

***2,2'-Bis(trifluoromethyl)biphenyl as a Building Block for Highly Ambient-Stable,
Amorphous Organic Field-Effect Transistors with Balanced Ambipolarity***

Chi-Jui Chaing,[†] Jyh-Chien Chen,^{} Yu-Ju Kuo,[†] Hsiang-Yen Tsao,[†] Kuan-Yi Wu,[‡]*

Chien-Lung Wang[‡]

[†] Department of Materials Science and Engineering, National Taiwan University of
Science and Technology, 43, Sec. 4 Keelung Road, Taipei 10607, Taiwan

[‡] Department of Applied Chemistry, National Chiao Tung University, 1001 Ta Hsueh
Road, Hsin-Chu 30010, Taiwan

* To whom correspondence should be addressed.

E-mail: jcchen@mail.ntust.edu.tw

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Monomer Synthesis

2,2'-Bis(trifluoromethyl)-4,4'-bis(diethyl methylenephosphonate)biphenyl

(dimethylenephosphonate of CF₃-BP):¹ To a 100-mL, three-necked, round-bottomed flask were added 2,2'-bis(trifluoromethyl)-4,4'-bis(bromomethyl)biphenyl (0.67 g, 1.41 mmol) and triethyl phosphate (0.72 mL, 4.22 mmol). The reaction mixture was stirred and heated to reflux for 24 h. The excess triethyl phosphate was removed by distillation at 120 °C to afford brown oil-like crude product. The crude product was further purified by column chromatography using ethyl acetate as eluent to afford 0.56 g of pale yellow oil-like product (68%): ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 7.75 (s, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.98 (m, *J* = 7.1 Hz, 8H), 3.43 (d, *J* = 21.7 Hz), 1.16 (m, *J*₁ = 7.1 Hz, *J*₂ = 2.4 Hz, 12H); ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 127.69, 127.45, 127.19, 126.98 (q), 127.17, 124.98, 122.80, 120.62, 134.87, 133.69, 132.87, 131.61, 129.49, 61.69, 31.73, 16.06; Anal. Calcd for C₂₄H₃₀F₆O₆P₂: C 48.82, H 5.12; found: C 48.92, H 5.32.

4,4'-Diformyltriphenylamine (DA-TPA):² To a 100-mL, three-necked, round-bottomed flask were added DMF (7.00 mL, 94.40 mmol) under N₂ atmosphere. After it was cooled to 0 °C with ice bath, POCl₃ (9.00 mL, 102.14 mmol) was added slowly by syringe. The reaction mixture was stirred for 1 h at 0 °C. After the addition of triphenylamine (1.00 g, 4.08 mmol), the reaction mixture was heated to 95 °C and

kept at that temperature for 4 h. After the reaction mixture was allowed to cool to room temperature, it was poured into iced water (200 mL) and stirred for 1 h. The reaction mixture was neutralized by sodium hydroxide aqueous solution (1.0 M). The mixture was extracted with dichloromethane. The organic phase was collected and washed with saturated brine. After dried with anhydrous magnesium sulfide, the organic phase was evaporated to dryness to afford yellow crude product. The crude product was further purified by column chromatography using dichloromethane as eluent to afford 1.11 g of yellow solid (90%): ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 9.87 (s, 2H), 7.83 (d, *J* = 8.6 Hz, 4H), 7.46 (dd, *J*₁ = 7.5 Hz, *J*₂ = 8.1 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.21 (dd, *J*₁ = 8.1 Hz, *J*₂ = 1.1 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 4H). Mp: 142-144 °C.

9-(2-Ethylhexyl)-3,6-diformylcarbazole (DA-CBZ):³ To a 100-mL, three-necked, round-bottomed flask were added DMF (13.00 mL, 166.82 mmol) under N₂ atmosphere. After it was cooled to 0 °C with ice bath, POCl₃ (17.00 mL, 181.70 mmol) was added slowly by syringe. The reaction mixture was stirred for 1 h at 0 °C. 9-(2-ethylhexyl)carbazole (2.03 g, 7.25 mmol) and 1,1,2-trichloroethane (5.00 mL) was added to the reaction mixture. After the addition, the reaction mixture was heated to 95 °C and kept at that temperature for 4 h. After the reaction mixture was allowed

to cool to room temperature, it was poured into iced water (400 mL) and stirred for 1 h. The reaction mixture was neutralized by sodium hydroxide aqueous solution (1.0 M). The mixture was extracted with chloroform. The organic phase was collected and washed with saturated brine. After dried with anhydrous magnesium sulfide, the organic phase was evaporated to dryness to afford yellow crude product. The crude product was further purified by column chromatography using ethyl acetate/n-hexane (1:3) as eluent to afford 2.45 g of yellow solid (83%): $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ , ppm): 10.10 (s, 2H), 8.91 (d, $J = 1.5$ Hz, 2H), 8.07 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz, 2H), 7.85 (d, $J = 8.5$ Hz, 2H), 4.42 (d, $J = 7.7$ Hz, 2H), 2.01 (m, 1H), 1.25 (m, 8H), 0.85 (t, $J = 7.5$ Hz, 3H), 0.75 (t, $J = 7.2$ Hz, 3H). Mp: 110-112 °C.

