ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.*, DOI: 10.1002/adma.201601957

Regioisomeric Effects of Donor–Acceptor–Acceptor# Small-Molecule Donors on the Open Circuit Voltage of Organic Photovoltaics

Xiaozhou Che, Chin-Lung Chung, Xiao Liu, Shu-Hua Chou, Yi-Hung Liu, Ken-Tsung Wong, and Stephen R. Forrest**

Supporting Information

Regioisomeric Effects of Donor-Acceptor-Acceptor' Small Molecule Donors on the Open Circuit Voltage of Organic Photovoltaics

Xiaozhou Che[#], Chin-Lung Chung[#], Xiao Liu, Shu-Hua Chou, Yi-Hung Liu, Ken-Tsung Wong[*], and Stephen R. Forrest[*]

# These authors contributed equally.

X. Che, Prof. S. R. Forrest
Applied Physics Program
University of Michigan
Ann Arbor, MI 48109, USA
E-mail: stevefor@umich.edu

C.-L. Chung, S.-H. Chou, Y.-H. Liu, Prof. K.-T. Wong
Department of Chemistry
National Taiwan University
Taipei, 10617, Taiwan
E-mail: kenwong@ntu.edu.tw

X. Liu, Prof. S. R. Forrest
Department of Electrical Engineering and Computer Science
University of Michigan
Ann Arbor, MI 48109, USA

Prof. K.-T. Wong
Institute of Atomic and Molecular Science Academia Sinica
Taipei, 10617, Taiwan

Prof. S. R. Forrest
Departments of Physics and Department of Materials Science and Engineering
University of Michigan
Ann Arbor, MI 48109, USA

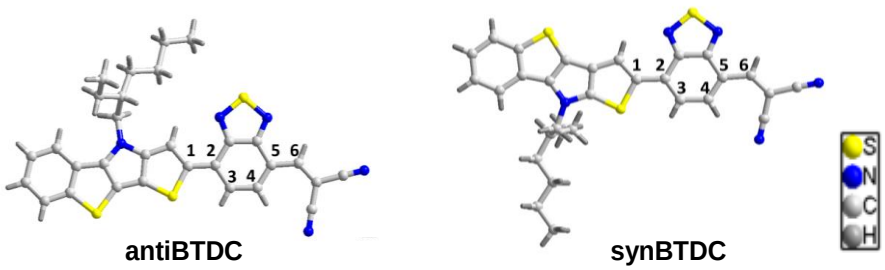


Figure S1. Crystal structures of antiBTDC and synBTDC with labeling of carbons. The detailed bond lengths are listed in Table S2.

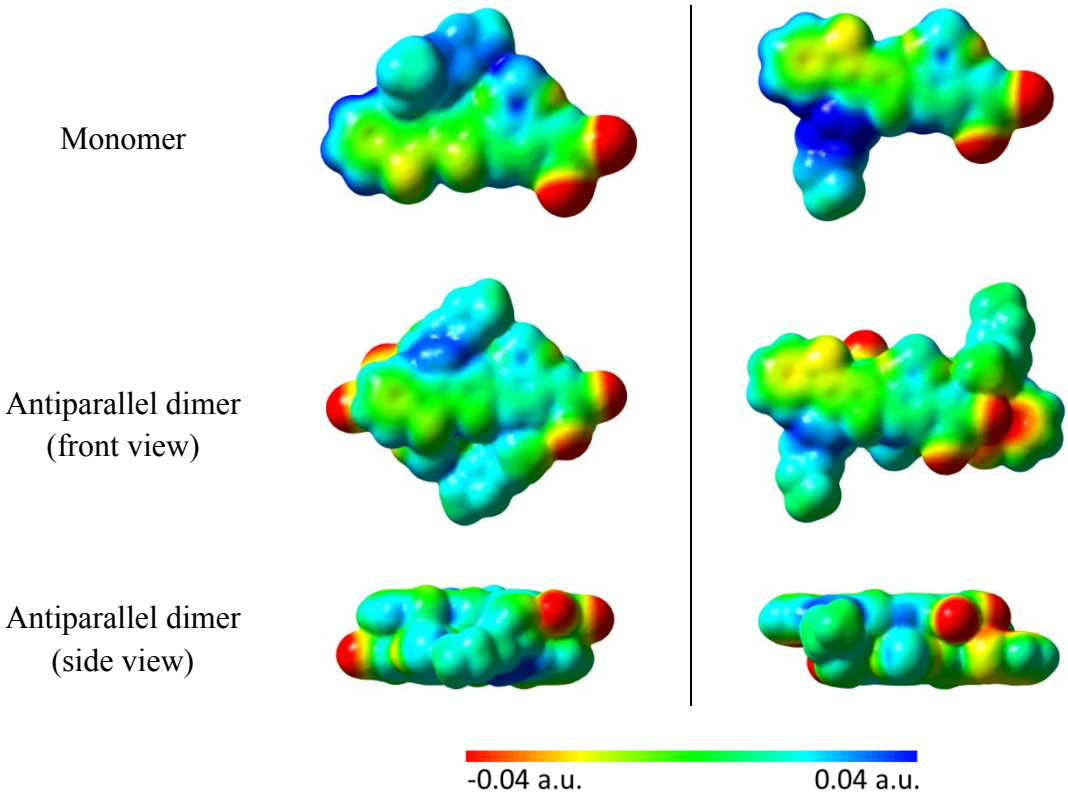


Figure S2. Electrostatic surface potential calculated from the crystal geometry of dyes taking an isovalue of 0.0004 for antiBTDC (left) and synBTDC (right).

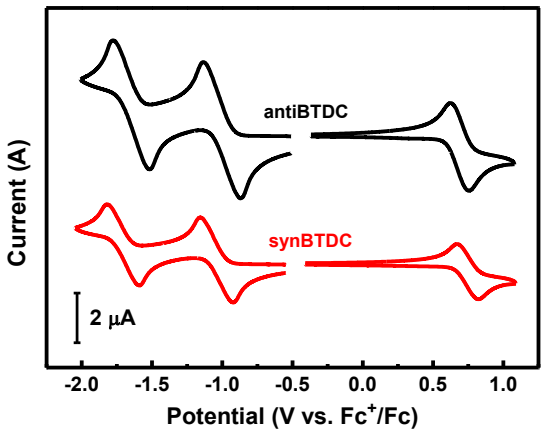


Figure S3. Cyclic voltammograms of antiBTDC and synBTDC.

Oxidation potentials were measured in dichloromethane solutions with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte. Reduction potentials were measured in tetrahydrofuran solutions with 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. These molecules exhibit one quasi-reversible oxidation wave assigned to the oxidation of the heteroacene donor moieties. The more positive oxidation potential of synBTDC relative antiBTDC is ascribed to the cross-conjugation in the donor unit. On the other hand, two reversible reduction waves were observed in the cathodic potential regime. The first wave is attributed to the reduction of the dicyanovinylene (DCV) segment, whereas the second wave is due to the reduction of benzothiadiazole (BT) fragment. Likewise, the reduction potential of synBTDC was negatively shifted because its conjugation is interrupted by the nitrogen atom in the donor moiety.

