

Supplementary Information

1,4-Azaborine Based Unfused Non-fullerene Acceptors for Organic Solar Cells

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Experimental Section

Materials

The commercial 2-butyloctan-1-amine, 2-decyltetradecan-1-amine and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile were purchased from Solarmer Materials Inc. Other chemicals and solvents are purchased from J&K, Alfa Aesar or Bide Pharmatech Ltd. (China).

Synthetic Procedures

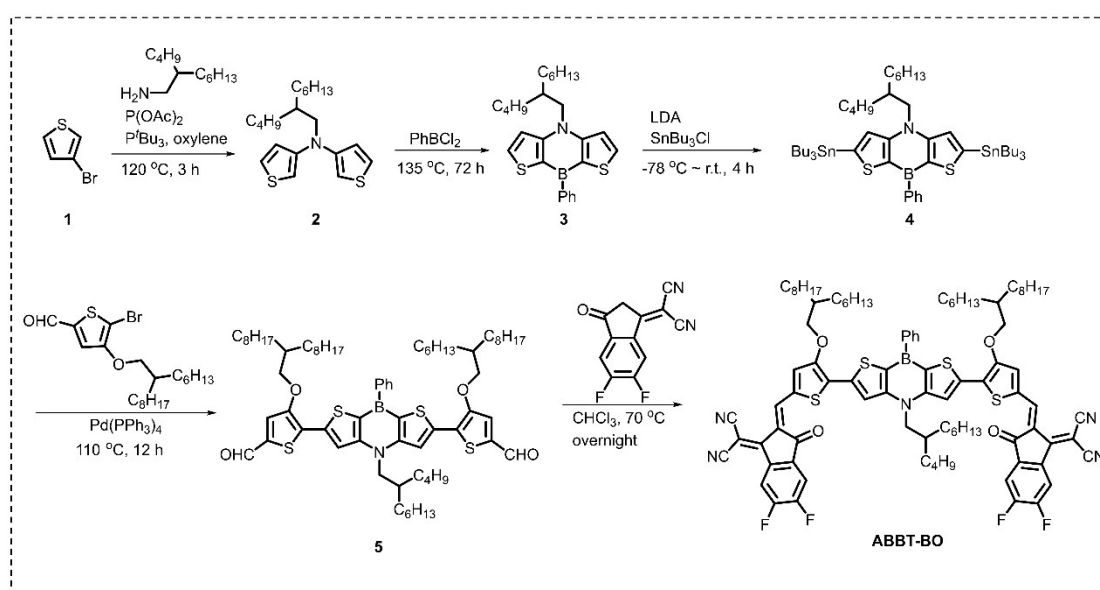


Figure S1. Synthetic routes of the intermediates and ABBT-BO.

Synthesis of *N*-(2-butyloctyl)-*N*-(thiophen-3-yl)thiophen-3-amine (2)

3-Bromothiophene (1.63 g, 10 mmol), 2-butyloctan-1-amine (463.0 mg, 2.5 mmol), sodium *tert*-butoxide (480.5 mg, 5 mmol), palladium acetate (41.6 mg, 0.25 mmol), and tri-*tert*-butylphosphine (101.16 mg, 0.5 mmol) were mixed in 30 mL of oxylene and refluxed at $120\text{ }^\circ\text{C}$ for 3 h. After the mixture was cooled, water was added and the reaction was extracted with hexanes for three times. The organic layers were combined and washed with saturated brine, and dried over Na_2SO_4 . After evaporation of the solvent, the residue was filtered through silica

gel and washed with petroleum ether (PE), the mixture was concentrated in vacuo and without further purification.

Synthesis of 4-(2-butyloctyl)-8-phenyl-4,8-dihydrodithieno[3,2-b:2',3'-e][1,4]azaborinine (3)

To a solution of compound **2** (crude, 2.5 mmol) in chlorobenzene (10 ml) was added Et₃N (252.9 mg, 2.5 mmol) and PhBCl₂ (635.28 mg, 4.0 mmol), and the mixture was stirred at 135 °C for 72 h. After cooling to room temperature, the resulting mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/DCM 5:1) to give the corresponding compound as a white solid (783 mg, 72%). **¹H NMR** (500 MHz, CDCl₃) δ 8.20–8.12 (m, 2H), 7.92 (d, *J* = 5.3 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.48–7.44 (m, 1H), 7.40 (d, *J* = 5.3 Hz, 2H), 4.44 (d, *J* = 7.5 Hz, 2H), 2.22–2.15 (m, 1H), 1.43–1.16 (m, 16H), 0.85 (t, *J* = 7.0 Hz, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 149.42, 134.51, 134.07, 128.66, 127.92, 117.25, 56.09, 37.77, 31.69, 31.66, 31.42, 29.53, 28.78, 26.56, 22.98, 22.56, 14.65, 13.95.

Synthesis of 4-(2-butyloctyl)-8-phenyl-2,6-bis(tributylstannyl)-4,8-dihydrodithieno[3,2-b:2',3'-e][1,4]azaborinine (4)

To a solution of compound **3** (700 mg, 1.6 mmol) in dry THF (20 ml) was added dropwise lithium diisopropyl solution (6 mmol) at -78 °C. After stirring for 2 h at -78 °C. To the mixture was added Bu₃SnCl (1.11 g, 3.4 mmol). After stirring for 2 h, the reaction was and further stirred for 2 h at -40 °C. The reaction mixture was quenched by methanol (1.0 mL), After warming to room temperature, the resulting mixture was concentrated in vacuo to give a black brown oil without further purification.

Synthesis of 5,5'-(4-(2-butyloctyl)-8-phenyl-4,8-dihydrodithieno[3,2-b:2',3'-e][1,4]azaborinine-2,6-diyl)bis(4-((2-hexyldecyl)oxy)thiophene-2-carbaldehyde) (5)

To a two-neck flask containing compound **4**, Pd(PPh₃)₄ (92.4 mg, 0.08 mmol) and 5-bromo-4-((2-hexyldecyl)oxy)thiophene-2-carbaldehyde, and dried PhMe (30 ml) were added under N₂ atmosphere. The reaction was stirred at 110 °C for 12 h. After cooling to room temperature, water was added and the reaction was extracted with ethyl acetate three times. The organic

layers were combined and washed with saturated brine, and dried over Na₂SO₄. The purified by column chromatography (PE:DCM = 2:1) to give the corresponding product **5** as an orange oil in 30% yield (545 mg). **¹H NMR** (500 MHz, CDCl₃) δ 9.82 (s, 2H), 8.21–8.15 (m, 2H), 7.69 (s, 2H), 7.55–7.44 (m, 5H), 4.39 (d, *J* = 7.5 Hz, 2H), 4.13 (d, *J* = 5.1 Hz, 4H), 2.25–2.17 (m, 1H), 1.90 (dt, *J* = 11.7, 5.7 Hz, 2H), 1.66–1.59 (m, 4H), 1.54–1.49 (m, 3H), 1.40–1.35 (m, 10H), 1.29–1.20 (m, 35H), 0.92–0.78 (m, 18H). **¹³C NMR** (126 MHz, CDCl₃) δ 181.84, 154.71, 148.83, 141.42, 137.37, 134.31, 128.93, 127.98, 127.11, 125.54, 123.11, 114.26, 74.75, 38.29, 37.62, 31.92, 31.91, 31.78, 31.75, 31.50, 31.24, 30.08, 29.74, 29.67, 29.37, 28.82, 26.88, 26.85, 26.66, 23.04, 22.69, 22.65, 14.12, 14.06, 14.00.

Synthesis of 2,2'-((2Z,2'Z)-(((4-(2-butyloctyl)-8-phenyl-4,8-dihydrodithieno[3,2-b:2',3'-e][1,4]azaborinine-2,6-diyl)bis(4-((2-hexyldecyl)oxy)thiophene-5,2-diyl))bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (ABB-BO)

To a two-neck flask containing compound **5** (300 mg, 0.26 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (202.4 mg, 0.88 mmol), CHCl₃ (30 ml) and pyridine (1 mL) were added under nitrogen atmosphere. The mixture was stirred at 70 °C overnight. After evaporation of the solvent, the residue was purified by column chromatography (PE/DCM = 1/1) to give the corresponding product **ABBT-BO** as a dark solid in 85% yield (344 mg). **¹H NMR** (400 MHz, CD₂Cl₂) δ 8.67 (s, 2H), 8.36 (s, 1H), 8.25 (s, 1H), 7.50 (s, 1H), 7.32 (s, 1H), 4.72 – 4.48 (m, 4H), 2.99 – 2.69 (m, 8H), 1.88 – 1.58 (m, 5H), 1.46 – 1.19 (m, 33H), 1.03 – 0.52 (m, 18H). **HR-MS** (MALDI-TOF) *m/z* calcd. for (C₉₂H₁₀₇BF₄N₅O₄S₄) (M+H⁺): 1560.72. Found: 1561.06.

