Supporting Information

D-π-A-π-D type benzothiadiazole-triphenylamine based small molecules containing cyano on π-bridge for solution-processed organic solar cells with high open-circuit voltage†

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1. Cyclic voltammetry curves of BDCTBT and BDETBT

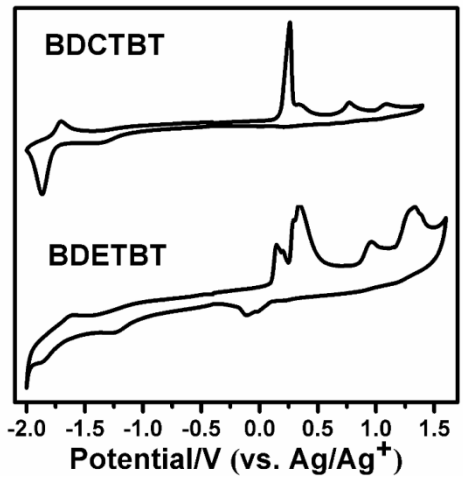

Fig. S1 Cyclic voltammetry curves of **BDCTBT** (top) and **BDETBT** (bottom) film on glass carbon electrode in 0.1 M Bu_4NBF_4/MeCN solution at scan rate of 100 $mV \cdot s^{-1}$.

2. Synthetic procedures

All reagents were purchased directly from commercial resource and used as received without further purification, unless noted otherwise. Tetrahydrofuran and toluene were dried by distillation from metallic sodium/benzophenone under nitrogen atmosphere before use. All reactions were carried out under an air atmosphere unless otherwise stated.

2-(4-bromophenyl)-3-[4-(N,N-diphenylamino)phenyl]-acrylonitrile (1) A solution of NaOH (0.14 g, 3.5 mmol) in 5 mL EtOH was added dropwise to the mixture of 4-(N,N-diphenylamine)-benzaldehyde (0.81 g, 3.0 mmol) and 4-bromobenzyl cyanide (0.69 g, 3.5 mmol) in ethanol (50 mL) at room temperature. After being stirred for 40 h, the yellow solid was filtered and washed by 3 x 150 mL water. The resulting solid was dried to afford compound **1** (1.2 g, 89%) without further purification. M.p.: 163-164 °C; ^{1}H-NMR(400MHz, $CDCl_3$, ppm): δ 7.77 (d, *J* = 8.8 Hz, 2H), 7.49-7.56 (m, 4H), 7.40 (s, 1H), 7.32 (t, 4H), 7.11-7.17 (m, 6H), 7.04 (d, *J* = 8.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 150.23, 146.51, 142.03, 134.08, 132.13, 130.81, 129.64, 127.18, 126.02, 125.84, 124.57, 122.62, 120.69, 118.46, 106.38; MALDI-TOF HRMS: 450.0752[M^+] (calcd for $C_{27}H_{19}N_2Br$: 450.0732).

N-{4-[2-(4-Bromophenyl)vinyl]phenyl}-diphenylamine (2) The mixture of N,N-diphenyl-4-iodoaniline (0.37 g, 1.0 mmol), 4-bromostyrene (0.19 mL, 0.27 g, 1.5 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), Na_2CO_3 (0.16 g, 1.5 mmol) and tetrabutyl ammonium bromide (TBAB, 0.32 g, 1.0 mmol) in 5 mL DMF was stirred at 60 °C under nitrogen atmosphere for 36 h. After being cooled to the room temperature, the

reaction mixture was poured into water (50 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3×20 mL), and the combined organic phases were washed with 20 mL brine and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 5:1) to obtain yellow powder. Then, the residue was washed with petroleum ether to afford pure compound **2** (0.20 g, 47%). M.p.: 183-185 °C; ^{1}H-NMR (400MHz, $CDCl_3$, ppm): δ 7.45 (d, *J* = 8.6 Hz, 2H), 7.36 (t, *J* = 8.6 Hz, 4H), 7.26 (t, *J* = 7.8 Hz, 4H), 7.11 (d, *J* = 7.8 Hz, 4 H), 7.06-7.02 (m, 5H), 6.91 (d, *J* = 16.4 Hz, 1H).[1]

2-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)phenyl]-3-[4-(N,N-diphenylamino)phenyl]-acrylonitrile (**D1**) A solution of compound 1 (2.3 g, 5.0 mmol), bis(pinacolato)diborane (1.4 g, 5.5 mmol), $Pd(PPh_3)_2Cl_2$ (0.18 g, 0.25 mmol), PPh_3 (0.13 g, 0.50 mmol) and KOAc (1.5 g, 15 mmol) in dry toluene (50 mL) was refluxed at 120 °C under nitrogen atmosphere for 24 h. After being cooled to the room temperature, the mixture was poured into water (100 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3×50 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 5:1) to afford compound **D1** as an orange solid (2.0 g, 81%). M.p.: 171-174 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.49 (s, 1H), 7.32 (t, 4H), 7.10-7.17 (m, 6H), 7.05 (d, *J* = 8.8Hz, 2H), 1.36 (s, 12H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 150.09, 146.58, 142.18, 137.52, 135.39, 130.83, 129.59, 129.54, 126.32, 125.77, 124.82, 124.44, 120.79, 118.69, 107.58, 84.01, 24.90; MALDI-TOF HRMS: 498.2490 [M^+] (calcd for $C_{33}H_{31}BN_2O_2$: 498.2479).

N-{4-{2-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)phenyl}vinylphenyl}-diphenylamine (**D2**) A solution of compound **2** (0.85 g, 2.0 mmol), bis(pinacolato)diborane (0.56 g, 2.2 mmol), $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol) and KOAc (0.59 g, 6.0 mmol) in dry toluene (50 mL) was refluxed at 120 °C under nitrogen atmosphere for 24 h. After being cooled to the room temperature, the mixture was poured into water (100 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3×50 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 10:1) to afford compound **D2** as a yellow solid (0.57 g, 60%). M.p.: 76-79 °C; ^{1}H-NMR(400 MHz, $CDCl_3$, ppm): δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.15-7.10 (m, 5H), 7.06-6.98 (m, 5H), 1.35 (s,

12H). ^{13}C-NMR(100 MHz, $CDCl_3$, ppm) δ147.55, 147.53, 140.36, 135.15, 131.32, 129.29, 129.14, 127.48, 126.94, 125.59, 124.57, 123.47, 123.10, 83.74, 24.88; MALDI-TOF HRMS: 473.2504[M^+] (calcd for $C_{33}H_{31}BN_2O_2$: 473.2526).

