Supporting Information

Synthesis of push-pull triarylamine dyes containing 5,6-difluoro-2,1,3-benzothiadiazole units by direct arylation and their evaluation as active material for organic photovoltaics

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1. Experimental procedure

General information. 5-Bromo-2-dicyanovinylthiophene was prepared according to an early reported procedure.[1] Reagents and chemicals from commercial sources were used without further purification. Solvents were dried and purified using standard techniques. Microwave assisted reactions were performed in the cavity of a Biotage Initiator+ system in sealed reactors. Flash chromatography was performed with analytical-grade solvents using Aldrich silica gel (technical grade, pore size 60 Å, 230-400 mesh particle size). Flexible plates ALUGRAM® Xtra SIL G UV254 from MACHEREY-NAGEL were used for TLC. Compounds were detected by UV irradiation (Bioblock Scientific). NMR spectra were recorded with a Bruker AVANCE III 300 (^{1}H, 300 MHz and ^{13}C, 75MHz) or a Bruker AVANCE DRX500 (^{1}H, 500 MHz; ^{13}C, 125 MHz). Chemical shifts are given in ppm relative to TMS and coupling constants J in Hz. UV-vis spectra were recorded with a Perkin Elmer 950 spectrometer. Matrix Assisted Laser Desorption/Ionization was performed on MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer. High-resolution mass spectrometry (HRMS) was performed with a JEOL JMS-700 B/E or a JEOL Spiral-TOF JMS3000. Photoelectron spectroscopy in air (PESA) measurements were recorded using a Riken Keiki PESA spectrometer (Model AC-2) with power settings of 50 nW.

General procedure for the synthesis of 4-Methoxy-N-(4-methoxyphenyl)-N-(4-(5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl) phenyl)aniline (2): To an oven-dried round bottom flask or microwave tube containing a stirring bar, difluorobenzothiadiazole (DFBT) (100 mg, 0.58 mmol) and 4-Bromo-4',4''-dimethoxytriphenylamine (1 and 0.5 eq.), the palladium source (0.058 mmol), the ligand (0.12 mmol), pivalic acid (59 mg, 0.58 mmol) and potassium carbonate (240 mg, 1.7 mmol) were sequentially added before a septum-cap was crimped on the vial/flask to form a seal. Solids were degassed 3 times by vacuum-argon filling cycles. Dry toluene (4 mL) was then added to the reaction mixture before being heated under conventional oil bath or microwave assisted conditions. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM/EP with 4/1 ratio) affording the corresponding product as an orange solid.

Table S1: Reactions conditions used to optimize the preparation of **2**

OMe-Br (eq)	Catalyst	Ligand	Heat source, temp./time	Yield OMe-BT2F (%)
1.0	$Pd(OAc)_2$	$P^tBu_3.HBF_4$	Oil bath 120°C; 16h	20%
0.5	$Pd(OAc)_2$	$P^tBu_3.HBF_4$	Oil bath (120°C; 16h)	33%
0.5	$Pd(OAc)_2$	$P^tBu_3.HBF_4$	μ-wave (150°C; 1h)	36%
0.5	$Pd(OAc)_2$	$P(OMePh)_3$	μ-wave (150°C; 1h)	40%
0.5	$Pd(OAc)_2$	$PCy_3.HBF_4$	μ-wave (150°C; 1h)	76%

Optimized synthesis of 4-Methoxy-N-(4-methoxyphenyl)-N-(4-(5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl) phenyl)aniline (2): To an oven-dried microwave tube containing a stirring bar, difluorobenzothiadiazole (DFBT) (100 mg, 0.58 mmol) and 4-bromo-4',4''-dimethoxytriphenylamine (111 mg, 0.29 mmol, 0.5 eq.), palladium acetate (13 mg, 0.058 mmol), tricyclohexylphosphinetetrafluoroborate (43 mg, 0.12 mmol), pivalic acid (59 mg, 0.58 mmol) and potassium carbonate (240 mg, 1.7 mmol) were sequentially added before a septum-cap was crimped on the vial to seal it. Solids were degassed 3 times by vacuum-argon filling cycles. Dry toluene (4 mL) was then added before exposing the reaction mixture to microwave irradiation for 1 hour at 150 °C. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM/EP with 4/1 ratio) affording the corresponding product as an orange solid (105 mg, 76%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 7.69 – 7.58 (m, 3H), 7.22 – 7.13 (m, 4H), 7.04 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 7.1 Hz, 4H), 3.81 (s, 6H). **^{13}C NMR** (75 MHz, Chloroform-d) δ 156.63, 151.08, 150.98, 150.82, 149.68, 140.27, 131.35, 131.31, 127.61, 121.05, 118.69, 115.01, 55.67. **HRMS** (EI) m/z: Calc for $C_{26}H_{19}F_2N_3O_2S$ (M+), 475.1166; Found, 475.1170.

Synthesis of 4-phenyl-N-(4-biphenylyl)-N-(4-(5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)phenyl)aniline (3): To an oven-dried microwave tube containing a stirring bar, DFBT (100 mg, 0.58 mmol) and N,N-Bis(4-biphenylyl)-N-(4-bromophenyl)amine (138 mg, 0.29 mmol, 0.5 eq.), palladium acetate (13 mg, 0.058 mmol), tricyclohexylphosphinetetrafluoroborate (43 mg, 0.12 mmol), pivalic acid (59 mg, 0.58 mmol) and potassium carbonate (240 mg, 1.7 mmol), were sequentially added and a septum-cap was crimped on the vial to form a seal. The solids were degassed 3 times under vacuum followed by a flow of argon. Dry toluene (4 mL) was added and the reaction mixture was heated under microwave irradiation at 150 °C for 1 hour. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM/EP with 4/1 ratio) affording the corresponding product as a yellowish solid (130 mg, 78%). **^{1}H NMR** (499 MHz, Chloroform-d) δ 7.75 (d, J = 7.9 Hz, 2H), 7.69 (dd, J = 9.0, 7.7 Hz, 1H), 7.63 – 7.55 (m, 8H), 7.45 (t, J = 7.6 Hz, 4H), 7.36 – 7.29 (m, 8H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 150.91, 150.84, 150.81, 148.49, 146.50, 140.62, 136.57, 131.62, 131.60, 128.93, 128.22, 127.18, 126.90, 125.44, 123.60, 122.49, 104.30, 104.14. **HRMS** (EI) m/z: Calc for $C_{36}H_{23}F_2N_3S$ (M+), 567.1581; Found, 567.1577.