2-(2-Ethylhexyloxy)-5-methoxybenzene-1,4-dicarbaldehyde (DA-MEH):⁴ To a 100-mL, three-necked, round-bottomed flask were added 1,4-bis(hydroxymethyl)-2-(2-ethylhexyloxy)-5-methoxybenzene (2.00 g, 7.00 mmol) and anhydrous dichloromethane (80.00 mL). The reaction mixture was stirred and cooled to 0 °C with ice bath. Pyridinium chlorochromate (PCC) (4.53 g, 21 mmol) was added portionwisely to the reaction mixture over a period of 20 min. The reaction mixture was then stirred for 8 h at room temperature. After a dark-brown suspension was formed, the reaction mixture was diluted with ether (200 mL) and stirred for further

30 min. The reaction mixture was then filtered through silica gel to remove the inorganic salt. The reaction mixture was extracted with ether. The organic phase was collected and washed with HCl aqueous solution (1.0 M) and saturated brine. After dried with anhydrous magnesium sulfide, the organic phase was evaporated to dryness to afford green crude product. The crude product was further purified by column chromatography using petroleum ether/ethyl acetate (10:1) as eluent to afford 1.80 g of yellow-green solid (87%). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 10.42 & 10.38 (s, 2H), 7.45 & 7.42(s, 2H), 4.04 (d, *J* = 5.5 Hz, 2H), 3.93 (s, 3H), 1.48 (m, 1H), 1.44 (m, 4H), 1.30 (m, 4H), 0.89 (m, 6H). Mp: 59-60 °C.

9,9-Dioctylfluorene-2,7-dicarbaldehyde (DA-FLO):⁵ To a 100-mL, three-necked, round-bottomed flask were added 2,7-dibromo-9,9-dioctylfluorene (0.60 g, 1.09 mmol) and anhydrous THF (16.00 mL). After the reaction mixture was cooled to -78 °C, *n*-BuLi (6.80 mL, 10.94 mmol, 1.6 M in *n*-hexane) was added dropwisely by syringe under N₂ atmosphere. After the reaction mixture was stirred at -78 °C for 1 h, anhydrous DMF (0.50 mL, 6.56 mmol) was added dropwisely by syringe. After the reaction mixture was stirred for 1 h at -78 °C, it was allowed to warm to room temperature and kept at that temperature for 18 h. The reaction mixture was quenched by HCl (20.00 mL, 2.0 M) and stirred for 2 h. The reaction mixture was extracted

with ether. The organic phase was collected and washed with saturated brine. After dried with anhydrous magnesium sulfide, the organic phase was evaporated to dryness to afford yellow oil-like crude product. The crude product was further purified by column chromatography using n-hexane/ethyl acetate (20:1) as eluent to afford 0.49 g of yellow oil-like product (27%): ^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ , ppm): 10.0 (s, 2H), 8.18 (d, $J_1 = 8.2$ Hz, 2H), 8.04 (s, 2H), 7.97 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.5$ Hz, 2H), 2.10 (m, 4H), 1.32-0.96 (m, 20H), 0.75 (t, $J = 7.2$ Hz, 6H), 0.46 (m, 4H).

^1H NMR ($\text{DMSO-}d_6$, 500 MHz)

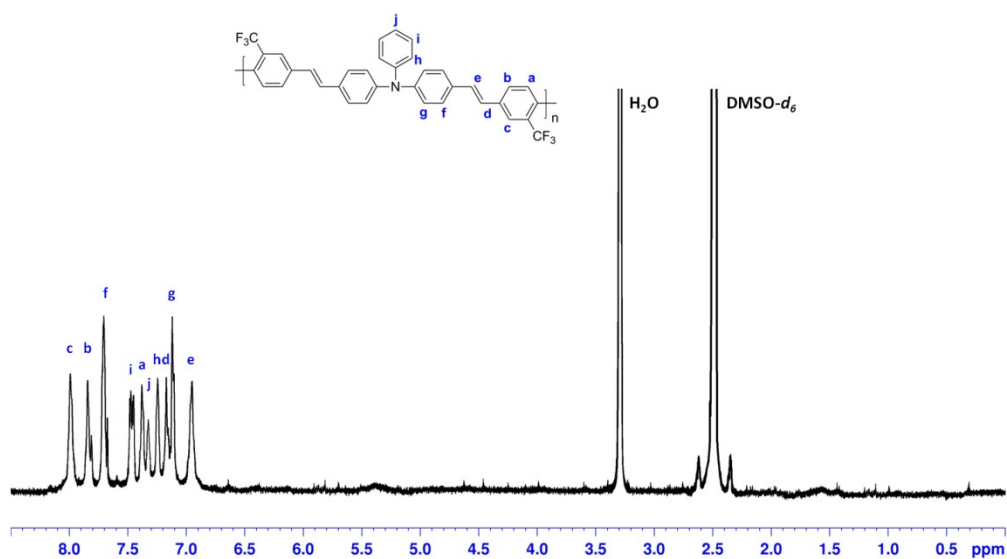


Fig. S1. ^1H NMR spectra of PBPV-TPA in $\text{DMSO-}d_6$.

