Supporting Information for

Optimized molecular aggregation and photophysical process synergistically promoted photovoltaic performance in low regularity benzo[c][1,2,5]-thiadiazole-based medium bandgap copolymers via modulating π bridges

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### Table S1: Bandgap, energy level and device parameters of the reported representative benzothiadiazole-based conjugated polymers.

<table>
<thead>
<tr>
<th>Polymer donors</th>
<th>Acceptors</th>
<th>$E_{\text{gopt}}$ (eV)</th>
<th>$E_{\text{HOMO}}$/$E_{\text{LUMO}}$ (eV)</th>
<th>$V_{\text{OC}}$ (V)</th>
<th>$J_{\text{SC}}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFBDT-BZS</td>
<td>IDIC</td>
<td>1.85</td>
<td>$-5.43/-3.58$</td>
<td>0.905</td>
<td>17.30</td>
<td>70.80</td>
<td>11.03</td>
<td>[1]</td>
</tr>
<tr>
<td>PBDTSF-FBT</td>
<td>ITIC</td>
<td>1.82</td>
<td>$-5.41/-3.59$</td>
<td>1.03</td>
<td>17.09</td>
<td>66.30</td>
<td>11.66</td>
<td>[2]</td>
</tr>
<tr>
<td>PBT-Cl</td>
<td>IT-4F</td>
<td>1.91</td>
<td>$-5.51/-3.60$</td>
<td>0.782</td>
<td>21.03</td>
<td>70.00</td>
<td>11.60</td>
<td>[3]</td>
</tr>
<tr>
<td>PBDT-AFBT</td>
<td>IDTCN-O</td>
<td>1.79</td>
<td>$-5.35/-3.56$</td>
<td>0.864</td>
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<td>66.35</td>
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<tr>
<td>PfBT4T-C$<em>{6}$C$</em>{13}$</td>
<td>PC$_{7}$BM</td>
<td>1.65</td>
<td>$-5.34/-3.69$</td>
<td>0.788</td>
<td>20.20</td>
<td>74.00</td>
<td>11.70</td>
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<tr>
<td>PfBT4T-2OD</td>
<td>ZITI-N-EH</td>
<td>1.79</td>
<td>$-5.30/-3.51$</td>
<td>0.805</td>
<td>22.13</td>
<td>73.35</td>
<td>13.07</td>
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<td>Phl-ffBT</td>
<td>IT-4F</td>
<td>1.75</td>
<td>$-5.55/-3.80$</td>
<td>0.91</td>
<td>19.41</td>
<td>76.00</td>
<td>13.31</td>
<td>[7]</td>
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<td>2TRA</td>
<td>IEICO-4F</td>
<td>1.62</td>
<td>$-5.27/-3.65$</td>
<td>0.73</td>
<td>23.74</td>
<td>70.04</td>
<td>12.10</td>
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<tr>
<td>PfBT-T3(1,2)-2</td>
<td>PC$_{7}$BM</td>
<td>1.63</td>
<td>$-5.31/-3.68$</td>
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<td>P3TEA</td>
<td>FTTB-PDI4</td>
<td>1.90</td>
<td>$-5.46/-3.56$</td>
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<td>14.05</td>
<td>66.40</td>
<td>10.58</td>
<td>[10]</td>
</tr>
</tbody>
</table>

### 1. Experimental section

#### 1.1. Materials and synthesis

All the available chemicals and solvents, unless otherwise specified, were purchased from Sigma-Aldrich Co., J&K, and Energy Chemical used without further purification. Electron acceptor material (2,2’-((2Z,2’Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro[1,2,5]thiadiazolo[3,4-e]thieno[2,’3’:4,5]pyrrolo[3,2-g]thieno[2’,3’:4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile) (Y6) and electron transfer material 3,3’-(1,3,8,10-tetraoxoanthra[2,1,9-def]:6,5,10-d’e’eff)diisoquinoline-2,9-(1H,3H,8H,10H)diyl)-bis(N,N-dimethylpropan-1-amine oxide) (PDINO) and 4,7-dibromobenzo[c][1,2,5]thiadiazole (BTBr$_2$) were purchased from Derthon Optoelectronic Materials Science Technology Co. LTD and SunaTech Inc., respectively. Chlorinated bistin 2,6-bis(trimethylstannanone)-4,8-bis(4-chloro-5-(2-butyloctyl)thien-2-yl)benzo-[1,2-b:4,5-b’]dithiophene (ClBDTSn) was synthesized on the basis of reference. Dibromide 4-bromo-7-(5-bromo-4-octylthien-2-yl)benzo[c][1,2,5]thiadiazole (TBTBr$_2$) and 4,7-di(5-bromo-4-octylthien-2-yl)benzo[c][1,2,5]thiadiazole (DTBTBr$_2$) were synthesized according to our reported method, and structures for all the monomers were confirmed and characterized by $^1$H NMR. The synthetic procedure for the medium band gap copolymers PCIBDT-BT, PCIBDT-TBT and PCIBDT-DTBT were as follows.
Scheme S1 Synthetic route for copolymers PCIBDT-BT, PCIBDT-TBT and PCIBDT-DTBT.