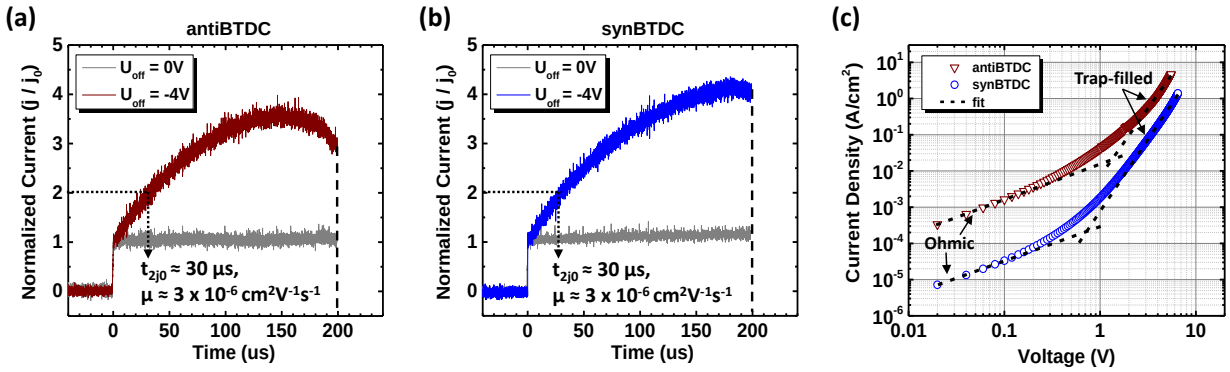


Figure S4. (a) / (b) MIS-CELIV (metal insulator semiconductor-charge extraction by linearly increasing voltage) hole mobility measurement of the donors, antiBTDC and synBTDC, respectively. The device structure is: ITO/d-a-a' donor (40 nm) /MgF_2 (15 nm)/Al. A waveform generator (Agilent 33120A) is used to shape the triangular voltage pulse that increases by 2 V in 200 µs, with an initial negative offset between 0 V and -4 V. The transient current is recorded by a digital oscilloscope (Tektronix TDS 3054B). For details of this method see [20] and [21] in text. (c) SCLC (space-charge limited current) hole mobility measurement with the fit to the ohmic and trap-filled limit regimes. The device structure is: ITO/MoO_3 (15 nm)/d-a-a' donor (40 nm)/MoO_3 (15 nm)/Al.

In the ohmic regime (Fig. S4c), there is linear relationship between current and voltage:

$$J_{ohm} = qp\mu\frac{V}{d} \qquad (1)$$

Here, p is the free carrier density, μ is the hole mobility, and d is the sample thickness. Assuming an exponential distribution of traps, the trap limited current is:[1]

$$J_{TFL} = q\mu N_V \left[\frac{\varepsilon m}{q(m+1)N_t}\right]^m \left(\frac{2m+1}{m+1}\right)^{m+1} \frac{V^{m+1}}{d^{2m+1}} \qquad (2)$$

Here, N_V is the HOMO density of states, N_t is the density of traps, m = T_t/T where T_t is the characteristic trap temperature. N_V is set to 10^{21} cm^{-3}, a typical value for organics; μ = 3×10^{-6} $cm^2V^{-1}s^{-1}$ as measured by MIS-CELIV. With Eqs. (1) and (2), we fit the ohmic and the trap-filled limit current respectively of the two donor materials. The parameters obtained from the fits are:

	m	N_t (cm^{-3})	p (cm^{-3})	σ (S/cm)*
antiBTDC	2.7 ± 0.1	8×10^{18}	1×10^{17}	5×10^{-8}
synBTDC	2.6 ± 0.3	1×10^{19}	3×10^{15}	2×10^{-9}

*σ: hole conductivity.

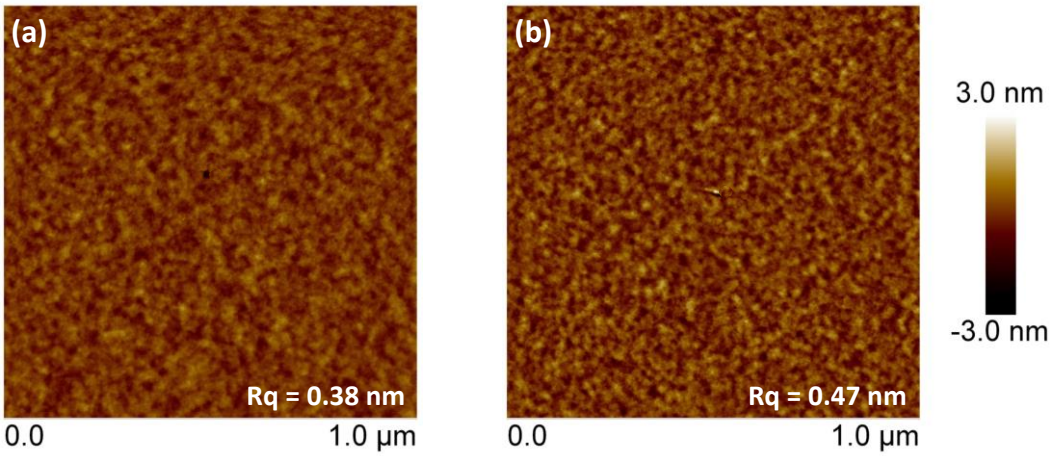


Figure S5. Atomic-force microscopy (AFM) images of (a) antiBTDC:C_{70} 1:2 and (b) synBTDC:C_{70} 1:2. R_q refers to the mean square roughness.

