ADVANCED ENERGY MATERIALS

Supporting Information

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Donor–Acceptor–Acceptor's Molecules for Vacuum-Deposited Organic Photovoltaics with Efficiency Exceeding 9%

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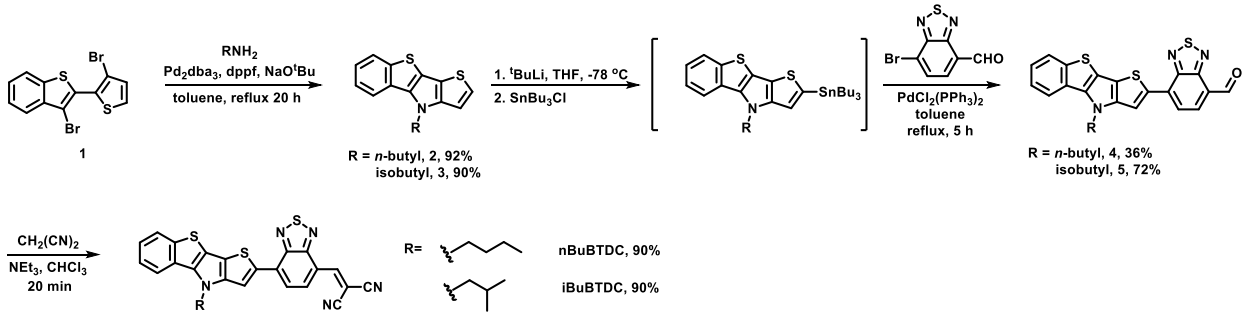
The syntheses of **nBuBTDC** and **iBuBTDC** are shown in Scheme S1. Compound **1** was cyclized by Pd-catalyzed tandem C-N bond coupling with butan-1-amine or 2-methylpropan-1-amine to afford the corresponding heterotetracene **2** and **3**, respectively. The final targeted isomers were obtained by the same synthetic protocols as those described for the synthesis of **antiBTDC**.[1] The detail procedures and characterizations of new compounds are shown in the last part of SI.



Scheme S1. Synthetic procedures for **nBuBTDC** and **iBuBTDC**.

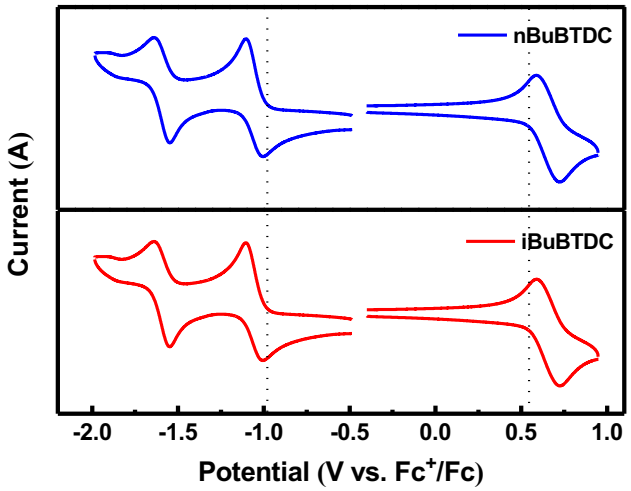


Figure S1. Cyclic voltammograms (CV) of **nBuBTDC** and **iBuBTDC**. It is referenced to the Ferrocenium/Ferrocene (Fc^+/Fc) redox couple, where the HOMO of Fc is assigned to be -4.8 eV relative to the vacuum level.