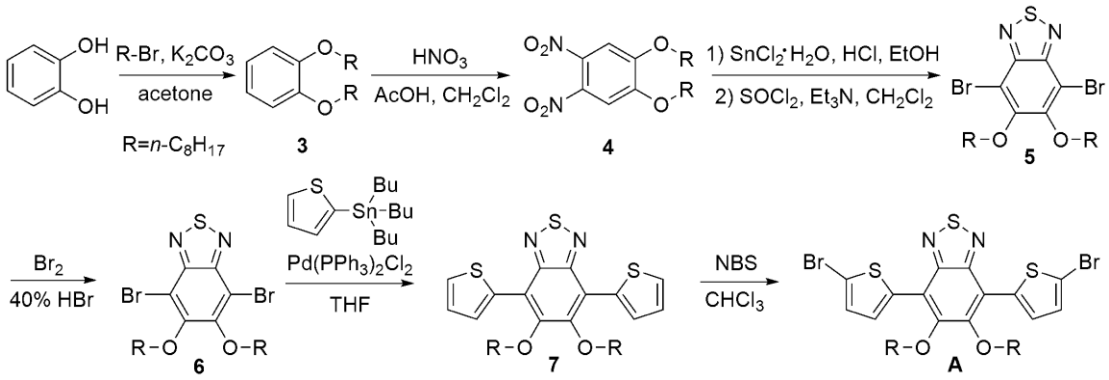

Fig. S2 Synthetic route for compound **A**

1,2-Bis(octyloxy)benzene (3) Catechol (1.1 g, 10 mmol), 1-bromooctane (4.8 g, 25 mmol) and K_2CO_3 (4.1 g, 30 mmol) were mixed in acetone (50 mL) under nitrogen atmosphere and the mixture was refluxed at 65 °C for 60 h. After being cooled to the room temperature, the water (200 mL) was added. Then, the mixture was extracted with ethyl acetate (3×50 mL); the combined organic layers was washed with brine and dried over anhydrous Na_2SO_4. The crude product was obtained by removing organic solvent under reduced pressure and purified through silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 10:1) to afford compound **3** as a colorless oil (2.6 g, 78%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 6.87 (s, 2H), 3.98 (t, *J* = 6.6 Hz, 4H), 1.88–1.77 (m, 4H), 1.49–1.28 (m, 20H), 0.88 (t, *J* = 6.6 Hz, 6H)

1,2-Dinitro-4,5-bis(octyloxy)benzene (4) A 65% nitric acid (10 mL) was added dropwise to the solution of compound 3 (3.3 g, 10 mmol) in acetic acid (70 mL) and CH_2Cl_2 (70 mL) at 0 °C. After being stirred at room temperature for 1 h, fuming nitric acid (25 mL) was added dropwise to the mixture. The reaction mixture was warmed up to the room temperature and stirred for 50 h. Then, the resulting mixture was slowly poured into ice-water (400 mL) and the CH_2Cl_2 layer was separated. The organic layer was washed by 3×150 mL water, 150 mL saturated $NaHCO_3$ solution and 50 mL brine, respectively, and dried over anhydrous Na_2SO_4. After the organic solvent was evaporated under reduced pressure, the crude product was recrystallized from EtOH to afford a light yellow solid (3.8 g, 90%). M.p.: 80-83 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.29 (s, 2H), 4.10 (t, *J* = 6.6 Hz, 4H), 1.91-1.84 (m, 4H), 1.50-1.44 (m, 4H), 1.39-1.30 (m, 16H), 0.89 (t, *J* = 6.6 Hz, 6H).

5,6-Bis(octyloxy)-benzo-2,1,3-thiadiazole (5) Concentrated hydrochloric acid (12 mL) was added in one portion to the mixture of compound **4** (0.85 g, 2.0 mmol)

and $SnCl_2 \cdot 2H_2O$ (3.6 g, 16 mmol) in EtOH (30 mL) at room temperature under nitrogen atmosphere. After being refluxed at 85 °C for 18 h, the mixture was completely cooled to the room temperature. The white solid was filtered and washed by 3×50 mL water and 50 mL MeOH. The resulting solid was dried at room temperature under vacuum condition and the crude 4,5-bis(octyloxy)-benzene-1,2 -diaminium chloride was used directly without further purification (0.57 g, 67%). To the mixture of triethylamine (1.4 mL, 1.0 g, 10 mmol) and 4,5-bis(octyloxy)-benzene-1,2-diaminium chloride (0.43 g, 1.0 mmol) in CH_2Cl_2 (20 mL) was dropwise added a solution of $SOCl_2$ (0.15 mL,0.24 g, 2.0 mmol) in 5 mL CH_2Cl_2 at room temperature under nitrogen atmosphere. After being refluxed at 50 °C for 6 h, the organic solvent was evaporated under reduced pressure. Then, the crude product was purified by silica column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 1:1) to afford compound **5** as a white solid (0.20 g, 52%). M.p.: 96-98 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.13 (s, 2H), 4.10 (t, *J* = 6.6 Hz, 4H), 1.94-1.87 (m, 4H), 1.58-1.48 (m, 4H), 1.42-1.30 (m, 16H), 0.89 (t, *J* = 6.6 Hz, 6H).

4,7-Dibromo-5,6-bis(octyloxy)-benzo-2,1,3-thiadiazole (6) A solution of bromine (0.15 mL, 0.48 g, 3.0 mmol) in 5 mL 40% hydrobromic acid was added dropwise to the mixture of compound **5** (0.39 g, 1.0 mmol) in 10 mL 40% hydrobromic acid at room temperature. After being refluxed at 120 °C for 6 h, the excess bromine was neutralized completely by saturated $NaHSO_3$ solution. Then, the reaction mixture was extracted by CH_2Cl_2 (3×50 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/ethyl acetate (v:v, 20:1) to afford compound **6** as a white solid (0.50 g, 90%). M.p.: 44-45 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 4.16 (t, *J* = 6.6 Hz, 4H), 1.92-1.85 (m, 4H), 1.58-1.50 (m, 4H), 1.41-1.30 (m, 16H), 0.90 (t, *J* = 6.6 Hz, 6H).

