Supporting Information

Substantial Photovoltaic Response and Morphology Tuning in Benzo[1,2-\(b\):6,5-\(b'\)]dithiophene (bBDT) Molecular Donors


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Materials and Methods

All reagents were commercially available and were used without further purification unless otherwise stated. THF and Et₂O were distilled from Na/benzophenone. Toluene was passed through activated alumina columns prior to use. Dimethylformamide (DMF) (anhydrous, 99.8%) was purchased from Sigma Aldrich. PC₇₁BM was purchased from American Dye Source, Inc. (ADS71BFA; purity >99%). The reagents 3,3’-dibromo-2,2’-bithiophene,¹ 5,10-diethyltetradec-7-yne (3a),² 2,6,13,17-tetramethyloctadec-9-yne (3b),³ and 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione⁴ were synthesized according to the literature. Unless otherwise stated, all reactions were carried out under inert atmosphere using standard Schlenk techniques. Thin-layer chromatography (TLC) was conducted with precoated glass-backed plates (silica gel 60 F254) and visualized by exposure to UV light (254 nm) or stained with KMnO₄ or Hanessian's Stain (CAM). Flash chromatography was performed with silica gel (43-60 µm). The eluent used is reported in parentheses. ¹H NMR spectra were recorded at 500 MHz and 400 MHz. ¹³C NMR spectra were recorded at 126 MHz or 101 MHz. Chemical shifts are reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets). Elemental analyses (EA) of starting materials and small molecule donors were performed by Midwest Microlab (Indianapolis, IN).
Synthesis and Characterization

**Scheme S1.** Synthetic route to bBDTTDPP2 derivatives 1a-c.

3,3'-diiodo-2,2'-bithiophene (2)

In a flame-dried round bottom flask 3,3'-dibromo-2,2'-bithiophene (5.39 g, 16.6 mmol) was dissolved in anhydrous Et₂O (170 ml) under a N₂-atmosphere and n-BuLi (2.5M in hexanes, 14.6 ml, 36.6 mmol, 2.2 equiv.) was added dropwise at -78 °C. The reaction mixture was stirred for 1 h. A solution of I₂ (9.29 g, 36.6 mmol, 2.2 equiv.) in Et₂O (35 ml) was added dropwise, the mixture was warmed to r.t. and was stirred for another hour. The reaction was quenched by addition of saturated Na₂S₂O₃ (100 ml) and the layers were separated. The aqueous layer was extracted with Et₂O (2×100 ml). The combined organic layer was washed with brine, dried over
Na$_2$SO$_4$ and the solvent was evaporated. The residue was recrystallized from hexanes/toluene 2:1. The diiodide 2 was isolated as an off-white crystalline solid (4.67 g, 11.2 mmol, 67%).

$R_t = 0.80$ (Hex) [UV] [CAM]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.41 (d, $J = 5.3$ Hz, 2H), 7.17 (d, $J = 5.3$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 135.8, 135.1, 129.5, 85.3.

The analytical data are in good accordance with those previously reported.$^3$

**General procedure A for the Palladium catalyzed carbocyclization of 2 and 3$^5$**

4,5-bis(2-ethylhexyl)benzo[1,2-b:6,5-b’]dithiophene

![Diagram of 4,5-bis(2-ethylhexyl)benzo[1,2-b:6,5-b’]dithiophene](image)

In a flame-dried round bottom flask 2 (100 mg, 239 µmol), 3a (120 mg, 479 µmol, 2 equiv.) and NBu$_3$ (114 µl, 88.9 mg, 479 µmol, 2 equiv.) were dissolved in anhydrous DMF (1.2 ml) and the solution was sparged with N$_2$. Pd(OAc)$_2$ (5.4 mg, 23.9 µmol, 10 mol%) was added and the reaction mixture was stirred at 130 °C for 4 h. The mixture was cooled to r.t., diluted with CH$_2$Cl$_2$ (15 ml) and poured into H$_2$O (30 ml). The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2×20 ml). The combined organic layer was dried over Na$_2$SO$_4$ and the solvent was removed. The residue was purified by flash chromatography on silica (hexanes). The title compound was isolated as a yellow resin (72.0 mg, 174 µmol, 73%).

$R_t = 0.82$ (Hex) [UV] [KMnO$_4$]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.47 (d, $J = 5.4$ Hz, 2H), 7.36 (d, $J = 5.4$ Hz, 2H), 3.05 – 2.94 (m, 4H), 1.72 – 1.62 (m, 2H), 1.44 – 1.21 (m, 16H), 0.90 – 0.85 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 138.1, 131.9, 131.4, 124.4, 123.2, 41.6, 35.1, 32.9, 29.3, 29.2, 26.0, 23.3, 14.3, 11.48, 11.45.

The analytical data are in good accordance with those previously reported.$^2$
General procedure B for the bromination of benzo[1,2-b:6,5-b’]dithiophene derivatives

2,7-dibromo-4,5-bis(2-ethylhexyl)benzo[1,2-b:6,5-b’]dithiophene

The above described benzo[1,2-b:6,5-b’]dithiophene (1.34 g, 3.22 mmol) was dissolved in CH$_2$Cl$_2$/AcOH 1:1 (20 ml) and $N$-bromosuccinimide (1.37 g, 7.73 mmol, 2.4 equiv.) was added at 0 °C. The mixture was warmed to r.t. and stirred for 1 h. The solution was diluted with CH$_2$Cl$_2$ (20 ml) and neutralized with saturated, aqueous NaHCO$_3$ solution. The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (2×30 ml). The combined organic layer was dried over Na$_2$SO$_4$ and the solvent was evaporated. The residue was purified by flash chromatography on silica (hexanes). The title compound was isolated as a yellow resin (1.48 g, 2.52 mmol, 78%).