^1H NMR ($\text{DMSO-}d_6$, 500 MHz)

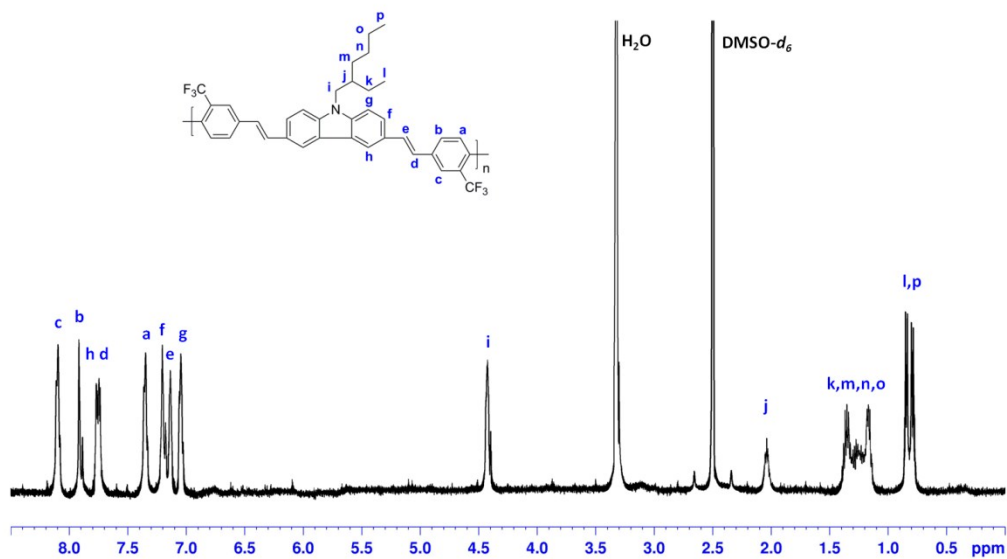


Fig. S2. ^1H NMR spectra of PBPV-CBZ in $\text{DMSO-}d_6$.

^1H NMR (DMSO- d_6 , 500 MHz)

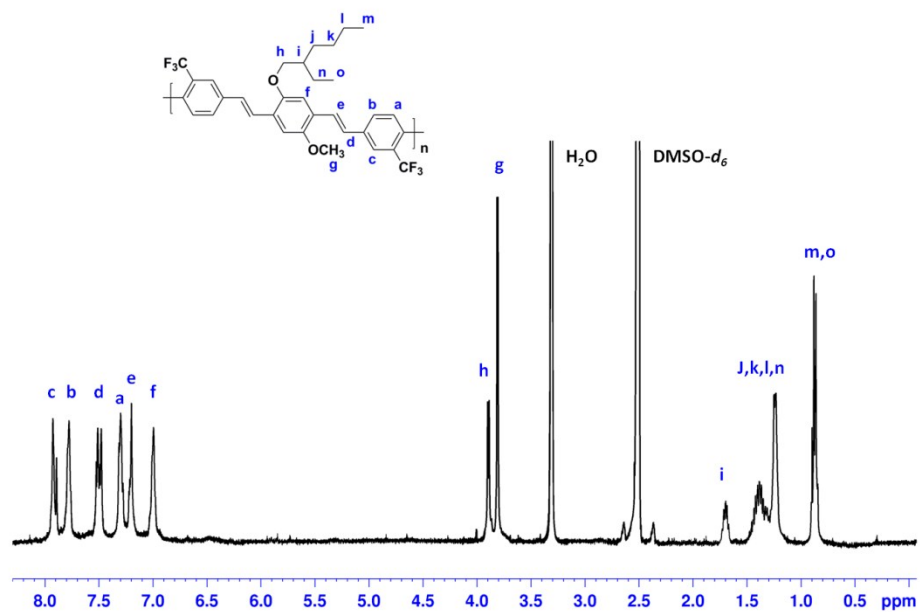


Fig. S3. ^1H NMR spectra of PBPV-MEH in DMSO- d_6 .