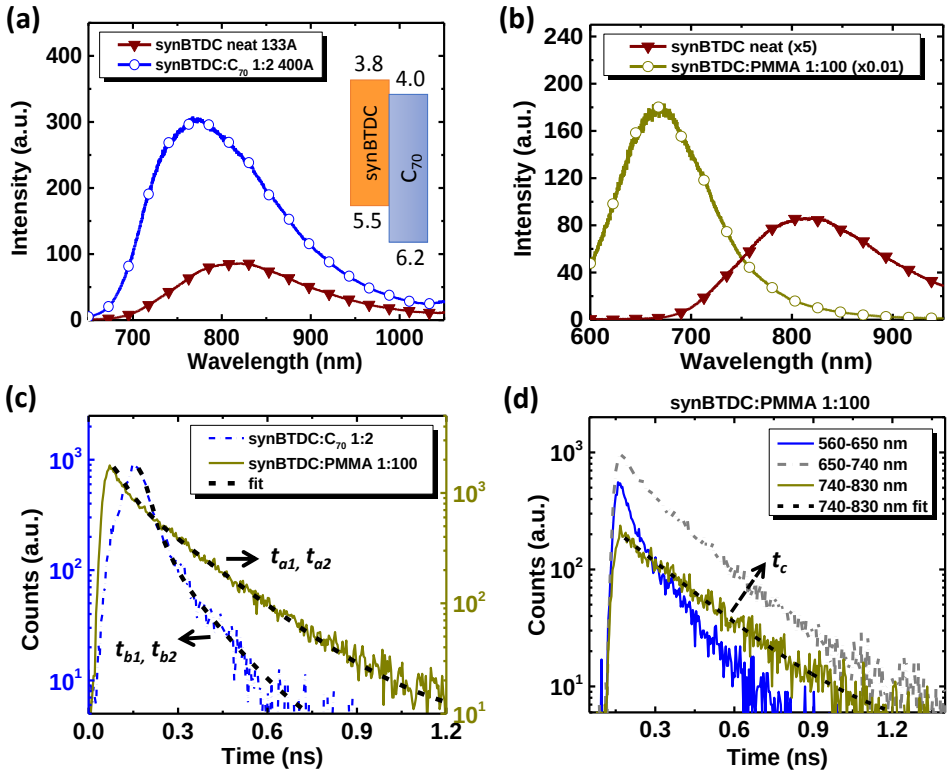


Figure S6. a) Steady state photoluminescence (PL) spectral intensity of synBTDC and a synBTDC:C_{70} 1:2 blend. *Inset:* Energy level diagram of synBTDC relative to C_{70}. Numbers

indicate energies in eV. b) PL spectra of 1% synBTDC diluted in poly(methyl methacrylate) (PMMA), and as a neat film. c) Time-resolved transient PL of synBTDC:PMMA 1:100 and antiBTDC:C_{70} 1:2 blends. d) Wavelength-resolved transient PL of synBTDC:PMMA. The time constants obtained from the fits (dashed lines) are: t_{a1} = 50 ± 10 ps, t_{a2} = 200 ± 20 ps; t_{b1} = 30 ± 10 ps, t_{b2} = 130 ± 10 ps; t_c = 230 ± 20 ps.

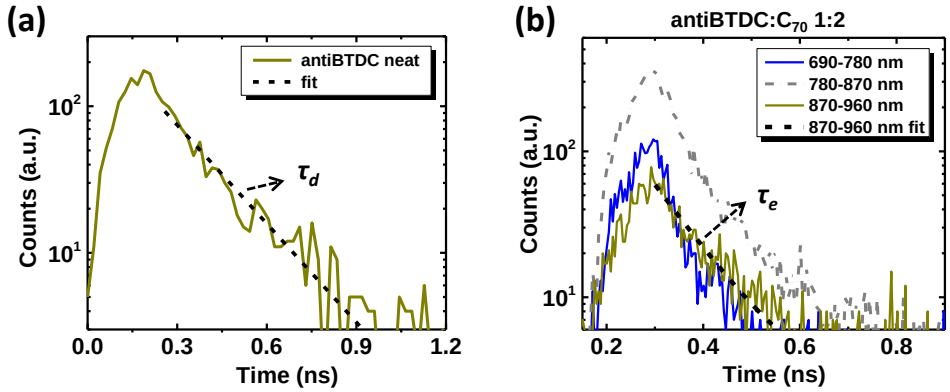


Figure S7. a) Transient PL emission of an antiBTDC film with a single exponential fit (dashed line). b) Wavelength-resolved transient PL of antiBTDC:C_{70} 1:2 blend film. The time constants obtained from the fits are: τ_d = 190 ± 30 ps, τ_e = 100 ± 20 ps.

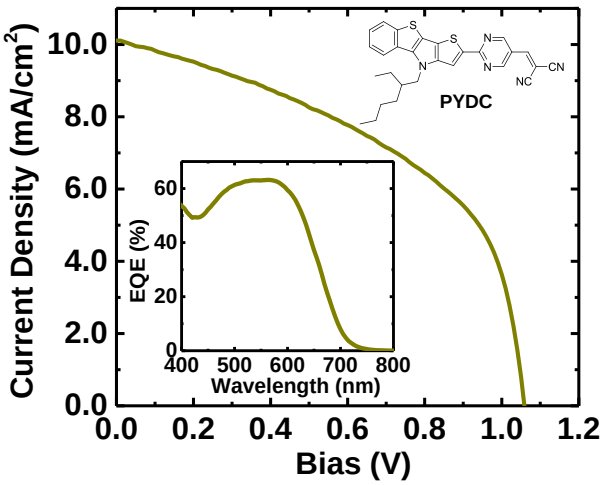
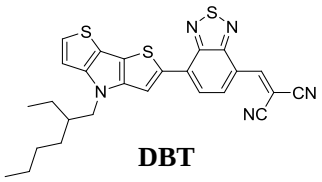
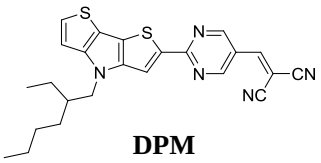


Figure S8. PYDC:C_{70} 1:2 organic photovoltaic cell *J-V* characteristics. *Inset:* Molecular structural formula of PYDC, and its *EQE* spectrum.



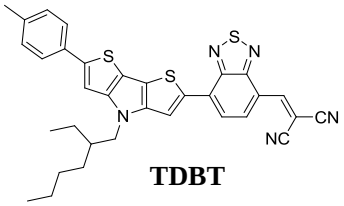
DBT

2-((7-(N-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]pyrrol-2-yl) benzo[c][1,2,5]thiadiazol-4-yl)methylene)malononitrile



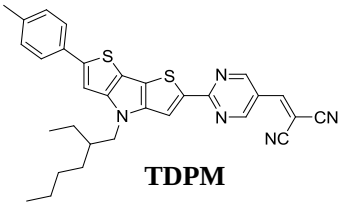
DPM

2-((2-(N-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)pyrimidin-5-yl)methylene)malononitrile



TDBT

2-((7-(N-(2-ethylhexyl)-6-p-tolyl-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)benzo[c][1,2,5]thiadiazol-4-yl)methylene)malononitrile



TDPM

2-((2-(N-(2-ethylhexyl)-6-p-tolyl-dithieno[3,2-b:2',3'-d]pyrrol-2-yl)pyrimidin-5-yl)methylene)malononitrile

Figure S9. Molecular structures of DBT, DPM, TDBT and TDPM.[2]

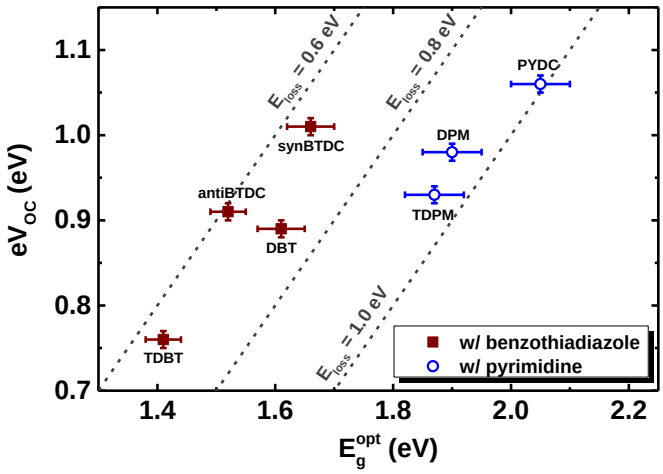


Figure S10. Plot of eV_{OC} *vs.* E_g^{opt} (optical energy gap) estimated from the absorption onset of the thin films. The dashed lines indicate E_{loss} (*i.e.* E_g^{opt} - eV_{OC}) of 0.6, 0.8 and 1.0 eV respectively.