$R_f = 0.89$ (Hex) [UV] [KMnO$_4$]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 7.39 (s, 2H), 2.98 – 2.78 (m, 4H), 1.64 – 1.56 (m, 2H), 1.37 – 1.17 (m, 16H), 0.90 – 0.86 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 137.8, 131.7, 131.5, 127.0, 112.4, 41.5, 35.0, 32.69, 32.66, 29.1, 29.06, 25.91, 25.88, 23.3, 14.3, 11.45, 11.41.

The analytical data are in good accordance with those previously reported.$^2$
General procedure C for the stannylation of 2,7-dibromo-benzo[1,2-b:6,5-b’]dithiophene derivatives

(4,5-bis(2-ethylhexyl)benzo[1,2-b:6,5-b’]dithiophene-2,7-diyl)bis(trimethylstannane) (4a)

In a flame-dried round bottom flask the above described dibromide (100 mg, 170 µmol) was dissolved in anhydrous THF (7 ml) under N₂-atmosphere and n-BuLi (2.5M in hexanes, 150 µl, 375 µmol, 2.2 equiv.) was added dropwise at -78 °C. The resulting yellow suspension was stirred for 2 h at -78 °C. Me₃SnCl (1M in hexanes, 544 µl, 544 µmol, 3.2 equiv.) was added at -78 °C and the reaction mixture was allowed to warm to r.t. over night. The reaction was quenched by addition of H₂O (20 ml). Hexanes (15 ml) was added and the layers were separated. The aqueous layer was extracted with hexanes (2×15 ml). The combined organic layer was washed with brine and dried over MgSO₄. The solvent was evaporated and the residue dried under high vacuum. Distannane 4a was isolated as a yellow resin (112 mg, 151 µmol, 89%) and was used without further purification.

¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.52 (s, 1H), 3.08 – 2.96 (m, 4H), 1.72 – 1.63 (m, 2H), 1.44 – 1.22 (m, 16H), 0.92 – 0.87 (m, 12H), 0.45 (s, 18H). ¹³C NMR (101 MHz, CDCl₃): δ [ppm] = 138.9, 138.8, 136.5, 135.8, 132.3, 131.1, 41.7, 35.04, 35.02, 33.01, 32.96, 29.43, 29.39, 26.02, 25.98, 23.4, 14.3, 11.6, 11.5, -8.1.

The analytical data are in good accordance with those previously reported.²
4,5-bis(3,7-dimethyloctyl)benzo[1,2-b:6,5-b']dithiophene

The title compound was synthesized according to general procedure A and was isolated as a yellow resin (61%).

\( R_f = 0.57 \) (Hex) [UV] [K\text{MnO}_4]. \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 7.46 (d, \( J = 5.4 \) Hz, 2H), 7.38 (d, \( J = 5.4 \) Hz, 2H), 3.09 – 2.92 (m, 4H), 1.70 – 1.16 (m, 20H), 1.06 (d, \( J = 6.4 \) Hz, 6H), 0.89 (d, \( J = 6.6 \) Hz, 12H). \textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 137.4, 131.7, 131.3, 123.6, 123.4, 39.4, 38.8, 37.2, 37.1, 33.7, 28.0, 28.0, 24.9, 22.8, 22.7, 19.8.

The analytical data are in good accordance with those previously reported.\(^3\)

2,7-dibromo-4,5-bis(3,7-dimethyloctyl)benzo[1,2-b:6,5-b']dithiophene

The title compound was synthesized according to general procedure B and was isolated as an off-white solid (73%).

\( R_f = 0.78 \) (Hex) [UV] [K\text{MnO}_4]. \textbf{\textsuperscript{1}H NMR} (400 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 7.38 (s, 2H), 2.96 – 2.79 (m, 4H), 1.65 – 1.50 (m, 6H), 1.48 – 1.14 (m, 14H), 1.04 (d, \( J = 6.4 \) Hz, 6H), 0.89 (d, \( J = 6.6 \) Hz, 12H). \textbf{\textsuperscript{13}C NMR} (101 MHz, CDCl\textsubscript{3}): \( \delta \) [ppm] = 137.4, 131.7, 131.5, 126.3, 112.8, 39.5, 38.8, 37.21, 37.19, 33.78, 33.77, 28.2, 28.1, 25.0, 22.9, 22.8, 19.9.
The analytical data are in good accordance with those previously reported.  

\[(4,5\text{-}\text{bis}(3,7\text{-}\text{dimethyloctyl})\text{benzo}[1,2\text{-}b\text{;}6,5\text{-}b']\text{dithiophene}-2,7\text{-}\text{diyl}}\text{bis}\text{(trimethylstannane)} \ (4b)\]

The title compound was synthesized according to general procedure C and was isolated as a dark-yellow resin (73%).

