## Electronic Supplementary Information

## Polythiophene derivatives compatible with both fullerene and non-

## fullerene acceptors for polymer solar cells

Xiao'e Jia, ${ }^{\text {à }}$ Zhiming Chen, ${ }^{\text {à }}$ Chunhui Duan, ${ }^{\text {a* }}$ Zhenfeng Wang, ${ }^{\text {a }}$ Qingwu Yin, ${ }^{\text {a }}$ Fei Huang, ${ }^{\text {a* }}$ and Yong Cao ${ }^{a}$
${ }^{\text {a }}$ Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China.
${ }^{\dagger}$ These authors contributed equally to this work.
*E-mail: duanchunhui@scut.edu.cn
*E-mail: msfhuang@scut.edu.cn

## Experimental Section

## Materials

All the chemicals and reagents were purchased from commercial sources (Solarmer Materials Inc., TCI, Alfa Aesar or Aldrich) and used as received unless otherwise indicated. Monomer 3 was purchased from SunaTech Inc.

## Synthesis of the monomers

2-Bromo-3-(2-butyloctyl)thiophene (1a). 3-(2-butyloctyl)thiophene (2.52 g, 10 mmol ) was dissolved in tetrahydrofuran $(50 \mathrm{~mL})$ and stirred at ambient temperature. A freshly recrystallized $N$-bromosuccinimide (1.78 g, 10 mmol ) was added in one portion. The mixture was left to stirring for 8 hours under dark. After the removal of solvent under reduced pressure, the crude product was purified with column chromatography using hexane as the eluent, then the final product was obtained as a pale yellow liquid ( $2.98 \mathrm{~g}, 90 \%$ ). ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}{ }_{3}\right) \delta(\mathrm{ppm})$ : $7.18(\mathrm{~d}, 1 \mathrm{H}), 6.76(\mathrm{~d}, 1 \mathrm{H}), 2.50(\mathrm{~d}, 2 \mathrm{H}), 1.64(\mathrm{~m}, 1 \mathrm{H}), 1.25(\mathrm{~m}, 16 \mathrm{H}), 0.89(\mathrm{t}, 6 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}):$ $141.32,128.96,125.06,109.56,38,68,34.18,33.50,33.20,32.04,29.83,28.92,26.66,23.20,22.84,14.28$. (APCIHRMS) Calculated for $\mathrm{C}_{16} \mathrm{H}_{27} \mathrm{BrS}$ : 331.4. Found: 330.1.

2-Bromo-3-(2-hexyldecyl)thiophene (1b). The synthetic procedure of 1 b was similar to the compound 1a with a yield of $92 \% .^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}): 7.18(\mathrm{~d}, 1 \mathrm{H}), 6.76(\mathrm{~d}, 1 \mathrm{H}), 2.50(\mathrm{~d}, 2 \mathrm{H}), 1.65(\mathrm{~m}, 1 \mathrm{H}), 1.26(\mathrm{~m}, 24 \mathrm{H})$, $0.90-0.87(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}^{\mathrm{CNMR}}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}): 141.33,128.96,125.05,109.56,38.70,34.19,33.52,33.51$, 32.07, 32.04, 30.15, 29.83, 29.76, 29.49, 26.68, 26.66, 22.85, 22.84, 14.28. (APCI-HRMS) Calculated for $\mathrm{C}_{20} \mathrm{H}_{35} \mathrm{BrS}$ : 387.5. Found: 386.2.