5-(7-(4-(Bis(4-methoxyphenyl)amino)phenyl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl) thiophene-2-carbaldehyde (4): To an oven-dried microwave tube containing a stirring bar and compound **2** (110 mg, 0.23 mmol), palladium acetate (4.19 mg, 0.023 mmol), tricyclohexylphosphinetetrafluoroborate (17 mg, 0.046 mmol), pivalic acid (23.6 mg, 0.23 mmol) and potassium carbonate (95.9 mg, 0.69 mmol) were added under a flow of argon and a septum-cap was crimped on the vial to form a seal. Dry toluene (4 mL) and 5-Bromo-2-thiophenecarboxaldehyde (53 mg, 0.28 mmol, 1.2 eq.) were added and the resulting mixture was heated under microwave irradiation at 150 °C for 1 hour. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM) affording the corresponding product as a dark orange solid (35 mg, 26%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 10.02 (s, 1H), 8.31 (d, J = 4.1 Hz, 1H), 7.86 (dd, J = 4.2, 1.1 Hz, 1H), 7.68 (d, J = 7.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 4H), 7.02 (d, J = 8.5 Hz, 2H), 6.91 – 6.84 (m, 4H), 3.82 (s, 6H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 183.20,

156.64, 150.45, 150.38, 149.82, 148.73, 144.58, 144.54, 139.88, 135.74, 131.44, 131.00, 130.92, 127.59, 120.36, 120.12, 118.27, 114.92, 110.02, 55.52. **HRMS** (EI) m/z: Calc for $C_{31}H_{21}F_2N_3O_3S_2$ (M+), 585.0992; Found, 585.0986.

5-(7-(4-(Bis(4-biphenylyl)amino)phenyl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl)thiophene-2-carbaldehyde (5): To an oven-dried microwave tube containing a stirring bar and compound **3** (145 mg, 0.25 mmol), palladium acetate (5.73 mg, 0.025 mmol), tricyclohexylphosphinetetrafluoroborate (18.81 mg, 0.051 mmol), pivalic acid (26 mg, 0.25 mmol) and potassium carbonate (105.9 mg, 0.76 mmol) were added under a flow of argon and a septum-cap was crimped on the vial to form a seal. Dry toluene (4 mL) and 5-Bromo-2-thiophenecarboxaldehyde (58.5 mg, 0.31 mmol) were added and the resulting mixture was heated under microwave irradiation at 150 °C for 1 hour. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM) affording the corresponding product as a red solid (60 mg, 34%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 10.05 (s, 1H), 8.36 (d, J = 3.9 Hz, 1H), 7.90 (d, J = 4.0 Hz, 1H), 7.80 (d, J = 7.8 Hz, 2H), 7.64 – 7.56 (m, 8H), 7.48 – 7.42 (m, 4H), 7.38 – 7.28 (m, 8H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 183.39, 148.84, 146.36, 140.61, 136.83, 135.88, 131.79, 131.76, 131.36, 131.28, 128.97, 128.29, 127.25, 126.94, 125.64, 123.08, 122.18, 77.16. **HRMS** (EI) m/z: Calc for $C_{41}H_{25}F_2N_3OS_2$ (M+), 677.1407; Found, 677.1407.

General procedure for the preparation of 4 and 5 through a "one-pot" reaction: To an oven-dried microwave tube containing a stirring bar, DFBT (1 eq.) and 4-Bromo-4',4''-dimethoxytriphenylamine or N,N-Bis(4-biphenylyl)-N-(4-bromophenyl)amine (0.5 eq.), palladium acetate (0.1 eq.), tricyclohexylphosphinetetrafluoroborate (0.2 eq.), pivalic acid (1 eq.) and potassium carbonate (3 eq.) were sequentially added before a septum-cap was crimped on the vial to seal it. Solids were degassed 3 times by vacuum-argon filling cycles. Dry toluene (4 mL) was then added before exposing the reaction mixture to microwave irradiation for 1 hour at 150 °C. Then, 5-bromo-2-thiophenecarboxaldehyde (1.2 eq.) was directly added to the reaction mixture through the septum and the tube was re-heated at 150°C for 30 minutes. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM/EP with 4/1 ratio) affording the corresponding products, namely **4** (18%) and **5** (17%).

Synthesis of 2-((5-(7-(4-(bis(4-methoxyphenyl)amino)phenyl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl) thiophen-2-yl)methylene)malononitrile (MD-OMe) from 2 by DHA cross-coupling reaction: To an oven-dried microwave tube containing a stirring bar, compound **2** (40 mg, 0.08 mmol) and 5-bromo-2-dicyanovinylthiophene (40 mg, 0.17 mmol), palladium acetate (1.9 mg, 0.008 mmol) ,tricyclohexylphosphinetetrafluoroborate (6.2 mg, 0.016 mmol), pivalic acid (8.6 mg, 0.08 mmol) and potassium carbonate (35 mg, 0.25 mmol), were sequentially added before a septum-cap was crimped on the vial to seal it. Solids were degassed 3 times by vacuum-argon filling cycles. Dry toluene (4 mL) was then added before exposing the reaction mixture to microwave irradiation for 1 hour at 150 °C. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM/EP with 4/1