\(1^H\text{ NMR (}400 \text{ MHz, CDCl}_3\): } \delta \text{ [ppm] = 7.48 (s, 2H), 3.11 – 2.92 (m, 4H), 1.75 – 1.15 (m, 20H), 1.07 (d, } J = 6.4 \text{ Hz, 6H), 0.89 (d, } J = 6.6 \text{ Hz, 12H), 0.45 (s, 18H).} \]

\(13^C\text{ NMR (}101 \text{ MHz, CDCl}_3\): } \delta \text{ [ppm] = 138.4, 137.2, 135.8, 131.3, 131.0, 39.5, 38.8, 37.29, 37.27, 33.82, 33.81, 28.2, 25.1, 22.9, 22.8, 20.0, -8.1.} \)

The analytical data are in good accordance with those previously reported.
**General procedure D for the alkylation of 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione**

2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione

![Chemical structure](image)

A flame-dried round bottom flask was charged with 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (6.00 g, 16.7 mmol), K$_2$CO$_3$ (6.83 g, 53.3 mmol, 3.2 equiv.) and anhydrous DMF (120 ml) and the mixture was stirred at 120 °C for 1 h. 2-Ethylhexyl bromide (8.9 ml, 9.65 g, 50.0 mmol, 3 equiv.) was added dropwise and the resulting mixture was stirred for 18 h at 120 °C. The reaction was cooled to r.t. and H$_2$O (500 ml) was added before stirring for 1 h. The solution was filtered and the residue was washed with H$_2$O (200 ml) and MeOH (200 ml) and subsequently purified by column chromatography (hex/CH$_2$Cl$_2$ 80:20 → 60:40). The title compound was isolated as a dark purple solid (2.30 g, 4.39 mmol, 26%).

$R_f = 0.47$ (hexanes/CHCl$_3$ 1:4) [UV]. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 8.89 (dd, $J = 3.9, 1.1$ Hz, 2H), 7.62 (dd, $J = 5.0, 1.1$ Hz, 2H), 7.27 (dd, $J = 5.0, 3.9$ Hz, 2H), 4.05 (dd, $J = 14.1, 7.1$ Hz, 2H), 4.00 (dd, $J = 13.9, 6.6$ Hz, 2H), 1.91 – 1.81 (m, 2H), 1.41 – 1.19 (m, 16H), 0.89 – 0.83 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ [ppm] = 161.9, 140.6, 135.4, 130.6, 130.0, 128.6, 108.1, 46.0, 39.2, 30.4, 30.4, 28.5, 23.7, 23.2, 14.2, 10.6.

The analytical data are in good accordance with those previously reported.$^6$
General procedure E for the mono-bromination of TDPP derivatives

3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5a)

![Chemical structure of 5a]

The above described TDPP derivative (525 mg, 1.00 mmol) was dissolved in CHCl₃ (30 ml) and N-bromosuccinimide (178 mg, 1.00 mmol, 1 equiv.) dissolved in CHCl₃ (15 ml) was added dropwise in the course of 8 h at 0 °C. The reaction mixture was allowed to warm to r.t. over night. The solvent was evaporated and the residue was purified by column chromatography (hex/EtOAc 98:2 → 90:10). TDPP-Br (5a) was isolated as a dark purple solid (311 mg, 516 μmol, 52%).

\( R_f = 0.63 \) (hexanes/CHCl₃ 1:4) [UV]. \(^1\)H NMR (400 MHz, CDCl₃): \( \delta [ppm] = 8.90 \) (dd, \( J = 3.9, 1.2 \) Hz, 1H), \( 8.63 \) (d, \( J = 4.2 \) Hz, 1H), \( 7.64 \) (dd, \( J = 5.0, 1.2 \) Hz, 1H), \( 7.27 \) (dd, \( J = 5.0, 3.9 \) Hz, 1H), \( 7.22 \) (d, \( J = 4.2 \) Hz, 1H), \( 4.07 - 3.98 \) (m, 2H), \( 3.98 - 3.89 \) (m, 2H), \( 1.89 - 1.81 \) (m, 2H), \( 1.40 - 1.21 \) (m, 16H), \( 0.91 - 0.83 \) (m, 12H). \(^1\)C NMR (101 MHz, CDCl₃): \( \delta [ppm] = 161.8, 161.6, 141.0, 139.1, 135.7, 135.2, 131.5, 131.4, 131.0, 129.9, 128.6, 118.8, 108.3, 107.9, 46.11, 46.07, 39.3, 39.2, 30.3, 28.5, 23.73, 23.69, 23.20, 23.18, 14.2, 10.6.

The analytical data are in good accordance with those previously reported.\(^7\)
2,5-bis(3,7-dimethyloctyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione

![Structure of 2,5-bis(3,7-dimethyloctyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione]

The title compound was synthesized according to general procedure D and was isolated as a dark purple solid (36%).

$R_f = 0.50$ (hexanes/CHCl$_3$ 1:4) [UV]. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 8.91 (dd, $J = 3.9$, 1.0 Hz, 2H), 7.64 (dd, $J = 5.0$, 1.0 Hz, 2H), 7.28 (dd, $J = 4.9$, 4.0 Hz, 2H), 4.17 – 4.04 (m, 4H), 1.80 – 1.71 (m, 2H), 1.63 – 1.55 (m, 4H), 1.52 – 1.47 (m, 2H), 1.37 – 1.12 (m, 12H), 1.00 (d, $J = 6.3$ Hz, 6H), 0.85 (d, $J = 6.6$ Hz, 12H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ [ppm] = 161.5, 140.2, 135.4, 130.8, 129.8, 128.8, 107.9, 41.0, 39.3, 37.3, 36.9, 31.4, 28.1, 24.8, 22.9, 22.8, 19.7. Anal. calcd. for C$_{34}$H$_{48}$N$_2$O$_2$S$_2$: C 70.30, H 8.33, N 4.82; found: C 70.50, H 8.10, N 4.97.