^1H NMR (DMSO- d_6 , 500 MHz)

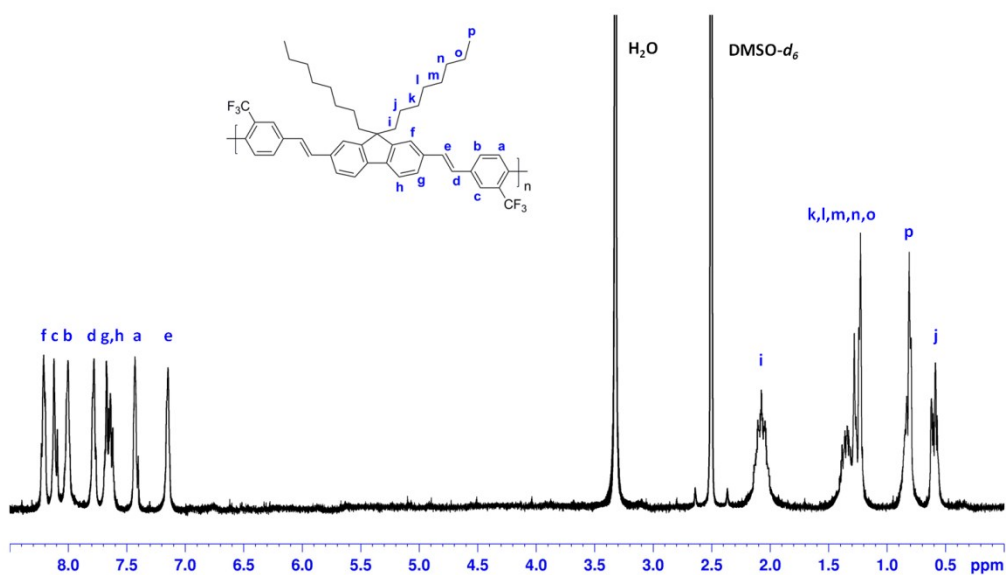


Fig. S4. ^1H NMR spectra of PBPV-FLO in DMSO- d_6 .

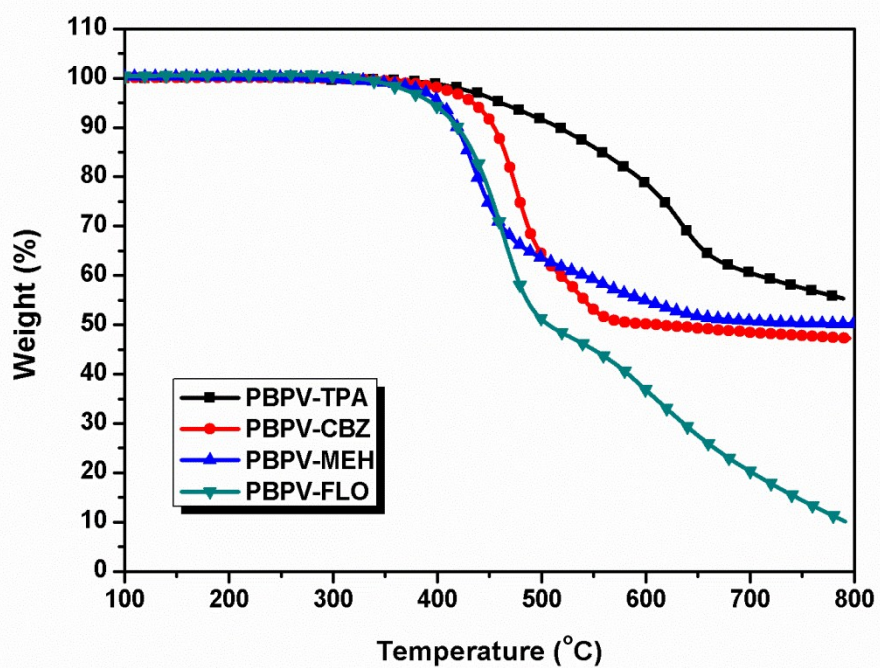


Fig. S5. TGA thermograms of polymers.