Table S1. Crystal Data for antiBTDC and synBTDC.

Compound	antiBTDC	synBTDC
Empirical formula	$C_{30}H_{25}N_5S_3$	$C_{30}H_{25}N_5S_3$
Formula weight	551.73	551.73
Crystal dimensions/mm^3	0.25×0.10×0.05	0.20×0.15×0.10
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/ Å	7.5639 (7)	8.8223 (7)
b/ Å	12.3326 (13)	9.5943 (7)
c/ Å	15.1168 (16)	16.6011 (9)
α (°)	112.01 (1)	100.667 (5)
β (°)	93.04 (1)	93.946 (6)
γ (°)	92.39 (1)	108.233 (7)
Cell volume/ Å^3	1302.63 (546)	1299.42 (16)
Z	2	2
Density (calc)/g cm^{-3}	1.407	1.410
F(000)	576	576
Temperature/K	150 (2)	150 (2)
Wavelength/ Å	1.54178	1.54178
No. of reflns collected	7306	8968
No. of indep reflns (R_{int})	4712 (0.1942)	5657 (0.1839)
R(F), wR_2 [all data]	0.0841 (3108)	0.0912 (2975)

Table S2. Bond lengths of carbon-carbon bonds measured in the crystal structures and the corresponding bond length alternation (BLA).

Dye	C1-C2 (Å)	C2-C3 (Å)	C3-C4 (Å)	C4-C5 (Å)	C5-C6 (Å)	BLA[a] (Å)
antiBTDC	1.426	1.398	1.417	1.375	1.433	0.031
synBTDC	1.450	1.374	1.420	1.375	1.450	0.046

[a] Calculated as (C3−C4)−[(C2−C3)+(C4−C5)]/2.

Table S3. Computed lowest-energy electronic transition ($S_1 \neg S_0$) parameters.

Dye	λ_{calc} (nm)[a]	HUMO/ LUMO (eV)[a]	f [b]	MO composition [Λ][c]	μ_g (D)[d]	μ_e (D)[e]	μ_{ge} (D)[f]	μ_{tr} (D)[g]
antiBTDC	676	-5.36/-3.33	1.12	98% HOMO→LUMO [43%] 2% HOMO−1→LUMO [16%]	15.42	16.48	1.08	5.00
synBTDC	652	-5.50/-3.29	0.25	66% HOMO→LUMO [30%] 34% HOMO−*1*→LUMO [22%]	14.84	13.77	1.07	2.31

[a] Calculated $S_1 \neg S_0$ transition energy levels.
[b] Oscillator strengths.
[c] Molecular orbital (MO) overlap [Λ].
[d] Total dipole moment at S_0.
[e] Total dipole moment at S_1.
[f] Total dipole moment change between S_0 and S_1.
[g] Total transition dipole moment between S_0 and S_1.

Table S4. Physical parameters of antiBTDC and synBTDC.

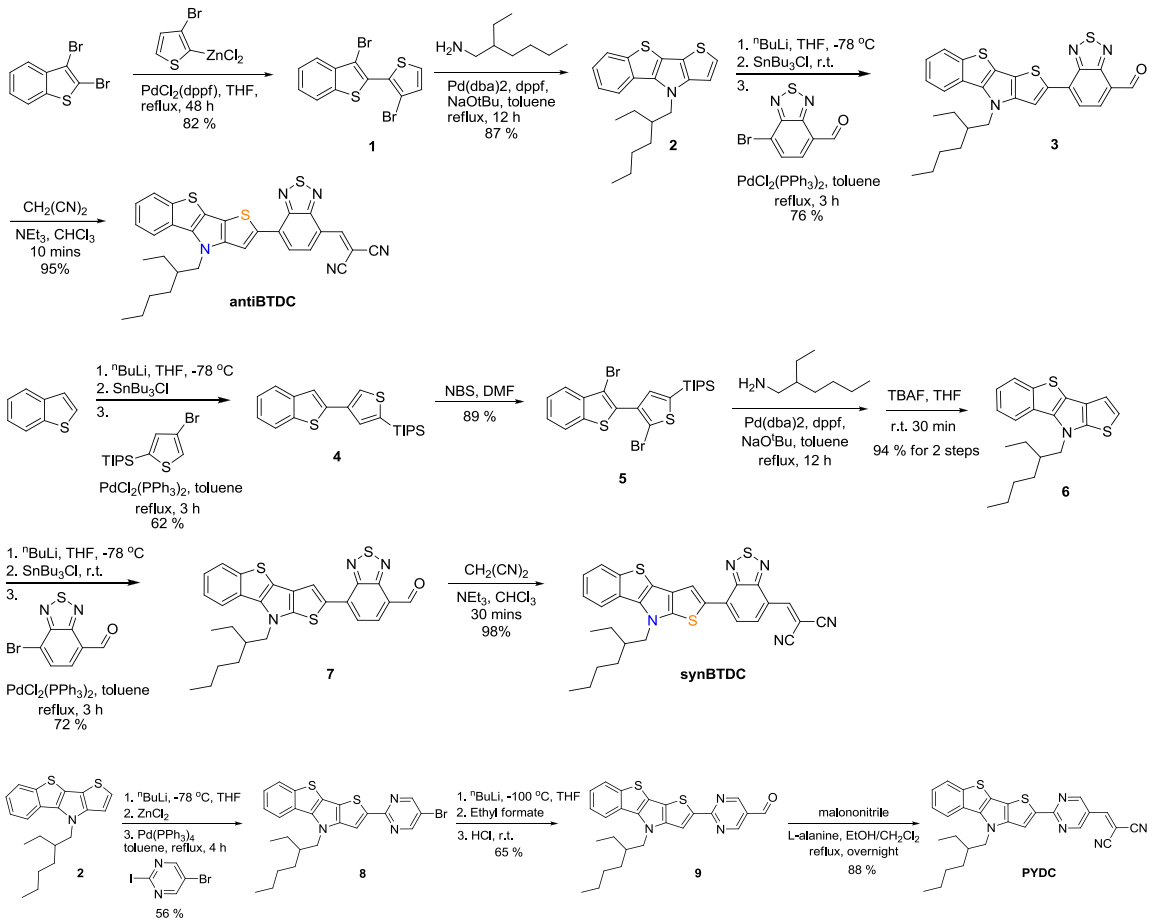
Dye	$\lambda_{max,solution}$ (nm)[a]	$\lambda_{max,film}$ (nm)	E_g^{opt} (eV)[b]	E_{ox} (V)[c]	E_{red} (V)[d]	ΔE_{CV} (eV)[e]	HOMO (eV)[f]	LUMO (eV)[g]	T_d (^oC)[i]
antiBTDC	612	619	1.52 ± 0.03	0.60	-0.92	1.52	-5.4 ± 0.05	-3.9	331
synBTDC	581	594	1.66 ± 0.04	0.66	-0.97	1.63	-5.5 ± 0.05	-3.8	319