3-(5-bromo thiophen-2-yl)-2,5-bis(3,7-dimethyloctyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5b)

![Structure of 3-(5-bromo thiophen-2-yl)-2,5-bis(3,7-dimethyloctyl)-6-(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (5b)]

5b was synthesized according to general procedure E and was isolated as a dark purple solid (53%).

$R_f = 0.69$ (hexanes/CHCl$_3$ 1:4) [UV]. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 8.92 (dd, $J = 3.9$, 1.1 Hz, 1H), 8.65 (d, $J = 4.2$ Hz, 1H), 7.65 (dd, $J = 5.0$, 1.1 Hz, 1H), 7.28 (dd, $J = 5.0$, 4.0 Hz,
1H), 7.23 (d, J = 4.2 Hz, 1H), 4.16 – 3.95 (m, 4H), 1.78 – 1.69 (m, 2H), 1.62 – 1.46 (m, 6H),
1.37 – 1.11 (m, 12H), 1.01 (d, J = 2.8 Hz, 3H), 0.99 (d, J = 2.7 Hz, 3H), 0.86 (d, J = 3.1 Hz, 6H),
0.85 (d, J = 3.1 Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ [ppm] = 161.4, 161.2, 140.6, 138.7,
135.6, 135.2, 131.7, 131.3, 131.1, 129.8, 128.8, 118.9, 108.12, 107.8, 41.0, 41.0, 39.3, 39.3, 37.2,
37.2, 36.9, 36.9, 31.4, 31.3, 28.1, 24.8, 24.8, 22.9, 22.8, 22.7, 19.7, 19.6. Anal. calcd. for
C$_{34}$H$_{47}$BrN$_2$O$_2$S$_2$: C 61.89, H 7.18, N 4.25; found: C 62.27, H 7.24, N 4.18.

General procedure F for Stille coupling of 4 and 5

EH-bBDTTDPP$_2$ (1a)

A flame-dried pressure flask was charged with distannane 5a (50.4 mg, 68.1 µmol), 4a (126 mg,
208 µmol, 2.5 eq.) and Pd(PPh$_3$)$_4$ (7.8 mg, 6.8 µmol, 10 mol%) under N$_2$-atmosphere. A mixture
of toluene and DMF (5:1, 10 ml) sparged with N$_2$ for 30 min, was added. The flask was sealed
and the solution was stirred at 130 °C for 24 h. The reaction mixture was cooled to r.t. and
poured into MeOH (150 ml). The mixture was stirred for 20 min and filtered off. The residue
was purified by column chromatography (hexanes/CHCl$_3$ 20:80 → 0:100). After purification the
product was precipitated into MeOH (100 ml), filtered off and dried under vacuum. 1a was
isolated as a blue solid (69.7 mg, 47.3 µmol, 70%).

$R_t$ = 0.59 (hexanes/EtOAc 4:1) [UV]. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 9.01 (d, J = 4.0
Hz, 2H), 8.91 (d, J = 3.4 Hz, 2H), 7.65 (s, 2H), 7.64 (d, J = 4.8 Hz, 2H), 7.44 (d, J = 4.1 Hz, 2H),
7.28 (dd, J = 4.8, 4.1 Hz, 2H), 4.13 – 4.01 (m, 8H), 3.04 – 2.95 (m, 4H), 2.00 – 1.94 (m, 2H),
1.92 – 1.85 (m, 2H), 1.71 – 1.64 (m, 2H), 1.45 – 1.21 (m, 48H), 0.96 – 0.93 (m, 12H), 0.91 –
0.85 (m, 24H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ [ppm] = 161.9, 161.8, 142.7, 140.3, 139.8,
139.4, 137.1, 135.5, 133.9, 133.0, 131.0, 130.8, 130.0, 129.1, 128.6, 126.0, 122.0, 108.6, 108.3,
46.1, 41.8, 39.4, 39.2, 35.0, 32.9, 30.4, 30.3, 29.9, 29.3, 29.2, 28.6, 28.5, 26.1, 26.0, 23.8, 23.7,
23.32, 23.28, 23.2, 14.3, 14.3, 14.2, 11.6, 11.5, 10.7, 10.6. Anal. calcd. for C$_{86}$H$_{114}$N$_4$O$_4$S$_6$: C 70.74, H 7.87, N 3.84; found: C 70.74, H 7.89, N 3.73.