ratio) affording the corresponding product as a dark purple solid (3.5 mg, 6%).**^{1}H NMR** (300 MHz, Chloroform-d) δ 8.38 (d, J = 4.3 Hz, 1H), 7.96 (d, J = 4.4 Hz, 1H), 7.88 (s, 1H), 7.71 (dd, J = 8.9, 1.7 Hz, 2H), 7.21 – 7.14 (m, 4H), 7.02 (d, J = 8.9 Hz, 2H), 6.92 – 6.85 (m, 4H), 3.82 (s, 6H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 156.72, 150.43, 150.37, 150.20, 150.03, 143.20, 139.78, 137.55, 136.69, 136.63, 131.53, 131.50, 131.43, 131.34, 127.64, 120.99, 120.18, 118.17, 114.93, 114.04, 113.23, 109.43, 109.34, 55.52, 30.94. **^{19}F NMR** (283 MHz, Chloroform-d) δ -123.01 (d, J = 16.3 Hz), -134.60 (d, J = 16.3 Hz). **HRMS** (EI) m/z: Calc for $C_{34}H_{21}F_2N_5O_2S_2$ (M+), 633.1105; Found, 633.1098.

Synthesis of 2-((5-(7-(4-(bis(4-methoxyphenyl)amino)phenyl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl) thiophen-2-yl)methylene)malononitrile (MD-OMe) from 4 by a Knoevenagel reaction: Five drops of triethylamine were added to a mixture of **4** (50 mg, 0.075 mmol) and malononitrile (10.33 mg, 0.16 mmol) in $CHCl_3$ (4mL). The reaction mixture was stirred under air at room temperature. After TLC analysis showed completion of the reaction, the desired product was obtained by precipitation in hexane as a dark purple solid (47 mg, 90%).

Synthesis of 2-((5-(7-(4-(bis(4-biphenylyl)amino)phenyl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl) thiophen-2-yl)methylene)malononitrile (MD-Ph) from 3 by DHA cross-coupling reaction: To an oven-dried microwave tube containing a stirring bar, compound **3** (40 mg, 0.07 mmol) and 5-Bromo-2-dicyanovinylthiophene (33 mg, 0.14 mmol), palladium acetate (1.6 mg, 0.007 mmol), tricyclohexylphosphinetetrafluoroborate (5.2 mg, 0.014 mmol), pivalic acid (7.2 mg, 0.07 mmol) and potassium carbonate (29 mg, 0.21 mmol) were sequentially added before a septum-cap was crimped on the vial to seal it. Solids were degassed 3 times by vacuum-argon filling cycles. Dry toluene (4 mL) was then added before exposing the reaction mixture to microwave irradiation for 1 hour at 150 °C. The resulting mixture was cooled to room temperature, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: DCM/EP with 4/1 ratio) affording the corresponding product as a purple solid (2.6 mg, 5%). **^{1}H NMR** (300 MHz, Chloroform-d) δ 8.40 (d, J = 4.2 Hz, 1H), 7.97 (d, J = 4.1 Hz, 1H), 7.90 (s, 1H), 7.81 (dd, J = 10.3 Hz, 2H), 7.64 – 7.54 (m, 8H), 7.50 – 7.41 (m, 4H), 7.38 – 7.29 (m, 8H). **^{13}C NMR** (125 MHz, Chloroform-d) δ 150.35, 149.02, 148.66, 148.59, 146.26, 140.57, 137.68, 136.95, 131.86, 131.83, 131.73, 131.65, 128.97, 128.31, 127.28, 126.94, 125.72, 122.01, 114.12, 113.33, 78.67. **^{19}F NMR** (283 MHz, Chloroform-d) δ -122.95 (d, J = 16.3 Hz), -133.85 (d, J = 16.3 Hz). **HRMS** (EI) m/z: Calc for $C_{44}H_{25}F_2N_5S_2$ (M+), 725.1519; Found, 725.1509.

Synthesis of 2-((5-(7-(4-(bis(4-biphenylyl)amino)phenyl)-5,6-difluorobenzo[c][1,2,5]thiadiazol-4-yl) thiophen-2-yl)methylene)malononitrile (MD-Ph) from 5 by a Knoevenagel reaction: Five drops of triethylamine were added to a mixture of **5** (23 mg, 0.034 mmol) and malononitrile (4.7 mg, 0.071 mmol) in $CHCl_3$ (4mL). The reaction mixture was stirred under air at room temperature. After TLC analysis showed completion of the reaction, the desired product was obtained by precipitation in hexane as a purple solid (13 mg, 53%).