1.1.1 2,6-Bis(trimethylstannane)-4,8-bis(4-chloro-5-(2-butyloctyl)thien-2-yl)benzo[1,2-b: 4,5-b']dithiophene (ClBDTSn)\(^\text{11}\)

M.p.: 122–125 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)), \(\delta\) (ppm): 7.62 (t, \(J = 14.5\) Hz, 2H), 7.24 (s, 2H), 2.85 (d, \(J = 5.5\) Hz, 4H), 1.80 (m, 2H), 1.40–1.30 (m, 32H), 0.90 (t, \(J = 7.0\) Hz, 12H), 0.42 (t, \(J = 26\) Hz, 18H). \(^1\)C NMR (500 MHz, CDCl\(_3\), 125 Hz): 143.36, 143.23, 137.95, 137.30, 136.64, 130.57, 127.75, 122.53, 121.55, 39.38, 33.12, 31.90, 29.69, 28.84, 26.61, 23.05, 22.69, 14.17, 14.14. Alal. Calcd for C\(_{48}\)H\(_{72}\)Cl\(_2\)S\(_2\)Sn\(_2\): C, 53.10%; H, 6.68%; Found: C, 54.00%; H, 6.51%.

1.1.2 4,7-Dibromobenzo[c][1,2,5]thiadiazole (BTBr\(_2\))

M.p.: 164–167 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.73 (s, 2H). Alal. Calcd for C\(_6\)H\(_2\)Br\(_2\)N\(_2\)S: C, 24.51%, H, 0.69%, N, 9.53%; Found: C, 24.40%; H, 0.58%; N, 9.61%.

1.1.3 4-Bromo-7-(5-bromo-4-octylthien-2-yl)benzo[c][1,2,5]thiadiazole (TBTBr\(_2\))\(^\text{12}\)

M.p.: 73–74 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)), \(\delta\) (ppm): 7.83 (d, \(J = 7.6\) Hz, 1H), 7.75 (s, 1H), 7.62 (d, \(J = 7.6\) Hz, 1H), 2.63 (t, \(J = 7.6\) Hz, 2H), 1.67 (m, 2H), 1.40–1.25 (m, 10H), 0.88 (t, \(J = 6.4\) Hz, 3H). Alal. Calcd for C\(_{18}\)H\(_{20}\)Br\(_2\)N\(_2\)S\(_2\): C, 44.27%; H, 4.13%; N, 5.74%. Found C, 44.24%; H, 4.01%; N, 5.84%.

1.1.4 4,7-Di(5-bromo-4-octylthien-2-yl)benzo[c][1,2,5]thiadiazole (DTBTBr\(_2\))\(^\text{12}\)
Syntheses of copolymers PClBDT-BT, PClBDT-TBT and PClBDT-DTBT

1.2.1 Poly[(4,8-bis(4-chloro-5-(2-butyloctyl)thien-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) -alt-(benzo[c][1,2,5]thiadiazole-4,7-diyl)] (PClBDT-BT)^13

Into a 25 mL two-neck round-bottom flask, carefully purified chlorinated bistin ClBDTSn (110.06 mg, 0.101 mmol), dibromide BTBr₂ (29.80 mg, 0.101 mmol), and 6 mL degassed toluene and 0.7 mL DMF was added, and the mixture was bubbled with Ar for another 20 min to remove O₂. And Pd₂(dba)₃ (1.0 mg), P(o-tolyl)₃ (2.0 mg) were added in one portion and the solution was bubbled with Ar for another 20 min. The mixture was vigorously stirred at 105 °C under Ar for 48 h. At the end of polymerization, the polymer was end-capped with 2-tributylstannylthiophene and 2-bromothiophene to remove bromo and trimethylstannyl end groups. Then, the mixture was poured into 300 mL methanol, and the polymer was precipitated and then collected by filtration. The crude polymer was purified by Soxhlet extraction with ethanol, acetone, hexane and toluene, respectively. The toluene fraction was condensed to approximately 6 mL and precipitated into methanol (300 mL). And the polymer PClBDT-BT was collected and dried under vacuum overnight as black solid (57.3 mg, yield: 63.3%). \( M_n = 19.0 \text{ kDa}, \text{polydisperse index (PDI} = M_w/M_n): 1.7. \) \(^1\)H NMR (400 MHz, o-DCB-d₄), \( \delta \) (ppm), 7.90−7.30 (m, ArH), 3.30–2.70 (br, CH₂), 2.15−1.25 (m, CH, CH₂), 1.10−0.75 (m, CH₃). Anal. Calcd for C₄₈H₅₆Cl₂N₂S₅: C, 65.11%; H, 6.78%; N, 3.04%. Found, C, 65.01%; H, 6.61%; N, 3.22%.

