Support information

Aldol Condensation-Polymerized Semiconducting Polymers Based on BDOPV Unit with Near Infrared Absorption and Better n-Doped Ability

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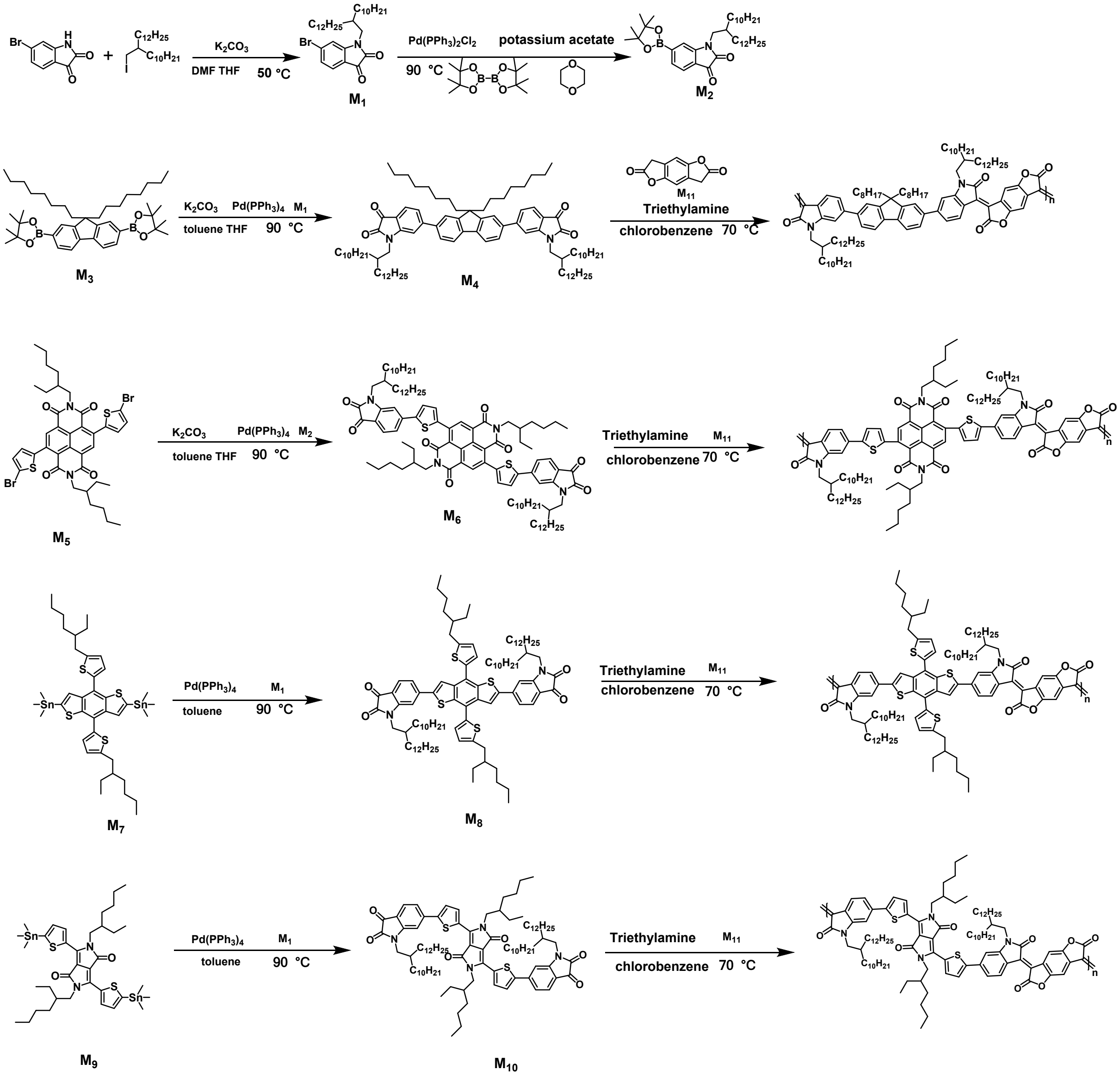

Experimental section:

Scheme S1 Synthetic procedures of monomers and polymers.