**EH-DMO-bBDTTDPP$_2$ (1b)**

$\text{R}_f = 0.63 \ (\text{CHCl}_3) \ [\text{UV}]. \ ^1\text{H NMR} \ (500 \text{ MHz, CDCl}_3): \delta \ [\text{ppm}] = 8.98 \ (d, J = 4.1 \text{ Hz, 2H}), 8.91 \ (dd, J = 4.8, 1.1 \text{ Hz, 2H}), 7.63 \ (dd, J = 5.0, 0.9 \text{ Hz, 2H}), 7.61 \ (s, 2H), 7.45 \ (d, J = 4.1 \text{ Hz, 2H}), 7.28 \ (dd, J = 6.1, 5.0 \text{ Hz, 2H}), 4.13 – 4.00 \ (m, 8H), 3.09 – 2.90 \ (m, 4H), 2.01 – 1.83 \ (m, 4H), 1.73 – 1.62 \ (m, 4H), 1.46 – 1.17 \ (m, 48H), 1.10 \ (d, J = 6.3 \text{ Hz, 6H}), 0.95 \ (t, J = 7.4 \text{ Hz, 6H}), 0.91 – 0.85 \ (m, 30H). \ ^{13}\text{C NMR} \ (126 \text{ MHz, CDCl}_3): \delta \ [\text{ppm}] = 161.9, 161.8, 142.6, 140.4, 139.7, 138.9, 136.9, 135.6, 134.3, 133.0, 130.9, 130.8, 130.0, 129.1, 128.6, 126.0, 121.1, 108.6, 108.3, 46.1, 39.5, 39.4, 39.2, 39.0, 37.3, 33.8, 30.4, 30.34, 30.32, 29.9, 28.6, 28.5, 28.2, 25.1, 23.8, 23.7, 23.3, 23.2, 22.9, 22.8, 19.9, 14.3, 14.2, 10.7, 10.6. Anal. calcd. for C$_{90}$H$_{122}$N$_4$O$_4$S$_6$: C 71.29, H 8.11, N 3.69; found: C 71.32, H 8.04, N 3.72.

**1b** was synthesized according to general procedure E and was isolated as a blue solid (92%).
DMO-bBDTTDPP$_2$ (1c)

1b was synthesized according to general procedure E and was isolated as a blue solid (80%).

$R_f = 0.69$ (CHCl$_3$) [UV]. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ [ppm] = 8.98 (d, $J = 4.1$ Hz, 2H), 8.93 (dd, $J = 3.9$, 1.1 Hz, 2H), 7.63 (dd, $J = 5.0$, 1.1 Hz, 2H), 7.59 (s, 2H), 7.42 (d, $J = 4.1$ Hz, 2H), 7.28 (dd, $J = 6.1$, 5.0 Hz, 2H), 4.21 – 4.05 (m, 8H), 3.09 – 2.90 (m, 4H), 1.85 – 1.51 (m, 16H), 1.41 – 1.14 (m, 44H), 1.10 (d, $J = 6.3$ Hz, 6H), 1.08 (d, $J = 6.3$ Hz, 6H), 1.02 (d, $J = 6.3$ Hz, 6H), 0.90 – 0.84 (m, 36H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ [ppm] = 161.4, 161.3, 142.7, 139.9, 139.3, 138.9, 136.8, 135.5, 134.3, 132.9, 130.9, 130.8, 129.9, 129.0, 128.8, 126.1, 121.0, 108.4, 108.1, 41.1, 39.5, 39.4, 39.3, 39.0, 37.4, 37.3, 37.0, 36.9, 33.8, 31.5, 31.4, 31.1, 29.9, 28.2, 28.1, 25.1, 24.9, 24.8, 22.90, 22.87, 22.81, 22.78, 19.9, 19.7, 19.6. Anal. calcd. for C$_{98}$H$_{138}$N$_4$O$_4$S$_6$: C 72.28, H 8.54, N 3.44; found: C 72.05, H 8.34, N 3.46.
Density Functional Theory (DFT) Calculations

DFT calculations were performed at the B3LYP/6-31G** level using QCHEM4.0. All relative donor-acceptor conformations were optimized and identified as local minima by frequency calculations. The lowest energy conformer is shown here.

Figure S1. (A) Chemical structure, FMO energies and (B) optimized geometry for \textit{bBDTTDPP}_2 (1) calculated at DFT//B3LYP/6-31G** level. Alkyl chains are replaced by methyl groups to simplify calculations.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry were collected on an Indium-calibrated Mettler-Toledo DSC822e equipped with a TSO801RO autosampler. The samples (weight range 1.5 - 3.0 mg) were placed in lidded 30 microliters Al pans and thermally cycled twice under nitrogen with a heating rate of 10°C/min and a slower cooling rate of 5°C/min to minimize overcooling effects. The reported cycles correspond to the second cycle and are all endo up.
Figure S2. DSC traces for 1a (green), 1b (blue) and 1c (red).

Table S1. Summary of melting ($T_m$) and freezing ($T_f$) temperatures of 1a-c.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$T_m$</th>
<th>$T_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>227</td>
<td>194</td>
</tr>
<tr>
<td>1b</td>
<td>228</td>
<td>207</td>
</tr>
<tr>
<td>1c</td>
<td>247</td>
<td>224</td>
</tr>
</tbody>
</table>

UV-Vis spectrometry

UV-Vis spectra were recorded on a Varian Cary 50 Scan UV-Vis spectrophotometer. The solution absorption spectra of the small molecules were recorded on $10^{-6}$ M chloroform solutions, and the small molecule film optical absorption spectra were recorded from films cast from 7 mg/mL chloroform solutions.