2. NMR spectra of MD-OMe and MD-Ph

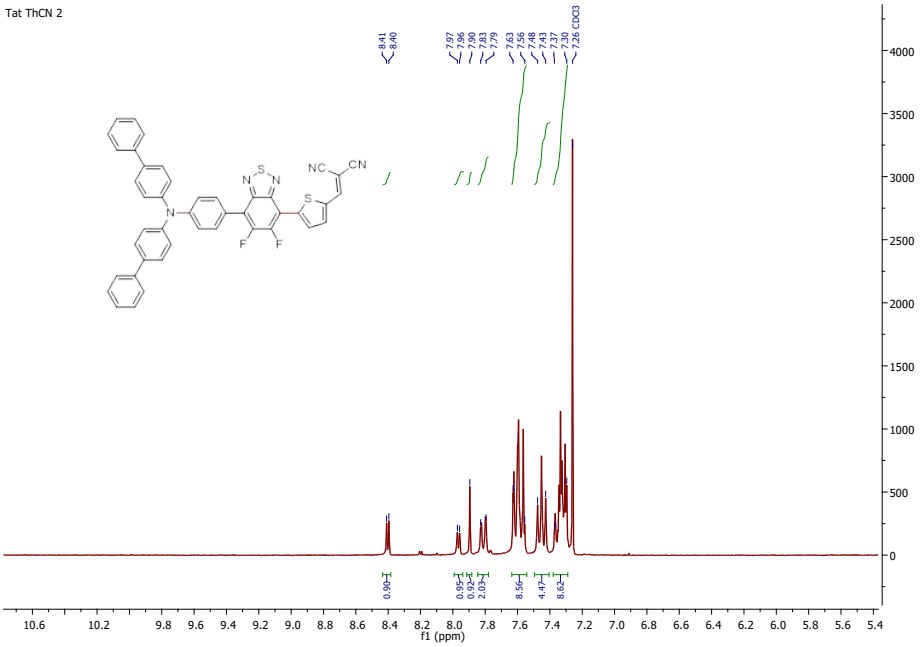

Figure S1: ^{1}H NMR spectrum of MD-Ph in $CDCl_3$

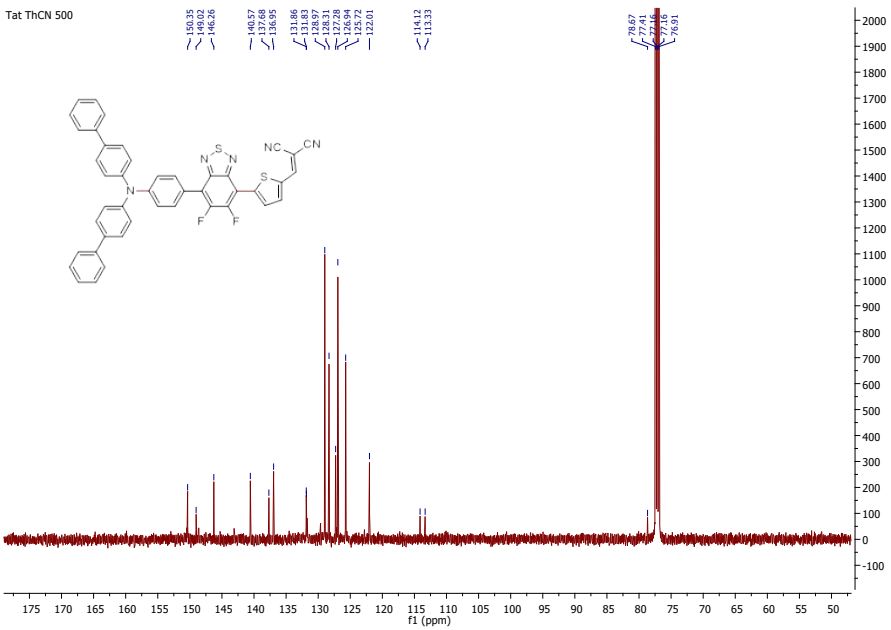

Figure S2: ^{13}C NMR spectrum of MD-Ph in $CDCl_3$

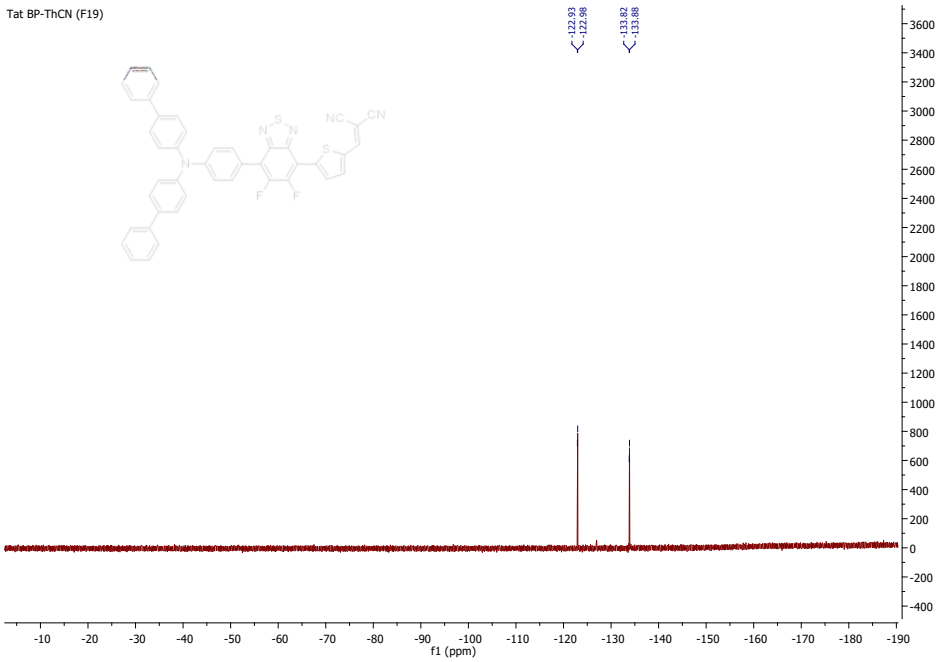

Figure S3: ^{19}F NMR spectrum of MD-Ph in $CDCl_3$