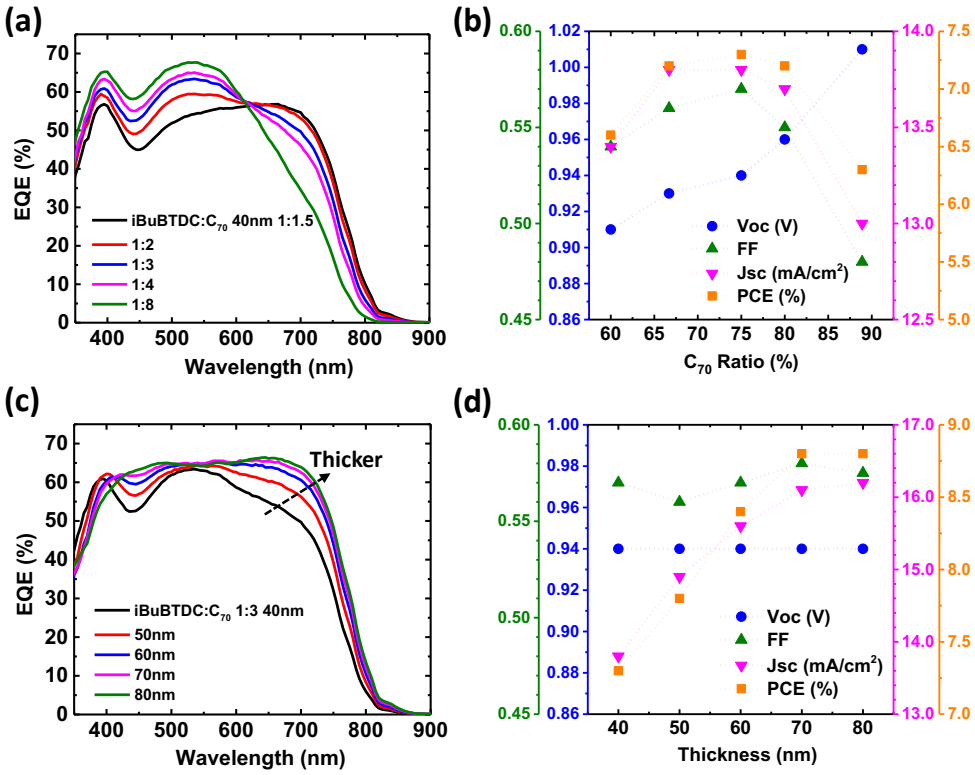


Figure S2. Optimization of the iBuBTDC:C_{70} cells. a)/c)External quantum efficiency (*EQE*) and b)/d) device parameter plots with different donor:acceptor ratios and active layer thicknesses. The active layer thickness of a) and b) is fixed at 40 nm; the D:A ratio of c) and d) is fixed at 1:3.

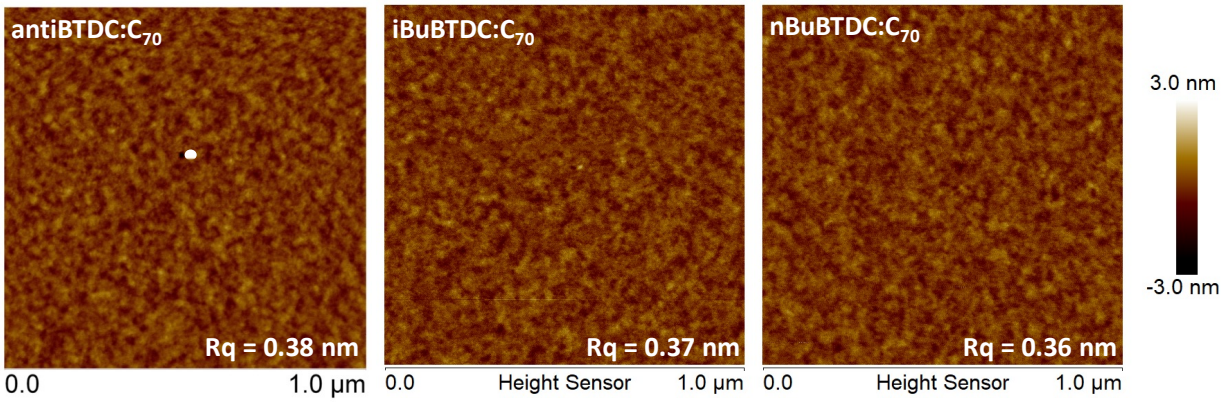


Figure S3. Atomic force microscopy (AFM) images of the three d-a-a':C_{70} blend thin films. R_q refers to the mean square roughness.