5,6-Bis(octyloxy)-4,7-di(thiophene-2-yl)-benzo-2,1,3-thiadiazole (7) A solution of *n*-BuLi (2.5 M in hexane, 3.2 mL, 8.0 mmol) was added dropwise to the mixture of thiophene (0.48 mL, 0.50 g, 6.0 mmol) in 30 mL dry THF under nitrogen atmosphere at -78 °C and the reaction mixture was stirred at that temperature for 1h. Then, tributylchlorostannane (2.2 mL, 2.6 g, 8.0 mmol) was added to the mixture in one portion. After being stirred at room temperature overnight, the resulting mixture was poured into water (50 mL) and the organic layer was separated. The aqueous layer was extracted with ethyl ether (3×30 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The crude product was obtained by removing organic solvent under reduced pressure and purified by silica column chromatography eluting with petroleum/triethylamine (v:v, 20:1) to afford 2-tri(*n*-butyl)stannylthiophene as a light yellow oil. The 2-tri(*n*-butyl)stannylthiophene (freshly prepared, about 6.0 mmol) and

compound **6** (1.0 g, 1.8 mmol) were dissolved in 30 mL dry THF. After being degassed with nitrogen, to the mixture was added $Pd(PPh_3)_2Cl_2$ (70 mg, 0.1 mmol) and the resulting mixture was heated at 70 °C for 40 h. Then, the organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 4:1) to afford compound **7** as an orange oil (0.96 g, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.43 (dd, J_a = 3.8 Hz, J_b = 1.0 Hz, 2H), 7.52 (dd, J_a = 5.0 Hz, J_b = 1.0 Hz, 2H), 7.22 (dd, J_a = 5.0 Hz, J_b = 3.8 Hz, 2H), 4.07 (t, J = 7.0 Hz, 4H), 1.94-1.85 (m, 4H), 1.58-1.30 (m, 20H), 0.90 (t, J = 6.6 Hz, 6H).

4,7-Bis(5-bromothiophene-2-yl)-5,6-bis(octyloxy)-benzo-2,1,3-thiadiazole (A) The mixture of compound **7** (0.96 g, 1.7 mmol) and N-Bromosuccinimide (NBS, 0.73 g, 4.1 mmol) in 30 mL $CHCl_3$ was stirred for 24 h in dark. Then, the organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 10:1) to afford compound **A** as an orange-red solid (1.1 g, 92%). M.p.: 74-76 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.33 (d, J = 4.0 Hz, 2H), 7.13 (d, J = 4.0 Hz, 2H), 4.10 (t, J = 7.2 Hz, 4H), 1.98-1.90 (m, 4H), 1.47-1.25 (m, 20H), 0.90 (t, J = 6.6 Hz, 6H).

4,7-Bis{5-{4-{2-[4-(N,N-diphenylamino)phenyl]-1-cyanoethenyl}phenyl}-2-thienyl}-5,6,-bis(otcyloxy)-benzo-2,1,3-thiadiazole (BDCTBT) Degassed EtOH (2 mL) and 2 M aqueous Na_2CO_3 (4 mL) were added to the solution of compound **D1** (0.25 g, 0.50 mmol), compound **A** (0.18 g, 0.25 mmol) and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) in 8 mL toluene under nitrogen atmosphere. After being refluxed at 110 ^{o}C for 24 h, the mixture was poured into water (50 mL) and the organic layer was separated. The aqueous layer was extracted with chloroform (3×20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 1:3) to afford compound **BDCTBT** as a red solid (0.28 g, 87%). M.p.: 106-109 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.53 (s, 2H), 7.78 (d, J = 8.8 Hz, 4H), 7.73 (d, J = 8.0 Hz, 4H), 7.67 (d, J = 8.0 Hz, 4H), 7.46-7.44 (m, 4H), 7.20 (t, J = 8.0 Hz, 8H), 7.17-7.10 (m, 12H), 7.05 (d, J = 8.8 Hz, 4H), 4.18 (t, J = 7.0 Hz, 4H), 2.03-1.96 (m, 4H), 1.56-1.30 (m, 20H), 0.88 (t, J = 6.6 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 151.82, 150.81, 150.00, 146.60, 144.47, 141.02, 134.57, 134.30, 134.04, 132.06, 130.73, 129.59, 126.41, 126.11, 126.10, 125.76, 124.44, 123.56, 120.84, 118.64, 117.45, 107.13, 74.57, 31.87, 30.54, 29.63, 29.39, 26.16, 22.73, 14.14; MALDI-TOF HRMS: 1296.5215 [M^+] (calcd for $C_{84}H_{76}N_6O_2S_3$: 1296.5192).

4,7-Bis{5-{4-{2-[4-(N,N-diphenylamino)phenyl]-1-ethenyl}phenyl}-2-thienyl}-5,6,-bis(otcyloxy)-benzo-2,1,3-thiadiazole (BDETBT) Degassed EtOH (2 mL) and 2 M aqueous Na_2CO_3 (4 mL) were added to the solution of compound **D2** (0.24 g,

0.50 mmol), compound **A** (0.18 g, 0.25 mmol) and $Pd(PPh_3)_4$ (15 mg, 0.013 mmol) in 8 mL toluene under nitrogen atmosphere. After being refluxed at 110 ^oC for 24 h, the mixture was poured into water (50 mL) and the organic layer was separated. The aqueous layer was extracted with chloroform (3×20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography eluting with petroleum ether/CH_2Cl_2 (v:v, 2:1) to afford compound **BDETBT** as a red solid (0.28 g, 88%). M.p.: 148-150 °C; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.51 (d, *J* = 4.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 4H), 7.51 (d, *J* = 8.0 Hz, 4H), 7.43 (d, *J* = 4.0 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.26 (t, *J* = 8.0 Hz, 8H), 7.12 (d, *J* = 8.0 Hz, 8H), 7.07-6.98 (m, 12H), 4.17 (t, *J* = 7.0 Hz, 4H), 2.03-1.95 (m, 4H), 1.53-1.29 (m, 20H), 0.89 (t, *J* = 6.0 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 151.75, 150.91, 147.54, 147.47, 145.38, 137.01, 133.67, 133.29, 131.99, 131.43, 129.31, 128.26, 127.42, 126.81, 126.43, 125.99, 124.56, 123.53, 123.10, 122.95, 117.47, 74.51, 31.87, 30.52, 29.62, 29.38, 26.16, 22.72, 14.13; MALDI-TOF HRMS: 1246.5316 [M^+] (calcd for $C_{84}H_{76}N_4O_2S_3$: 1246.5287).