5,5'-Dibromo-4,4'-bis(2-butyloctyl)-2,2'-bithiophene (2a). The compound 1a (1.66 g, 5 mmol ), dry dimethyl sulfoxide ( 50 mL ) were added to a two-neck round flask and degassed with argon for 15 min . Then potassium fluoride (KF) ( $0.58 \mathrm{~g}, 10 \mathrm{mmol})$, silver nitrate $\left(\mathrm{AgNO}_{3}\right)(1.7 \mathrm{~g}, 10 \mathrm{mmol})$, and $2 \mathrm{~mol} \%$ of bis(benzonitrile)palladium (II) chloride ( $38.4 \mathrm{mg}, 0.1 \mathrm{mmol}$ ) were added quickly into the solution successively under a stream of argon, and then the mixture was purged with argon again for 15 min . Subsequently, the reaction mixture was heated to $60^{\circ} \mathrm{C}$ with stirring. Two additional portions of $\mathrm{AgNO}_{3}$ and KF (same quantities as above) were added to the reaction mixture with 3 hours interval, and the reaction was continued for further 12 hours at the same temperature. The resulting black suspension was cooled to room temperature, washed three times with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous magnesium sulfate and filtered. After the removal of solvent under reduced pressure, the crude product was purified with column chromatography using hexane as the eluent, then the final product was obtained as a yellow oil ( $1.40 \mathrm{~g}, 85 \%$ ). ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$
$\delta(p p m): 6.73(\mathrm{~s}, 2 \mathrm{H}), 2.46(\mathrm{~d}, 4 \mathrm{H}), 1.65(\mathrm{~m}, 2 \mathrm{H}), 1.26(\mathrm{~m}, 32 \mathrm{H}), 0.90-0.86(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (125 MHz, CDCl$\left.)_{3}\right) \delta$ (ppm): 142.33, 136.13, 125.06, 108.64, 38.64, 34.34, 33.44, 33.16, 32.04, 29.82, 28.89, 26.63, 23.20, 22.84, 14.28. (APCI-HRMS) Calculated for $\mathrm{C}_{32} \mathrm{H}_{52} \mathrm{Br}_{2} \mathrm{~S}_{2}$ : 660.7. Found: 660.2.

5,5'-Dibromo-4,4'-bis(2-hexyldecyl)-2,2'-bithiophene (2b). The synthetic procedure of 2 b was similar to the compound 2 a with a yield of $88 \%{ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}): 6.73(\mathrm{~s}, 2 \mathrm{H}), 2.46(\mathrm{~d}, 4 \mathrm{H}), 1.65(\mathrm{~m}, 2 \mathrm{H}), 1.26$ $(\mathrm{m}, 48 \mathrm{H}), 0.89(\mathrm{t}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (125 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta(\mathrm{ppm}): 142.34,136.14,125.05,108.63,38.66,34.35,33.48$, $33.45,32.08,32.05,30.14,29.82,29.77,29.50,26.65,26.64,22.85,22.84,14.29$. (APCI-HRMS) Calculated for $\mathrm{C}_{40} \mathrm{H}_{68} \mathrm{Br}_{2} \mathrm{~S}_{2}$ : 772.9. Found: 772.3.

## Synthesis of the polymers

P4T2F-BO. In a glove box filled with nitrogen $\left(\mathrm{N}_{2}\right)$, monomer 2a ( $165.2 \mathrm{mg}, 0.25 \mathrm{mmol}$ ), monomer 3 ( 132.0 mg , $0.25 \mathrm{mmol})$, tris(dibenzylideneacetone)dipalladium(0) $\left(\mathrm{Pd}_{2}(\mathrm{dba})_{3}\right)(4.6 \mathrm{mg}, 0.005 \mathrm{mmol})$ and tri(o-tolyl)phosphine $\left(\mathrm{P}(\mathrm{o}-\mathrm{tol})_{3}\right)(12.2 \mathrm{mg}, 0.04 \mathrm{mmol})$ were dissolved in 2.5 mL dry chlorobenzene in a 15 mL reaction tube. After stirred at $110^{\circ} \mathrm{C}$ for 24 hours, 2-(tributylstannyl)thiophene and 2-bromothiophene were added to the reaction mixture sequentially with 2 hours interval to complete end-capping. Then the reaction mixture was diluted with chlorobenzene, and refluxed with sodium $N, N$-diethylcarbamodithioate trihydrate ( 100 mg ) for another 2 hours. Subsequently, the reactant was cooled to room temperature and precipitated into methanol, filtered. The solid was further purified by Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform, and chlorobenzene under argon protection. Finally, the polymer was collected from chlorobenzene. The solution was concentrated by rotary evaporation, precipitated into methanol. The polymer was collected via filter paper and dried over in the vacuum to give red solid (154 mg, 88\%). Anal. calcd for C40H54F2S4: C 68.52, H 7.76, S 18.29; found: C 66.41, H 7.57, S 17.53. $\bar{M}_{\mathrm{n}}=42 \mathrm{kDa}, \oplus_{\mathrm{M}}=1.7$.