6-Bromoisatin (97%), triethylamine (99.5%), iodomethane (99.5%), bromoethane (99.5%) and tetrahydrofuran (99.5%) were purchased from Energy Chemical and used directly without further treatment. 3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (M6) (98%) was purchased from COSPAR industry (China) Co. Ltd. Chlorobenzene (99.5%) and Pd(PPh$_3$)$_4$ were purchased from

Acros Co. Ltd. 6,6'-(2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene-9,9-diyl)bis(N,N-diethylhexan-1-amine),[1] M1[2] and M2[3] were synthetized according to the published literatures. The synthetic steps of monomers are presented in **Scheme S1**.

6,6'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(1-(2-decyltetradecyl)indoline-2,3-dione) (M4)

Toluene (12 mL), M1(1.1 g, 1.96 mmol) and 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M3) (0.53 g, 0.82 mmol) were added to a 50 mL of flask. Then potassium carbonate (2.0 M aqueous solution, 6 mL) and THF (4 mL) were added. The reaction was then purged with argon for 20 min, then $Pd(PPh_3)_4$ (5 mg) was added. The mixture was then stirred under 90°C overnight. The orange mixture was extracted with dichloromethane and water, washed by water for two times. The organic phase was then dried with anhydrous $MgSO_4$, and was evaporated under vacuum to obtain the crude product. After purifying by column chromatography with petroleum ether/dichloromethane (1:1) as eluent, the pure product (M2) was obtained as orange oil with a yield of 87%.

^{1}H NMR (500 MHz, $CDCl_3$) δ =7.86 (d, *J*=7.9, 2H), 7.71 (d, *J*=7.8, 2H), 7.63 (dd, *J*=7.9, 1.5, 2H), 7.60 (s, 2H), 7.40 (dd, *J*=7.8, 1.0, 2H), 7.12 (s, 2H), 3.70 (d, *J*=7.3, 4H), 2.12-2.04 (m, 4H), 1.98-1.91 (m, 2H), 1.41-1.06 (m, 100H), 0.87 (t, *J*=6.9, 12H), 0.78 (t, *J*=7.1, 6H), 0.72 (s, 4H).

4,9-bis(5-(1-(2-decyltetradecyl)-2,3-dioxoindolin-6-yl)thiophen-2-yl)-2,7-bis(2-ethylhexyl) benzo [3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (M6)

Toluene (3 mL), M2 (217 mg，0.36 mmol) and 4,9-bis(5-bromothiophen-2-yl)-2,7-bis(2-ethylhexyl)benzo [3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (M5) (100 mg， 0.16 mmol) were added to a 15 mL of pressure tubes. Then potassium carbonate (2.0 M aqueous solution, 2 mL) and THF (1 mL) were added. The reaction was then purged with argon for 20 min, then $Pd(PPh_3)_4$ (5 mg) was added. The mixture was then stirred under 90°C overnight. The orange mixture was extracted with dichloromethane and water, washed by water for two times. The organic phase was then dried with anhydrous $MgSO_4$, and was evaporated under vacuum to obtain the crude product. After purifying by column chromatography (SiO2；PE/DCM =1:1), the pure product (M6) was obtained as orange oil with a yield of 87%.

^{1}H NMR (400 MHz, $CDCl_3$) δ =8.82 (s, 2H), 7.66 (d, *J*=7.8, 2H), 7.57 (d, *J*=3.8, 2H), 7.39 (d, *J*=7.9, 2H), 7.36 (d, *J*=3.8, 2H), 7.13 (s, 2H), 4.11 (dd, *J*=7.1, 4.3, 4H), 3.67 (d, *J*=7.3, 4H), 1.91 (d, *J*=6.2, 4H), 1.40-1.35 (m, 16H), 1.31-1.17 (m, 80H), 0.92-0.83 (m, 24H).

6,6'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(1-(2-decyltetradecyl)indoline-2,3-dione) (M8)

Toluene (5 mL), M1 (202 mg，0.36 mmol) and M7 (145 mg，0.16 mmol) were added to a 10 mL of pressure tubes. The reaction was then purged with argon for 20 min, then $Pd(PPh_3)_4$ (5 mg) was added. The mixture was then stirred under 90°C overnight. The orange mixture was extracted with dichloromethane and water, washed by water for two times. The organic phase was then dried with anhydrous $MgSO_4$, and was evaporated under vacuum to obtain the crude product. After purifying by column chromatography (SiO2；PE/DCM =1:1), the pure product (M8) was obtained as orange oil with a yield of 90%.