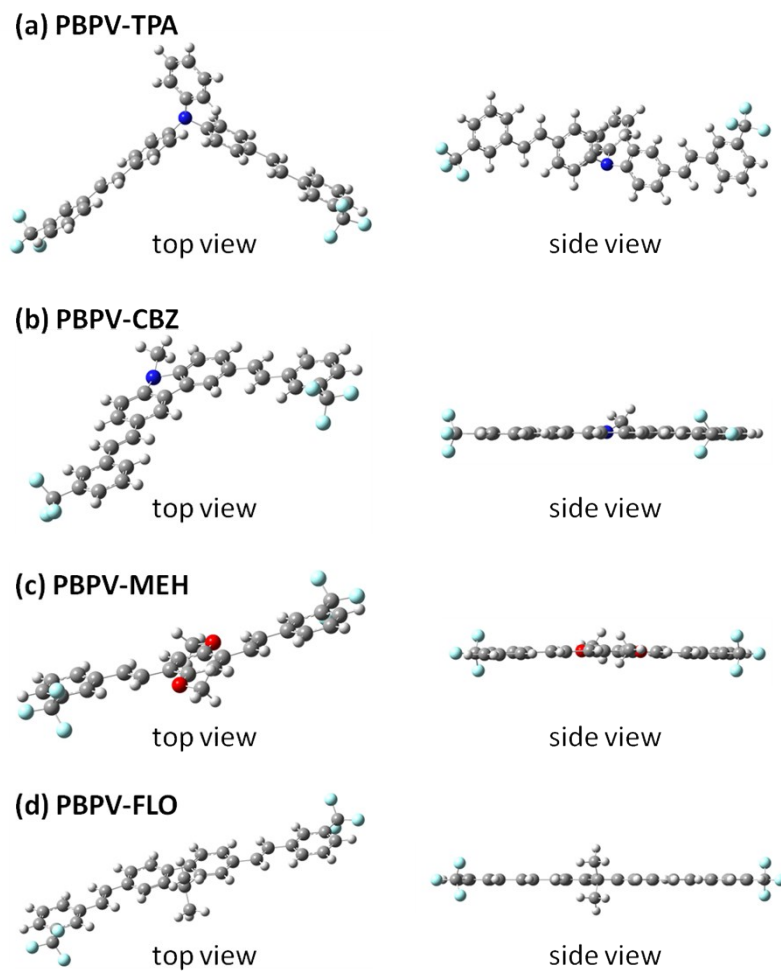


Fig. S6. Top and side view of DFT-optimized geometries of (a) PBPV-TPA, (b) PBPV-CBZ, (c) PBPV-MEH and (d) PBPV-FLO.

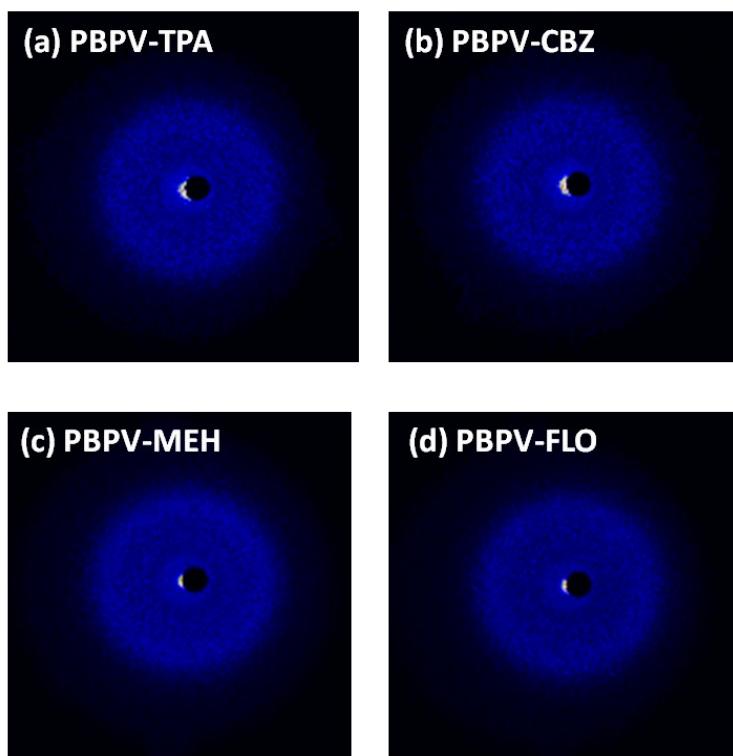


Fig. S7. WAXS ring patterns of (a) PBPV-TPA, (b) PBPV-CBZ, (c) PBPV-MEH and (d) PBPV-FLO.