1.2.2 Poly[(4,8-bis(4-chloro-5-(2-butyloctyl)thien-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)-co-(7-(4-octylthien-2-yl)benzo[c][1,2,5]thiadiazole-4,5'-diyl)] (PClBDT-TBT)

A procedure similar to that of PClBDT-BT was used with bistin ClBDTSn (109.6 mg, 0.101 mmol), TBTBr₂ (49.3 mg, 0.101 mmol). The title polymer was collected as black solid. (90.4 mg, yield: 83.0%). \( M_n = 22.3 \text{ kDa}, \text{PDI} = 1.8. \) \(^1\)H NMR (400 MHz, o-DCB-d₄), \( \delta \) (ppm), 8.00−7.30 (m, ArH), 3.30–2.70 (br, CH₂), 2.10−1.25 (m, CH, CH₂), 1.10–0.75 (m, CH₃). Anal. Calcd for C₆₀H₇₄Cl₂N₂S₆: C, 66.32%; H, 6.86%; N, 2.58%. Found, C, 66.21%; H, 6.69%; N, 2.70%.

1.2.3 Poly[(4,8-bis(4-chloro-5-(2-butyloctyl)thien-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-4,7-di(3-octylthien-2-yl)benzo[c][1,2,5]thiadiazole-5,5'-diyl)] (PClBDT-DTBT)

A procedure similar to that of PClBDT-TBT was used with ClBDTSn (107.2 mg, 0.099
The polymer was collected as black solid. (128 mg, yield: 76.1%). $M_n = 21.6$ kDa, PDI = 1.8. $^1$H NMR (400 MHz, o-DCB-d$_4$), $\delta$ (ppm), 8.16 (br, ArH, 2H), 7.91 (br, ArH, 2H), 7.76 (br, ArH, 2H), 7.48 (br, ArH, 2H), 3.02 (br, CH$_2$ of ClBDT, 4H), 2.93 (br, CH$_2$ of octylthienyl, 4H), 2.00–1.80 (m, CH, CH$_2$, 6H), 1.50–1.25 (m, CH$_2$, 58H), 0.95–0.85 (m, CH$_3$, 18H). Anal. Calcd for C$_{72}$H$_{92}$Cl$_2$N$_2$S$_7$: C, 67.51%; H, 7.24%; N, 2.19%. Found, C, 67.36%; H, 7.13%; N, 2.29%.

1.3 Measurement and characterization

$^1$H NMR spectra was measured on a Bruker 500 MHz AVANCE NEO (Rheinstetten, Germany) spectrometer, with tetramethylsilane (TMS) as the internal reference. Chemical shifts ($\delta$) were recorded in units of ppm and their splitting patterns were designed as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broaden). Note that o-dichlorobenzene-d4 (o-DCB-d4) residual peak was taken as internal reference at 7.20 ppm for $^1$H NMR. Melting points were obtained on a microscopic melting point apparat (Beijing Taike), and the temperature gauge was uncorrected. C, H and N elemental analyses (EAs) were carried out on a Vario EL Elemental Analysis Instrument (Elementar Co.). TGA curves were collected on a TGA 2050 instruments (New Castle, DE, USA) at the heating rate of 10 °C·min$^{-1}$ and under a N$_2$ flow rate (20 mL·min$^{-1}$). UV-Vis absorption measurement was performed on a UV-1800 spectrophotometer (Shimadzu, Kyoto, Japan). Thin film X-ray diffraction (XRD) was recorded on a PANalytical X'Pert PRO diffractometer equipped with a rotating anode (Cu K$_\alpha$ radiation, $\lambda$ = 1.54056 Å). The electrochemical properties of films were measured on a CHI600D electro-chemical instrument (Chenhua, Shanghai, China) in anhydrous CH$_3$CN at a scan rate of 100 mV·s$^{-1}$ under N$_2$. Tetra(n-butyl)ammonium hexafluorophosphate (Bu$_4$NPF$_6$) (0.1 mol·L$^{-1}$) was utilized as the electrolyte. A three-electrode cell was used in all experimental, wherein glassy carbon electrode coated by polymer film, platinum wire and Ag/AgNO$_3$ (0.01 M of AgNO$_3$ in CH$_3$CN) electrode were used as the working, counter and reference electrode, respectively. The potential of Ag/AgNO$_3$ reference electrode was calibrated by the ferrocene/ferrocenium couple (Fc/Fc$^+$), whose energy level was –4.80 eV. Note that small molecule thin films were obtained by dropcasting 1 µL studied material chlorobenzene solution with the concentration of 1 mg·mL$^{-1}$ onto the glass carbon electrode, and then dried in the air. Atomic force microscopy (AFM) images were acquired on an MFP-3D-SA (Asylum Research, Santa Barbara, CA, USA) in a tapping mode. Transmission electron microscopy (TEM) images were were obtained on a Tecnai G$^2$ F20 at accelerating voltage of 200 kV.
1.4 Fabrication of PSCs and mobility characterization