3. ^{1}H-NMR and ^{13}C-NMR spectra

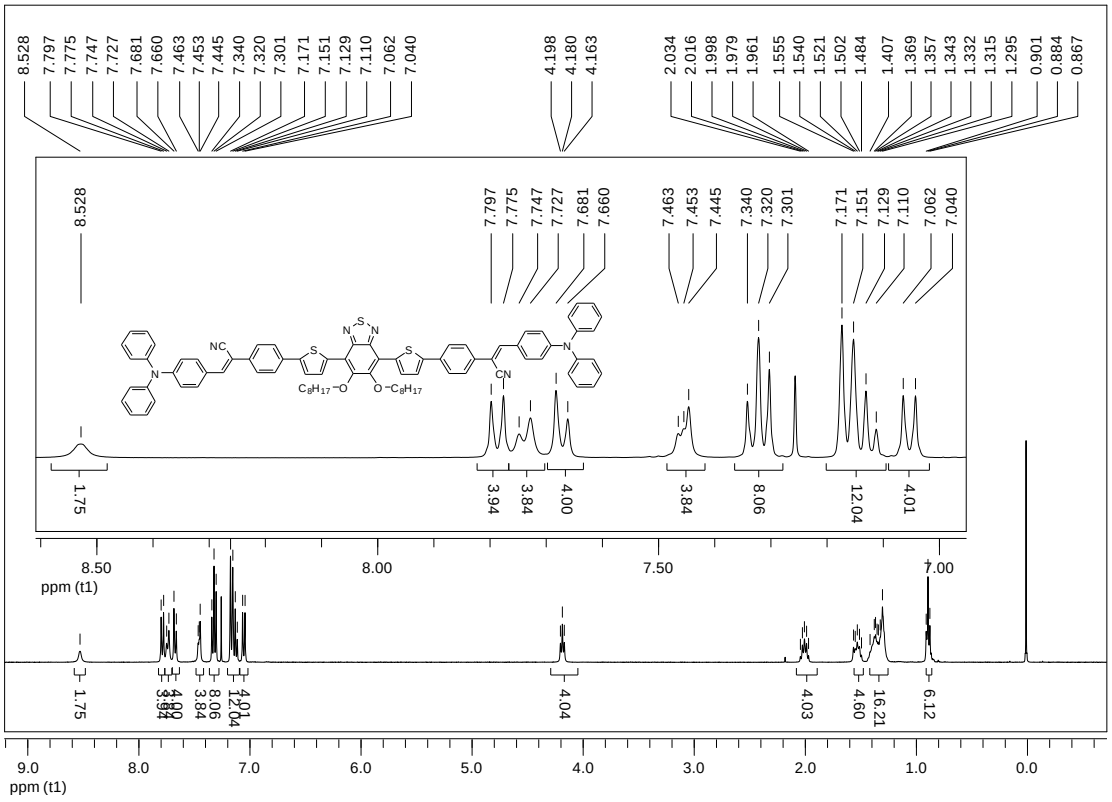

Fig. S3 ^{1}H-NMR spectrum of **BDCTBT**

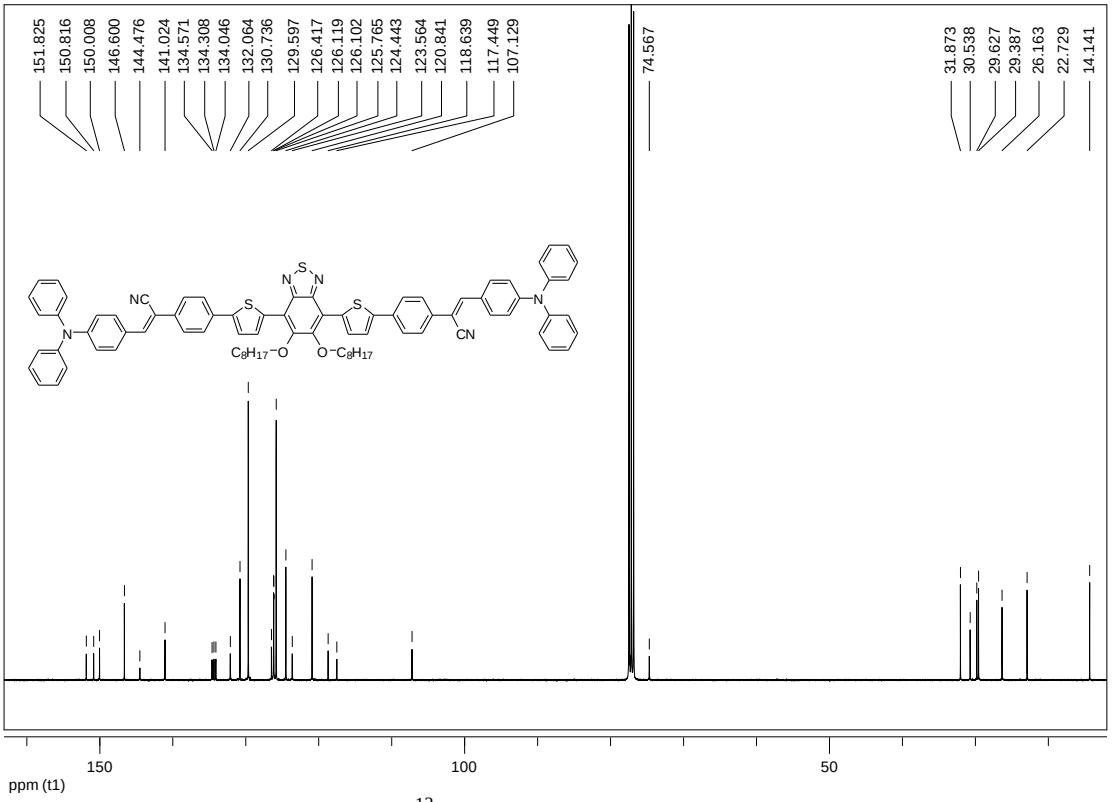

Fig. S4 ^{13}C-NMR spectrum of **BDCTBT**

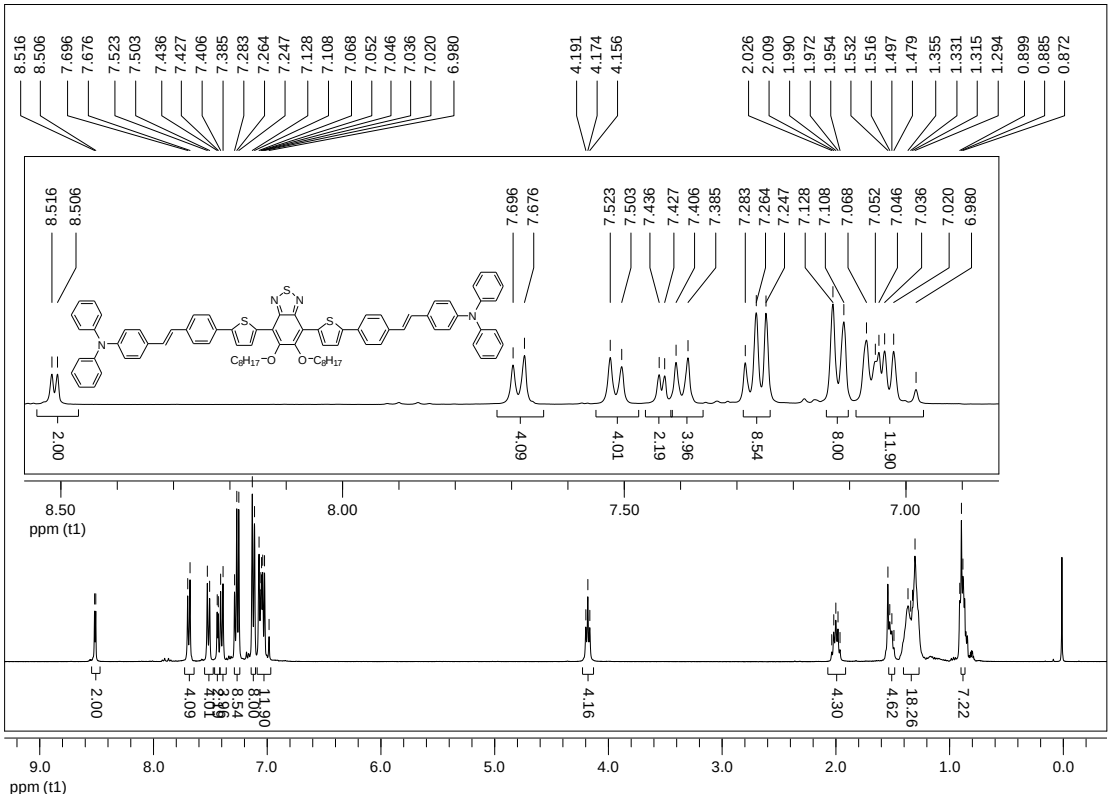

Fig. S5 ^{1}H-NMR spectrum of **BDETBT**

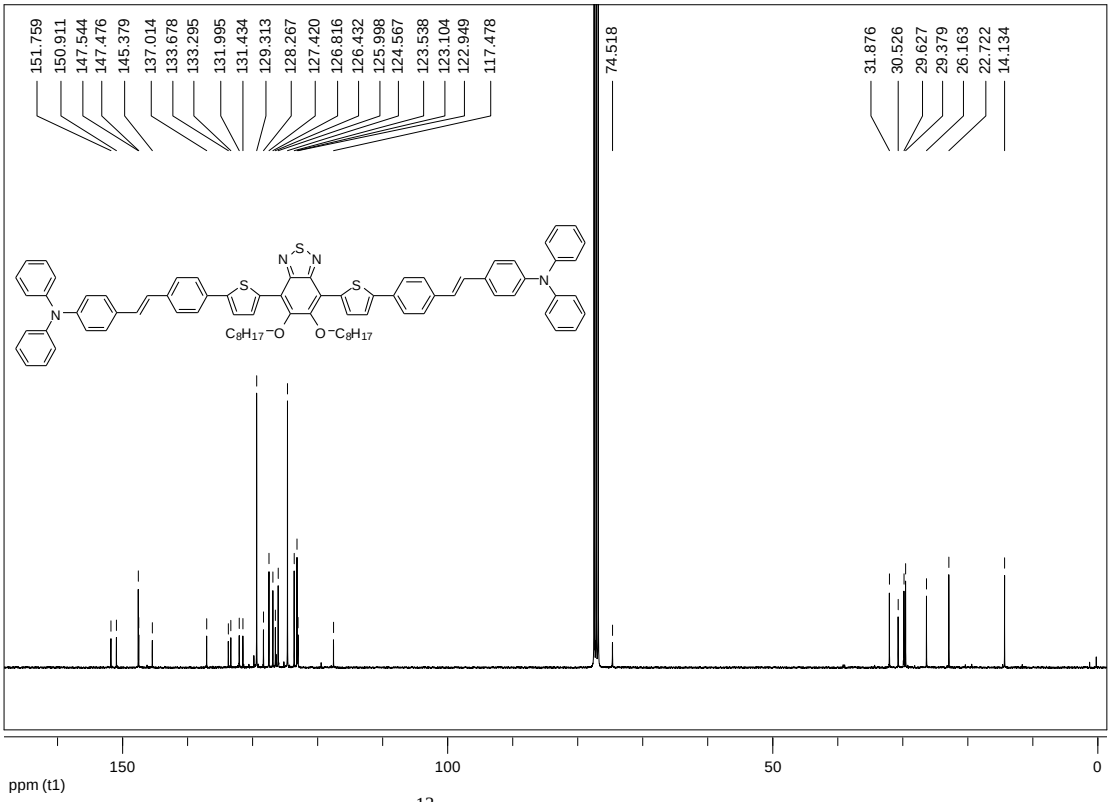

Fig. S6 ^{13}C-NMR spectrum of **BDETBT**

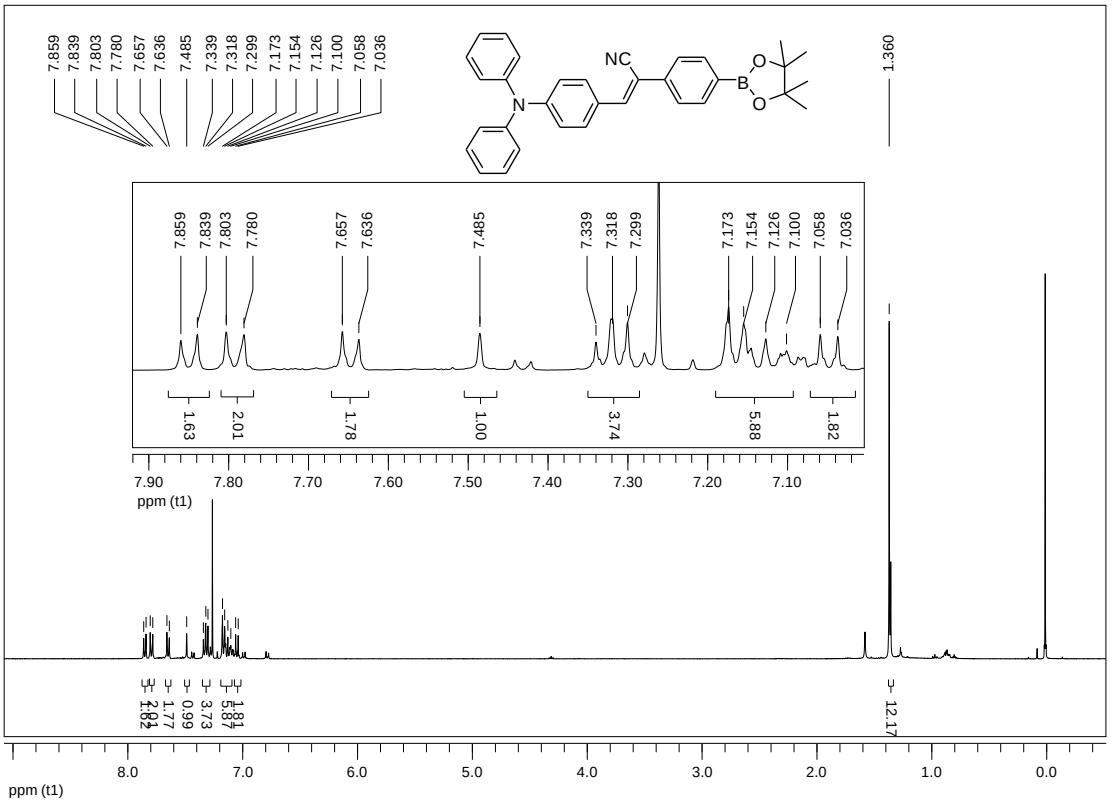

Fig. S7 ^{1}H-NMR spectrum of compound **D1**

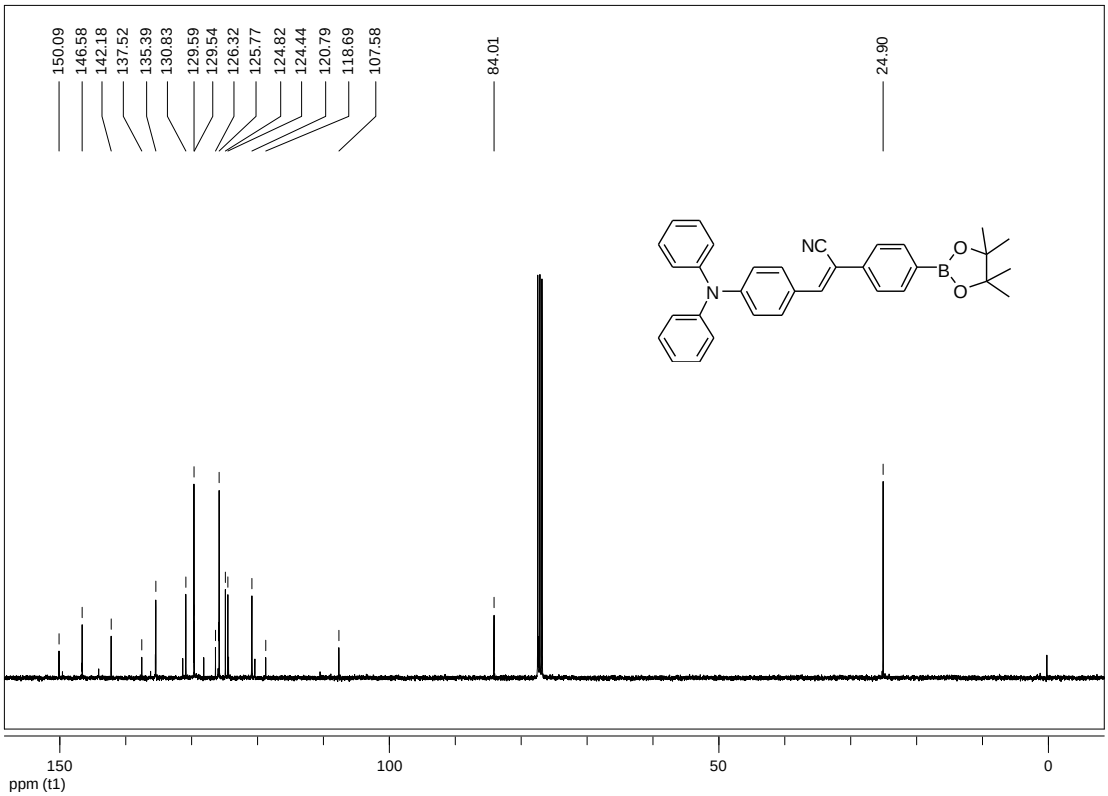

Fig. S8 ^{13}C-NMR spectrum of compound **D1**

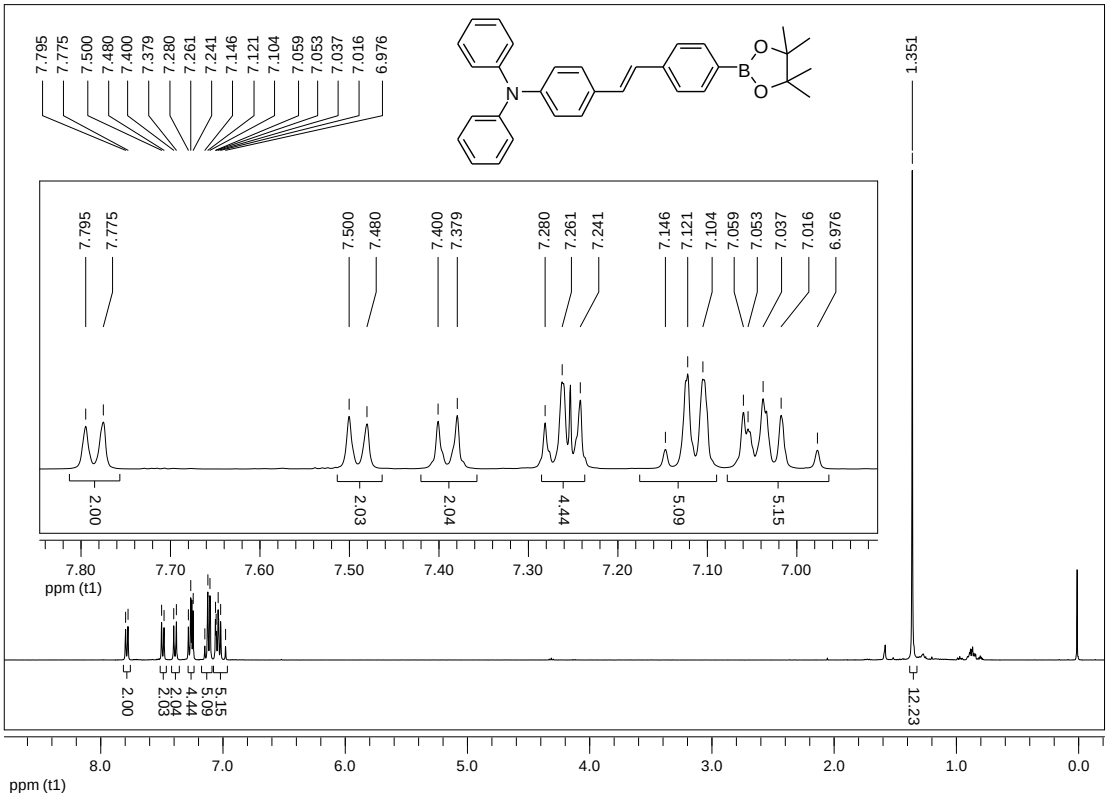

Fig. S9 ^{1}H-NMR spectrum of compound **D2**

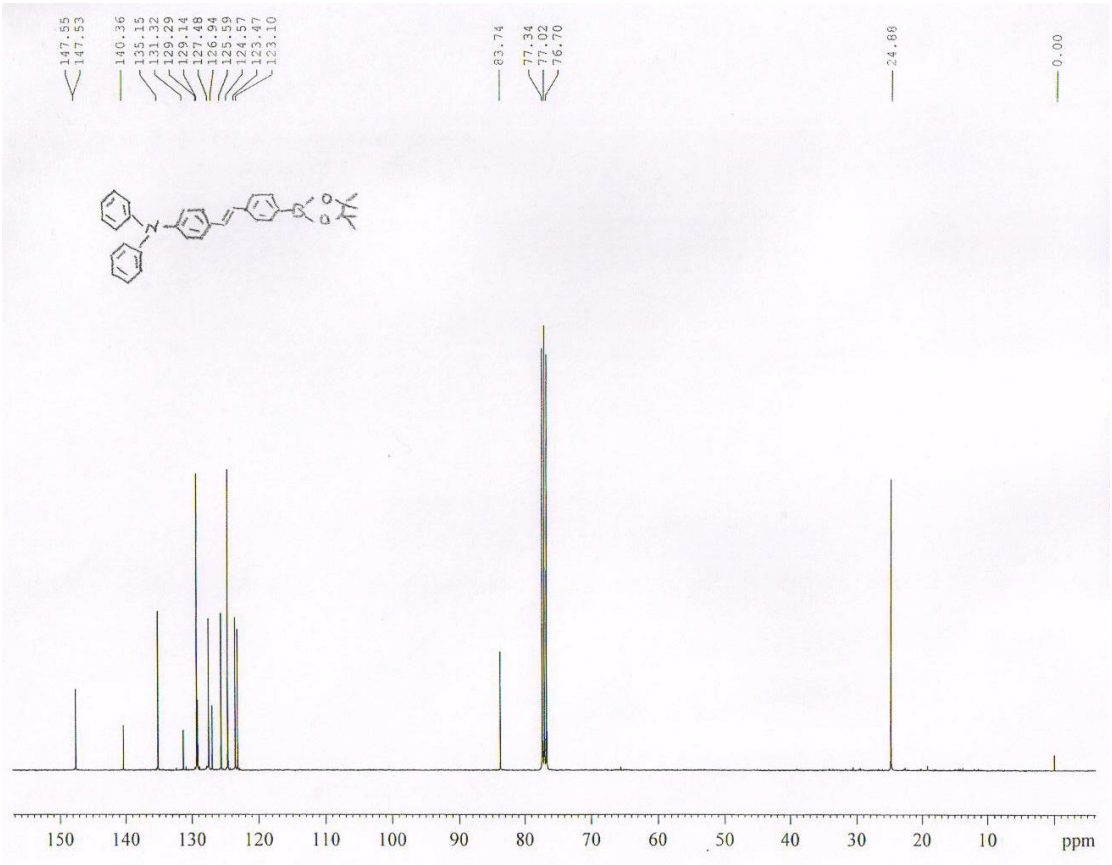

Fig. S10 ^{13}C-NMR spectrum of compound **D2**

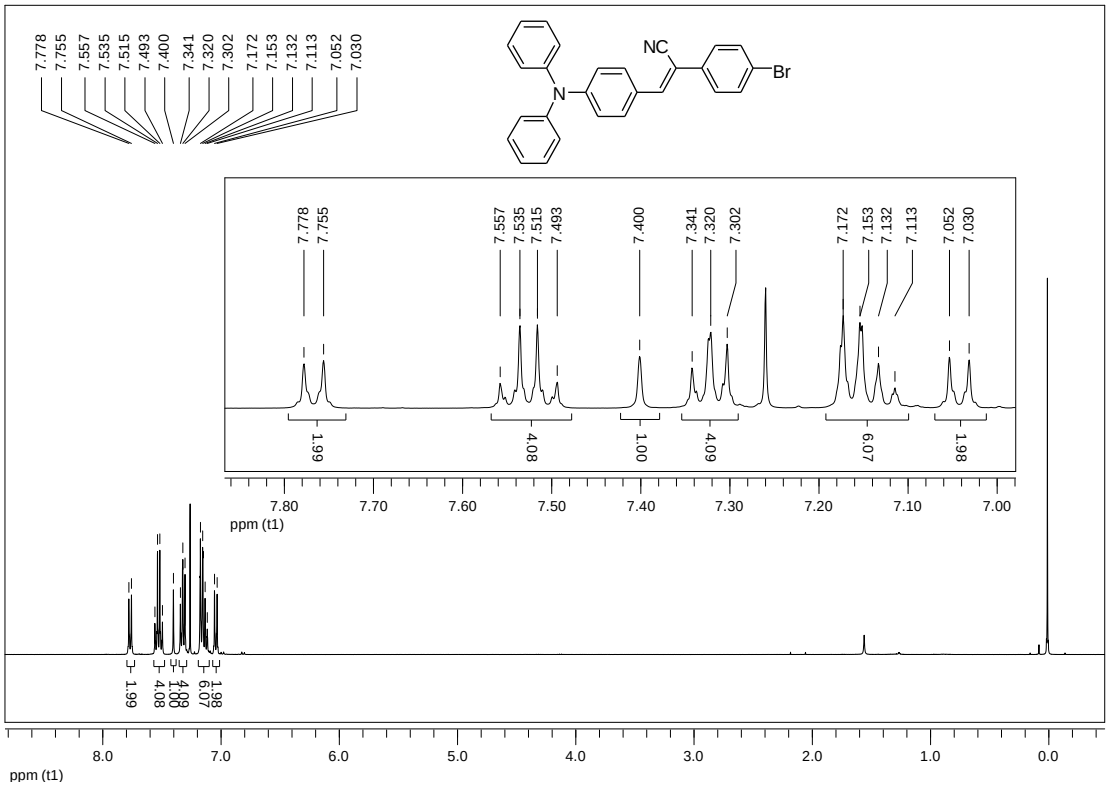

Fig. S11 ^{1}H-NMR spectrum of compound **1**

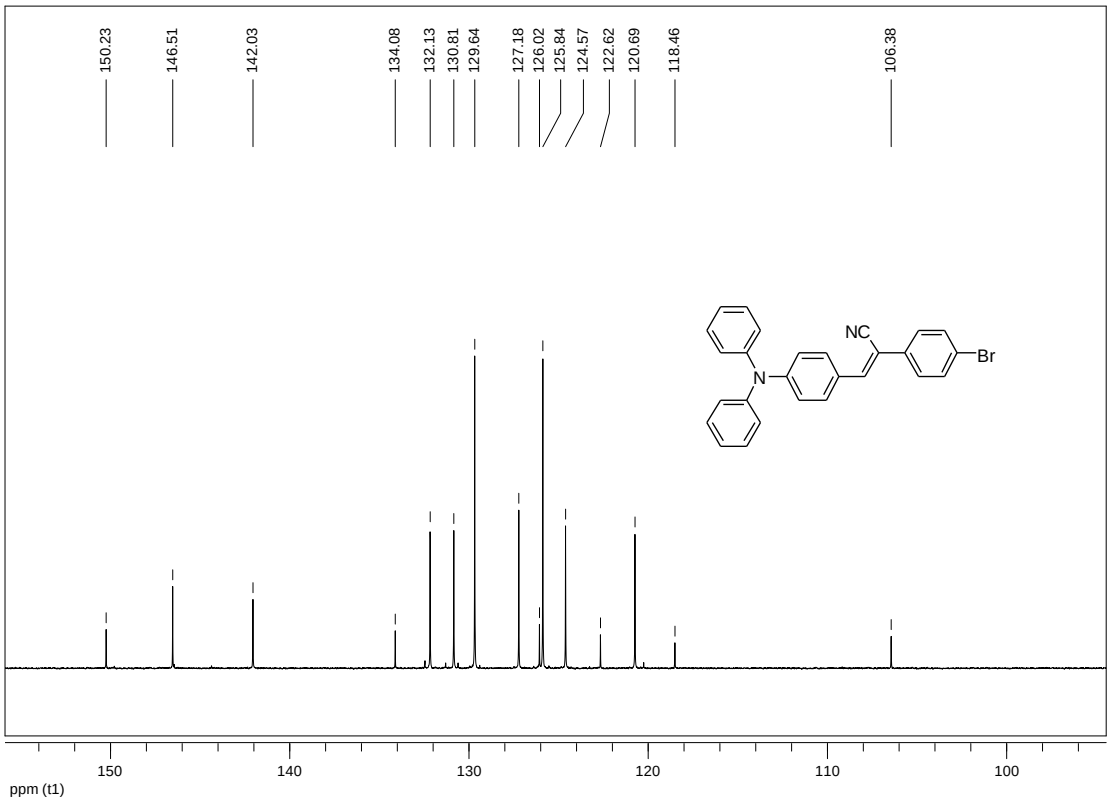