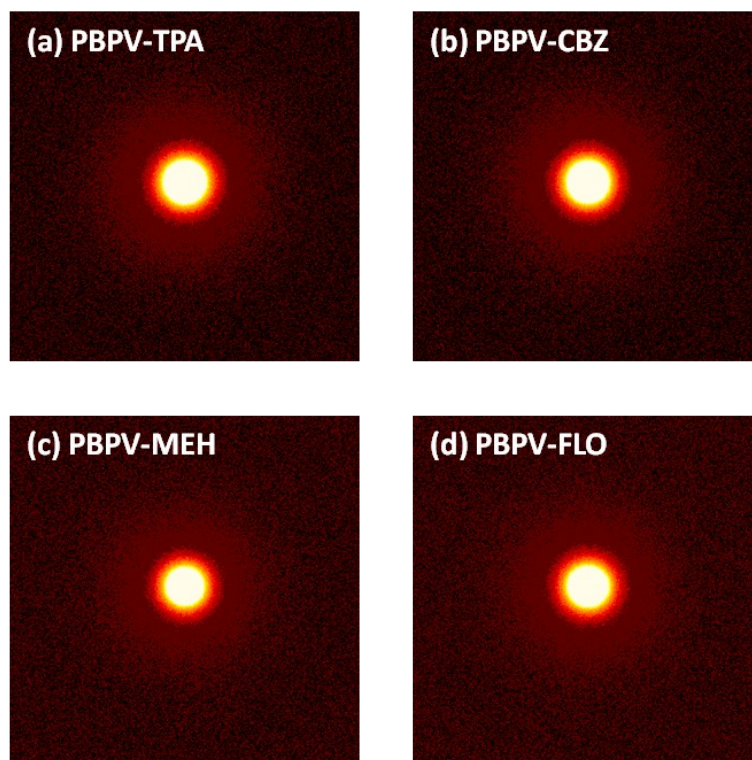


Fig. S8. SAXS ring patterns of (a) PBPV-TPA, (b) PBPV-CBZ, (c) PBPV-MEH and (d) PBPV-FLO.

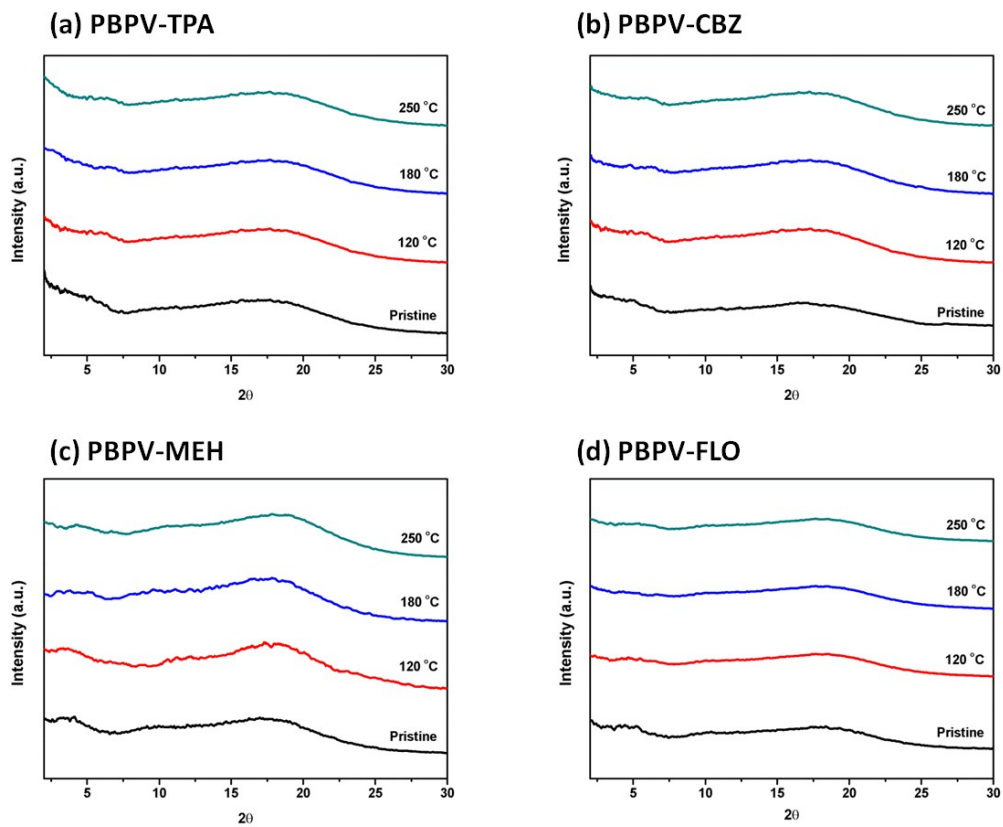


Fig. S9. WAXS patterns of (a) PBPV-TPA, (b) PBPV-CBZ, (c) PBPV-MEH and (d) PBPV-FLO annealed at different temperatures.