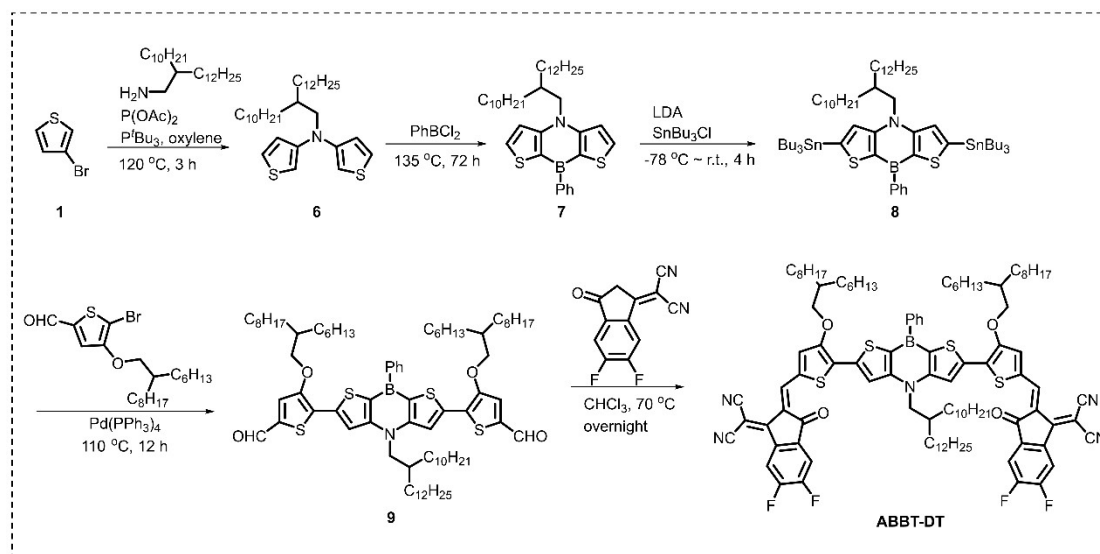


Figure S2. Synthetic routes of the intermediates and ABBT-DT.

Synthesis of *N*-(2-decyltetradecyl)-*N*-(thiophen-3-yl)thiophen-3-amine (**6**)

3-Bromothiophene (1.63 g, 10 mmol), 2-decyltetradecan-1-amine (883.5 mg, 2.5 mmol), sodium *tert*-butoxide (480.5 mg, 5 mmol), palladium acetate (41.6 mg, 0.25 mmol), and tri-*tert*-butylphosphine (101.16 mg, 0.5 mmol) were mixed in 30 mL of oxylene and refluxed at 120 °C for 3 h. After the mixture was cooled, water was added and the reaction was extracted with hexanes for three times. The organic layers were combined and washed with saturated brine, and dried over Na₂SO₄. After evaporation of the solvent, the residue was filtered through silica gel and washed with petroleum ether (PE), the mixture was concentrated in vacuo and without further purification.

Synthesis of 4-(2-decyltetradecyl)-8-phenyl-4,8-dihydrodithieno[3,2-*b*:2',3'-*e*][1,4]azaborinine (**7**)

To a solution of compound **6** (crude, 2.5 mmol) in chlorobenzene (10 ml) was added Et₃N (252.9 mg, 2.5 mmol) and PhBCl₂ (635.3 mg, 4.0 mmol), and the mixture was stirred at 135 °C for 72 h. After cooling to room temperature, the resulting mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/DCM 5:1) to give the corresponding compound **7** as a white solid (870 mg, 58%). ¹H NMR (500 MHz,

CDCl₃) δ 8.20–8.12 (m, 2H), 7.92 (d, *J* = 5.3 Hz, 2H), 7.55–7.50 (m, 2H), 7.46 (ddd, *J* = 7.4, 3.9, 1.3 Hz, 1H), 7.40 (d, *J* = 5.3 Hz, 2H), 4.44 (d, *J* = 7.5 Hz, 2H), 2.19 (s, 1H), 1.43–1.16 (m, 16H), 0.85 (t, *J* = 7.0 Hz, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 149.44, 141.72, 134.52, 134.09, 128.68, 127.93, 126.10, 117.26, 56.14, 37.77, 31.93, 31.91, 31.72, 29.89, 29.67, 29.66, 29.60, 29.59, 29.50, 29.37, 29.33, 26.62, 22.70, 14.13.

Synthesis of 4-(2-decyltetradecyl)-8-phenyl-2,6-bis(tributylstannyl)-4,8-dihydrodithieno[3,2-b:2',3'-e][1,4]azaborinine (8)

To a solution of compound **7** (800 mg, 1.3 mmol) in dry THF (20 ml) was added dropwise lithium diisopropyl solution (5.2 mmol) at -78 °C. After stirring for 2 h at -78 °C. To the mixture was added Bu₃SnCl (1.11 g, 2.6 mmol). After stirring for 2 h, the reaction was and further stirred for 2 h at -40 °C. The reaction mixture was quenched by methanol (1.0 mL), After warming to room temperature, the resulting mixture was concentrated in vacuo to give a black brown oil without further purification.

Synthesis of 5,5'-(4-(2-decyltetradecyl)-8-phenyl-4,8-dihydrodithieno[3,2-b:2',3'-e][1,4]azaborinine-2,6-diyl)bis(4-((2-hexyldecyl)oxy)thiophene-2-carbaldehyde) (9)

To a two-neck flask containing compound **8**, Pd(PPh₃)₄ (92.4 mg, 0.08 mmol) and 5-bromo-4-((2-hexyldecyl)oxy)thiophene-2-carbaldehyde, and dried PhMe (30 ml) were added under N₂ atmosphere. The reaction was stirred at 110 °C for 12 h. After cooling to room temperature, water was added and the reaction was extracted with ethyl acetate three times. The organic layers were combined and washed with saturated brine, and dried over Na₂SO₄. The purified by column chromatography (PE:DCM = 2:1) to give the corresponding product **9** as an orange oil in 34% yield (575 mg). **¹H NMR** (400 MHz, CDCl₃) δ 8.17–8.12 (m, 2H), 7.92 (d, *J* = 5.3 Hz, 2H), 7.56–7.49 (m, 2H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.40 (d, *J* = 5.3 Hz, 2H), 4.44 (d, *J* = 7.5 Hz, 2H), 2.18 (s, 1H), 1.50–1.11 (m, 44H), 0.87 (dt, *J* = 7.0, 3.3 Hz, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 181.93, 154.77, 149.01, 141.67, 137.55, 134.24, 129.24, 128.00, 127.98, 127.28, 125.61, 124.39, 123.22, 114.50, 38.34, 37.72, 32.0, 31.95, 31.93, 31.90, 31.79, 31.53, 31.46,

31.33, 30.21, 30.16. 30.06, 29.72, 29.66, 29.54, 29.39, 29.37, 26.92, 26.90, 26.71, 22.70.
14.14, 14.12.

Synthesis of 2,2'-((2Z,2'Z)-(((4-(2-decyltetradecyl)-8-phenyl-4,8-dihydrodithieno[3,2-b:2',3'-e][1,4]azaborinine-2,6-diyl)bis(4-((2-hexyldecyl)oxy)thiophene-5,2-diyl))bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (ABB-DT)

To a two-neck flask containing compound **9** (300 mg, 0.22 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (184 mg, 0.80 mmol), CHCl₃ (30 ml) and pyridine (1 mL) were added under nitrogen atmosphere. The mixture was stirred at 70 °C overnight. After evaporation of the solvent, the residue was purified by column chromatography (PE/DCM = 1/1) to give the corresponding product **ABB-DT** as a dark solid in 87% yield (330 mg). **¹H NMR** (400 MHz, CDCl₃) δ 8.60 (s, 2H), 8.30 (d, *J* = 7.0 Hz, 4H), 7.78–7.70 (m, 2H), 7.76–7.49 (m, 6H), 4.45 (s, 2H), 3.82 (s, 4H), 2.05 (s, 1H), 1.94 (s, 2H), 1.51–1.05 (m, 88H), 0.89–0.78 (ddd, *J* = 19.0, 10.5, 4.6 Hz, 18H). **HR-MS** (MALDI-TOF) *m/z* calcd. for (C₁₀₄H₁₃₁BF₄N₅O₄S₄) (M+H⁺): 1728.90. Found: 1728.29.