[a] Measured in CH_2Cl_2 solution.
[b] Optical gap estimated from the absorption onset of the thin films.
[c] Oxidation potential in CH_2Cl_2 solution.
[d] Reduction potential in tetrahydrofuran (THF).
[e] Difference between E_{ox} and E_{red}.
[f] Highest occupied molecular orbital (HOMO) level determined by ultraviolet photoelectron spectroscopy (UPS).
[g] Lowest unoccupied molecular orbital (LUMO) = HOMO + E_g^{opt}.
[I] Decomposition temperature obtained from thermogravimetry analysis (TGA).

Table S5. Device performance of antiBTDC:C_{70} cells with different blend ratios.

Device (40 nm)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
antiBTDC:C_{70} 1:1	11.4 ± 0.5	0.92 ± 0.01	0.47 ± 0.01	4.9 ± 0.2
antiBTDC:C_{70} 1:2	12.1 ± 0.6	0.94 ± 0.01	0.49 ± 0.01	5.6 ± 0.3
antiBTDC:C_{70} 1:3	11.9 ± 0.6	0.94 ± 0.01	0.47 ± 0.01	5.3 ± 0.3
antiBTDC:C_{70} 1:4	11.2 ± 0.5	0.94 ± 0.01	0.45 ± 0.01	4.7 ± 0.2

We optimized the D:A ratio of each donor material with fixed active layer thickness of 40 nm. The table lists the result for antiBTDC cells. It is worth noting that the cells have lower *PCEs* than the values reported in Table 1 due to: 1) The active layer is thinner than later optimized thickness of 1:2 ratio (60 nm); 2) The type of ITO used is different from the one in the final structure which gives a lower V_{OC} but much higher *FF* and overall *PCE*. The trend is clear nevertheless. The V_{OC} is insensitive to the blend ratio, increasing to 0.94 eV as the ratio increases. Both J_{SC} and *FF* reaches their peak value at 1:2 ratio. The synBTDC cells show similar trend.



Scheme S1. Synthetic routes for **antiBTDC**, **synBTDC** and **PYDC**.

The synthetic pathways to **antiBTDC, synBTDC** and **PYDC** are outlined in Scheme 1. Solvents for chemical synthesis were freshly distillated before use. All chemical reactions were performed under an Ar or N_2 atmosphere. Starting from 2,3-dibromobenzo[*b*]thiophene, compound **1** was synthesized by regioselective Negishi coupling with (3-bromothiophen-2-yl)zinc(II) chloride in the presence of dichloro[1,10-bis(diphenylphosphino)ferrocene] palladium (Pd(dppf)Cl_2). The Pd-catalyzed tandem Buchwald-Hartwig cyclization reaction of compound 1 with 2-ethyl-1-hexylamine gave the asymmetric heterotetracene **2**. Compound 2 was then converted to stannyl reagent by the treatment of ^{n}BuLi and subsequently quenched by $SnBu_3Cl$. The resulting crude was directly subject to the Stille coupling reaction of 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde to afford aldehyde **3** which was then condensed with malononitrile to yield the desired product antiBTDC. The synthesis of regioisomer synBTDC started from benzo[*b*]thiophene was then reacted with (4-bromothiophen-2-yl)triisopropylsilane by Stille coupling reaction to yield compound **4**. The bromination of compound **4** with *N*-bromosuccinimide (NBS) proceeded smoothly to afford compound **5** which was then cyclized by palladium-catalyzed two-fold C-N bond coupling with alkyl amine. Without further purification, the triisopropylsilyl (TIPS) protecting group of coupled intermediate was cleanly removed by tetra-*n*-butylammonium fluoride (TBAF) to give the corresponding heterotetracene **6**. From compound **6**, the

final target synBTDC was obtained by the same synthetic protocols as those described for the synthesis of antiBTDC. It is noteworthy that the synthetic routes provide a versatile method for developing asymmetric heteroacene derivatives as organic semiconductors. In addition, the electron-deficient pyrimidine group was introduced to the heteroacene **2** through a selective Stille coupling reaction with 5-bromo-2-iodopyrimidine, affording the compound **8**. Then, the treatment of compound **8** with ^{n}BuLi at −100 °C gave the lithiated intermediate, which was quenched with ethyl formate to afford the carbaldehyde **9**. Finally, a Knoevenagel condensation of the aldehyde **9** with malononitrile under the L-alanine catalyzed condition furnished **PYDC**.

Synthesis of **1**:

To a solution of 2,3-dibromothiophene (7.3 g, 30 mmol) in diethyl ether (60 mL) was added dropwise *n*-butyllithium (18.8 mL, 1.6 M in hexane) at -78 °C. After being stirred for 1 h at the same temperature, to the solution was added a solution of zinc chloride (4.3 g, 31.5 mol) in THF (60 mL) via a syringe. The mixture was stirred at 0 °C for 1 h, and then transferred to a rounded bottle containing 2,3-dibromobenzo[*b*]thiophene (5.8 g, 20.0 mmol) and Pd(dppf)Cl_2 (1.5 g, 2.0 mmol). The resulting mixture was refluxed under Ar for 48 h. After being cooled to room temperature, to the mixture solution was added aq. NH_4Cl, and extracted with ethyl acetate. The combined organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as eluent to afford compound **1** as a white solid (6.1 g, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.52-7.43 (m, 2H), 7.49 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.7, 130.7, 128.7, 127.9, 125.8, 125.0, 123.6, 121.9, 112.7, 110.0; IR (KBr) *v* 3105, 3057, 2920, 2850, 1744, 1689, 1658, 1632, 1565, 1476, 1455, 1435, 1411, 1344, 1302, 1250, 1152, 1080, 1018, 942, 866, 752, 724 cm^{-1}; mp: 87-89 °C; HRMS (FAB) m/z calcd for $C_{12}H_6{}^{79}Br_2S_2$: 371.8278, found 371.8278; calcd for $C_{12}H_6{}^{79}Br^{81}BrS_2$: 373.8257, found 373.8257; calcd for $C_{12}H_6{}^{81}Br_2S_2$: 375.8237, found 375.8228.