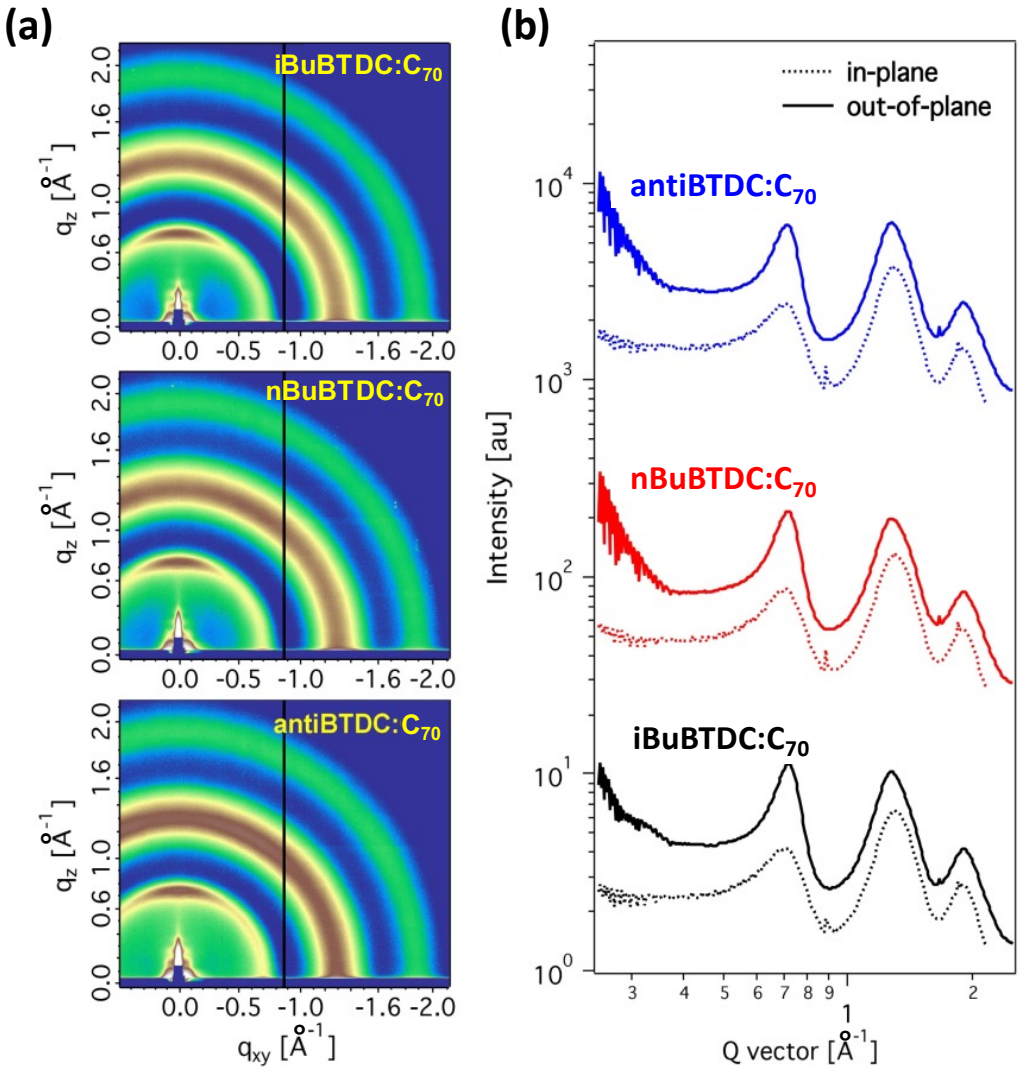


Figure S4. a) Two-dimensional grazing incidence X-ray diffraction (GIXD) scattering patterns of d-a-a':C_{70} 1:3 blend thin films; and b) the corresponding line cut profiles.

Table S1. Computed lowest-energy electronic transition ($S_1 \leftarrow S_0$) parameters.

Dye	λ_{calc} (nm)[a]	HUMO/ LUMO (eV)[b]	f[c]	MO composition[c]
antiBTDC	676	-5.36/-3.33	1.12	98% HOMO→LUMO 2% HOMO−1→LUMO
iBuBTDC	676	-5.33/-3.33	1.09	98% HOMO→LUMO 2% HOMO−1→LUMO
nBuBTDC	678	-5.33/-3.33	1.10	98% HOMO→LUMO 2% HOMO−1→LUMO

[a] Calculated $S_1 \leftarrow S_0$ transition energy levels.