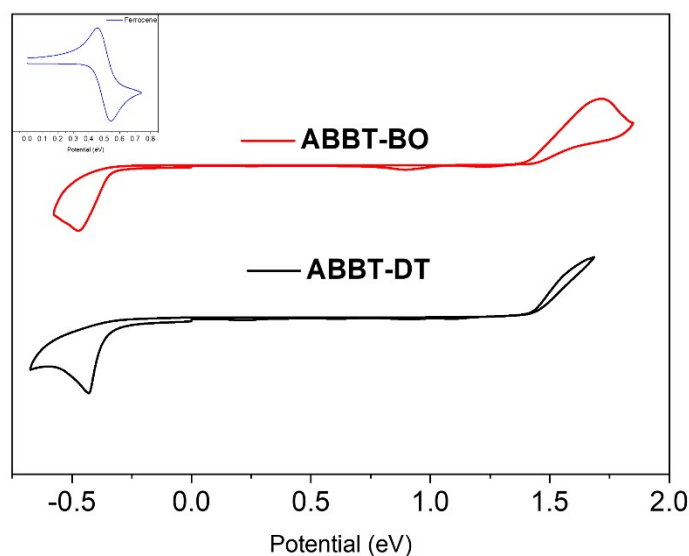


Figure S3. Cyclic voltammograms of ABBT-BO and ABBT-DT.

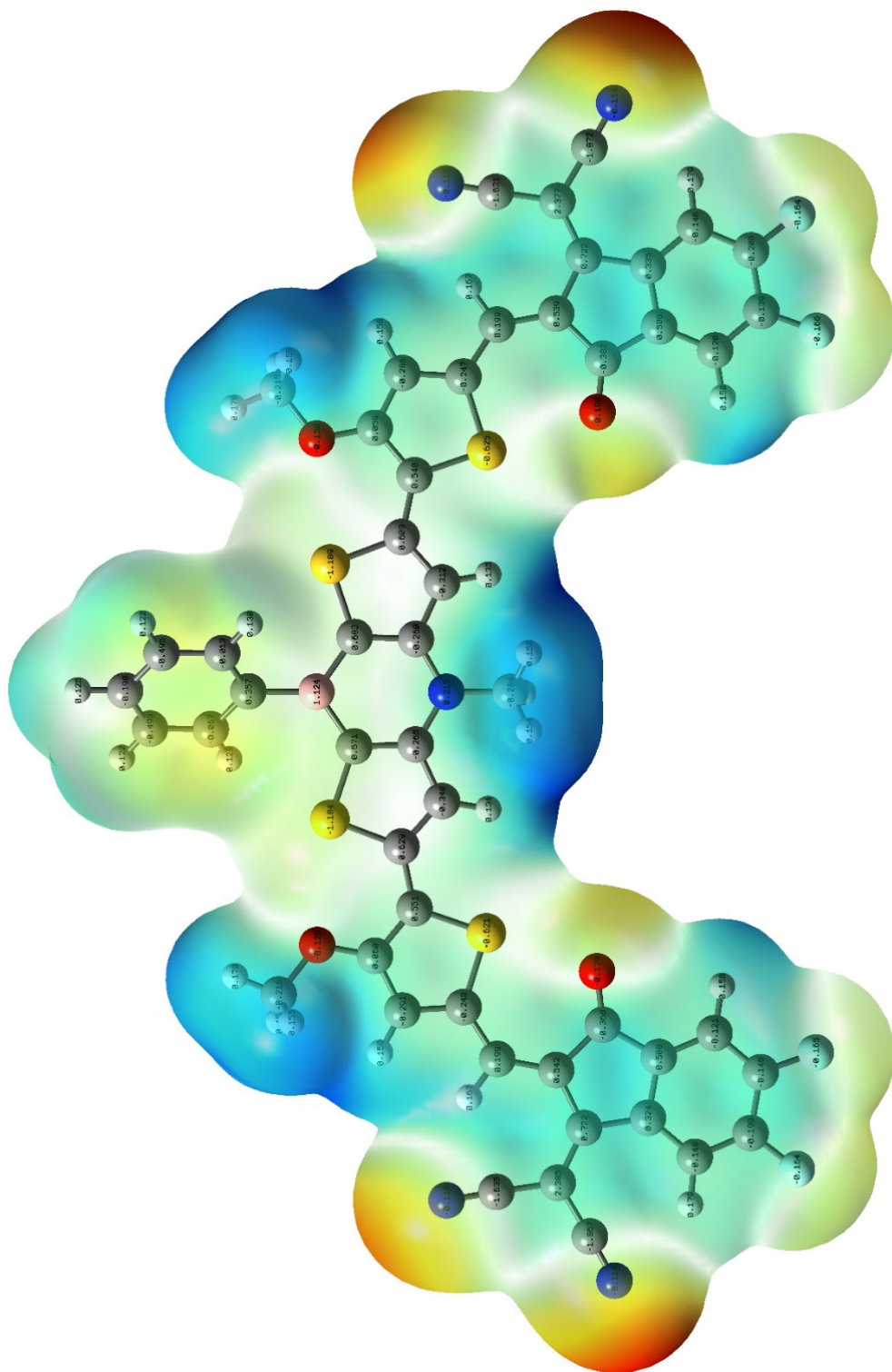


Figure S4. ESP distribution of the ABBT-BO(DT).

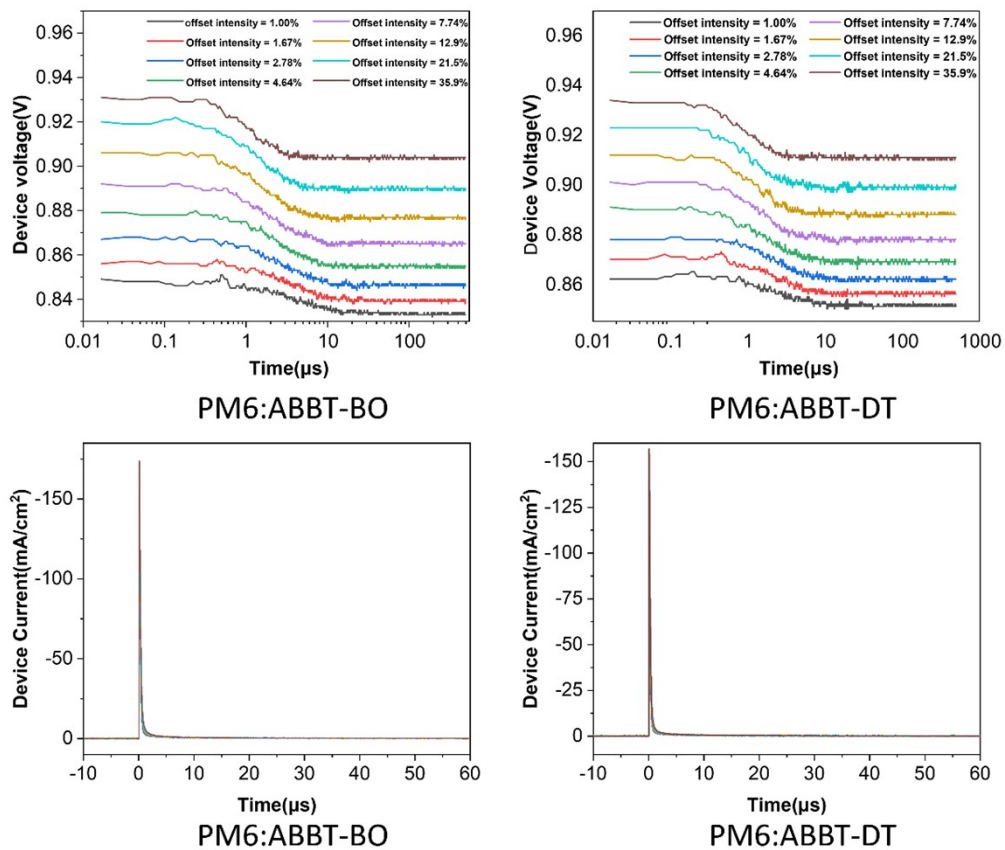


Figure S5. (a-b) Transient photovoltage and (c-d) charge extraction traces under different illumination intensities.