Synthesis of **2**:

A solution of **1** (6.1 g, 16.4 mmol), sodium *t*-butoxide (12.6 g, 131.2 mmol), $Pd(dba)_2$ (943 mg, 1.6 mmol), and dppf (1.8 g, 3.3 mmol) in toluene (330 mL) was stirred at room temperature for 30 min. To the resulting solution was added 2-ethyl-1-hexylamine (3.3 mL, 19.7 mmol), and the mixture was stirred at 110 °C for 12 h. After the resulting mixture was cooled to room temperature, H_2O was added to the mixture and extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with hexane as eluent to afford compound **2** as a white solid (5.6 g, 87 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.43-7.39 (m, 1H), 7.30-7.26 (m, 1H), 7.22 (d, *J* = 5.2 Hz, 1H), 7.08 (d, *J* = 5.2 Hz, 1H), 4.43-4.32 (m, 2H), 2.11-2.05 (m, 1H), 1.45-1.22 (m, 8H), 0.90 (t, *J* = 7.6 Hz, 3H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 141.5, 137.1, 128.0, 124.5, 124.3, 124.0, 122.9, 119.0, 115.0, 114.3, 111.3, 51.7, 40.7, 30.7, 28.7, 24.0, 23.3, 14.3, 10.9; IR (KBr) *v* 3102, 3080, 3050, 2958, 2928, 2871, 2857, 1766, 1690, 1590, 1516, 1488, 1468, 1408, 1384, 1363, 1299, 1268, 1241, 1165, 1137, 1094, 1026, 964, 926, 850, 804, 804, 747, 723, 708; mp: 68-70 °C; HRMS (FAB) m/z calcd for $C_{20}H_{23}NS_2$: 341.1272, found 341.1265.

Synthesis of **3**:

To a solution of compound **2** (683 mg, 2 mmol) in THF (30 mL) was added dropwise *n*-butyllithium (1.9 mL, 1.6 M in hexane) at -78 °C. After stirring for 1 hour, tributyltin chloride (1.1 mL, 4 mmol) was injected by a syringe and the resulting mixture was warm to room temperature for 12 h, then quenched with H_2O and extracted with diethyl ether. The combined organic phase was washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. A mixture of stannylated heteroacene (2 mmol), 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (438 mg, 1.8 mmol), and $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol) in toluene (20 mL) was stirred and heated at reflux temperature under argon for 3 hours. After cooling, the resulting mixture was extracted with dichloromethane and aq. NH_4Cl. The organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel with dichloromethane/hexane (v/v:1/1) as eluent to afford **3** as a purple solid (0.8 g, 76 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.53 (s, 1H), 8.36 (s, 1H), 7.99 (d, *J* = 7.6 Hz), 7.78-7.75 (m, 2H), 7.69 (d, *J* = 8 Hz, 1H), 7.34-7.31 (m, 1H), 7.28-7.24 (m, 1H), 4.29-4.18 (m, 2H), 2.03-2.00 (m, 1H), 1.42-1.20 (m, 8H), 0.90 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 188.4, 154.5, 152.5, 147.6, 142.8, 139.8, 137.0, 134.3, 132.6, 127.5, 125.1, 125.0, 124.8, 124.3, 122.9, 120.1, 118.4, 115.6, 114.7, 52.0, 41.1, 30.9, 29.0, 24.5, 23.6, 14.4, 11.1; IR (KBr) *v* 2961, 2934, 2876, 2856, 2829, 1698, 1590, 1541, 1519, 1494, 1466, 1411, 1356, 1267, 1240, 1179, 1154, 1102, 1091, 1008, 832, 807, 752, 721; mp: 218-220 °C; HRMS (FAB) m/z calcd for $C_{27}H_{25}N_3OS_3$: 503.1160, found 503.1164.

Synthesis of **antiBTDC**:

A mixture of **3** (200 mg, 0.4 mmol), malononitrile (40 mg, 0.6 mmol) and 3 drops of triethylamine was stirred at room temperature in $CHCl_3$ (5 mL) under N_2 for 10 minutes. The solvent was removed by rotary evaporation and the reaction mixture was directly precipitated with CH_2Cl_2 and MeOH. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/hexane (v/v, 1:2) as eluent to afford **antiBTDC** as a metallic green solid (210 mg, 95 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8 Hz, 1H), 8.43 (s, 1H), 8.35 (s, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 8 Hz, 1H), 7.68 (d, *J* = 8 Hz, 1H), 7.43-7.39 (m, 1H), 7.36-7.32 (m, 1H), 4.27-4.16 (m, 2H), 2.03-2.00 (m, 1H), 1.42-1.24 (m, 8H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 151.3, 150.7, 147.2, 142.6, 140.1, 136.6, 134.1, 130.2, 126.7, 124.7, 124.6, 124.5, 122.4, 120.2, 119.7, 119.2, 115.6, 114.5, 114.2, 113.5, 80.0, 51.5, 40.5, 30.4, 28.4, 23.9, 23.0, 14.0, 10.7; IR (KBr) *v* 2956, 2928, 2870, 2851, 2225, 1698, 1659, 1582, 1538, 1513, 1485, 1461, 1411, 1372, 1353, 1320, 1270, 1226, 1163, 1102, 1041, 1025, 928, 906, 840, 826, 804, 754, 730; mp: 237 °C (DSC); HRMS (FAB) m/z calcd for $C_{30}H_{25}N_5S_3$: 551.1272, found 551.1278.

Synthesis of **4**:

To a solution of benzo[*b*]thiophene (4.8 g, 36 mmol) in THF (120 mL) was added dropwise *n*-butyllithium (26.8 mL, 1.6 M in hexane) at -78 °C. After stirring for 1 hour, tributyltin chloride (15 mL, 54 mmol) was injected by a syringe and the resulting mixture was warm to room temperature for 12 h,

then quenched with H_2O and extracted with diethyl ether. The combined organic phase was washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. A mixture of benzo[*b*]thiophen-2-yltributylstannane (36 mmol), (4-bromothiophen-2-yl)triisopropylsilane (11.5 g, 36 mmol), and $Pd(PPh_3)_4$ (2.1 g, 1.8 mmol) in toluene (120 mL) was stirred and heated at reflux temperature under argon for 12 hours. After cooling, the resulting mixture was extracted with dichloromethane. The organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel with hexane as eluent to afford **4** as a colorless solid (8.4 g, 62 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.82 (s, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.60 (s, 1H), 7.48 (s, 1H), 7.39-7.30 (m, 2H), 1.45-1.33 (m, 3H), 1.17 (d, *J* = 7.6 Hz, 18 H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 140.5, 138.2, 137.9, 135.0, 129.2, 127.5, 127.4, 126.8, 125.7, 123.0, 121.6, 120.0, 19.3, 12.8; IR (KBr) *v* 3062, 2942, 2895, 2865, 2729, 1789, 1690, 1678, 1591, 1570, 1545, 1468, 1434, 1393, 1363, 1350, 1313, 1261, 1199, 1159, 1066, 1020, 976, 924, 887, 846, 825, 748, 723; mp: 58-60 °C; HRMS (FAB) m/z calcd for $C_{21}H_{28}S_2Si$: 372.1402, found 372.1406.