[b] Oscillator strengths.

[c] Molecular orbital (MO) compositions in terms of the corresponding contribution.

Table S2. Physical parameters of antiBTDC, iBuBTDC and nBuBTDC.

Dye	λ_{max} (nm)	$\lambda_{onset, film}$ (nm)	ΔE_{opt} (eV)[c]	HOMO (eV)[d]	LUMO (eV)[e]	ΔE_{CV} (eV)[g]	T_d (°C)[h]
antiBTDC	612[a]	815	1.52	-5.40	-3.88	1.52	331
iBuBTDC	630[b]	809	1.53	-5.35[f]	-3.83[f]	1.52	339
nBuBTDC	630[b]	809	1.53	-5.35[f]	-3.83[f]	1.52	341

[a] Measured in CH_2Cl_2 solution.

[b] Measure in $CHCl_3$ solution.

[c] Optical bandgap estimated from the film absorption onset.

[d] Highest occupied molecular orbital (HOMO) level measured in CH_2Cl_2.

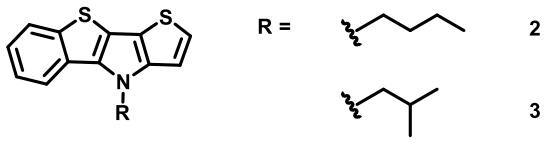
[e] Lowest unoccupied molecular orbital (LUMO) Measured in THF.

[f] Measured in CH_2ClCH_2Cl.

[g] Electrochemical bandgaps, calculated from CV.

[h] Decomposition temperature, obtained by thermogravimetric analysis (TGA).

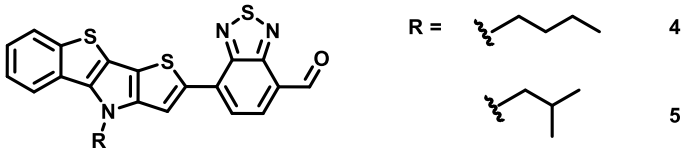
Procedures and characterizations of new compounds.



Synthesis of 4-(n-butyl)-4H-benzo[4,5]thieno[3,2-b]thieno[2,3-d]pyrrole (2)

A solution of **1** (5.13 g, 13.7 mmol), sodium *t*-butoxide (10.5 g, 0.11 mol), $Pd(dba)_2$ (776 mg, 1.37 mmol), and dppf (3.04 g, 5.48 mmol) in toluene (300 mL) was stirred at room temperature for 30 min. To the resulting solution was added *n*-butyl-1-amine (1.62 mL, 16.4 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 **4** as a pale yellow solid (3.6 g, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.90-7.84 (m, 2H), 7.44-7.40 (m, 1H), 7.31-7.26 (m, 1H), 7.22 (d, *J* = 5.2 Hz, 1H), 7.10 (d, *J* = 5.2 Hz, 1H), 4.53-4.50 (m, 2H), 1.97-1.90 (m, 2H), 1.47-1.38 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 146.5, 141.8, 137.3, 128.3, 124.9, 124.8, 124.5, 123.4, 119.5, 115.3, 114.4, 111.6, 47.9, 33.6, 20.7, 14.2; IR (KBr) *v* 3100, 3079, 3051, 2956, 2929, 2870, 1590, 1518, 1490, 1469, 1427, 1406, 1385, 1369, 1356, 1300, 1288, 1265, 1236, 1162, 1148, 1133, 1111, 1092, 1077, 1027, 846, 794, 774, 747, 723, 709; M. p.:135-137 °C; HRMS (FAB^+) m/z calcd for $C_{16}H_{15}NS_2$: 285.0646, found 285.0641.