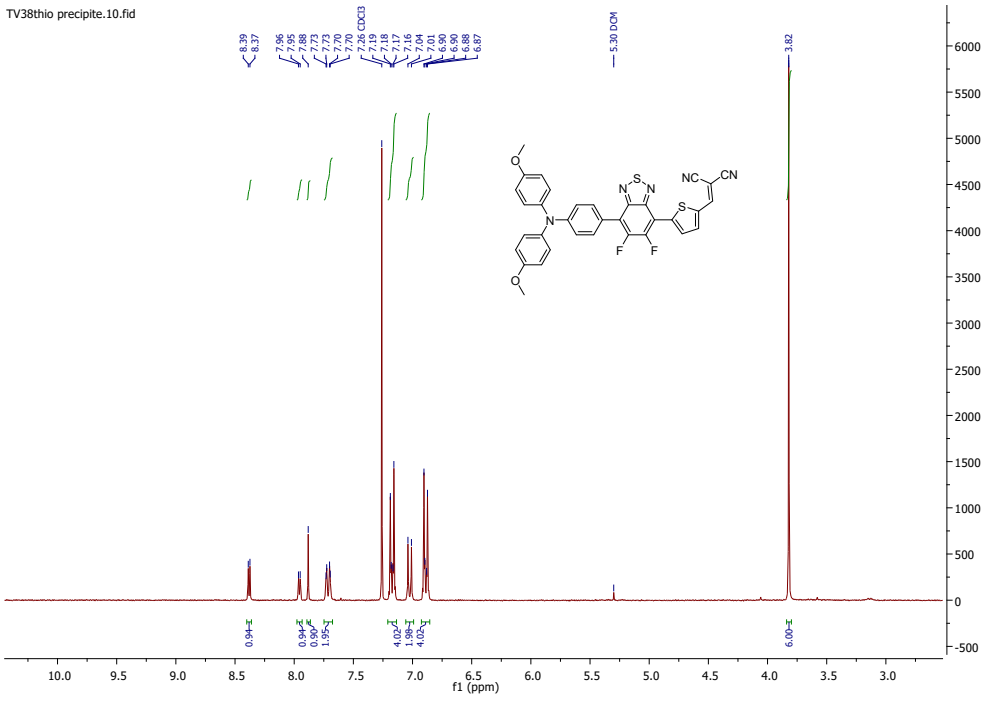

Figure S4: ^{1}H NMR spectrum of MD-OMe in $CDCl_3$

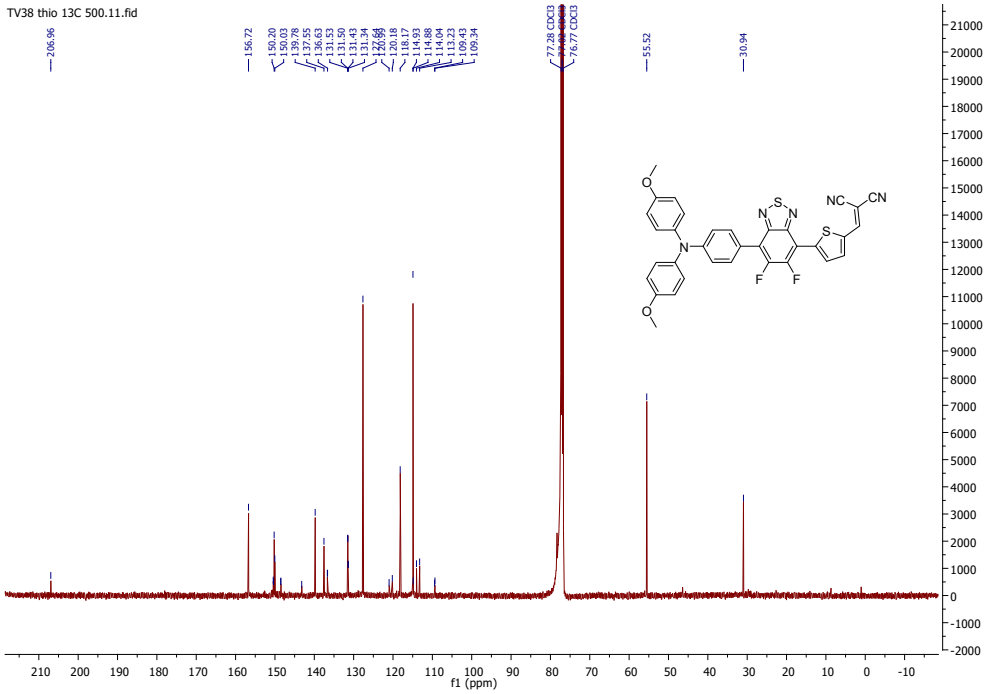

Figure S5: ^{13}C NMR spectrum of MD-OMe in $CDCl_3$

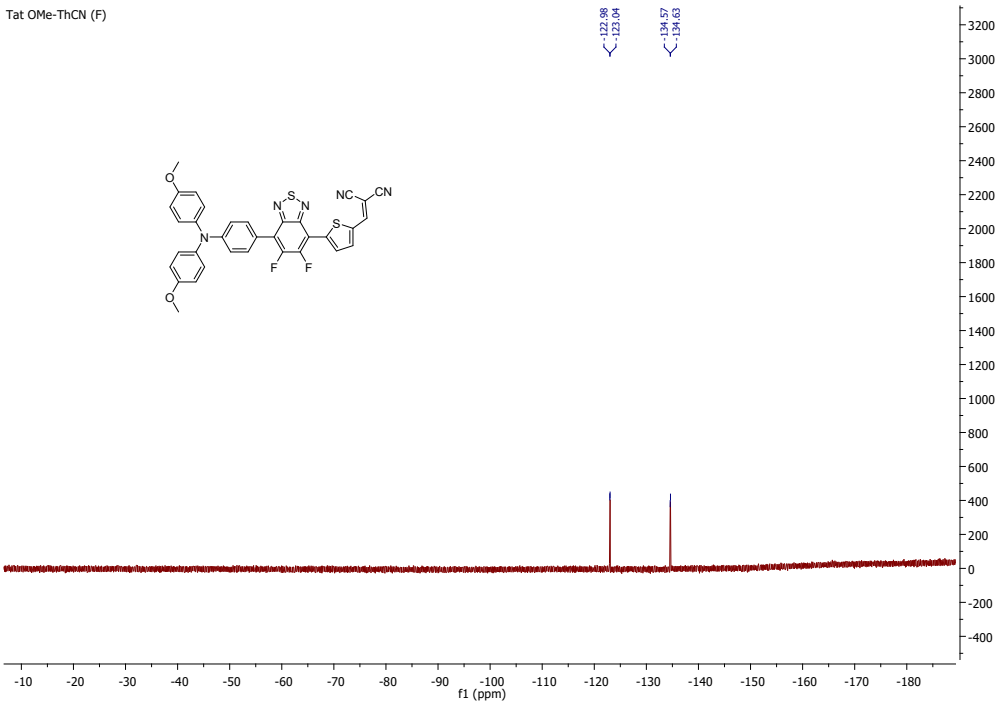

Figure S6: ^{19}F NMR spectrum of MD-OMe in $CDCl_3$

3. HRMS spectra of MD-OMe and MD-Ph

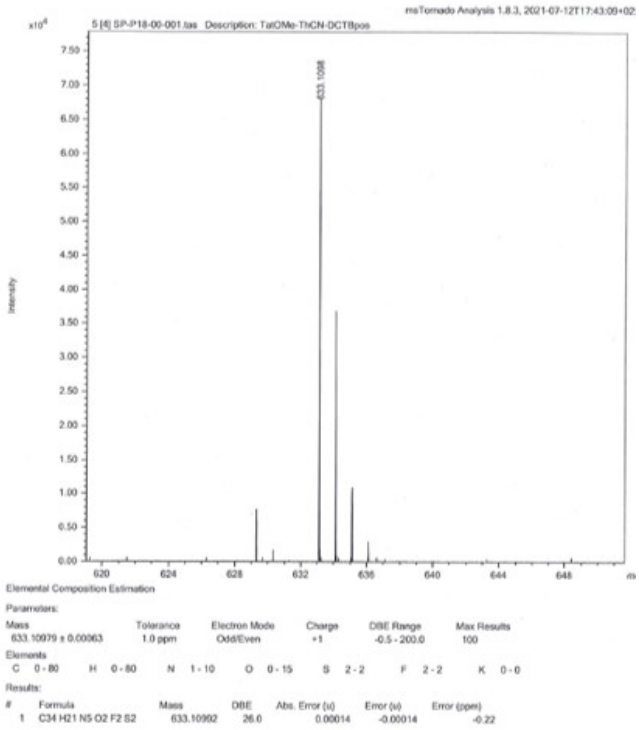