Table S2. Summary of the optical properties of 1a-c in CHCl$_3$ solution and spun-cast films.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)$^a$</th>
<th>$\lambda_{\text{max}}$ (nm)$^b$</th>
<th>$\lambda_{\text{onset}}$ (nm)$^b$</th>
<th>$E_g^{\text{opt}}$ (eV)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>$8.41 \times 10^4$</td>
<td>607</td>
<td>724</td>
<td>1.72</td>
</tr>
<tr>
<td>1b</td>
<td>$8.05 \times 10^4$</td>
<td>611</td>
<td>725</td>
<td>1.71</td>
</tr>
<tr>
<td>1c</td>
<td>$9.02 \times 10^4$</td>
<td>615</td>
<td>732</td>
<td>1.70</td>
</tr>
</tbody>
</table>

$^a$derived from solution UV-VIS. $^b$thin-film properties.
Cyclic Voltammetry (CV)

The electrochemical properties of the small molecule donor materials were investigated in CH₂Cl₂ solution (0.3 mg/ml) under N₂ at a scan rate of 100 mV/s using 0.1 M tetrakis(n-butyl)ammonium hexafluorophosphate [(n-Bu)₄N⁺PF₆⁻] as the supporting electrolyte, Pt as the working, glassy carbon as the counter electrode, and an Ag wire was used as the pseudoreference electrode. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal standard and was assigned an absolute energy level of -4.88 eV vs. vacuum. The HOMO levels of 1a-c were determined by eq 1, where $E_{ox}^{onset}$ is the onset of oxidation potential vs. Fc/Fc⁺. The LUMO levels of 1a-c were determined by eq 2, where $E_{g}^{opt}$ is the optical band gap. The electron affinities (EA) of 1a-c were determined by eq 3, where $E_{red}^{onset}$ is the onset of reduction potential vs. Fc/Fc⁺.

$$E_{HOMO} = e(E_{ox}^{onset} + 4.88 \text{ eV}) \quad (1)$$

$$E_{LUMO} = E_{HOMO} + E_{g}^{opt} \quad (2)$$

$$EA = e(E_{red}^{onset} + 4.88 \text{ eV}) \quad (3)$$

Table S3. Summary of the FMO energies of 1a-c determined by cyclic voltammetry in CH₂Cl₂ solution.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{LUMO}$ (eV)</th>
<th>$EA$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>-5.20</td>
<td>-3.48</td>
<td>-3.40</td>
</tr>
<tr>
<td>1b</td>
<td>-5.19</td>
<td>-3.48</td>
<td>-3.56</td>
</tr>
<tr>
<td>1c</td>
<td>-5.21</td>
<td>-3.51</td>
<td>-3.44</td>
</tr>
</tbody>
</table>

TFT and SCLC mobility measurements

Bottom-gate/top-contact (BGTC) organic thin-film transistors (OTFTs) were fabricated by spin-coating (1000 rpm for 30 sec) a small molecule solution in CF under ambient conditions on OTS (octadecyltrichlorosilane)-treated, p-doped Si/SiO₂ substrates (300 nm SiO₂; capacitance: ~11 nFcm⁻²; Montco Silicon Technologies Inc.). Prior to OTS deposition, the wafers were solvent-cleaned by immersion in ethanol with sonication, and were then dried in a filtered stream of N₂, followed by 5 min plasma cleaning. Alkylsilation of the Si/SiO₂ surface was carried out by
submerging the silicon wafers in a 0.5 M solution of OTS in hexanes at 55-60% relative humidity. OTFT devices were completed by vapor deposition of Au source/drain electrodes through a shadow mask (channel length: 100 µm; channel width: 5000 µm). OFET characterization was performed under vacuum or ambient conditions in a probe station with a Keithley 6430 subfemtoamp meter (drain) and a Keithley 2400 (gate) source meter, operated by a locally written Labview program.

Figure S4. OFET measurements of (A) 1a, (B) 1b and (C) 1c.

Table S4. Summary of TFT performance metrics.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\mu_h$ (cm²/Vs)</th>
<th>$V_T$ (V)</th>
<th>$I_{on}:I_{off}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>$6.39 \times 10^{-3}$</td>
<td>-8.4</td>
<td>$10^5$</td>
</tr>
<tr>
<td>1b</td>
<td>$3.71 \times 10^{-3}$</td>
<td>-2.1</td>
<td>$10^6$</td>
</tr>
<tr>
<td>1c</td>
<td>$1.16 \times 10^{-2}$</td>
<td>+4.9</td>
<td>$10^5$</td>
</tr>
</tbody>
</table>

For SCLC mobility measurements, hole-only diodes were fabricated on ITO coated glass with a PEDOT:PSS bottom contact and a MoO$_3$/Au top contact. The top contact was the injecting electrode. The semiconducting layer was either neat polymer or polymer blend (as used in the optimal solar cell devices). Device areas ($A$) were $200 \times 200$ µm$^2$.

In these diodes, the current density ($J$) as a function of applied electric field ($E$) in the space charge limited regime is given by eq. 3, where by fitting the $J$-$E$ curve it is possible to extract the zero-field mobility, $\mu_0$, and the field dependence coefficient, $\gamma$, where $\varepsilon_s$ and $L$ are the semiconductor permittivity (taken as $3\varepsilon_0$) and thickness, respectively.$^{10}$
Figure S5. SCLC measurements of 1a (green), 1b (blue) and 1c (red) as neat films.