Indium tin oxide (ITO) coated glass substrates were washed by a wet-cleaning process inside an ultrasonic bath, with de-ionized water, acetone, de-ionized water and isopropanol in turn. After drying under nitrogen flow, the substrates were treated with oxygen plasma for 10 min, then a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS, ca. 40 nm, Clevios PVP Al4083) was spin-coated onto the ITO substrates and annealed at 150 ºC for 20 min. After that the substrates were transferred into a nitrogen-filled glove box and the active layer was prepared. The active layer, with a thickness in the 100–120 nm range, was deposited on top of the PEDOT:PSS layer by spin-casting from chloroform solution containing the studied materials. The thickness of the active layer was verified by a surface profilometer (DektakXT, Bruker). Then, an ultrathin layer of PDINO (1 mg·mL⁻¹ in methanol) was spin-coated on the active layer. Finally, the Al layer (~55 nm) as the cathode was thermally evaporated under a vacuum pressure of 10⁻⁴ Pa. Moreover, the all effective device area in this work was 0.1 cm², which was ascertained by a shadow mask. The thickness values of the evaporated Al was monitored by a quartz crystal thickness/ratio monitor (SI-TM206, Shenyang Sciens Co.). The PCEs of the resulting PSCs were measured under 1 sun, AM 1.5 G (Air mass 1.5 global) condition using a solar simulator (XES-70S1, San-EI Electric Co.) with irradiation of 100 mW·cm⁻². The current density-voltage (\(J-V\)) characteristics were recorded with a Keithley 2400 source-measurement unit. The spectral responses of the devices were measured with a commercial external quantum efficiency (EQE)/incident photon to charge carrier efficiency (IPCE) setup (7-SCSpecIII, Beijing 7-star Opt. In. Co.) equipped with a standard Si diode.

The hole-only and electron-only devices were prepared with a diode configuration of ITO/PEDOT:PSS/active layer/MoO₃/Ag or ITO/ZnO/active layer/PDINO/Ag, respectively. The device characteristics were extracted by modeling the dark current under an applied forward bias. The hole and electron mobilities of the active layers were extracted by fitting the current-voltage curves using the Mott-Gurney relationships\(^{14}\) (space-charge-limited current, SCLC). The field dependent SCLC behavior can be expressed as:

\[
J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}.
\]

Where \(J\) stands for the current density, \(\varepsilon_0\) is the permittivity of free space \((8.85 \times 10^{-12} \text{ F·m}^{-1})\), \(\varepsilon_r\) is the relative permittivity of the transport medium (assumed to be 3, which is a typical value for CPs), \(\mu\) is the zero-field mobility of hole or electron, \(L\) is the thickness of the active layer, and effective voltage \(V = (V_{\text{appl}} - V_{\text{bi}})\), where \(V_{\text{appl}}\) is the applied voltage to the device and \(V_{\text{bi}}\) is the built-in voltage. By linearly fitting \(J^{1/2}\)
with $V$, the mobilities were extracted from the slope and $L$: 
$$
\mu = \frac{slope^2 \times 8L^3}{9\varepsilon_0\varepsilon_r}
$$
For the hole-only devices, $V_{bi}$ is 0 V, while $V_{bi} = 0.7$ V in the electron-only devices.