Synthesis of **5**:

To a solution of **4** (8.3 g, 22.3 mmol) in DMF (75 mL) was added N-bromosuccinimide (7.9 g, 44.5 mmol) in the dark. The resulting solution was stirred for 12 h at room temperature under nitrogen and then was extracted with ether and water. The combined organic layer was dried over $MgSO_4$. After removal the solvent under reduced pressure, the residue was directly precipitated with CH_2Cl_2 and MeOH to afford compound **5** as a white solid (10.5 g, 89%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.50-7.42 (m, 2H), 7.32 (s, 1H), 1.38-1.31 (m, 3H), 1.14 (d, *J* = 7.2 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 138.2, 137.9, 136.2, 134.2, 125.6, 125.1, 123.6, 122.2, 117.7, 107.9, 18.5, 11.6; IR (KBr) *v* 3059, 2945, 2892, 2865, 1783, 1662, 1628, 1604, 1570, 1477, 1431, 1390, 1307, 1248, 1199, 1159, 1069, 1023, 1001, 973, 927, 887, 834, 760, 726; mp: 87-89 °C; HRMS (FAB) m/z calcd for $C_{21}H_{26}{}^{79}Br_2S_2Si$: 527.9612, found 527.9604; calcd for $C_{21}H_{26}{}^{79}Br^{81}Br\ S_2Si$: 529.9591, found 529.9585; calcd for $C_{21}H_{26}{}^{81}Br_2S_2Si$: 531.9571, found 531.9577.

Synthesis of **6**:

A solution of **5** (7.0 g, 13 mmol), sodium *t*-butoxide (10.0 g, 104 mmol), $Pd(dba)_2$ (748 mg, 1.3 mmol), and dppf (1.44 g, 2.6 mmol) in toluene (250 mL) was stirred at room temperature for 30 min. To the resulting solution was added 2-ethyl-1-hexylamine (2.6 mL, 15.8 mmol), and the mixture was stirred at 110 °C for 12 h. After the resulting mixture was cooled to room temperature, H_2O was added to the mixture and extracted with ethyl acetate. The combined organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. After flash column chromatography, to a solution of the residue in THF (130 mL) was added a tetrabutylammonium fluoride (TBAF) solution (20 mL, 20 mmol, 1 M in THF). The solution was stirred for 30 minutes at room temperature, then poured into water, and extracted with ethyl acetate. The combined organic layer was dried over $MgSO_4$ and concentrated in vacuo to give a residue, which was purified by column chromatography on silica gel with hexane as eluent to afford compound **6** as a white solid (4.2 g, 94 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.88 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.43-7.39 (m, 1H), 7.29-7.25 (m, 1H), 7.15 (d, *J* = 5.2 Hz, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 4.37-4.27 (m, 2H), 2.20-2.16 (m, 1H), 1.48-1.22 (m, 8H), 0.92 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 7.6 Hz,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 140.9, 136.9, 127.5, 124.3, 124.0, 122.3, 121.8, 118.4, 117.1, 117.0, 114.0, 52.9, 39.9, 30.5, 28.4, 23.9, 23.0, 14.0, 10.6; IR (KBr) *v* 3109, 3078, 3059, 2963, 2929, 2871, 2852, 1771, 1591, 1520, 1468, 1415, 1400, 1307, 1273, 1199, 1128, 1069, 1023, 880, 806, 751, 723, 714; mp: 87-89 °C; HRMS (FAB) m/z calcd for $C_{20}H_{23}NS_2$: 341.1272, found 341.1269.

Synthesis of **7**:

To a solution of compound **6** (490 mg, 1.4 mmol) in THF (14 mL) was added dropwise *n*-butyllithium (1.1 mL, 1.6 M in hexane) at -78 °C. After stirring for 1 hour, tributyltin chloride (0.6 mL, 2.2 mmol) was injected by a syringe and the resulting mixture was warm to room temperature for 12 h, then quenched with H_2O and extracted with diethyl ether. The combined organic phase was washed with H_2O and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. A mixture of stannylated heteroacene **6** (1.43 mmol), 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (313 mg, 1.3 mmol), and $Pd(PPh_3)_2Cl_2$ (50 mg, 0.1 mmol) in toluene was stirred and heated at reflux temperature under argon for 3 hours. After cooling, the resulting mixture was extracted with dichloromethane and aq. NH_4Cl. The organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel with dichloromethane/hexane (v/v:1/1.5) as eluent to afford **7** as a red solid (470 mg, 72 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.46 (s, 1H), 8.31 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.62-7.59 (m, 2H), 7.35-7.31 (m, 1H), 7.27-7.23 (m, 1H), 4.10-4.00 (m, 2H), 2.10-2.07 (m, 1H), 1.43-1.23 (m, 8H), 0.90 (t, *J* = 7.6 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 188.3, 154.3, 152.2, 145.7, 141.8, 138.1, 134.4, 132.5, 131.6, 127.4, 124.9, 124.8, 124.6, 123.7, 123.5, 122.0, 121.9, 119.2, 115.4, 53.6, 40.5, 31.1, 29.0, 24.5, 23.6, 14.3, 11.0; IR (KBr) *v* 2961, 2931, 2878, 2859, 1687, 1599, 1541, 1516, 1469, 1419, 1394, 1383, 1353, 1331, 1259, 1226, 1179, 1091, 1077, 1041, 1011, 909, 829, 807, 752, 719; mp: 179-180 °C; HRMS (FAB) m/z calcd for $C_{27}H_{25}N_3OS_3$: 503.1160, found 503.1155.

Synthesis of **synBTDC**:

A mixture of **7** (200 mg, 0.4 mmol), malononitrile (40 mg, 0.6 mmol) and 5 drops of triethylamine was stirred at room temperature in $CHCl_3$ (5 mL) under N_2 for 30 minutes. The solvent was removed by rotary evaporation and the reaction mixture was directly precipitated with CH_2Cl_2 and MeOH. The crude product was purified by column chromatography on silica gel with $CHCl_3$ as eluent to afford **synBTDC** as a dark purple solid (216 mg, 98 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.6 Hz, 1H), 8.66 (s, 1H), 8.57 (s, 1H), 7.88 (d, *J* = 8 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.46-7.43 (m, 1H), 7.36-7.32 (m, 1H), 4.32-4.29 (m, 2H), 2.22 (brs, 1H), 1.53-1.30 (m, 8H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 151.9, 150.9, 146.3, 141.7, 138.3, 135.0, 131.3, 130.8, 127.0, 124.6, 124.0, 123.3, 122.9, 122.2, 120.2, 118.8, 115.4, 114.3, 113.6, 80.3, 53.4, 40.0, 30.6, 28.4, 24.0, 23.0, 14.0, 10.7; IR (KBr) *v* 2950, 2917, 2854, 2230, 2214, 1739, 1634, 1574, 1538, 1510, 1496, 1466, 1447, 1433, 1405, 1370, 1350, 1273, 1229, 1201, 1157, 1105, 1072, 1025, 931, 909, 876, 859, 834, 821, 804, 782, 752, 727, 710; mp: 228 °C (DSC); HRMS (FAB) m/z calcd for $C_{30}H_{25}N_5S_3$: 551.1272, found 551.1281.