^{1}H NMR (400 MHz, $CDCl_3$), δ=8.92 (d, 2H, *J* =3.9 Hz), 7.46 (d, *J*=7.9, 2H) 7.30 (d, *J*=4.3 Hz, 2H), 7.27 (dd, *J*=7.9, 1.5, 2H), 7.02 (d, *J*=1.4, 2H),4.13-3.98 (m, 4H), 3.57 (d, *J*=7.5, 4H),1.89 (p, *J* = 6.3 Hz, 2H), 1.83 (s, 2H), 1.43-1.15 (m, 96H), 0.89 (dt, *J* = 9.1, 7.1 Hz, 12H), 0.88 (t, *J*=6.8, 12H)

6,6'-((2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis (thiophene-5,2-diyl))bis(1-(2-decyltetradecyl)indoline-2,3-dione) (M10)

Toluene (5 mL), M1 (151.5 mg，0.27 mmol) and M9 (102.2 mg，0.12 mmol) were added to a 10 mL of pressure tubes. The reaction was then purged with argon for 15 min, then $Pd(PPh_3)_4$ (5 mg) was added. The mixture was then stirred under 90°C overnight. The blue mixture was extracted with dichloromethane and water, washed by water for two times. The blue phase was then dried with anhydrous $MgSO_4$, and was evaporated under vacuum to obtain the crude product. After purifying by column chromatography (SiO2；PE/DCM =1:2), the pure product (M10) was obtained as blue soild with a yield of 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.64 (d, *J* =5.7 Hz, 2H), 7.46 (d, *J*=7.9, 2H),7.29 (d, J =3.4 Hz, 2H), 7.27 (dd, *J*=7.9, 1.5, 2H), 7.02 (d, *J*=1.4, 2H),6.89 (d, *J* =3.5 Hz, 2H) , 3.57 (d, *J*=7.5, 4H), 2.86 (d, *J* = 6.8 Hz, 4H), 1.83 (s, 2H), 1.73-1.64 (m, 2H), 1.43-1.15 (m, 96H), 1.05-0.88 (m, 12H) , 0.84 (t, *J*=6.8, 12H).