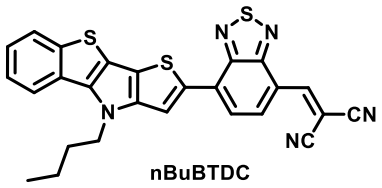
4-(isobutyl)-4H-benzo[4,5]thieno[3,2-b]thieno[2,3-d]pyrrole (3): using **1** (5.13 g, 13.7 mmol), sodium *tert*-butoxide (10.5 g, 0.11 mol), $Pd(dba)_2$ (776 mg, 1.37 mmol), and dppf (3.04 g, 5.48 mmol), 2-methylpropan-1-amine (isobutylamine) (1.63 mL, 16.4 mmol) and toluene (300 mL) to afford **12** as a pale yellow solid (3.55 g, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.87-7.84 (m, 2H), 7.44-7.40 (m, 1H), 7.30-7.26 (m, 1H), 7.22 (d, *J* = 5.6 Hz, 1H), 7.09 (d, *J* = 4.8 Hz, 1H), 4.30 (d, *J* = 8.0 Hz, 2H), 2.38-2.31 (m, 1H), 1.00 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 146.9, 141.9, 137.5, 128.4, 124.9, 124.8, 124.5, 123.4, 119.5, 115.2, 114.5, 111.9, 55.5, 30.9, 20.4; IR (KBr) *v* 3101, 3079, 3050, 2958, 2928, 2869, 1590, 1516, 1490, 1468, 1446, 1426, 1407, 1387, 1356, 1296, 1268, 1252, 1216, 1163, 1135, 1093, 1076, 1058, 1025, 948, 925, 904, 847, 818, 800, 748, 723, 709; M. p.: 109-111 °C; HRMS (FAB^+) m/z calcd for $C_{16}H_{15}NS_2$: 285.0646, found 285.0645.



Synthesis of 7-(4-(n-butyl)-4H-benzo[4,5]thieno[3,2-b]thieno[2,3-d]pyrrol-2-yl)benzo[c][1,2,5] thiadiazole-4-carbaldehyde (4)

To a solution of compound **2** (2.85 g, 10 mmol) in THF (100 mL) was added dropwise *n*-butyllithium (19 mL, 1.6 M in hexane) at -78 °C. After stirring for 1 hour, tributyltin chloride (5.5 mL, 20 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 **2** (10 mmol), 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (2.43 g, 10 mmol), and $Pd(PPh_3)_2Cl_2$ (702 mg, 1.0 mmol) in toluene (100 mL) was stirred and heated at reflux temperature under argon for 5 hours to afford **4** as a purple solid (1.2 g, 36%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.68 (s, 1H), 8.58 (s, 1H), 8.18 (d, *J* = 7.2 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H),7.92-7.85 (m, 2H), 7.46-7.42 (m, 1H), 7.36-7.32 (m, 1H), 4.60 (t, *J* = 7.2 Hz, 2H), 2.02-1.99 (m, 2H), 1.52-1.46 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 153.9, 152.2, 146.7, 142.5, 139.2, 136.6, 134.3, 133.0, 127.0, 124.7, 124.6, 124.5, 123.9, 122.6, 119.4, 118.3, 114.9, 114.4, 47.4, 33.0, 20.2, 13.8; IR (KBr) *v* 3051, 2953, 2866, 2837, 1683, 1666, 1589, 1567, 1538, 1522, 1495, 1468, 1428, 1398, 1358, 1327, 1259, 1230, 1203, 1179, 1148, 1133, 1088, 1062, 1011, 931, 891, 856, 839, 810, 803, 775, 750, 723; M. p.: 246-248 °C; HRMS (FAB^+) m/z calcd for $C_{23}H_{17}N_3OS_3$: 447.0534, found 447.0542.