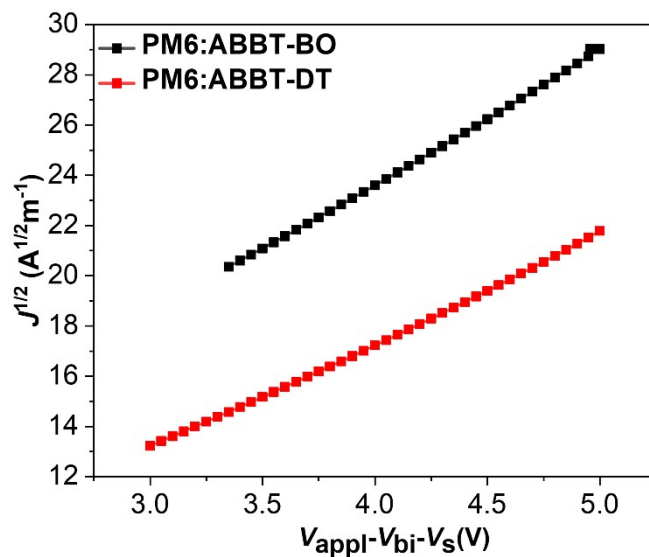


Figure S6 The electron mobilities of PM6:ABBT-BO and PM6:ABBT-DT

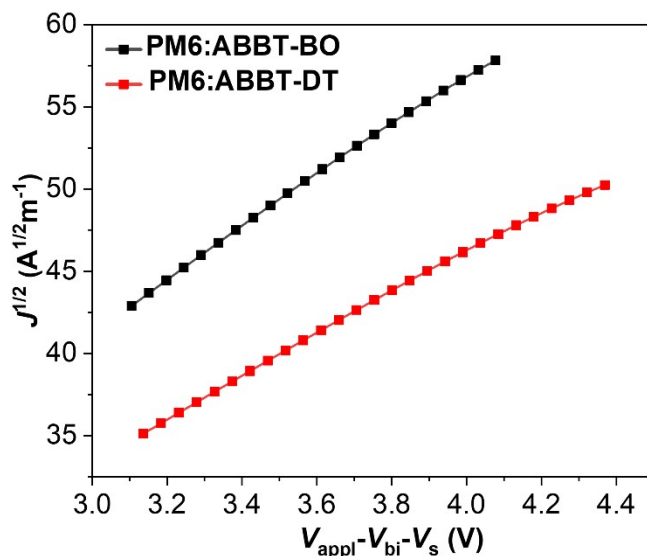


Figure S7 The hole mobilities of PM6:ABBT-BO and PM6:ABBT-DT.

Instruments and Measurement

^1H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 MHz or Bruker AVANCE III 500 MHz spectrometer. UV-Vis absorption spectra were recorded on a PerkinElmer Lambda UV-Vis spectrophotometer. The absorption coefficient was calculated through Lambert-Beer law $A = Kcd$, where A is absorbance (no units), K is absorption coefficient ($\text{M}^{-1} \text{cm}^{-1}$), c is concentration (mol L^{-1}), and d is distance light travels (cm^{-1}). Cyclic voltammetry (CV) was measured on a CHI660e Electrochemical Workstation equipped with a glass carbon working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode. The potential of saturated calomel electrodes (SCE) was internally calibrated as 0.43 V by using the ferrocene/ferrocenium redox couple (Fc/Fc^+), which has a known reduction potential of -4.80 eV. The scan rate is 50 mV/s. Tapping-mode atomic force microscopy (AFM) images were obtained by using a Bruker Multimode 8 Microscope. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F instrument. 2D-GIWAXS measurements were performed Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The crystal coherence length (CCL) was estimated from the full width half maxima (FWHM) of

peaks by using the formula ($CCL = 1.8\pi/(FWHM)$). The d-spacing of molecular stacking can be calculated by the equation: $d = 2\pi/q$.^[1]

The photo-CELIV, TPV and CE measurements reported here were performed by the all-in-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland. Dynamic X-ray photoelectron spectroscopy (DXPS) were determined by X-ray photoelectron spectroscopy (XPS, LVAC-PHI-5000 VersaProbe III) for element distribution and binding energy analysis.

The hole-only and electron-only devices were fabricated with the architectures of ITO/PEDOT:PSS/active layer/MoO₃/Ag and ITO/ZnO/active layer/PNDIT-F3N/Ag, respectively. Hole-only and electron-only devices were recorded with a Keithley 236 source meter under dark. The hole and electron mobility were determined by fitting the dark current to the model of single-carrier SCLC, which is described by the equation,

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layers, and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole and electron mobilities can be calculated from the slope of the $J^{1/2}$ - V curves.

The electroluminescence (EL) spectra were acquired by a spectroradiometer (PR745, Photo Research) or a high-sensitivity spectrometer (QE Pro or NIR Quest 512, Ocean Optics). The radiation flux of EL was determined by measuring the emitted photons in all direction through an integrated sphere by using calibrated spectrometers (QE Pro, and NIRQuest-512, Ocean Optics), under a constant current density with a Keithley 2400 source measure unit.

The dielectric constants of PM6, ABBT-BO and ABBT-DT were measured using the parallel-plate capacitance measurement with impedance spectroscopy. The device structure was indium tin oxide ITO/PEDOT:PSS/test film/ PNDIT-F3N/Ag. The *Capacitance–Voltage* measurements of the molecules were performed using a HP 4192A LCR meter by sweeping the voltage from -30 V to 10 V at room temperature, with a ramping rate of 0.5 V s⁻¹ and 30

mV of oscillator levels. The measurements were performed under the frequency from 1×10^3 to 1×10^6 Hz.

Device Fabrication and characterization

All solar cells were fabricated with a conventional architecture of ITO/PEDOT:PSS/active layer/PNDIT-F3N/Ag. The ITO-coated glass substrates were cleaned by sequentially ultrasonic bath with detergent, deionized water, and isopropanol. After being dried in the oven at 60 °C overnight, the ITO-coated glass substrates were treated with an oxygen plasma for 5 min. Then, 30 nm PEDOT:PSS was spin-coated onto the ITO surface and annealed at 150 °C in the air for 15 min. The substrates were then moved into an N₂-filled glovebox. All the active layers (D/A=1:1.5) were obtained by spin-coating at a total concentration of 18.8 mg mL⁻¹ and 1 vol% of 1,8-diiodooctane. The optimal film thickness of ca. 100 nm was obtained, measured by a Bruker AXS Dektak stylus surface profiling system. All the active layers were thermal annealed at 50 °C for 10 min. Subsequently, ~10 nm PNDIT-F3N was spin-coated onto the active layers. Finally, 100 nm Ag was thermally deposited in a vacuum chamber at a pressure of 3×10^{-7} torr. The current density–voltage (*J*–*V*) characteristics were measured under a computer-controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The light intensity was calibrated by a standard silicon solar cell (certified by NREL) before the testing, giving a value of 100 mW cm⁻² during the test of *J*–*V* characteristics. The external quantum efficiency (EQE) spectra were recorded with a QE-R measurement system (Enlitech, QE-R3011, Taiwan).

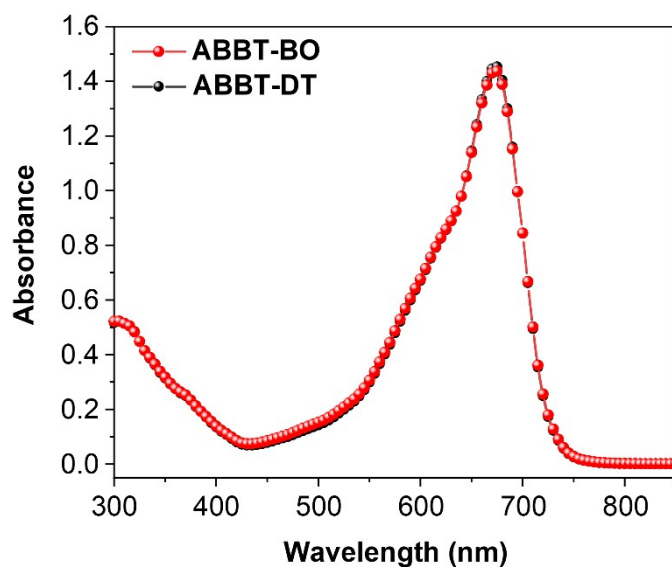


Figure S8 UV-vis absorption spectrum of ABBT-BO and ABBT-DT in 10^{-5} M chloroform solution with 1 cm light path length.