P4T2F-BO/HD. P4T2F-BO/HD was synthesized by following the same procedure as P4T2F-BO. The resulting polymer P4T2F-BO/HD was collected from chlorobenzene and obtained as a red solid (55\%). Anal. calcd for C88H124F4S8: C 69.79, H 8.25, S 16.94; found: C 68.74, H 8.08, S $16.79 . \bar{M}_{\mathrm{n}}=46 \mathrm{kDa}, \oplus_{\mathrm{M}}=1.4$.

P4T2F-HD. P4T2F-HD was synthesized by following the same procedure as P4T2F-BO. The resulting polymer P4T2FHD was collected from chloroform and obtained as a red solid (80\%). Anal. calcd for C40H54F2S4: C 70.88, H 8.68, S 15.77; found: C 70.74, H 8.59, S 15.96. $\bar{M}_{\mathrm{n}}=46 \mathrm{kDa}, \bigoplus_{\mathrm{M}}=1.6$.

## Instruments and Characterization

${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR spectra were characterized on a Bruker AV-500 in $d$-chloroform solvent with tetramethylsilane (TMS) as an internal reference at room temperature. MS was performed by using a Waters ACQUITY ${ }^{\circledR}$ SQD/TQD for APCI-HRMS. High-temperature gel permeation chromatograph (GPC) was operated on an Agilent Technologies PL-GPC 220 at $150^{\circ} \mathrm{C}$ using 1,2,4-trichlorobenzene as the eluent versus polystyrene standards. Thermogravimetric analyses (TGA) were performed on NETZSCH TG 209 at a heating rate of $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$ under a nitrogen flow rate of $20 \mathrm{~mL} \mathrm{~min}^{-1}$. Differential scanning calorimetry (DSC) were conducted on a NETZSCH (DSC200F3) apparatus at a heating or cooling rate of $10^{\circ} \mathrm{C} \mathrm{min}^{-1}$ with a nitrogen atmosphere. UV-vis absorption spectra were recorded on a Shimadzu UV3600 spectrophotometer. The electrochemical cyclic voltammetry (CV) experiments were carried out on a CHI600D electrochemical workstation at a scan rate of $100 \mathrm{mV} \mathrm{s}^{-1}$ with $^{\text {Bu }} \mathrm{NPFF}_{6}$ (0.1 M) in acetonitrile as the electrolyte, and glassy-carbon, platinum wire, and saturated calomel electrode as the working, counter, and reference electrode, respectively. Potentials were calibrated using ferrocence as an external standard. or polymer. Photoluminescence (PL) spectra were acquired on an FLS920 spectrofluorimeter (Edinburgh Instruments). The transmission electron microscopy (TEM) images were obtained from a JEM-2100F instrument.