### 1.5 Surface energy calculation

The surface tension ($\gamma$) can be evaluated using the Wu model, via Equations (1), (2), and (3), on the basis of the measured contact angles ($\theta$) information.

\[
\gamma_{water}(1 + \cos\theta_{water}) = \frac{4\gamma_{water}\gamma^d}{\gamma_{water} + \gamma^d} + \frac{4\gamma_{water}\gamma^p}{\gamma_{water} + \gamma^p} \tag{1}
\]

\[
\gamma_{EG}(1 + \cos\theta_{EG}) = \frac{4\gamma_{EG}\gamma^d}{\gamma_{EG} + \gamma^d} + \frac{4\gamma_{EG}\gamma^p}{\gamma_{EG} + \gamma^p} \tag{2}
\]

\[
\gamma = \gamma^d + \gamma^p \tag{3}
\]

Where, $\gamma$ is the surface energy of the studied semiconductor; $\gamma^d$ and $\gamma^p$ are the dispersion and polar components of $\gamma$; $\gamma^i$ is the total surface energy of the $i$ material ($i = \text{water or ethylene glycol}$); $\gamma^d$ and $\gamma^p$ are the dispersion and polar components of $\gamma^i$; and $\theta$ is the droplet contact angle (water or ethylene glycol) on the semiconductor film. Flory–Huggins interaction parameter $\chi_{\text{donor-acceptor}}$, which is a parameter to evaluate the interaction between polymer donor and polymer acceptor, based on this, the miscibility of the two components can be objectively judged. The smaller the difference of surface energy between donor and acceptor, the lower the value of $\chi_{\text{donor-acceptor}}$ and the better the miscibility.

### 1.6 Femtosecond time-resolved Transient Absorption (fs-TA) Measurements

Fs-TA spectroscopy was performed to measure the temporal evolution of the absorption changes in the excited states, through which the carrier dynamics in femtosecond to nanosecond regime could be revealed. The laser beam is supplied by amplified Ti: sapphire laser source (800 nm, Coherent) that provides 100 fs pulses with a repetition rate of 1 kHz. The output was split into two beams, the stronger one of which was frequency doubled to generate a 400 nm pump light, and the other one was focused into a sapphire plate to generate a broadband supercontinuum probe light. Using an optical chopper, the repetition rate of the pump pulses was adjusted to 500 Hz, and were focused on the sample with the probe pulse (white light). The TA spectra were obtained by comparing the probe light spectra with and without pump light excitation. The photo-induced absorption change as a function of wavelength was described using optical density (absorbance) changes ($\Delta OD(\lambda)$). By adjusting the delay time between the pump and probe pulses, a 3D transient
spectral image $\Delta \text{OD}(\lambda, t)$ was formed.
2 Supplementary figures and tables

Fig. S1 $^1$H NMR spectrum of CIBDTSn in CDCl$_3$.

Fig. S2 $^{13}$C NMR spectrum of CIBDTSn in CDCl$_3$.
Fig. S3 $^1$H NMR spectrum of BTBr$_2$ in CDCl$_3$.

Fig. S4 $^1$H NMR spectrum of TBTBr$_2$ in CDCl$_3$. 
Fig. S5 $^1$H NMR spectrum of DTBTBr$_2$ in CDCl$_3$.

Fig. S6 $^1$H NMR spectrum of PCIBDT-BT o-DCB-d4 at 85 °C.
Fig. S7 $^1$H NMR spectrum of PClBDT-TBT in $o$-DCB-d$_4$ at 85 °C.

Fig. S8 $^1$H NMR spectrum of PClBDT-DTBT $o$-DCB-d$_4$ at 85 °C.
Table S2 Yield, molecular weight, TGA and absorption coefficients for the studied copolymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_n$ (kDa)</th>
<th>$M_w$ (kDa)</th>
<th>PDI</th>
<th>$T_D$ (°C)</th>
<th>$\varepsilon_{\text{soln}}$ ($M^{-1} \text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PClBDT-BT</td>
<td>63.3</td>
<td>19.0</td>
<td>32.3</td>
<td>1.7</td>
<td>416</td>
<td>$3.27 \times 10^4$ (λ = 639 nm)</td>
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<tr>
<td>PClBDT-TBT</td>
<td>83.0</td>
<td>22.3</td>
<td>40.1</td>
<td>1.8</td>
<td>371</td>
<td>$3.24 \times 10^4$ (λ = 639 nm)</td>
</tr>
<tr>
<td>PClBDT-DTBT</td>
<td>76.1</td>
<td>21.6</td>
<td>38.9</td>
<td>1.8</td>
<td>386</td>
<td>$3.58 \times 10^4$ (λ = 608 nm)</td>
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</tbody>
</table>

Fig. S9 TGA curves for copolymers PClBDT-BT, PClBDT-TBT and PClBDT-DTBT.