Fig. S12 ^{13}C-NMR spectrum of compound **1**

4. Measurements and characterization

^{1}H-NMR and ^{13}C-NMR spectra were collected on a Bruker AVANCE II 400-MHz spectrometer with $CDCl_3$ as solvent and TMS as the internal standard. The ground-state geometries and electronic structures of **BDCTBT** and **BDETBT** were calculated with Gaussian 09 software, using density functional theory (DFT) based on the Becke's three-parameter gradient-corrected functional (B3LYP) with a polarized 6-31G(d) basis.[2] HRMS data were measured with MALDI Micro MX spectrometer. UV-vis absorption spectra were recorded on a HP8453 UV-vis spectrophotometer at room temperature using a quartz cuvette as container and chloroform as solvent. For the thin film spectra, the materials were firstly dissolved in chloroform, and then spin-casted on glass slide. Fluorescence spectra and fluorescence quenching experiments were carried out with a Shimadzu RF-5301PC spectrofluorometer. Cyclic voltammetry (CV) was performed using a CHI 610D electrochemical workstation from CH Instruments, Inc. On these analyses, the synthesized materials were drop-casted on glass-carbon electrode which was used as the working electrode, and Ag/Ag^{+} electrode (Ag in 0.1 M $AgNO_3$ solution of MeCN) and platinum wire were used as the reference electrode and the count electrode, respectively. Ferrocene-ferrocenium (Fc/Fc^{+}) couple was chosen as internal standard. The energy levels and the electrochemical band gaps of two compounds were calculated from

onset oxidation potentials (E_{ox}) and onset reduction potentials (E_{red}) according to the following equations:

$$HOMO^{CV} = - (E_{ox} - E_{1/2}^{ferrocene} + 4.8)\ eV$$

$$LUMO^{CV} = - (E_{red} - E_{1/2}^{ferrocene} + 4.8)\ eV$$

$$E_g^{CV} = LUMO\text{-}HOMO$$