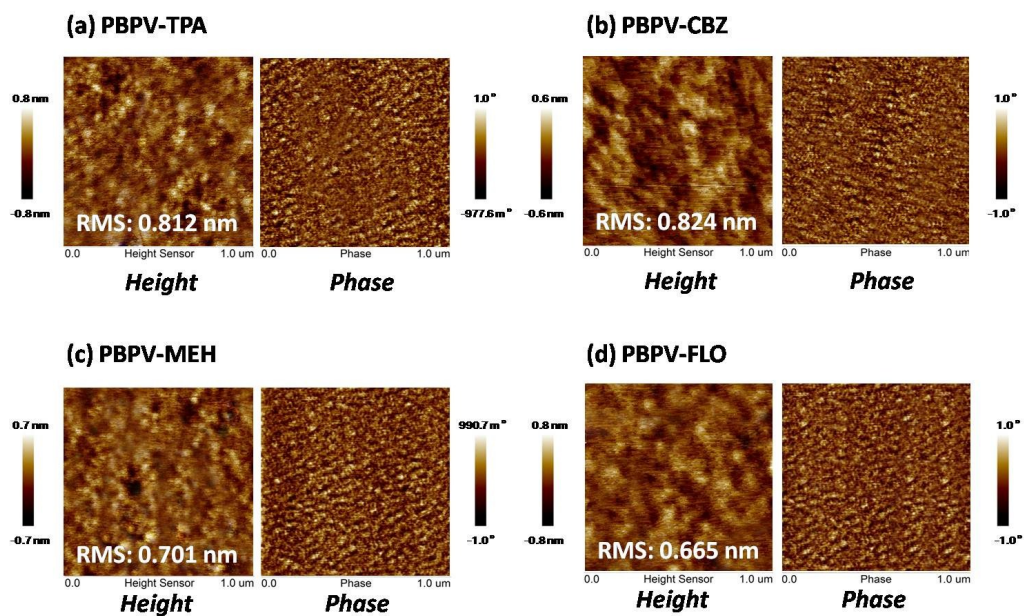


Fig. S10. AFM height and phase images (1 $\mu\text{m} \times 1 \mu\text{m}$) of spin-coated (a) PBPV-TPA, (b) PBPV-CBZ, (c) PBPV-MEH and (d) PBPV-FLO films annealed at 120 $^{\circ}\text{C}$.

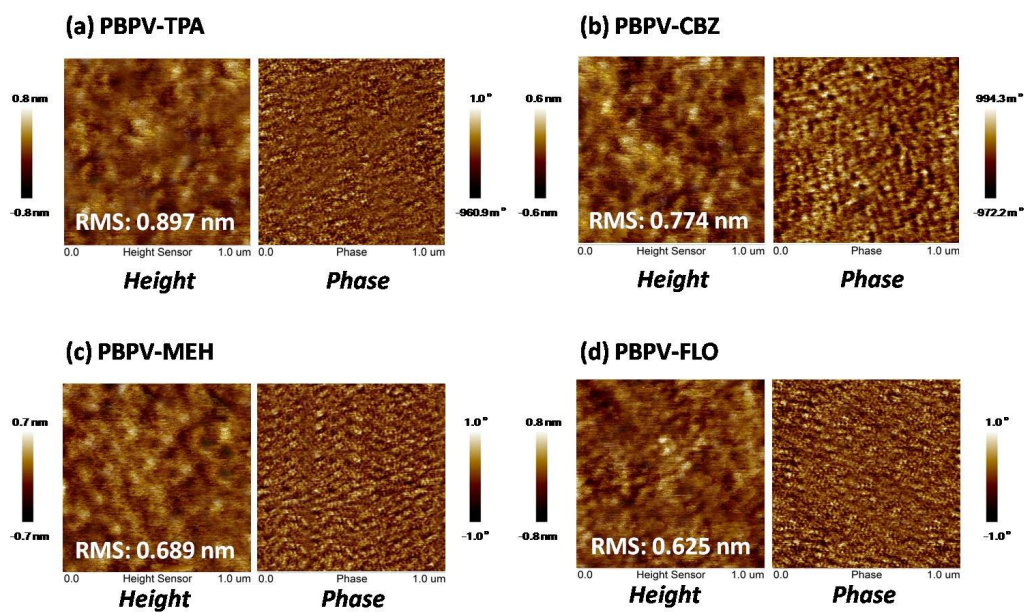


Fig. S11. AFM height and phase images ($1 \mu\text{m} \times 1 \mu\text{m}$) of spin-coated (a) PBPV-TPA, (b) PBPV-CBZ, (c) PBPV-MEH and (d) PBPV-FLO films annealed at 180 °C.