## Device Fabrication and Characterization

Fabrication of PSCs. The polymer solar cells were fabricated with a conventional configuration of indium tin oxide (ITO)/PEDOT:PSS/active layer/PFN-Br/Ag, where poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and poly[(9,9-bis(3'-((N,N-dimethyl)-N-ethylammonium)-propyl)-2,7-fluorene)-alt-2,7-(9,9dioctylfluorene)]dibromide (PFN-Br) were used as anode and cathode interlayer, respectively. The ITO-coated glass substrates were cleaned sequentially under sonication with detergent, deionized water, acetone, and isopropyl alcohol and then dried at $80^{\circ} \mathrm{C}$ in a baking oven overnight, followed by a 4 min oxygen plasma treatment. PEDOT:PSS (Heraeus Clevios P VP A 4083) was spin-coated onto the above ITO glass substrates and annealed at $150^{\circ} \mathrm{C}$ on a hot plate for 10 min in air. Afterwards, the substrates were transferred into a nitrogen protected glove box, and the active layer of donor:[70]PCBM or P4T2F-HD:O-IDTBR were formed by spin-coating from their mixed solutions (D/A weight ratio 1:1.5 for donor:[70]PCBM blend solutions, D/A weight ratio 1:1 for P4T2F-HD:O-IDTBR blend solution). Different concentrations and rotating speed were used to regulate the film thickness, and then the active layers were treated by thermal annealing for 5 minutes at different temperatures. After spin-coating of 5 nm PFN-Br as cathode interface, a 100 nm Ag layer was sequentially deposited by thermal evaporation through a shadow mask in a vacuum chamber with a base pressure of $2 \times 10^{-6} \mathrm{mbar}$. The active layer area of the device was $0.04 \mathrm{~cm}^{2}$.

Characterization of the PSCs. The photovoltaic performance of the devices was measured using an AM1.5G solar simulator (Taiwan, Enlitech SS-F5). The current density-voltage ( $J-V$ ) characteristics were recorded with a Keithley 2400 source meter. The illumination intensity of the light source was $100 \mathrm{~mW} \mathrm{~cm}{ }^{-2}$ in the test, which was calibrated on a National Renewable Energy Laboratory calibrated silicon photodiode using a standard silicon solar cell. The external quantum efficiency (EQE) spectra were determined from a commercial EQE measurement system (Taiwan, Enlitech, QE-R3011).

## Fabrication and Characterization of Single-Carrier Devices

Space-charge-limited current (SCLC) method was exploited to determine the charge carrier mobility of donoracceptor blend films from single-carrier device. The device structures are ITO/PEDOT:PSS/blend films/ $\mathrm{MoO}_{3} / \mathrm{Ag}$ for hole-only devices and ITO/ZnO/blend films/PFN-Br/Ag for electron-only devices, respectively. The J-V characteristics of each single-carrier device were recorded with a Keithley 2400 source meter in the dark under a nitrogen atmosphere. The mobility was determined by fitting the dark J-V current to the model of a single-carrier SCLC, according to the equation $J=9 \varepsilon_{0} \varepsilon_{r} \mu V^{2} / 8 d^{3}$, where $J$ is the current density, $d$ is the thickness of the blend films, $\varepsilon_{0}$ and $\varepsilon_{\mathrm{r}}$ represent the permittivity of free space and relative permittivity of the material, respectively, $\mu$ is the zero-field mobility, and $V$ is the effective voltage. $V=V_{a p p l}-V_{b i}-V_{s}$, where $V_{a p p l}, V_{b i}$, and $V_{s}$ denoted as the applied voltage, built-in voltage, and the voltage drop from the series resistance, respectively.

Table S1. Summary of the device performance parameters of P3HT: acceptor blend films with PCE $\geq 6.0 \%$.

| Donor | Acceptor | $V_{\text {oc }}(\mathrm{V})$ | $J_{\text {sc }}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P3HT | $1 \mathrm{C}_{60} \mathrm{BA}$ | 0.84 | 10.6 | 0.73 | 6.5 | (1) |
|  | $1 \mathrm{C}_{70} \mathrm{BA}$ | 0.87 | 11.4 | 0.75 | 7.4 | (2) |
|  | trans-3 | 0.88 | 10.2 | 0.71 | 6.3 | (3) |
|  | $1 \mathrm{C}_{60} \mathrm{BA}$ | 0.85 | 10.3 | 0.75 | 6.6 | (4) |
|  | O-IDTBR | 0.72 | 13.9 | 0.60 | 6.3 | (5) |
|  | EH-IDTBR | 0.76 | 12.1 | 0.62 | 6.0 | (5) |
|  | SF(DPPB) ${ }_{4}$ | 1.11 | 10.2 | 0.54 | 6.1 | (6) |
|  | $1 \mathrm{C}_{70} \mathrm{BA}$ | 0.85 | 10.0 | 0.70 | 6.7 | (7) |
|  | BT2b | 0.92 | 10.0 | 0.66 | 6.1 | (8) |