Synthesis of **8**:

To a solution of compound **2** (1.5 g, 4.4 mmol) in THF (20 mL) was added dropwise *n*-butyllithium (3 mL, 1.6 M in hexane) at -78 °C. After stirring for 1 hour, zinc chloride (718 mg, 5.3 mmol) in THF (20 mL) solution was injected by a syringe and the resulting mixture was warm to room temperature for 30 minutes, and the resulting solution was then directly transferred to a rounded bottle containing a mixture of 5-bromo-2-iodopyrimidine (1.3 g, 4.4 mmol) and $Pd(PPh_3)_4$ (254 mg, 0.2 mmol). The resulting mixture was stirred and heated at reflux temperature under argon for 4 hours. After cooling, the resulting mixture was extracted with dichloromethane and aq. NH_4Cl. The organic phase was dried over $MgSO_4$ and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel with dichloromethane/hexane (v/v:1/2) as eluent to afford compound **8** as a yellowish green solid (1.2 g, 56 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.70 (s, 2H), 7.99 (s, 1H), 7.91 (d, *J* = 7.6 Hz, 1H), 7.86 (d, 8 Hz, 1H), 7.45-7.41 (m, 1H), 7.35-7.31 (m, 1H), 4.42-4.39 (m, 2H), 2.11-2.09 (m, 1H), 1.46-1.22 (m, 8H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.84 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 158.3, 146.9, 142.9, 140.0, 139.8, 127.8, 125.0, 124.9, 124.3, 120.2, 119.7, 116.7, 114.9, 114.0, 52.4, 41.2, 31.1, 29.1, 24.5, 23.6, 14.3, 11.1; IR (KBr) *ν* 3055, 3019, 2969, 2926, 2880, 2860, 2662, 1767, 1731, 1662, 1586, 1503, 1460, 1407, 1358, 1272, 1219, 1146, 1120, 1097, 1071, 919, 829, 787, 747, 724; mp: 180-182 °C; HRMS (FAB) m/z calcd for $C_{24}H_{24}{}^{79}BrN_3S_2$: 497.0595, found 497.0587; calcd for $C_{24}H_{24}{}^{81}BrN_3S_2$: 499.0575, found 499.0570.

Synthesis of **9**:

To a stirred solution of **8** (2.0 g, 4.0 mmol) in anhydrous THF (50 mL) at -100 ^{o}C was added dropwise a solution of *n*-butyllithium (2.6 mL, 1.6 M in hexane) under argon and stirred for a further 30 min. Freshly distillated ethyl formate (3.3 ml, 40 mmol) was added to the reaction mixture and then stirred for 30 min. The resulting mixture was quenched with 1.5 M HCl in THF solution (2.7 mL). The ice bath was removed and the resulting solution was stirred for 1.5 h at room temperature. Then, the reaction mixture was extracted with H_2O and ethyl acetate, the combined organic phase was washed with brine and dried over $MgSO_4$. After removal of solvent under reduced pressure, the crude was purified by column chromatography on silica gel (gradient eluent: dichloromethane/hexane = 1.5/1 to 5/1) to yield **9** as an orange solid (1.2 g, 65 %). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.01 (s, 1H), 9.03 (s, 1H), 8.14 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.47-7.42 (m, 1H), 7.37-7.33 (m, 1H), 4.48-4.37 (m, 2H), 2.14-2.11 (m, 1H), 1.47-1.22 (m, 8H), 0.92 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.6 Hz, 3H) ; ^{13}C NMR (100 MHz, CD_2Cl_2) δ 189.0, 165.8, 159.2, 147.2, 143.3, 141.0, 140.0, 127.6, 126.1, 125.2, 125.1, 124.8, 122.1, 120.6, 116.0, 115.0, 52.4, 43.5, 41.1, 31.1, 29.1, 24.5, 23.6, 14.3, 11.1; IR (KBr) *ν* 2962, 2927, 2868, 2849, 1695, 1671, 1577, 1523, 1507, 1490, 1469, 1415, 1399, 1366, 1261, 1218, 1154, 1038, 981, 935, 906, 860, 838, 798, 755, 725, 706; mp: 216-218 °C; HRMS (FAB) m/z calcd for $C_{25}H_{25}N_3OS_2$: 447.1439, found 447.1435.

Synthesis of **PYDC**:

Compound **9** (150 mg, 0.3 mmol) and malononitrile (33 mg, 0.5 mmol) was dissolved in dichloromethane (30 mL). A solution of trace amount of L-alanine in 15 mL of anhydrous ethanol was poured into the mixture. The reaction was stirred overnight at reflux. After cooling, the mixture was extracted with dichloromethane and brine. The organic layer was dried over $MgSO_4$ and the solvent was removed by

rotary evaporation. The crude product was purified by column chromatography on silica gel with dichloromethane as eluent to afford **PYDC** as a dark red solid (148 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.11 (s, 1H), 7.90-7.86 (m, 2H), 7.49 (s, 1H), 7.47-7.43 (m, 1H), 7.39-7.36 (m, 1H), 4.46-4.35 (m, 2H), 2.11 (brs, 1H), 1.47-1.25 (m, 8H), 0.93 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 152.6, 146.8, 143.1, 141.3, 139.0, 126.8, 124.7, 123.2, 121.3, 120.0, 116.1, 113.3, 112.6, 82.3, 51.9, 40.5, 30.5, 29.7, 28.5, 23.9, 23.0, 14.0, 10.7; IR (KBr) *v* 2960, 2919, 2872, 2860, 2226, 1665, 1631, 1573, 1509, 1467, 1420, 1398, 1250, 1231, 1150, 1038, 985, 952, 790, 757, 726, 704; mp: 280 °C (DSC); HRMS (FAB) m/z calcd for $C_{28}H_{25}N_5S_2$: 495.1551, found 495.1550.

[1] P. Mark, W. Helfrich, *J. Appl. Phys.* **1962**, *33*, 205.
[2] H.-I. Lu, C.-W. Lu, Y.-C. Lee, H.-W. Lin, L.-Y. Lin, F. Lin, J.-H. Chang, C.-I. Wu, K.-T. Wong, *Chemistry of Materials* **2014**, *26*, 4361.