where E_{ox} and E_{red} are the measured onset potentials relative to Ag/Ag^+. $E_{1/2}^{ferrocene}$ = 0.05 V versus Ag/Ag^+.

5. Device fabrications and characterization

Bulk-heterojunction organic solar cells were fabricated with a conventional device configuration of ITO/PEDOT:PSS/donors:$PC_{61}BM$ (1:2, w/w)/Al. The conductivity of ITO was 20Ω/□ and the ITO-coated glass was ultrasonicated in detergent, acetone, toluene and isopropyl alcohol for 30 min, respectively. After being dried with nitrogen airflow, the ITO substrates were spin-coated a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) at 4000 $rpm \cdot s^{-1}$ for 1 min and subsequently baked at 140 °C for 30 min on a hot plate. The active layer was prepared by spin-coating at 800 $rpm \cdot s^{-1}$ for 1 min with the dichlorobenzene solution of blended small molecules and $PC_{61}BM$ (total concentration of 21 $mg \cdot mL^{-1}$) on the top of ITO/PEDOT:PSS. An aluminum layer was then evaporated onto the surface of the active layer under vacuum (ca. 10^{-4} Pa) to form the negative electrode. Six OSCs were fabricated on one substrate, and the effective area of one cell was the overlap between ITO and aluminum, which was 4 mm^2. *J-V* curves were recorded using a computer-controlled Keithley 2400 Source Measure Unit under AM 1.5G illumination with an intensity of 100 $mW \cdot cm^{-2}$. A controlled OSC with configuration of ITO/PEDOT:PSS/P3HT:$PC_{61}BM$/Al was fabricated and characterized at same conditions.

6. J-V characterization for P3HT:$PC_{61}BM$ blended device

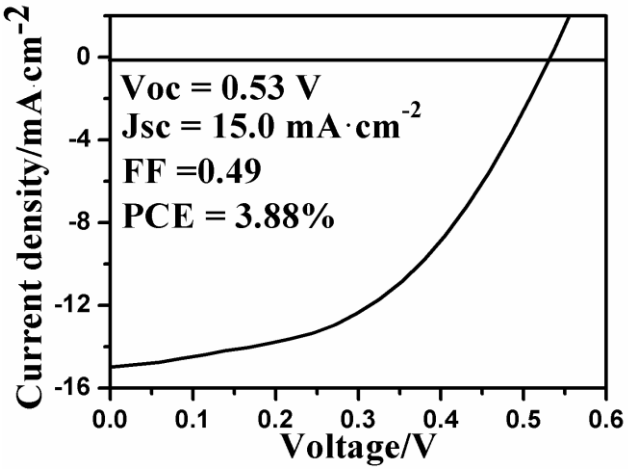

Fig. S13 J-V Characterization of OSC with configuration of ITO/PEDOT:PSS/P3HT:$PC_{61}BM$/Al.

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