Fig. S10 UV-vis absorption spectra for PClBDT-BT, PClBDT-TBT and PClBDT-DTBT dissolved in solution at varied concentrations and calculation of molar absorption coefficient.
Fig. S11 CV curves for polymer donors (a) and Y6 under the similar testing condition.
### Table S3: Dihedral angles of model molecules (ClBDT-BT)$_3$, (ClBDT-TBT-1)$_3$, (ClBDT-TBT-2)$_3$ and (ClBDT-TBT-3)$_3$, (ClBDT-TBT-4)$_3$ and (ClBDT-DTBT)$_3$ through DFT calculation.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Structure</th>
<th>Dihedral angle (deg)</th>
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</thead>
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<td>(ClBDT-BT)$_3$</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>$\theta_1 = -11.48$, $\theta_2 = 7.70$.</td>
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<td>(ClBDT-TBT-1)$_3$</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>$\theta_1 = 5.48$, $\theta_2 = 8.79$, $\theta_3 = -12.44$.</td>
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<td>(ClBDT-TBT-2)$_3$</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>$\theta_1 = -3.81$, $\theta_2 = -1.74$, $\theta_3 = 8.88$.</td>
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<tr>
<td>(ClBDT-TBT-3)$_3$</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>$\theta_1 = -1.17$, $\theta_2 = 0.65$, $\theta_3 = 11.23$.</td>
</tr>
<tr>
<td>(ClBDT-TBT-4)$_3$</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>$\theta_1 = -11.89$, $\theta_2 = 2.52$, $\theta_3 = -3.83$.</td>
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<tr>
<td>(ClBDT-DTBT)$_3$</td>
<td><img src="image6.png" alt="Structure" /></td>
<td>$\theta_1 = 3.13$, $\theta_2 = 3.13$, $\theta_3 = -12.97$, $\theta_4 = -7.18$.</td>
</tr>
</tbody>
</table>
Table S4 Molecular surface area, MPI, extreme ESP value and total average ESP for (CIBDT-BT)$_3$, (CIBDT-TBT-1)$_3$, (CIBDT-TBT-2)$_3$, (CIBDT-TBT-3)$_3$, (CIBDT-TBT-4)$_3$, (CIBDT-DTBT)$_3$ and Y6.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Overall surface area ($\text{Å}^2$)</th>
<th>MPI (kcal·mol$^{-1}$)</th>
<th>Minimal/maximal values (kcal·mol$^{-1}$)</th>
<th>Overall average value (kcal·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CIBDT-BT)$_3$</td>
<td>1444.64</td>
<td>7.13</td>
<td>$-26.12/22.66$</td>
<td>0.26</td>
</tr>
<tr>
<td>(CIBDT-TBT-1)$_3$</td>
<td>1703.39</td>
<td>7.16</td>
<td>$-26.28/25.35$</td>
<td>-0.25</td>
</tr>
<tr>
<td>(CIBDT-TBT-2)$_3$</td>
<td>1705.22</td>
<td>7.19</td>
<td>$-22.67/24.97$</td>
<td>-0.25</td>
</tr>
<tr>
<td>(CIBDT-TBT-3)$_3$</td>
<td>1977.97</td>
<td>6.37</td>
<td>$-26.26/24.92$</td>
<td>0.02</td>
</tr>
<tr>
<td>(CIBDT-TBT-4)$_3$</td>
<td>1997.19</td>
<td>6.40</td>
<td>$-22.19/24.63$</td>
<td>0.16</td>
</tr>
<tr>
<td>(CIBDT-DTBT)$_3$</td>
<td>1967.87</td>
<td>6.99</td>
<td>$-21.24/24.57$</td>
<td>-0.13</td>
</tr>
<tr>
<td>Y6</td>
<td>811.49</td>
<td>11.96</td>
<td>$-33.14/41.44$</td>
<td>5.49</td>
</tr>
</tbody>
</table>

Fig. S12 ESP area distribution for model molecules of donor polymers and acceptor Y6.