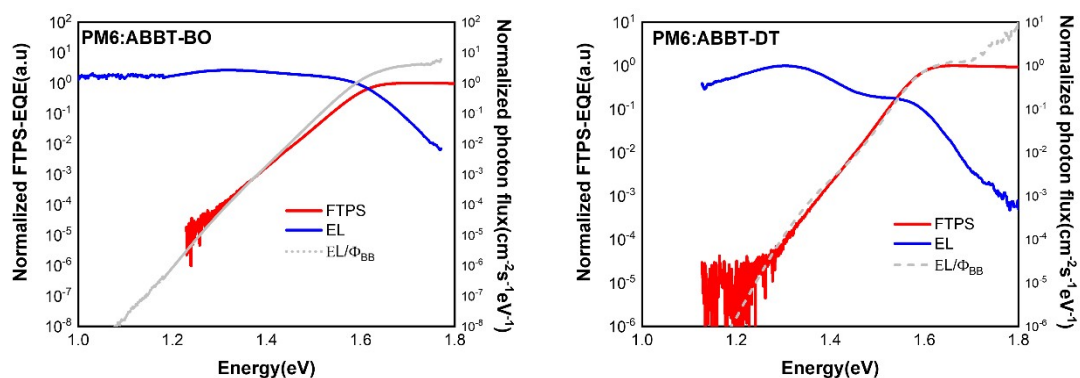


Figure S9. The measured EL spectrum and experimental EQE spectrum of (a) PM6:ABBT-BO and (b) PM6:ABBT-DT.

Table S1. Summary of energy loss data of PM6:ABBT-BO and PM6:ABBT-DT-based devices.

Active layer	E_g [eV]	$qV_{OC,SQ}$ [eV]	$qV_{OC,Rad}$ [eV]	ΔE_1 [eV]	ΔE_2 [eV]	ΔE_3 [eV]	E_{loss} [eV]
PM6:ABBT-BO	1.60	1.31	1.17	0.29	0.14	0.28	0.71
PM6:ABBT-DT	1.59	1.29	1.14	0.30	0.15	0.27	0.72

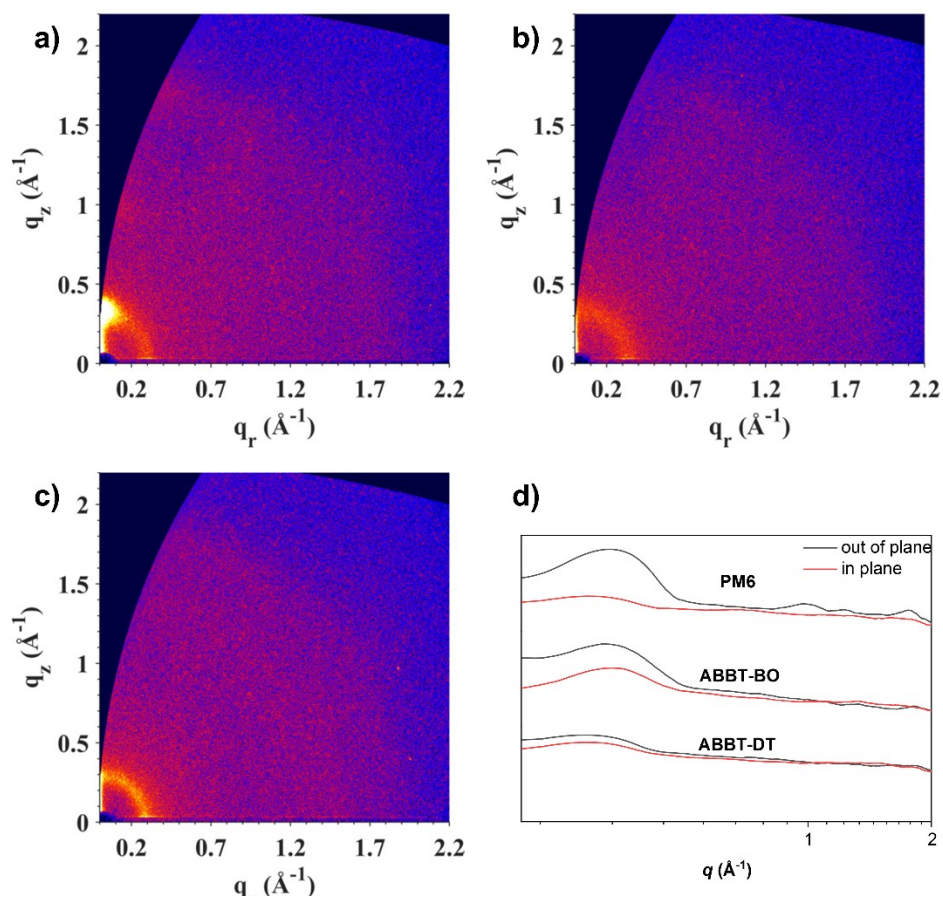


Figure S10. 2D GIWAXS patterns of (a) PM6, (b) ABBT-BO and (c) ABBT-DT; and (d) integrated scattering profiles for the corresponding neat films.

Table S2. The CCL and d-spacing values of PM6 and blend films.

Film	q_0 [\AA^{-1}]	w [\AA^{-1}]	CCL [\AA]	d-spacing [\AA]
PM6	1.74	0.284	21.97	3.22
PM6:ABBT-BO	1.83	0.192	32.50	3.07
PM6:ABBT-DT	1.80	0.164	32.84	3.12