Table S5. Summary of SCLC mobilities of 1a-c.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Solvent</th>
<th>$\mu_{th}$ (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>CHCl$_3$</td>
<td>$(1.1 \pm 0.1) \times 10^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>1a:PC$_{71}$BM 1:1.5</td>
<td>CHCl$_3$</td>
<td>$(1.2 \pm 0.1) \times 10^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>1a:PC$_{71}$BM 1:1.5</td>
<td>CHCl$_3$:DIO (99%:1%)</td>
<td>$(3.6 \pm 0.1) \times 10^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>CHCl$_3$</td>
<td>$(5.2 \pm 0.1) \times 10^{-5}$</td>
</tr>
<tr>
<td>5</td>
<td>1b:PC$_{71}$BM 1:1</td>
<td>CHCl$_3$</td>
<td>$(3.4 \pm 0.1) \times 10^{-5}$</td>
</tr>
<tr>
<td>6</td>
<td>1b:PC$_{71}$BM 1:1</td>
<td>CHCl$_3$:DIO (99%:1%)</td>
<td>$(4.1 \pm 0.1) \times 10^{-5}$</td>
</tr>
<tr>
<td>7</td>
<td>1c</td>
<td>CHCl$_3$</td>
<td>$(5.5 \pm 0.1) \times 10^{-4}$</td>
</tr>
<tr>
<td>8</td>
<td>1c:PC$_{71}$BM 1:1</td>
<td>CHCl$_3$</td>
<td>$(2.3 \pm 0.1) \times 10^{-4}$</td>
</tr>
<tr>
<td>9</td>
<td>1c:PC$_{71}$BM 1:1</td>
<td>CHCl$_3$:DIO (99%:1%)</td>
<td>$(3.2 \pm 0.1) \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Atomic Force and Transmission Electron Microscopy (AFM, TEM)

AFM measurements were performed using a Dimension Icon Scanning Probe Microscope (Veeco) in tapping mode. For TEM measurements a JEOL JEM-2100F instrument was used, with samples transferred from films made under identical conditions as actual devices. Slightly defocus mode is used to increase the contrast between small molecule donors and PC$_{71}$BM.
Figure S6. AFM images of (A) 1a:PC$_{70}$BM 1:1.5 (B) 1b:PC$_{71}$BM 1:1 and (C) 1c:PC$_{71}$BM 1:1 blend films spun-cast from CHCl$_3$ (top) and CHCl$_3$/DIO (99:1) (bottom).

Figure S7. TEM and AFM (insert) images of (A) 1a:PC$_{70}$BM 1:1.5 (B) 1b:PC$_{71}$BM 1:1 and (C) 1c:PC$_{71}$BM 1:1 blend films spun-cast from CHCl$_3$/DIO (97:3).

**Grazing Incidence Wide-Angle X-Ray Scattering (GIWAXS) Data**

Grazing incidence x-ray scattering measurements were performed at Beamline 8-ID-E$^4$ of the Advanced Photon Source at Argonne National Laboratory as described by Jiang et al.$^{11}$ An x-ray wavelength of $\lambda = 1.6868$ Å was used, and data were collected on a Pilatus 1M pixel array detector at a sample-detector distance of 204 mm. Spectra were collected at an incidence angle of 0.2°; exposure times were varied from 4 to 11 seconds to maximize the signal and the x-ray beam was attenuated between a factor of 0 and 2. All spectra were normalized with respect to exposure time and attenuation.
Figure S8. GIWAXS data of pristine films (top) of (A) 1a, (B) 1b and (C) 1c fabricated from CHCl₃/DIO (99:1) and blend films (bottom) of (A) 1a:PC₇₁BM (1:1.5), (B) 1b:PC₇₁BM (1:1) and (C) 1c:PC₇₁BM (1:1) fabricated from CHCl₃.

Figure S9. In-plane (A) and out-of-plane (B) line-cuts of GIWAXS spectra of blend films of 1a:PC₇₁BM (1:1.5) (green), 1b:PC₇₁BM (1:1) (blue) and 1c:PC₇₁BM (1:1) (red) fabricated from CHCl₃/DIO (99:1).
Table S6. $d$-spacing resulting from line-cuts in Figure S9.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>lamellar</th>
<th>$\pi-\pi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>in-plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>18.3</td>
<td>3.85</td>
</tr>
<tr>
<td>1b</td>
<td>18.1, 21.7</td>
<td>3.73</td>
</tr>
<tr>
<td>1c</td>
<td>21.3</td>
<td>3.71</td>
</tr>
<tr>
<td>out-of-plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>17.4</td>
<td>n/a</td>
</tr>
<tr>
<td>1b</td>
<td>17.2, 20.4</td>
<td>n/a</td>
</tr>
<tr>
<td>1c</td>
<td>20.1</td>
<td>3.74</td>
</tr>
</tbody>
</table>

Solar Cell Fabrication and Characterization

Pre-patterned ITO-coated glass (Thin Film Devices, Inc.) with a sheet resistance of $\sim 10\Omega/\square$ is used as the substrate. It is cleaned by sequential sonication in hexane, DI water, methanol, isopropanol, and acetone. After UV/ozone treatment (Jelight Co.) for 20 min, $\sim 20$ nm ZnO electron transport/hole blocking layer is prepared by spin-coating at 5000 rpm a precursor solution prepared from 0.5 M zinc acetate dehydrate in 0.5 M monoethanolamine and 2-methoxyethanol under air. After cleaning the electrical contacts, the ZnO substrates are immediately baked in air at 170 °C for 10 min, then rinsed with DI water, isopropanol, and acetone, and then dried in a glovebox. Active layer solutions are prepared from 10-15 mg/mL solutions of 1a, 1b and 1c molecules in (chloroform) CF/DIO in various ratios. For optimum device performance, active layers of 1a, 1b, and 1c are spun cast at 4000, 6000, and 3000 rpm, respectively. Thin 7.5 nm layers of MoO$_x$ and 120 nm of Ag are then thermally evaporated through a shadow mask at $\sim 10^{-6}$ Torr. For the fabrication of conventional solar cells, PEDOT:PSS (Clevios P VP Al 4083) was spun-cast at 5000 rpm for 30 sec and annealed at 150 °C. Active layers are prepared under the same conditions as the inverted solar cells. LiF(1.0 nm)/Al(100 nm) were then thermally evaporated through a shadow mask at $\sim 10^{-6}$ Torr. For device characterization, $J-V$ characteristics are measured under AM1.5G light (100 mW/cm$^2$) using the Xe arc lamp of a Spectra-Nova Class A solar simulator. The light intensity is calibrated using an NREL-certified monocrystalline Si diode coupled to a KG3 filter to bring spectral mismatch to unity. A Keithley 2400 source meter is used for electrical characterization. The area of all devices is 6 mm$^2$, and a 6 mm$^2$ aperture is placed on top of cells during all measurements.
EQEs are characterized using an Oriel model QE-PV-SI instrument equipped with a NIST-certified Si diode. Monochromatic light is generated from an Oriel 300W lamp source.