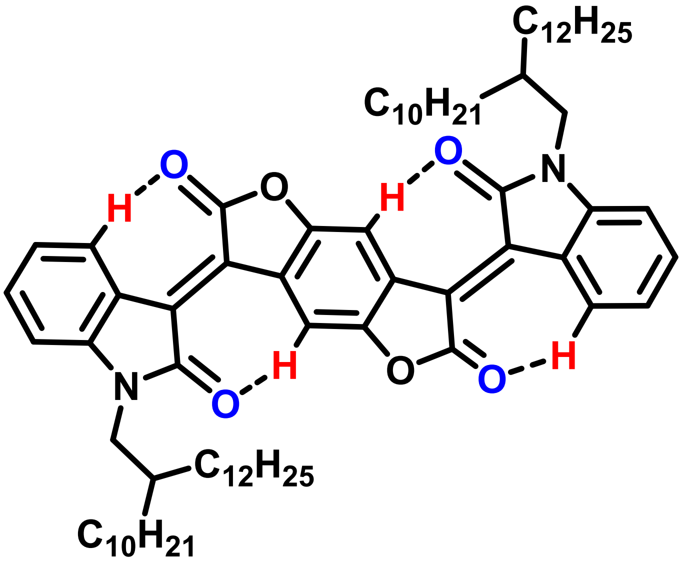

Figure S1 The diagram of hydrogen bonds in BDOPV unit

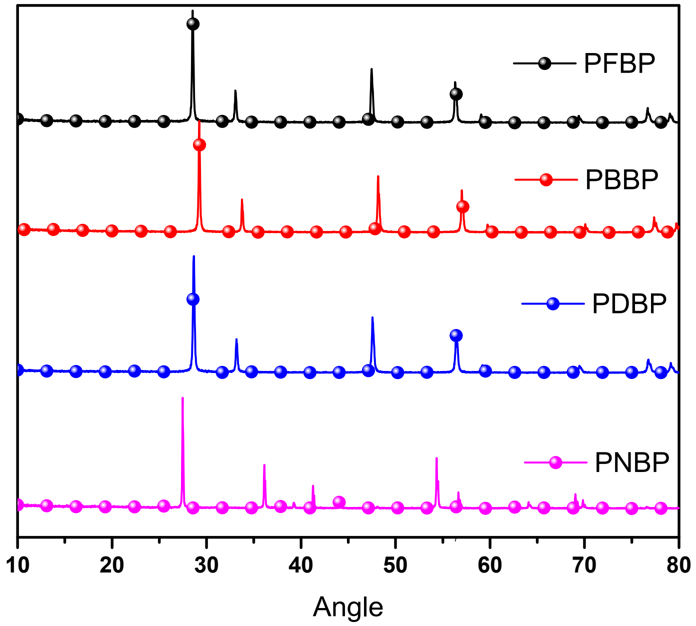

Figure S2 XRD spectra of BCF doped PFBP(a); PBBP(b); PDBP(c); PNBP(d) films

Table S1. Electron/hole mobilities of pure narrow-bandgap semiconducting polymers and polymers:PTB7-Th blend electron/hole-only devices

Acceptor		$\mu_e(\mathrm{cm}^2V^{-1}s^{-1})$	$\mu_h(\mathrm{cm}^2V^{-1}s^{-1})$
PBBP	Blend(PTB7-Th)	1.012×10^{-7}	5.820×10^{-4}
	pure	1.157×10^{-7}	4.565×10^{-5}
PNBP	Blend(PTB7-Th)	2.228×10^{-8}	1.529×10^{-4}
	pure	3.514×10^{-4}	1.750×10^{-4}
PDBP	Blend(PTB7-Th)	2.067×10^{-8}	9.047×10^{-4}
	pure	4.607×10^{-6}	1.465×10^{-5}
PFBP	Blend(PTB7-Th)	1.459×10^{-7}	3.150×10^{-3}

pure	1.237×10^{-4}	1.579×10^{-6}

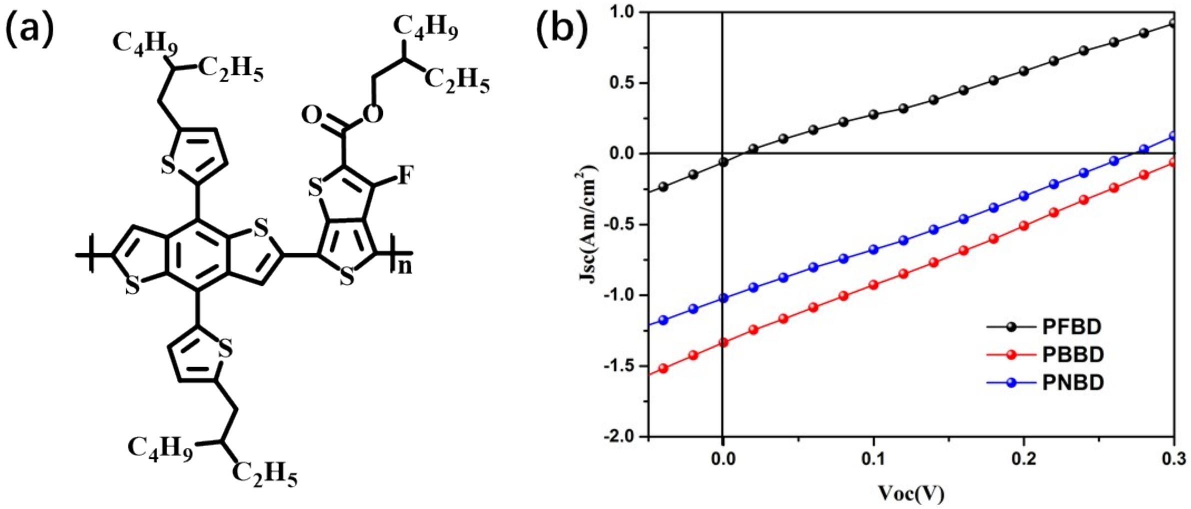

Figure S3 Chemical structures of PTB7-Th (a); J-V curves of devices based on PFBP, PBBP, PDBP and PNBP(b);

