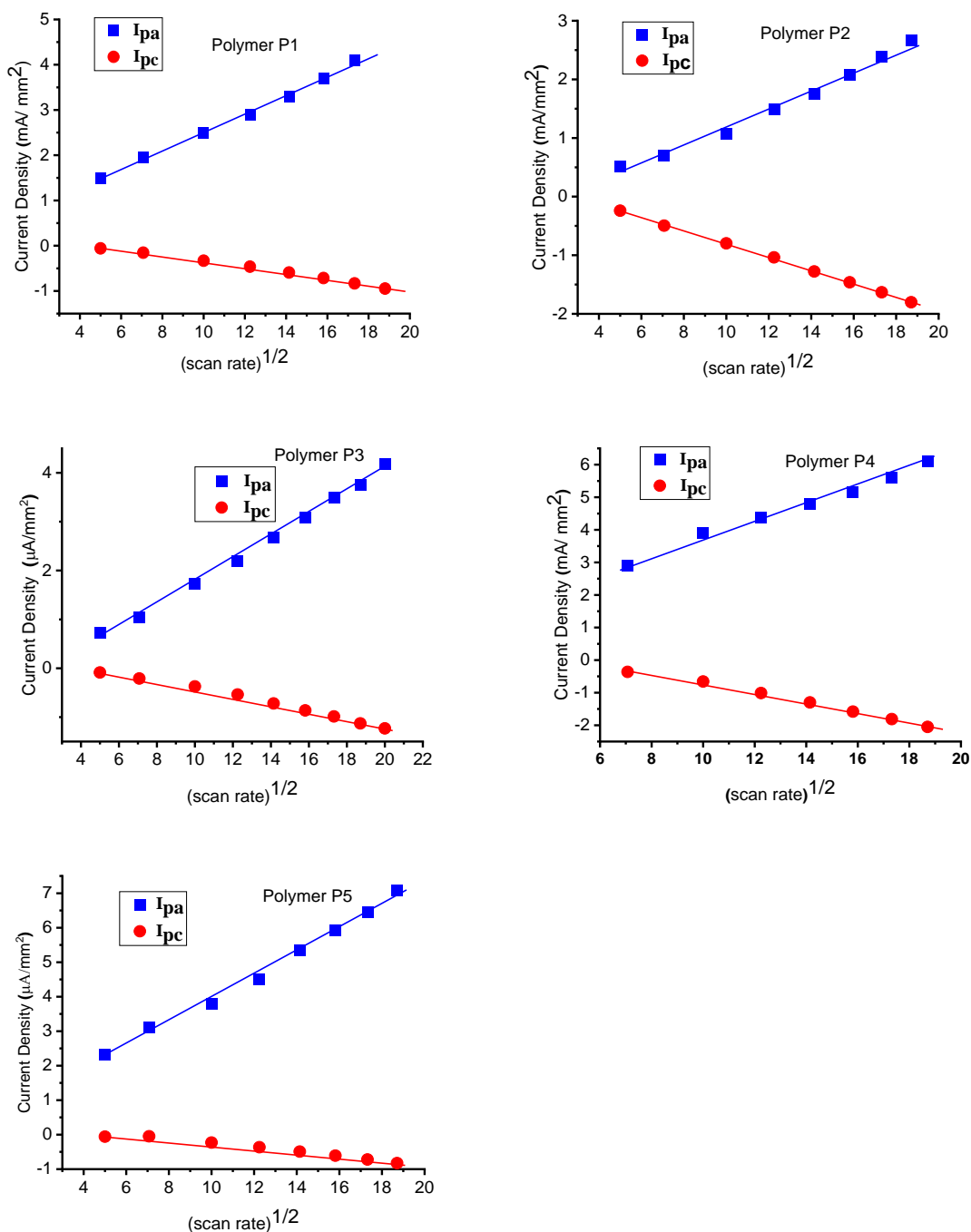


Figure S5. For polymers **P1-5** current density versus square root of different scan rates (25 mV/s, 50 mV/s, 100 mV/s, 150 mV/s, 200 mV/s, 250 mV/s, 300mV/s and 350 mV/s).

(1) S. Albrecht, S. Janietz, W. Schindler, J. Frisch, J. Kurpiers, J. Kniepert, D. Neher, Fluorinated copolymer PCPDTBT with enhanced open-circuit voltage and reduced recombination for highly efficient polymer solar cells. *J. Am. Chem. Soc.* 2012, **134**, 14932-14944.