Figure S7: HRMS spectrum of MD-OMe

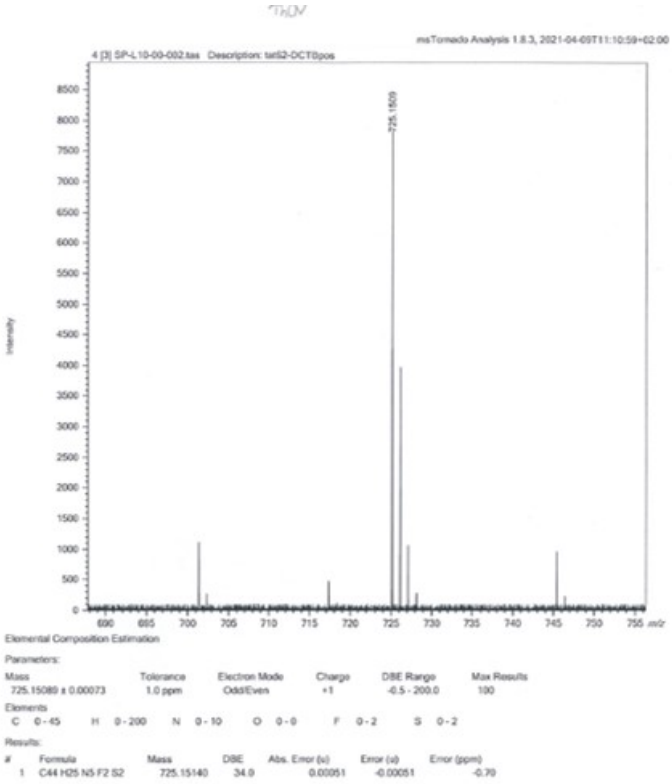

Figure S8: HRMS spectrum of MD-Ph

4. Thermogravimetric Analyses (TGAs)

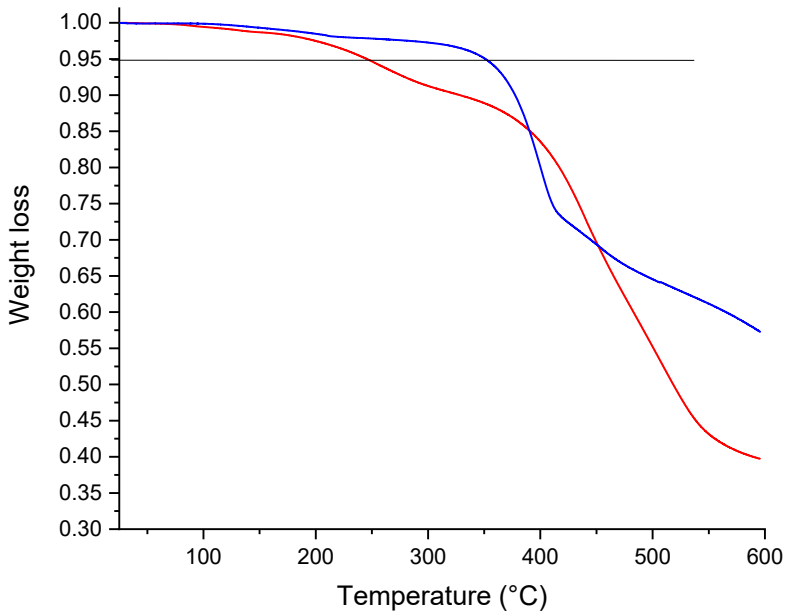

Figure S9: Thermogravimetric analyses (TGA) at a heating rate of 10 °C/min in air of **MD-OMe** (bleu) and **MD-Ph** (red)