Acceptor	V_{oc}(V)	J_{sc}(mA/cm^2)	*FF*	PCE(%)	PCE (max%)
PFBP	0.01±0.00	0.06±0.00	0.00±0.00	0.00±0.00	0
PBBP	0.29±0.03	1.39±0.08	26.20±0.00	0.11±0.00	0.11
PNBP	0.27±0.00	0.97±0.07	27.38±0.52	0.07±0.00	0.08

Table S2. Device parameters of photovoltaic devices based on PTB7-Th: acceptor.

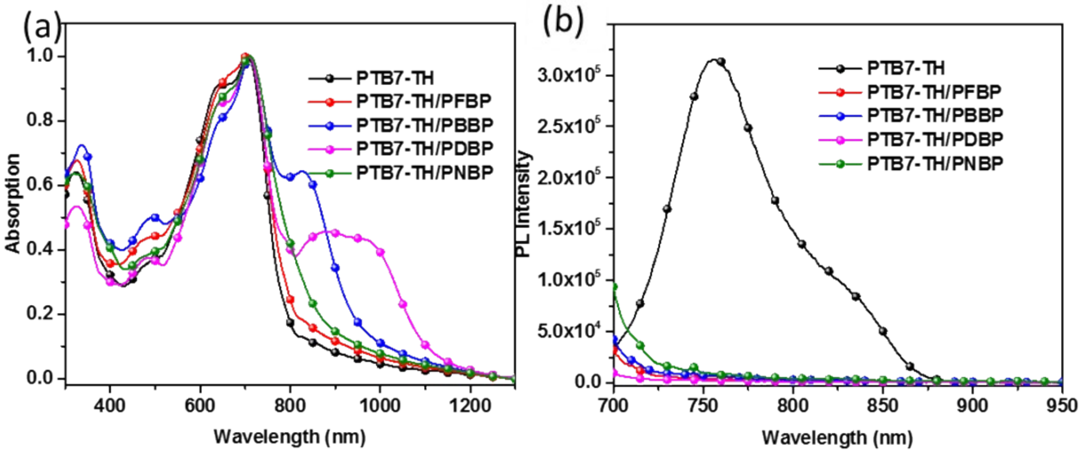

Figure S4 UV–vis absorption spectra (a) and steady state PL spectra (b) for PTB7-Th and PTB7-Th/polymers blend films

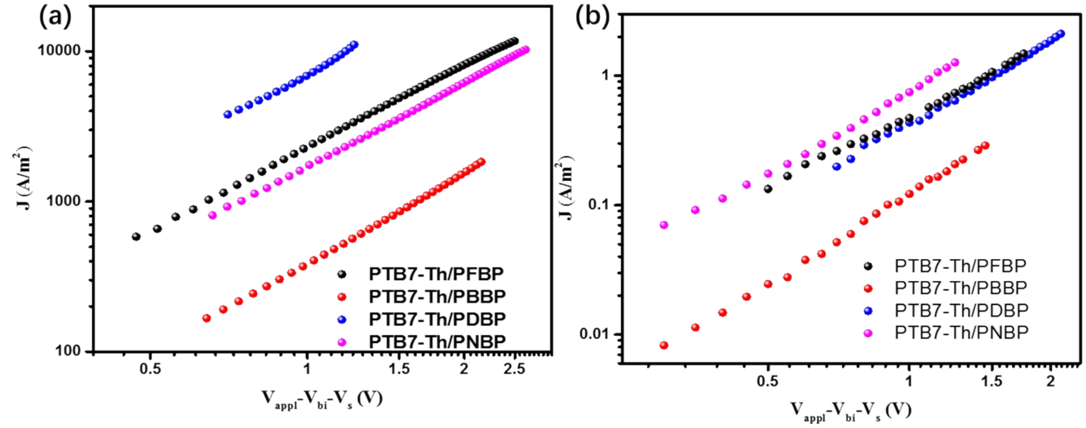

Figure S5 The J-V curves of (a)electron-only devices with structure of ITO/ZnO/polymers:PTB7-TH/Ag; (b)hole-only devices with structure of ITO/PEDOT:PSS/ polymers:PTB7-TH /MoO3/Ag for semiconducting polymer films;