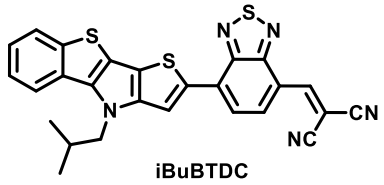
7-(4-(isobutyl)-4H-benzo[4,5]thieno[3,2-b]thieno[2,3-d]pyrrol-2-yl)benzo[c][1,2,5]thiadiazole-4-carbaldehyde (5): A mixture of stannylated **3** (10.5 mmol), 7-bromobenzo[*c*][1,2,5]thiadiazole-4-carbaldehyde (2.43 g, 10 mmol), and $Pd(PPh_3)_2Cl_2$ (702 mg, 1.0 mmol) in toluene (100 mL) was stirred and heated at reflux temperature under argon for 5 hours to afford **5** as a purple solid (2.4 g, 72%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.69 (s, 1H), 8.57 (s, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.0 Hz, 1H), 7.90-7.86 (m, 2H), 7.46-7.42 (m, 1H), 7.36-7.34 (m, 1H), 4.39 (d, *J* = 7 Hz, 2H), 2.45-2.38 (m, 1H), 1.07 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.4, 153.9, 152.2, 147.1, 142.5, 139.4, 136.6, 134.3, 132.9, 127.1, 124.7, 124.6, 124.5, 123.9, 122.7, 119.4, 118.2, 115.2, 114.5, 55.0, 30.3, 20.3; IR (KBr) *v* 3013, 2963, 1804, 1673, 1537, 1516, 1489, 1465, 1402, 1352, 1338, 1272, 1260, 1231, 1199, 1184, 1155, 1102, 1064, 1052, 1012, 953, 926, 909, 861, 836, 818, 792, 782, 741, 722; M. p.: 296-298 °C; HRMS (FAB^+) m/z calcd for $C_{23}H_{17}N_3OS_3$: 447.0534, found 447.0530.



nBuBTDC

Synthesis of nBuBTDC

A mixture of **4** (250 mg, 0.56 mmol), malononitrile (55 mg, 0.84 mmol) and 3 drops of triethylamine was stirred at room temperature in $CHCl_3$ (10 mL) under N_2 for 20 minutes. The reaction mixture was directly precipitated with EA. The crude product was washed with CH_2Cl_2, EA and pentane to afford **nBuBTDC** as a blue-violet solid (250 mg, 90 %). ^{1}H NMR (400 MHz, CD_2ClCD_2Cl) δ 8.73 (s, 1H), 8.71 (d, J = 8.4 Hz, 1H), 8.51 (s, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.91-7.89 (m, 2H), 7.49-7.47 (m, 1H), 7.41-7.37 (m, 1H), 4.58 (brs, 2H), 2.05-1.99 (m, 2H), 1.52-1.47 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H); ^{13}C NMR could not be recorded due to the low solubility of **nBuBTDC**. IR (KBr) v 3094, 3050, 2956, 2217, 1676, 1571, 1523, 1429, 1415, 1337, 1270, 1230, 1160, 1079, 1062, 1040, 1027, 934, 895, 862, 848, 831, 798, 747, 720; M. p.: 314 °C (DSC); HRMS (MALDI) m/z calcd for $C_{26}H_{17}N_5S_3$: 495.0646, found 495.0660.



iBuBTDC

Synthesis of **iBuBTDC**

A mixture of **5** (250 mg, 0.56 mmol), malononitrile (55 mg, 0.84 mmol) and 3 drops of triethylamine was stirred at room temperature in $CHCl_3$ (10 mL) under N_2 for 20 minutes. The reaction mixture was directly poured into methanol. The precipitate was purified by flash column with $CHCl_3$ as eluent to afford **iBuBTDC** as a blue-violet solid (250 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 6.8 Hz, 1H), 8.70 (s, 1H), 8.53 (s, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.87-7.83 (m, 2H), 7.44-7.42 (m, 1H), 7.37-7.35 (m, 1H), 4.35 (d, J = 7.2 Hz, 2H), 2.42-2.38 (m, 1H), 1.08 (d, J = 6.4 Hz, 6H); ^{13}C NMR could not be recorded due to the low solubility of **iBuBTDC.** IR (KBr) v 3093, 2961, 2218, 1849, 1732, 1644, 1571, 1536, 1519, 1463, 1428, 1399, 1337, 1271, 1230, 1165, 1102, 1080, 1064, 1040, 1027, 932, 888, 860, 845, 827, 793, 748, 719, 706; M. p.: 316 °C (DSC); HRMS (MALDI) m/z calcd for $C_{26}H_{17}N_5S_3$: 495.0646, found 495.0620.

[1] X. Che, C.-L. Chung, X. Liu, S.-H. Chou, Y.-H. Liu, K.-T. Wong, S. R. Forrest, Advanced Materials 2016, 28, 8248.