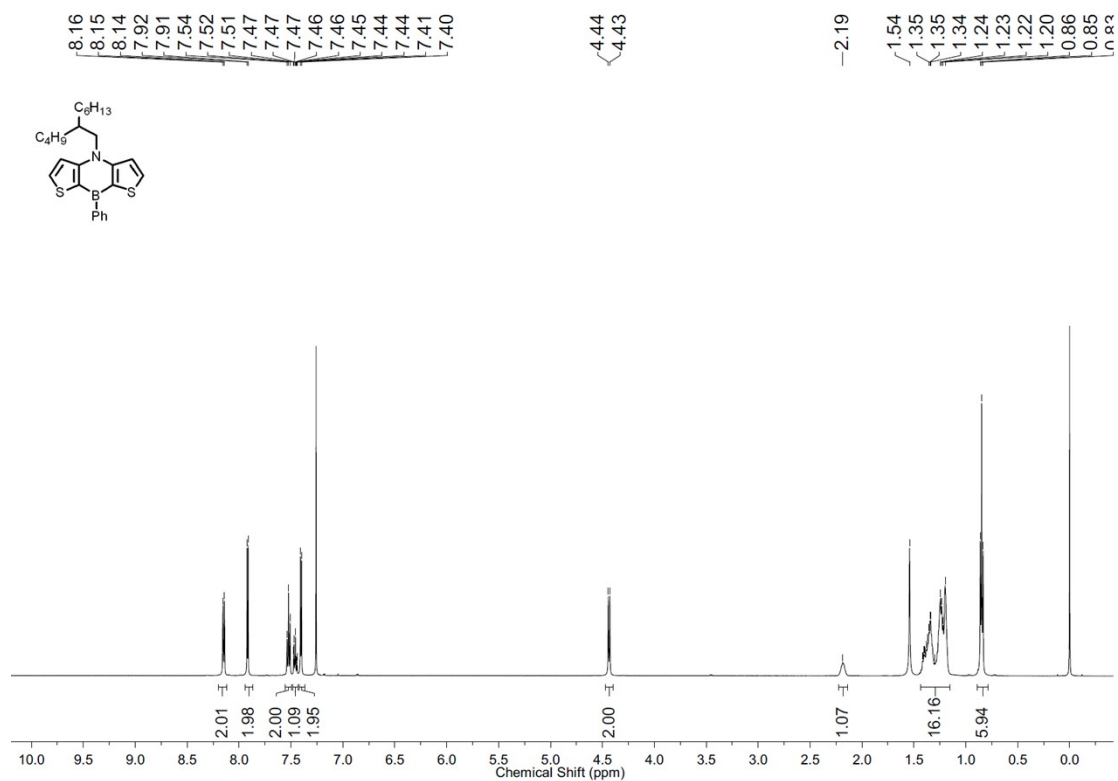


Figure S11. ^1H NMR spectrum of compound **3** in CDCl_3

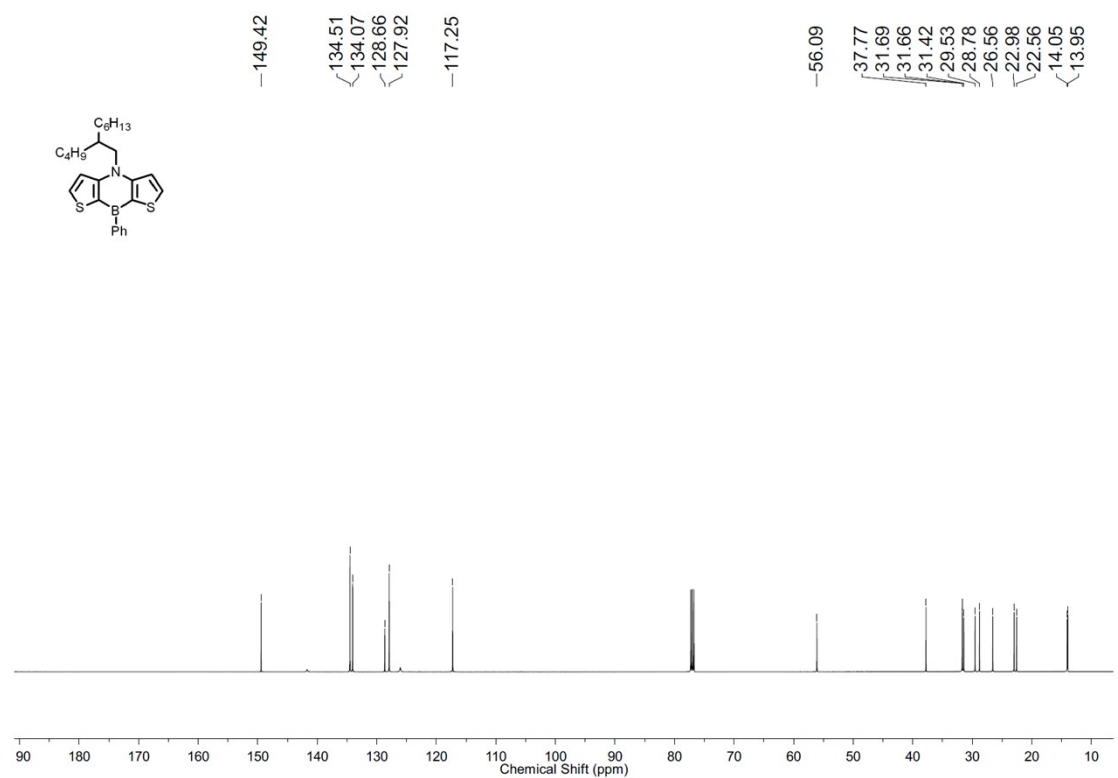


Figure S12. ^{13}C NMR spectrum of compound **3** in CDCl_3

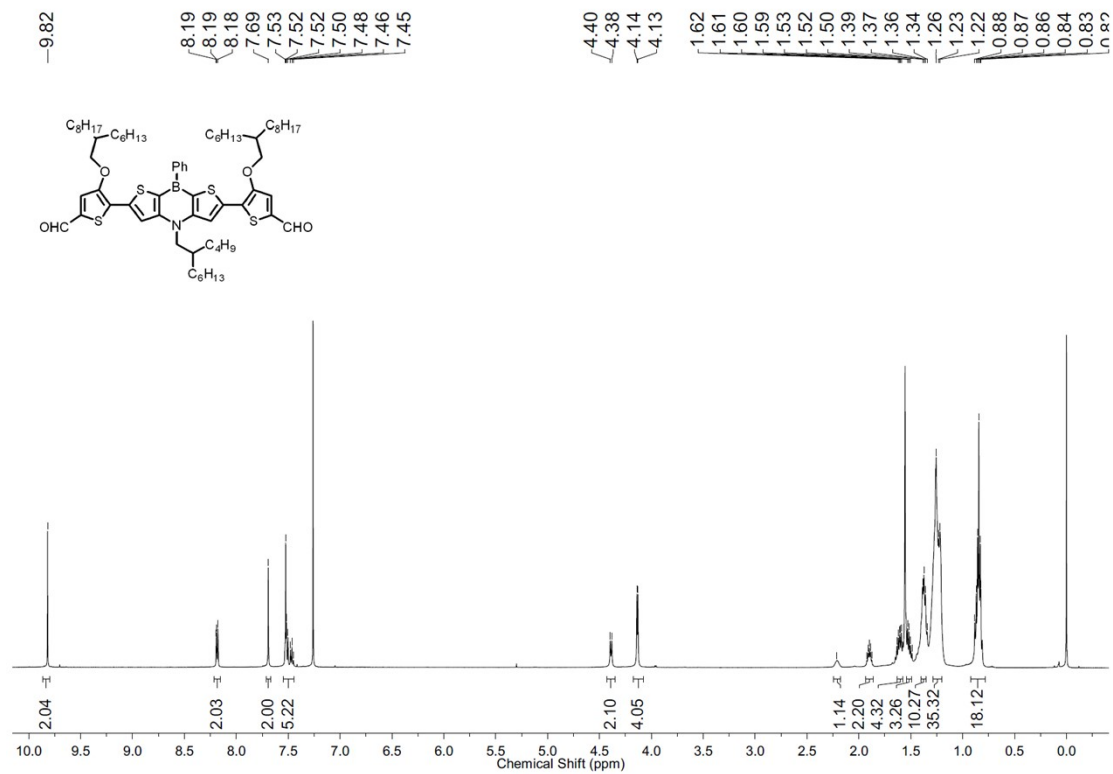


Figure S13. ¹H NMR spectrum of compound **5** in CDCl₃.

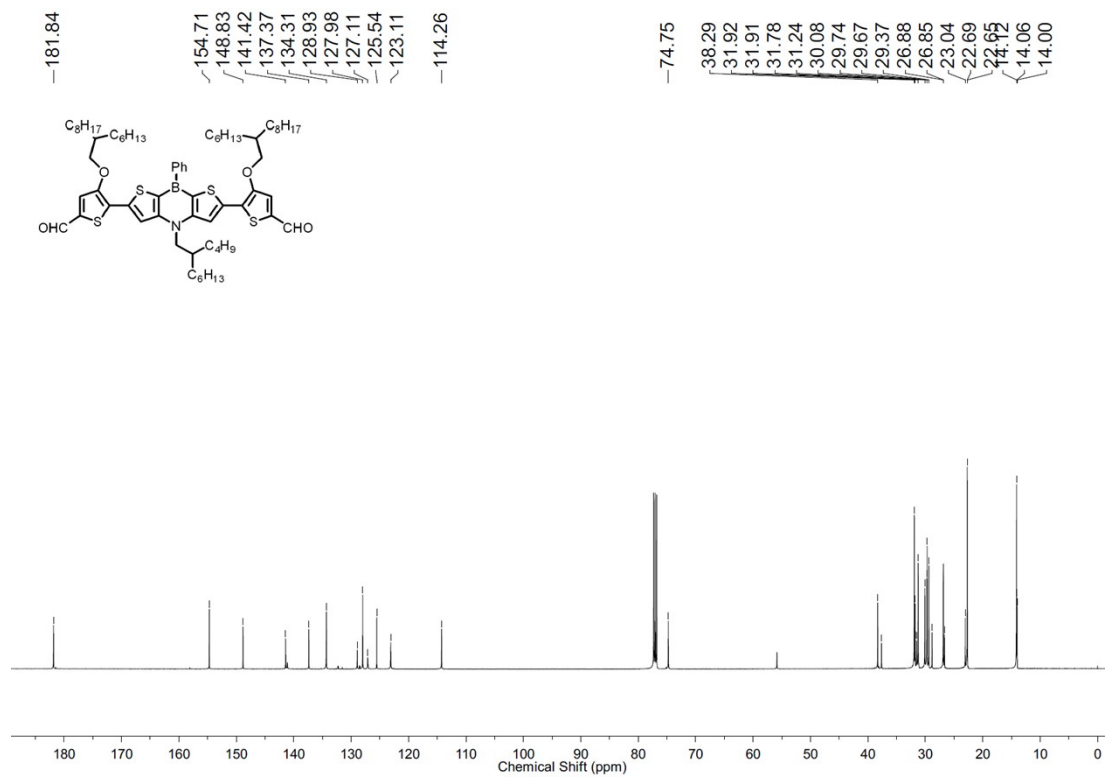


Figure S14. ¹³C NMR spectrum of **5** in CDCl₃.