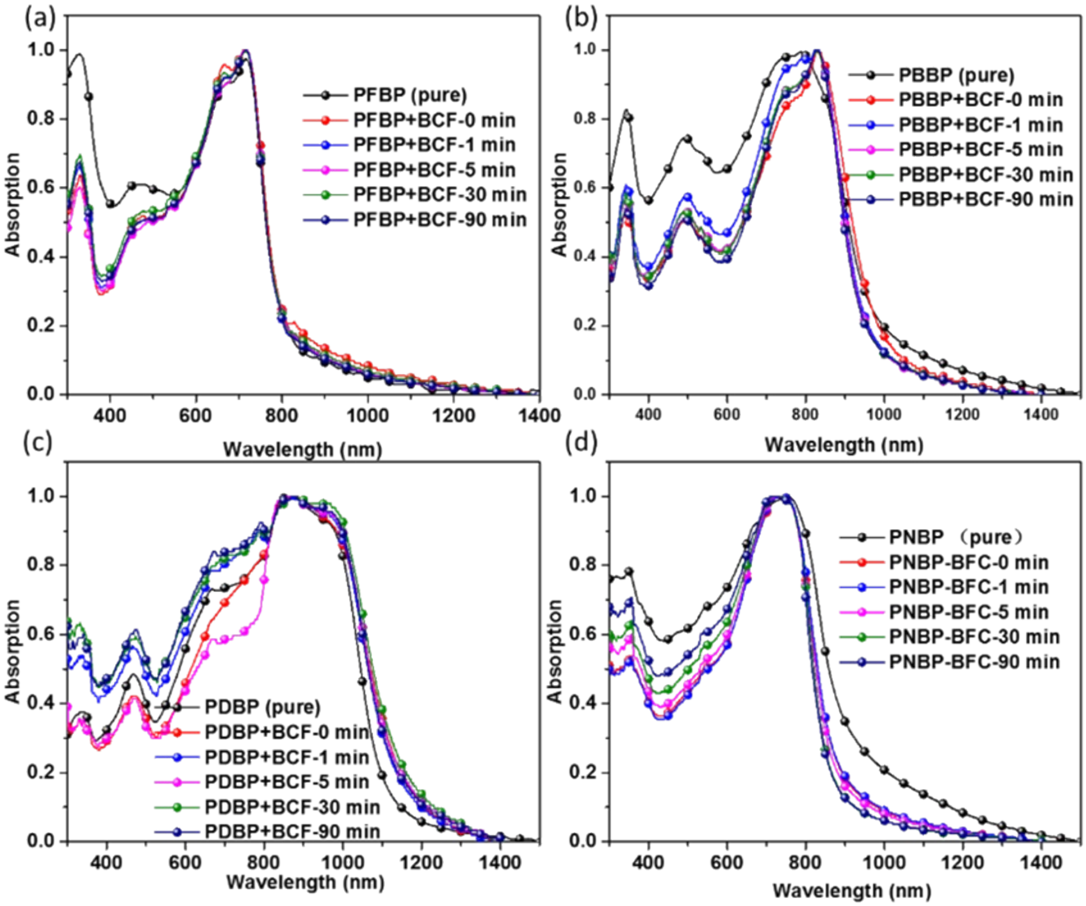

Figure S6 UV–vis absorption spectra of BCF doped PFBP(a); PBBP(b); PDBP(c); PNBP(d) films after thermal annealing at 120^{o}C for different time;

Reference:

1. C. Duan, L. Wang, K. Zhang, X. Guan, F. Huang, *Adv. Mater*. **2011**, *23*, 1665-1669.
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3. H. Liao, C. Xiao, M. K. Ravva, Y. Wang, M. Little, M. V. C. Jenart, A. Onwubiko, Z. Li, Z. Wang, J.-L. Brédas, I. McCulloch, W. Yue, *Chem. Commun.*, **2018**, 54, 11152-11155