Table S2. Chemical structures and device performance parameters of the representative polythiophene
derivatives

| Polymer | Acceptor | $V_{\text {oc }}(\mathrm{V})$ | $J_{\text {sc }}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) | Ref. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | [60]PCBM | 0.61 | 10.3 | 0.60 | 3.7 | (9) |
|  | [60]PCBM | 0.72 | 10.3 | 0.43 | 3.2 | (10) |
| $+\sqrt{\left(\pi_{s}\right.} \psi_{n}^{c_{12} H_{25}}$ | [60]PCBM | 0.68 | 5.8 | 0.47 | 1.8 | (11) |
|  | [70]PCBM | 0.60 | 8.4 | 0.59 | 3.0 | (12) |
|  | [60]PCBM | 0.61 | 11.3 | 0.60 | 4.1 | (13) |
|  | [60]PCBM | 0.64 | 7.6 | 0.65 | 3.2 | (14) |
|  | [70]PCBM | 0.56 | 9.6 | 0.69 | 3.7 | (15) |
|  | [60]PCBM | 0.82 | 6.3 | 0.66 | 3.4 | (16) |
| Hexime | [60]PCBM | 0.60 | 10.9 | 0.69 | 4.5 | (17) |
|  | [70]PCBM | 0.59 | 8.1 | 0.63 | 3.0 | (18) |




Figure S1. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of 1 a in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 2} .{ }^{13} \mathrm{C}-\mathrm{NMR}$ spectrum of $\mathbf{1 a}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 3} \mathbf{}^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{1 b}$ in $\mathrm{CDCl}_{3}$.


Figure S4. ${ }^{13} \mathrm{C}$-NMR spectrum of $\mathbf{1 b}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 5}{ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{2 a}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 6} \cdot{ }^{13} \mathrm{C}$-NMR spectrum of $\mathbf{2 a}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 7}$. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectrum of $\mathbf{2 b}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 8} .{ }^{13} \mathrm{C}-\mathrm{NMR}$ spectrum of $\mathbf{2 b}$ in $\mathrm{CDCl}_{3}$.


Figure S9. Temperature-dependent UV-vis absorption spectra of (a) P4T2F-BO, (b) P4T2F-BO/HD, and (c) P4T2FHD.


Figure S10. The absorption coefficients of P4T2F-BO, P4T2F-BO/HD, P4T2F-HD in chlorobenzene solutions (a) and in thin films (b).


Figure S11. (a) Cyclic voltammograms of P4T2F-BO, P4T2F-BO/HD, P4T2F-HD, and P3HT, (b) energy levels of donor polymers and acceptor molecules used in this study.

Table S3. Device characteristics of the PSCs based on P4T2F-BO:[70]PCBM with different D:A ratio under AM1.5G illumination, $100 \mathrm{~mW} \mathrm{~cm}{ }^{-2}$.

| $\mathrm{D}: \mathrm{A}(\mathrm{w} / \mathrm{w})$ | $V_{\text {oc }}(\mathrm{V})$ | $J_{\mathrm{SC}}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) |
| :--- | :--- | :--- | :--- | :--- |
| $1: 1$ | 0.75 | 8.6 | 0.64 | 4.2 |
| $1: 1.5$ | 0.79 | 9.3 | 0.64 | 4.7 |
| $1: 2$ | 0.74 | 9.1 | 0.61 | 4.1 |

Table S4. Device characteristics of the PSCs based on P4T2F-BO:[70]PCBM with different thermal annealing temperature under AM1.5G illumination, $100 \mathrm{~mW} \mathrm{~cm}^{-2}$.