Table S7. Summary of PV metrics of optimized devices.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>0.782</td>
<td>4.57</td>
<td>38.9</td>
<td>1.39 (1.27)</td>
</tr>
<tr>
<td>1b</td>
<td>0.766</td>
<td>11.4</td>
<td>63.2</td>
<td>5.53 (5.46)</td>
</tr>
<tr>
<td>1c</td>
<td>0.756</td>
<td>8.47</td>
<td>61.8</td>
<td>3.96 (3.88)</td>
</tr>
</tbody>
</table>

$^a$All devices use inverted device architecture: ITO/ZnO/1:PC$_{71}$BM/MoO$_x$/Ag (1a:PC$_{70}$BM 1:1.5, 1b:PC$_{71}$BM 1:1, and 1c:PC$_{71}$BM 1:1). Active layers are spun cast from CHCl$_3$/DIO (99:1) solution. $^b$Data represent best performance device and average values of at least 16 devices are shown in parantheses.

Table S8. Optimization of the solvent composition for active layer deposition.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Molecule</th>
<th>Solvent</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>CHCl$_3$</td>
<td>0.819</td>
<td>3.41</td>
<td>39.0</td>
<td>1.09 (1.03)</td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>CHCl$_3$:DIO (97%:3%)</td>
<td>0.754</td>
<td>4.01</td>
<td>39.1</td>
<td>1.18 (1.14)</td>
</tr>
<tr>
<td>3</td>
<td>1b</td>
<td>CHCl$_3$</td>
<td>0.808</td>
<td>3.62</td>
<td>50.6</td>
<td>1.48 (1.47)</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>CHCl$_3$:DIO (97%:3%)</td>
<td>0.742</td>
<td>9.91</td>
<td>60.2</td>
<td>4.43 (4.40)</td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>C$_6$H$_5$Cl:DIO (99%:1%)</td>
<td>0.763</td>
<td>9.88</td>
<td>61.8</td>
<td>4.66 (4.62)</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>C$_6$H$_4$Cl$_2$:DIO (99%:1%)</td>
<td>0.708</td>
<td>6.69</td>
<td>51.5</td>
<td>2.44 (2.38)</td>
</tr>
<tr>
<td>7</td>
<td>1c</td>
<td>CHCl$_3$</td>
<td>0.764</td>
<td>3.02</td>
<td>57.4</td>
<td>1.32 (1.28)</td>
</tr>
<tr>
<td>8</td>
<td>1c</td>
<td>CHCl$_3$:DIO (97%:3%)</td>
<td>0.753</td>
<td>6.46</td>
<td>60.4</td>
<td>2.94 (2.87)</td>
</tr>
</tbody>
</table>

$^a$All devices use inverted device architecture: ITO/ZnO/1:PC$_{71}$BM/MoO$_x$/Ag (1a:PC$_{70}$BM 1:1.5, 1b:PC$_{71}$BM 1:1, and 1c:PC$_{71}$BM 1:1). $^b$Data represent best performance device and average values of at least 8 devices are shown in parantheses.
Figure S10. J-V plots for 1a:PC71BM (1:1.5) (green), 1b:PC71BM (1:1) (blue) and 1c:PC71BM (1:1)-based (red) inverted OPVs fabricated from CHCl3 without DIO. (B) EQE plots for 1a-c-based solar cells.

Table S9. PV metrics of conventional architectures.\(^a\)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(V_{oc}) (V)</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>PCE (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.787</td>
<td>4.28</td>
<td>37.8</td>
<td>1.27 (1.24)</td>
</tr>
<tr>
<td>3</td>
<td>0.769</td>
<td>10.9</td>
<td>61.9</td>
<td>5.18 (5.07)</td>
</tr>
<tr>
<td>7</td>
<td>0.754</td>
<td>7.93</td>
<td>61.1</td>
<td>3.65 (3.58)</td>
</tr>
</tbody>
</table>

\(^a\)All devices use conventional device architecture: ITO/PEDOT:PSS/1:PC71BM/LiF/Al (1a:PC70BM 1:1.5, 1b:PC71BM 1:1 and 1c:PC71BM 1:1). Active layers are spun cast from CHCl3/DIO (99:1) solution. \(^b\)Data represent best performance device and average values of at least 16 devices are shown in parantheses.

Literature

$R^1 = 2$-ethylhexyl
$R^2 = 3,7$-dimethyloctyl