Fig. S13 ESP distribution for Y6.
Table S5 Calculated dipole moments for model molecules (CIBDT-BT)$_3$, (CIBDT-TBT-1)$_3$, (CIBDT-TBT-2)$_3$, (CIBDT-TBT-3)$_3$, (CIBDT-TBT-4)$_3$ and (CIBDT-DTBT)$_3$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>State</th>
<th>X(D)</th>
<th>Y(D)</th>
<th>Z(D)</th>
<th>$\Delta\mu_{g-e}$ (Deby)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CIBDT-BT)$_3$</td>
<td>$S_0$</td>
<td>0.2768</td>
<td>0.8646</td>
<td>0.1879</td>
<td>7.2371</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>-6.95548</td>
<td>1.0015</td>
<td>-0.0403</td>
<td></td>
</tr>
<tr>
<td>(CIBDT-TBT-1)$_3$</td>
<td>$S_0$</td>
<td>-1.4355</td>
<td>-0.7823</td>
<td>0.3626</td>
<td>9.3952</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>7.9158</td>
<td>0.0630</td>
<td>0.0320</td>
<td></td>
</tr>
<tr>
<td>(CIBDT-TBT-2)$_3$</td>
<td>$S_0$</td>
<td>-0.6683</td>
<td>-0.6106</td>
<td>0.5430</td>
<td>8.7782</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>8.0761</td>
<td>-0.0092</td>
<td>0.0640</td>
<td></td>
</tr>
<tr>
<td>(CIBDT-TBT-3)$_3$</td>
<td>$S_0$</td>
<td>-2.8396</td>
<td>-2.5498</td>
<td>2.8608</td>
<td>7.8432</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>-7.8401</td>
<td>0.2210</td>
<td>0.0103</td>
<td></td>
</tr>
<tr>
<td>(CIBDT-TBT-4)$_3$</td>
<td>$S_0$</td>
<td>-2.0084</td>
<td>-1.1782</td>
<td>0.6030</td>
<td>8.0629</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>8.0517</td>
<td>0.4167</td>
<td>0.4279</td>
<td></td>
</tr>
<tr>
<td>(CIBDT-DTBT)$_3$</td>
<td>$S_0$</td>
<td>1.0826</td>
<td>0.6803</td>
<td>0.5402</td>
<td>8.1802</td>
</tr>
<tr>
<td></td>
<td>$S_1$</td>
<td>9.2380</td>
<td>0.2857</td>
<td>0.0395</td>
<td></td>
</tr>
</tbody>
</table>

$^a\Delta\mu_{g-e} = [(\mu_{gx} - \mu_{ex})^2 + (\mu_{gy} - \mu_{ey})^2 + (\mu_{gz} - \mu_{ez})^2]^{1/2}$.

Fig. S14 $J$-$V$ curves for the copolymers under different weight ratio.

Fig. S15 $J$-$V$ curves for the copolymers under different condition of additive and thermal annealing.
Table S6 Photovoltaic performance of devices with different blend ratio, additive or thermal annealing (TA).

<table>
<thead>
<tr>
<th>Active layer</th>
<th>condition</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE$^a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PClBDT-BT:Y6</td>
<td>1:1</td>
<td>0.89±0.01</td>
<td>8.61±0.13</td>
<td>53.22±0.51</td>
<td>4.05±0.13</td>
</tr>
<tr>
<td>PCIBDT-BT:Y6</td>
<td>1:1.2</td>
<td>0.88±0.01</td>
<td>9.23±0.15</td>
<td>52.62±0.53</td>
<td>4.26±0.15</td>
</tr>
<tr>
<td>PCIBDT-BT:Y6</td>
<td>1:1.5</td>
<td>0.89±0.01</td>
<td>10.32±0.22</td>
<td>44.33±0.48</td>
<td>4.05±0.12</td>
</tr>
<tr>
<td>PCIBDT-BT:Y6</td>
<td>1:1.2+TA$^b$</td>
<td>0.87±0.02</td>
<td>10.67±0.23</td>
<td>52.33±0.52</td>
<td>4.86±0.11</td>
</tr>
<tr>
<td>PCIBDT-BT:Y6</td>
<td>1:1.2+TA$^b$+3%DIO</td>
<td>0.82±0.01</td>
<td>9.44±0.25</td>
<td>50.02±0.50</td>
<td>3.87±0.10</td>
</tr>
<tr>
<td>PCIBDT-BT:Y6</td>
<td>1:1.2+TA$^b$+0.5%CN</td>
<td>0.84±0.01</td>
<td>12.04±0.26</td>
<td>52.88±0.63</td>
<td>5.54±0.13</td>
</tr>
<tr>
<td>PClBDT-TBT:Y6</td>
<td>1:1</td>
<td>0.82±0.01</td>
<td>19.52±0.28</td>
<td>51.71±0.52</td>
<td>8.26±0.26</td>
</tr>
<tr>
<td>PCIBDT-TBT:Y6</td>
<td>1:1.2</td>
<td>0.83±0.01</td>
<td>18.61±0.26</td>
<td>67.54±0.56</td>
<td>10.42±0.28</td>
</tr>
<tr>
<td>PCIBDT-TBT:Y6</td>
<td>1:1.5</td>
<td>0.82±0.01</td>
<td>21.65±0.29</td>
<td>50.78±0.48</td>
<td>8.99±0.26</td>
</tr>
<tr>
<td>PCIBDT-TBT:Y6</td>
<td>1:1.2+TA$^c$</td>
<td>0.81±0.01</td>
<td>23.72±0.16</td>
<td>67.63±0.54</td>
<td>13.04±0.31</td>
</tr>
<tr>
<td>PCIBDT-TBT:Y6</td>
<td>1:1.2+TA$^c$+3%DIO</td>
<td>0.76±0.02</td>
<td>20.11±0.46</td>
<td>67.07±0.58</td>
<td>10.22±0.25</td>
</tr>
<tr>
<td>PCIBDT-TBT:Y6</td>
<td>1:1.2+TA$^c$+0.5%CN</td>
<td>0.82±0.01</td>
<td>18.68±0.42</td>
<td>66.83±0.53</td>
<td>10.19±0.19</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1:1</td>
<td>0.75±0.01</td>
<td>20.90±0.27</td>
<td>62.11±0.49</td>
<td>9.79±0.16</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1:1.2</td>
<td>0.75±0.01</td>
<td>22.97±0.29</td>
<td>59.72±0.46</td>
<td>10.29±0.20</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1:1.5</td>
<td>0.75±0.01</td>
<td>20.59±0.28</td>
<td>56.51±0.52</td>
<td>8.72±0.17</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1:1.2+TA$^d$</td>
<td>0.74±0.01</td>
<td>23.88±0.31</td>
<td>62.94±0.75</td>
<td>11.12±0.24</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1:1.2+TA$^d$+3%DIO</td>
<td>0.67±0.01</td>
<td>18.10±0.33</td>
<td>66.80±0.71</td>
<td>8.10±0.23</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1:1.2+TA$^d$+0.5%CN</td>
<td>0.75±0.02</td>
<td>20.38±0.27</td>
<td>71.05±0.54</td>
<td>10.89±0.21</td>
</tr>
</tbody>
</table>