| Annealing $\left({ }^{\circ} \mathrm{C}\right)$ | $V_{\text {oc }}(\mathrm{V})$ | $J_{\mathrm{sC}}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) |
| :--- | :--- | :--- | :--- | :--- |
| 80 | 0.82 | 8.6 | 0.65 | 4.7 |
| 100 | 0.82 | 9.4 | 0.65 | 5.0 |
| 120 | 0.82 | 9.1 | 0.64 | 4.8 |

Table S5. Device characteristics of the PSCs based on P4T2F-BO:[70]PCBM with different types and contents of additives under AM1.5G illumination, $100 \mathrm{~mW} \mathrm{~cm}{ }^{-2}$.

| Additive $(\mathrm{v} / \mathrm{v})$ | $V_{\text {oc }}(\mathrm{V})$ | $J_{\mathrm{sC}}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) |
| :--- | :--- | :--- | :--- | :--- |
| $1 \% \mathrm{CN}$ | 0.77 | 9.9 | 0.66 | 5.0 |
| $2 \% \mathrm{CN}$ | 0.78 | 9.7 | 0.68 | 5.2 |
| $3 \% \mathrm{CN}$ | 0.78 | 10.0 | 0.68 | 5.3 |
| $3 \% \mathrm{CN}^{a}$ | 0.75 | 9.3 | 0.68 | 4.7 |
| $5 \% \mathrm{CN}$ | 0.76 | 10.0 | 0.67 | 5.1 |
| $3 \%$ DPE | 0.76 | 10.0 | 0.65 | 4.9 |
| $3 \%$ NMP | 0.75 | 9.6 | 0.65 | 4.7 |
| $3 \%$ DIO | 0.77 | 9.9 | 0.65 | 5.0 |

${ }^{a}$ 1, 2-Dichlorobenzene was used as the host solvent.

Table S6. Effects of spin-coating temperature on the performances of the devices of P4T2F-HD:[70]PCBM under AM1.5G illumination, $100 \mathrm{~mW} \mathrm{~cm}{ }^{-2}$.

| D:A | Temperature $\left({ }^{\circ} \mathrm{C}\right)$ | $V_{\text {oc }}(\mathrm{V})$ | $J_{\mathrm{SC}}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| RT | 0.82 | 6.9 | 0.74 | 4.2 |  |
| $1: 1.5$ | 00 | 0.79 | 6.5 | 0.71 | 3.7 |
|  | 00 | 0.77 | 5.0 | 0.68 | 2.6 |
|  | 100 | 0.79 | 3.8 | 0.68 | 2.0 |
|  | 120 | 0.83 | 4.2 | 0.66 | 2.3 |
|  | 140 | 0.84 |  |  | 2.3 |

Table S7. Device characteristics of the PSCs of P4T2F-HD:[70]PCBM spin-coated from different solvents under AM1.5G illumination, $100 \mathrm{~mW} \mathrm{~cm}{ }^{-2}$.

| D:A | Solvent | $V_{\text {oc }}(V)$ | $J_{\text {SC }}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | CB+2\%DPE | 0.80 | 8.5 | 0.72 | 4.9 |
| $1: 1.5$ | DCB+2\%DPE | 0.77 | 7.7 | 0.69 | 4.1 |
|  | CF+2\%DPE | 0.79 | 9.6 | 0.74 | 5.6 |

Table S8. The performance parameters of the solar cells based on P4T2F-HD:[70]PCBM with different layer thickness under AM 1.5 G illumination ( $100 \mathrm{~mW} \mathrm{~cm}^{-2}$ ).

| $\mathrm{D}: \mathrm{A}$ | Thickness $(\mathrm{nm})$ | $V_{\text {oc }}(\mathrm{V})$ | $J_{\mathrm{SC}}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | $\mathrm{PCE}_{\max }(\%)$ | $\mathrm{PCE}_{\text {ave }}(\%)^{a}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 0.81 | 10.2 | 0.74 | 6.0 | 5.9 |  |
| $1: 1.5$ | 240 | 0.80 | 10.1 | 0.74 | 6.0 | 5.7 |
|  | 270 | 0.78 | 9.8 | 0.72 | 5.5 | 5.4 |
|  | 300 | 0.78 | 10.0 | 0.72 | 5.6 | 5.5 |
|  | 320 | 0.78 | 11.5 | 0.66 | 5.9 | 5.8 |

${ }^{a}$ The average PCE values obtained from 12 devices.