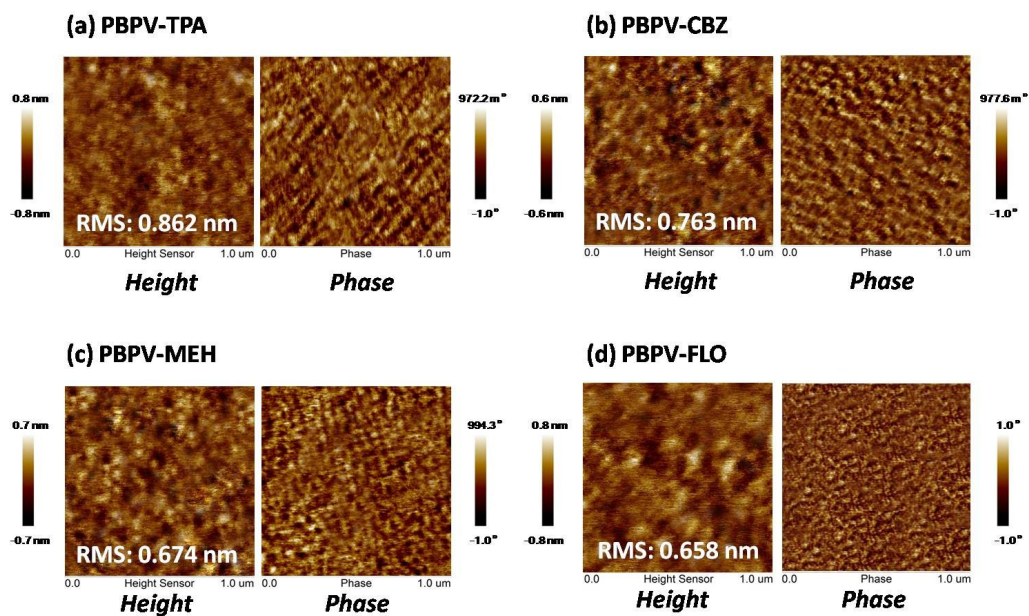
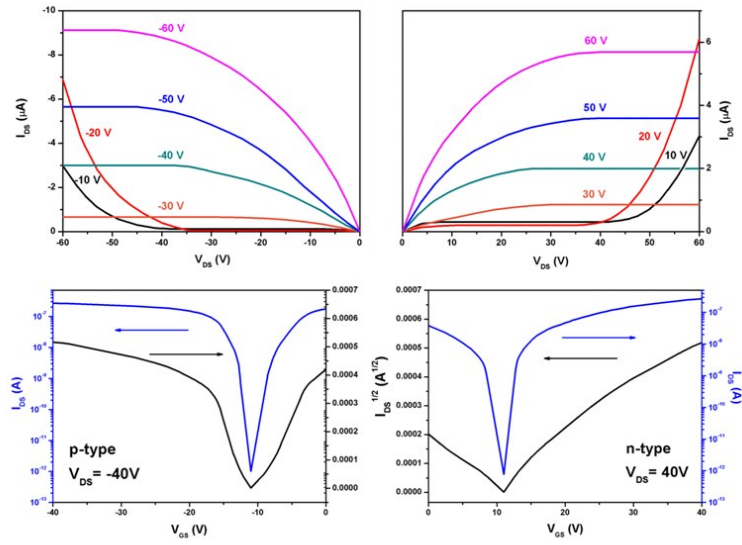


Fig. S12. AFM height and phase images ($1 \mu\text{m} \times 1 \mu\text{m}$) of spin-coated (a) PBPV-TPA, (b) PBPV-CBZ, (c) PBPV-MEH and (d) PBPV-FLO films annealed at 250 °C.

(a) PBPV-TPA



(b) PBPV-CBZ

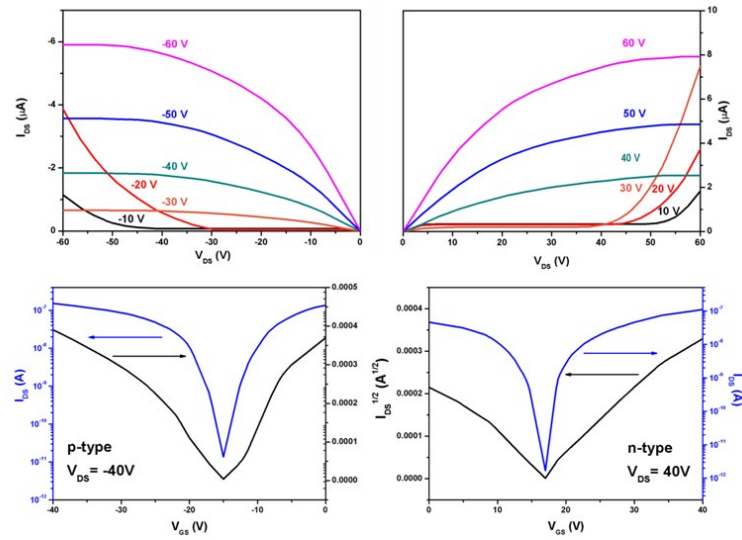


Fig. S13. Ambipolar output and transfer characteristics of OFET based on (a) PBPV-TPA and (b) PBPV-CBZ.

Table S1. Solubility^{a)} of polymers.

Polymer	Solvent							
	DMSO	NMP	DMAc	DMF	CHCl ₃	THF	T	DCB
PBPV-TPA	+-	++	++	+-	+-	+-	+-	+-
PBPV-CBZ	+	++	++	+	+	++	+-	++
PBPV-MEH	+	++	++	++	+	++	+	+-
PBPV-FLO	+	++	++	++	+	++	+	++

^{a)} The solubility was determined by using 5 mg of sample in 1 mL of stirred solvent. ++: Soluble at room temperature ; +: Soluble on heating ; +- : Partially soluble on heating ; - : Insoluble even on heating.

Abbreviation :

DMSO, dimethyl sulfoxide ; NMP, *N*-methyl-2-pyrrolidone ; DMAc, *N,N*-dimethylacetamide ; DMF, *N,N*-dimethylformamide ; CHCl₃, chloroform ; THF, tetrahydrofuran ; T, toluene ; DCB, 1,2-dichlorobenzene.

Notes and references

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