5. Photoelectron spectroscopy in air (PESA) analyses

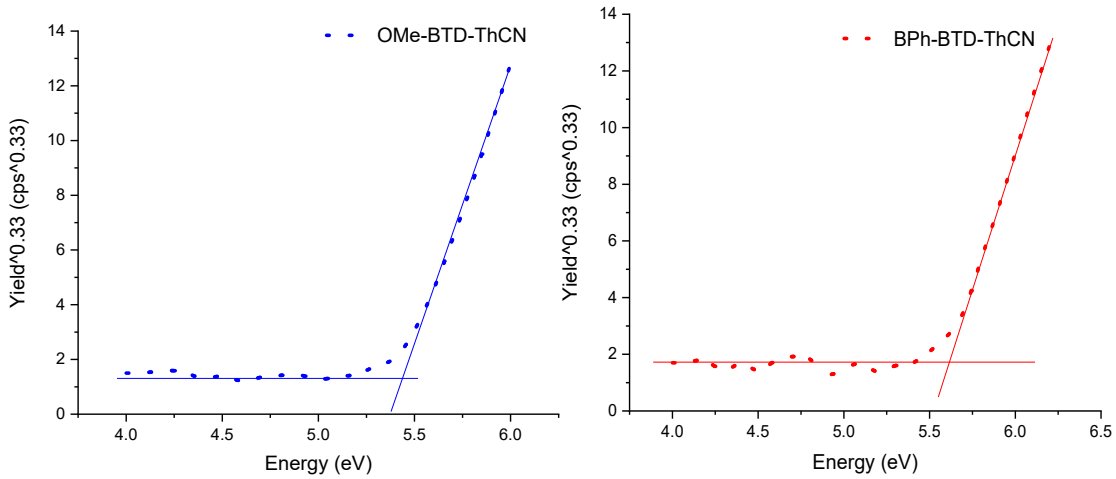

Figure S10: Photoelectron spectroscopy in air (PESA) analysis of MD-OMe (left) and MD-Ph (right) in thin film.

6. Device characterization and testing

OSCs: Indium tin oxide (ITO) pre-coated glass slides of 24×25×1.1 mm with a sheet resistance of RS = 7 Ω/sq were purchased from Visiontek Systems LTD. The substrates were washed with a diluted Deconex® 12 PA-x solution (2% in water) and scrubbed using dishwashing soap before being cleaned by a series of ultrasonic treatments in distilled water (15.3 MΩ cm-1), acetone and isopropanol for 15 min each. Once dried under a steam of nitrogen, a UV-ozone plasma treatment (UV/Ozone ProCleaner Plus, Bioforce Nanosciences) was performed for 15 min. An aqueous solution of poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS; Ossila), filtered through a 0.45 µm RC membrane (Millex®), was spun-casted onto the patterned ITO surface at 6000 rpm for 40 s before being baked at 140 °C for 30 min. Then, blends of MD-OMe or MD-Ph and PC71BM at different weight to weight ratios were dissolved in chloroform at a total concentration of 10 mg mL-1, stirred at 30 °C for 30 minutes and spun-casted on the PEDOT:PSS layer. Finally, devices were completed by the successive thermal deposition of Ca (7 nm) and aluminium (100 nm) at a pressure of 1.5 × 10-6 Torr through a shadow mask defining six cells of 27 mm2 each (13.5 mm x 2 mm). J-V curves were recorded using a Keithley 236 source-measure unit and a homemade acquisition program. The light source was an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttecknik, equipped with a metal halogen lamp). The light intensity was measured by a broadband power meter (13PEM001, Melles Griot). Atomic Force Microscopy (AFM) experiments were performed using the Nano-Observer microscope from CS Instrument.

AFM: The topographic images were obtained in tapping mode. Images were processed using Gwyddion SPM data analysis software. Optimized blends were spun cast on the above described PEDOT:PSS modified ITO substrates.

Hole only devices (SCLC devices and measurements): Gold electrodes (100 nm) were subsequently and thermally evaporated under a vacuum of 1.5 x 10^{-5} Torr, through a shadow mask defining actives area of 10 mm², 5 mm², 1.5 mm² and 0.8 mm² per substrates. Hole mobilities μ_h were evaluated using the Mott-Gurney law, ie, $J_{SCLC} = (9/8)\varepsilon_0\varepsilon_r\mu e(V^2/d^3)$ where εr is the static dielectric constant of the medium ($\varepsilon_r = 3$) and d, the thickness of the active layer.

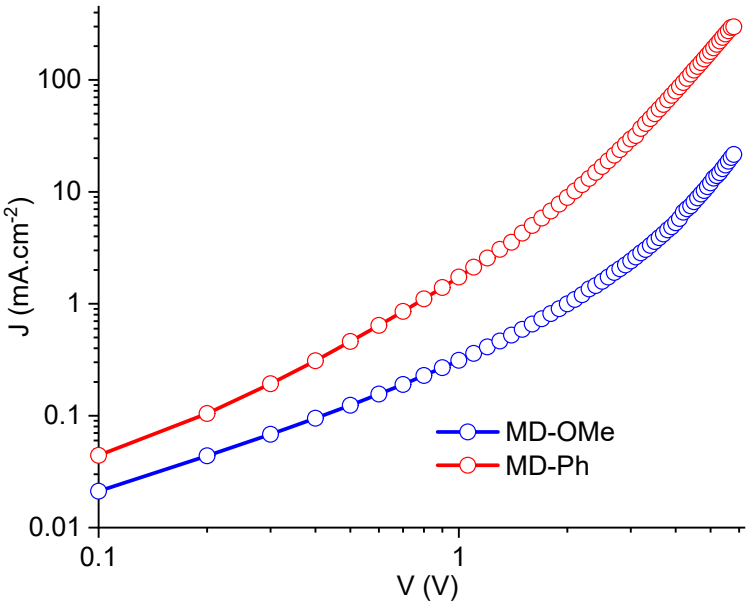

Figure S11: J–V characteristics of hole only devices ITO/PEDOT:PSS/ **MD-OMe** or **MD-Ph** :$PC_{71}BM$/Au

7. Computational chemistry

Ground-state density-functional theory (DFT) geometry optimiza- tions and time-dependent density-functional theory (TD-DFT) calculations were carried out using B3LYP/6–311G* basis sets for all the atomic species. In order to take into account solvation effects in the reproduction of the absorption spectra, solvent dichloromethane molecules were treated as a polarizable continuum (PCM).