Table S9. The photovoltaic parameters of the solar cells with or without thermal annealing treatment under AM 1.5 G illumination ( $100 \mathrm{~mW} \mathrm{~cm}^{-2}$ ).

| Donor | Acceptor | Thermal annealing | $V_{\text {oc }}(\mathrm{V})$ | $J_{\text {SC }}\left(\mathrm{mA} \mathrm{cm}^{-2}\right)$ | FF | PCE (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| P4T2F-BO | [70]PCBM | N | 0.79 | 9.6 | 0.67 | 5.1 |
|  |  | Y | 0.78 | 10.2 | 0.68 | 5.4 |
|  | O-IDTBR | N | 1.05 | 9.2 | 0.57 | 5.5 |
|  |  | $Y$ | 1.06 | 9.9 | 0.60 | 6.3 |
| P4T2F-BO/HD | [70]PCBM | N | 0.81 | 9.6 | 0.70 | 5.4 |
|  |  | Y | 0.80 | 10.4 | 0.74 | 6.1 |
|  | O-IDTBR | N | 1.03 | 10.1 | 0.58 | 6.0 |
|  |  | Y | 1.02 | 10.7 | 0.60 | 6.5 |
| P4T2F-HD | [70]PCBM | N | 0.81 | 9.9 | 0.72 | 5.8 |
|  |  | Y | 0.82 | 10.4 | 0.74 | 6.3 |
|  | O-IDTBR | N | 1.06 | 8.9 | 0.66 | 6.2 |
|  |  | Y | 1.04 | 10.0 | 0.67 | 7.0 |



Figure S12. Photoluminescence spectra of the pure donor films and corresponding blend films.


Figure S13. Current-voltage characteristics of (a) hole-only devices and (b) electron-only devices for fitting with a space-charge-limited-current (SCLC) model.


Figure S14. AFM height images of the blend films without thermal annealing treatments: (a) P4T2F-BO:[70]PCBM,
(b) P4T2F-BO/HD:[70]PCBM, (c) P4T2F-HD:[70]PCBM, (d) P4T2F-BO:O-IDTBR, (e) P4T2F-BO/HD:O-IDTBR, and (f) P4T2F-HD:O-IDTBR.


Figure S15. AFM phase images of the blend films: (a1, a2) P4T2F-BO:[70]PCBM, (a3, a4) P4T2F-BO:O-IDTBR, (b1,
b2) P4T2F-BO/HD:[70]PCBM, (b3,b4) P4T2F-BO/HD:O-IDTBR, (c1, c2) P4T2F-HD:[70]PCBM, (c3, c4) P4T2F-HD:OIDTBR.