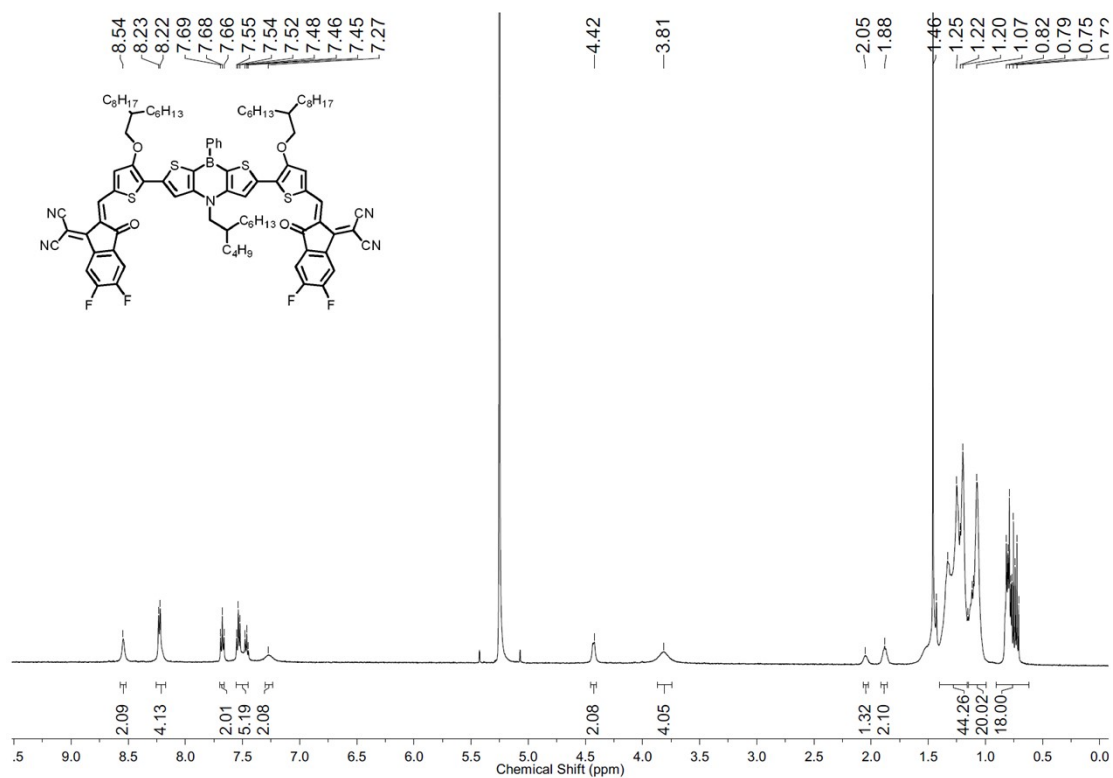


Figure S15. ^1H NMR spectrum of **ABBT-BO** in CD_2Cl_2

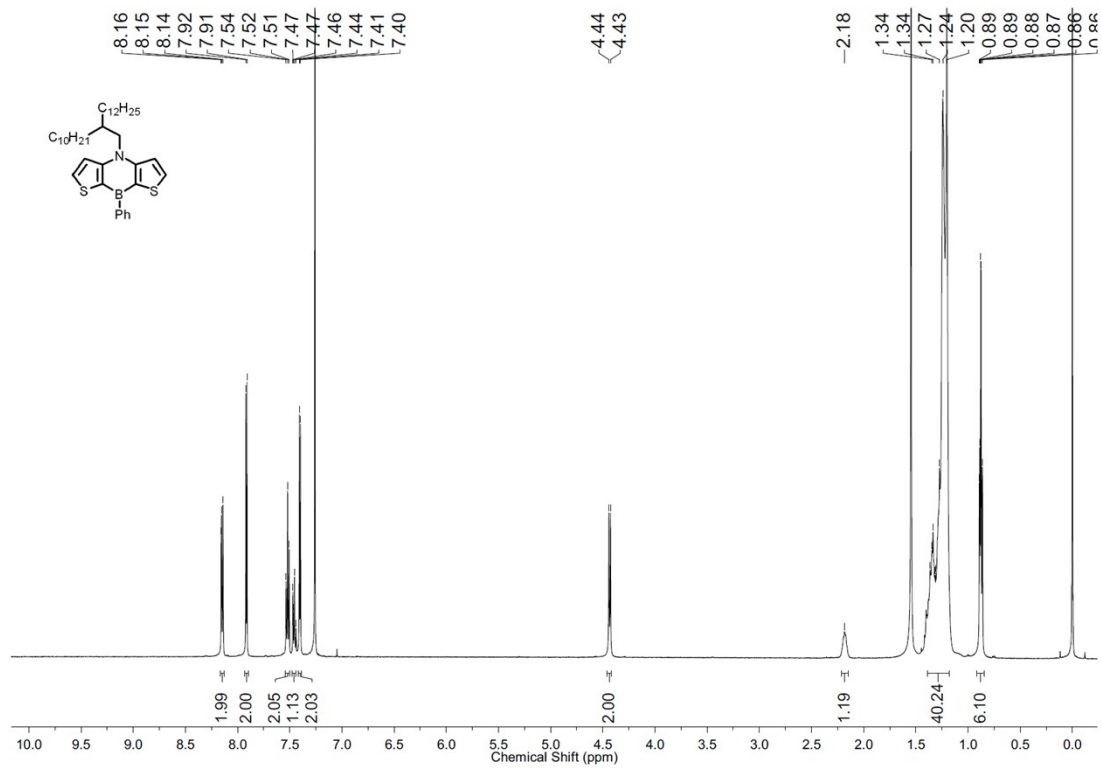


Figure S16. ^1H NMR spectrum of compound **7** in CDCl_3

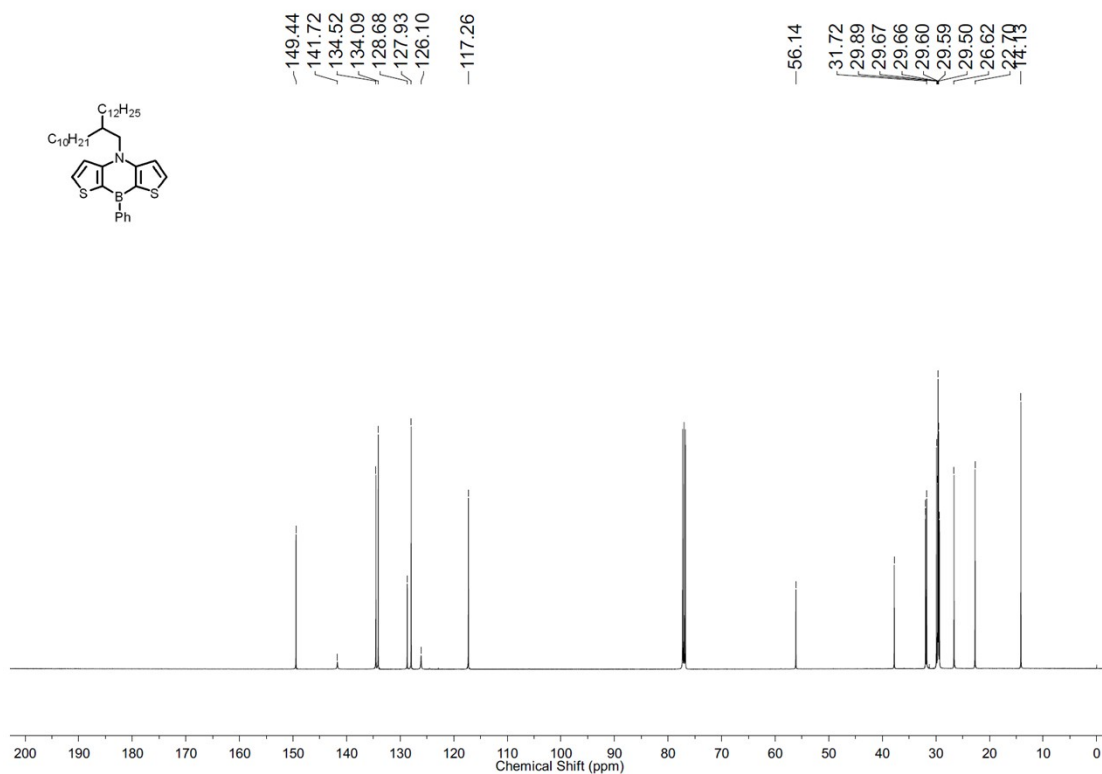


Figure S17. ^{13}C NMR spectrum of compound **7** in CDCl_3