$^a$Average values of 10 devices. $^b$TA at 100 °C for 10 min. $^c$TA at 120 °C for 10 min. $^d$TA at 110 °C for 10 min.

Fig. S16 $J$-$V$ curves of hole-only (a) and electron-only (b) devices under the best fabrication condition.

Table S7 Hole and electron mobilities of the optimized devices measured by SCLC model.

<table>
<thead>
<tr>
<th>Active layer</th>
<th>Ratios/Additive</th>
<th>Thickness (nm)</th>
<th>$k_h/k_e$</th>
<th>$\mu_h/\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCIBDT-BT:Y6</td>
<td>1:1.2/TA+0.5%C</td>
<td>100</td>
<td>17.01/20.96</td>
<td>1.53×10$^{-4}$/8.63×10$^{-5}$</td>
</tr>
<tr>
<td>PCIBDT-TBT:Y6</td>
<td>1:1.2/TA</td>
<td>120</td>
<td>29.00/28.38</td>
<td>3.90×10$^{-4}$/3.74×10$^{-4}$</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1:1.2/TA</td>
<td>105</td>
<td>28.50/24.60</td>
<td>3.76×10$^{-4}$/2.81×10$^{-4}$</td>
</tr>
</tbody>
</table>
Table S8: Surface tensions (γ) and interaction parameters (χ) for the studied copolymers and Y6.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Water (°)</th>
<th>EG(°)</th>
<th>γ(mN/m)</th>
<th>χ&lt;sub&gt;donor-acceptor&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y6</td>
<td>96.8</td>
<td>67.7</td>
<td>29.66</td>
<td></td>
</tr>
<tr>
<td>PCIBDT-BT</td>
<td>105.8</td>
<td>77.9</td>
<td>26.04</td>
<td>0.1177K</td>
</tr>
<tr>
<td>PCIBDT-TBT</td>
<td>103.9</td>
<td>75.9</td>
<td>26.59</td>
<td>0.0838K</td>
</tr>
<tr>
<td>DCIBDT-DTBT</td>
<td>103.7</td>
<td>75.7</td>
<td>26.36</td>
<td>0.0818K</td>
</tr>
</tbody>
</table>

Table S9: Experimental data obtained from GIWAXS characterization.

<table>
<thead>
<tr>
<th>Blend film</th>
<th>Out-of-plane (010)</th>
<th>In-plane (100)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Location (Å&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>d-spacing (Å)</td>
</tr>
<tr>
<td>PCIBDT-BT:Y6</td>
<td>1.78</td>
<td>3.52</td>
</tr>
<tr>
<td>PCIBDT-TBT:Y6</td>
<td>1.83</td>
<td>3.43</td>
</tr>
<tr>
<td>PCIBDT-DTBT:Y6</td>
<td>1.76</td>
<td>3.57</td>
</tr>
</tbody>
</table>

Reference

12 L. An, J. Tong, Y. Huang, Z. Liang, J. Li, C. Yang and X. Wang, Polymers 2020, 12, 368.