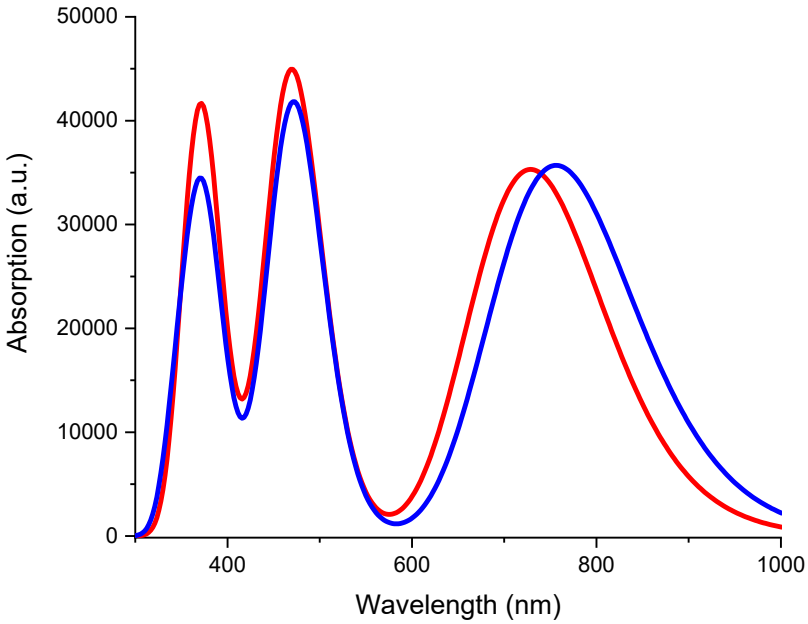

Figure S12: Simulated UV-visible spectra of **MD-OMe** (blue) and **MD-Ph** (red).

Table S2: TD-DFT calculated states and electronic transitions that rule the UV-vis optical absorption of **MD-Ph** and **MD-OMe**

Molecular Donor	Wavelength (nm)	Oscilator	Major transition	Minor transition
MD-Ph	728	0.524	HOMO->LUMO	-
	469	0.655	HOMO-1->LUMO (62%)	H-1->L+1 (12%), H->L+1 (12%)
	376	0.463	HOMO-1->LUMO+1 (46%)	H-3->L (30%), H->L+2 (26%)
MD-OMe	756	0.529	HOMO->LUMO	-
	471	0.619	HOMO-1->LUMO (67%)	H-1->L+1 (13%), H->L+1 (20%)
	375	0.407	HOMO-1->LUMO+1 (41%)	H-3->L (34%), H->L+2 (25%)

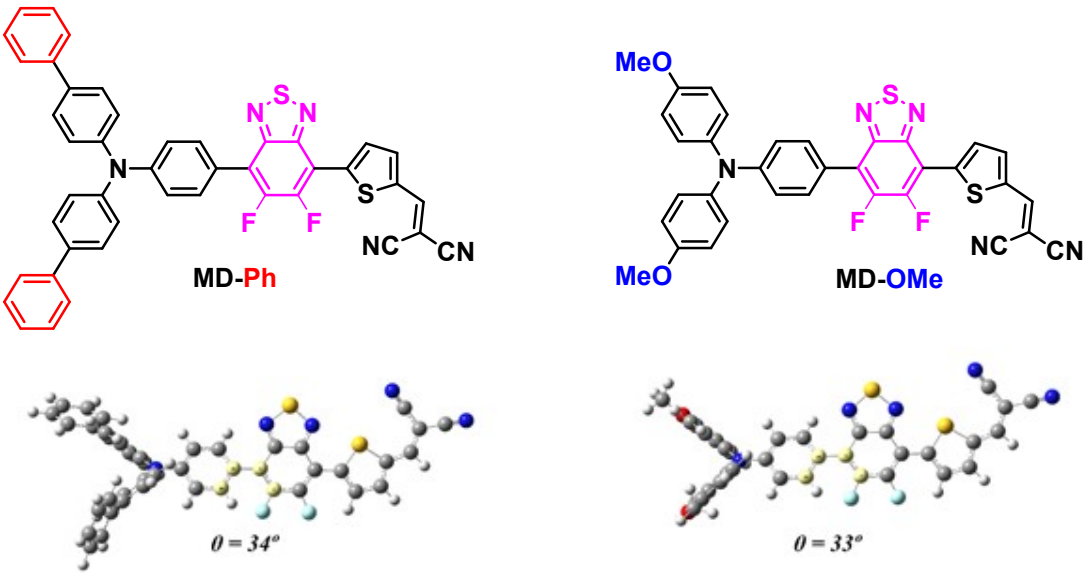

Figure S13: Optimized geometries of **MD-Ph** and **MD-OMe.**

8. Reference

(1) Fitzner, R.; Reinold, E.; Mishra, A.; Mena-Osteritz, E.; Bäuerle, P.; Ziehlke, H.; Körner, C.; Leo, K.; Riede, M.; Weil, M.; et al. *Adv. Funct. Mater.* **2011**, *21*, 897–910.