## REFERENCES

(1) G. Zhao, Y. He and Y. Li, Adv. Mater., 2010, 22, 4355.
(2) X. Guo, C. Cui, M. Zhang, L. Huo, Y. Huang, J. Hou and Y. Li, Energy Environ. Sci., 2012, 5, 7943.
(3) X. Meng, G. Zhao, Q. Xu, Z. Tan, Z. Zhang, L. Jiang, C. Shu, C. Wang and Y. Li, Adv. Funct. Mater., 2014, 24, 158.
(4) X. Guo, M. Zhang, C. Cui, J. Hou and Y. Li, ACS Appl. Mater. Interfaces, 2014, 6, 8190.
(5) S. Holliday, R. Ashraf, A. Wadsworth, D. Baran, S. Yousaf, C. Nielsen, C. -H. Tan, S. Dimitrov, Z. Shang, N. Gasparini, M. Alamoudi, F. Laquai, C. Brabec, A. Salleo, J. Durrant and I. McCulloch, Nat. Commun., 2016, 7, 11585. (6) W. Liu, S. Li, J. Huang, S. Yang, J. Chen, L. Zuo, M. Shi, X. Zhan, C. -Z. Li and H. Chen, Adv. Mater., 2016, 28, 9729. (7) D. Kutsarov, I. Rašović, A. Zachariadis, A. Laskarakis, M. Lebedeva, K. Porfyrakis, C. Mills, M. Beliatis, B. Fisher, K. Bruchlos, S. Ludwigs, S. Logothetidis and S. Silva, Adv. Electron. Mater., 2016, 2, 1600362.
(8) B. Xiao, A. Tang, L. Cheng, J. Zhang, Z. Wei, Q. Zeng and E. Zhou, Sol. RRL, 2017, 1, 1700166.
(9) K. Sivula, C. Luscombe, B. Thompson and J. Fréchet, J. Am. Chem. Soc., 2006, 128, 13988.
(10) J. Hou, Z. Tan, Y. Yan, Y. He, C. Yang and Y. Li, J. Am. Chem. Soc., 2006, 128, 4911.
(11) B. Thompson, B. Kim, D. Kavulak, K. Sivula, C. Mauldin and J. Fréchet, Macromolecules, 2007, 40, 7425.
(12) H. Xin, F. Kim and S. Jenekhe, J. Am. Chem. Soc., 2008, 130, 5424.
(13) Y. -T. Chang, S. -L. Hsu, M. -H. Su and K. -H. Wei, Adv. Mater., 2009, 21, 2093.
(14) S. Miyanishi, K. Tajima and K. Hashimoto, Macromolecules, 2009, 42, 1610.
(15) P. -T. Wu, H. Xin, F. Kim, G. Ren and S. Jenekhe, Macromolecules, 2009, 42, 8817.
(16) J. Hou, T. Chen, S. Zhang, L. Huo, S. Sista and Y. Yang, Macromolecules, 2009, 42, 9217.
(17) J. Kim, Y. Lee, J. Lee, J. Park, J. Kim and K. Cho, Adv. Mater., 2010, 22, 1355.
(18) G. Ren, P. -T. Wu and S. Jenekhe, Chem. Mater., 2010, 22, 2020.
(19) M. Zhang, X. Guo, Y. Yang, J. Zhang, Z. -G. Zhang and Y. Li, Polym. Chem., 2011, 2, 2900.
(20) S. Ko, E. Hoke, L. Pandey, S. Hong, R. Mondal, C. Risko, Y. Yi, R. Noriega, M. McGehee, J. -L. Brédas, A. Salleo and Z. Bao, J. Am. Chem. Soc., 2012, 134, 5222.
(21) Z. -G. Zhang, S. Zhang, J. Min, C. Cui, H. Geng, Z. Shuai and Y. Li, Macromolecules, 2012, 45, 2312.
(22) C. Lu, H. Wu, Y. Chiu, W. Lee and W. Chen, Macromolecules, 2012, 45, 3047.
(23) C. -H. Cho, H. Kim, H. Kang, T. Shin and B. Kim, J. Mater. Chem., 2012, 22, 14236.
(24) C. Cui, Y. Sun, Z. -G. Zhang, M. Zhang, J. Zhang and Y. Li, Macromol. Chem. Phys., 2012, 213, 2267.
(25) J. Jo, J. Jung, H. -W. Wang, P. Kim, T. Russell and W. Jo, Chem. Mater., 2014, 26, 4214.
(26) M. Zhang, X. Guo, W. Ma, H. Ade and J. Hou, Adv. Mater., 2014, 26, 5880.
(27) Y. Qin, M. Uddin, Y. Chen, B. Jang, K. Zhao, Z. Zheng, R. Yu, T. Shin, H. Woo and J. Hou, Adv. Mater., 2016, 28, 9416.
(28) H. Zhang, S. Li, B. Xu, H. Yao, B. Yang and J. Hou, J. Mater. Chem. A, 2016, 4, 18043.