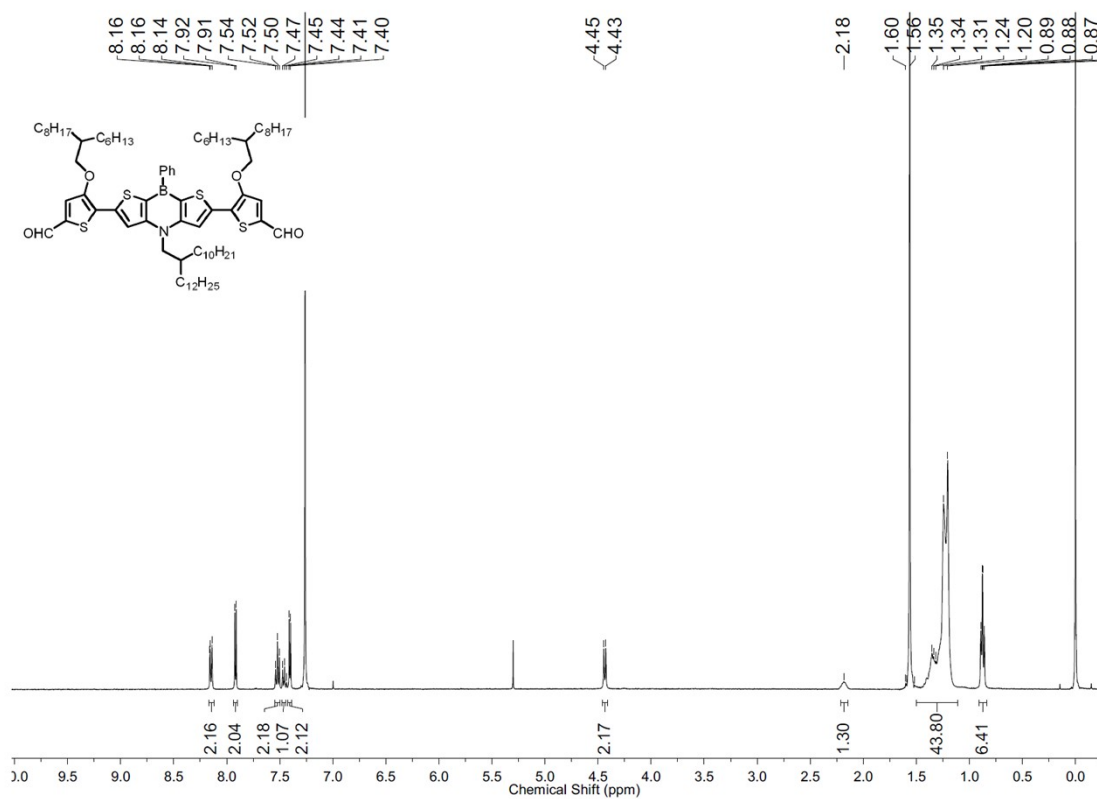


Figure S18. ^1H NMR spectrum of **9** in CDCl_3

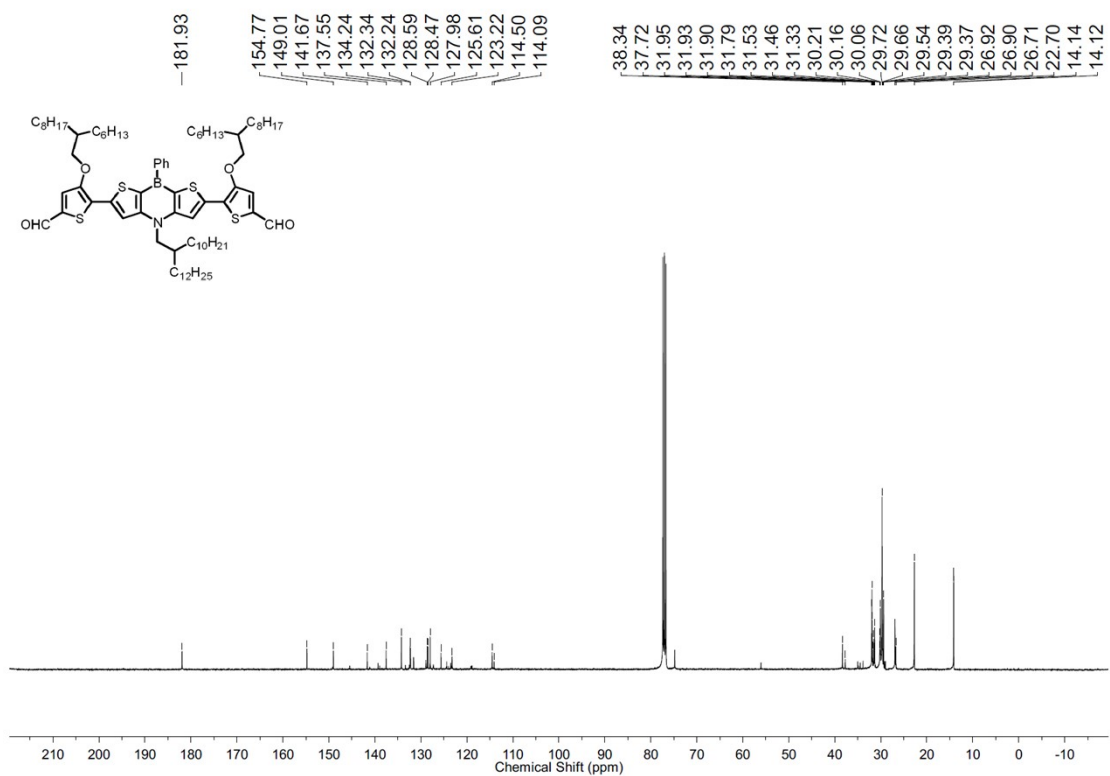


Figure S19. ^{13}C NMR spectrum of **9** in $CDCl_3$

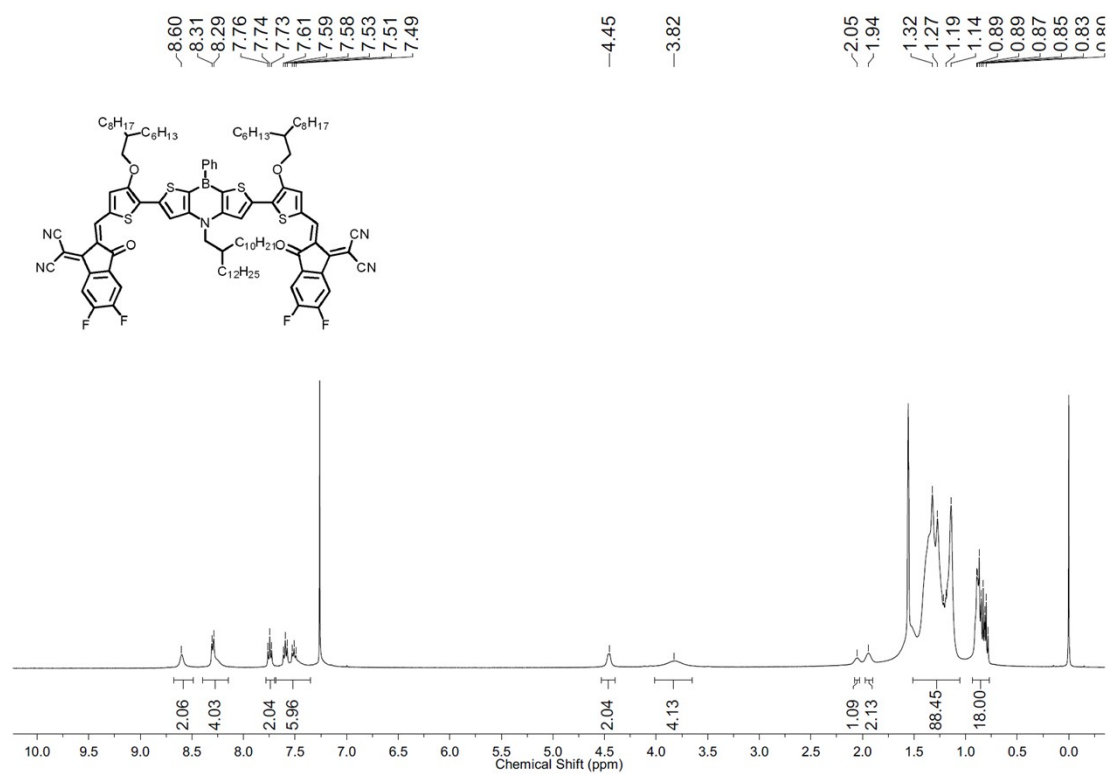


Figure S20. 1H NMR spectrum of **ABBT-DT** in $CDCl_3$

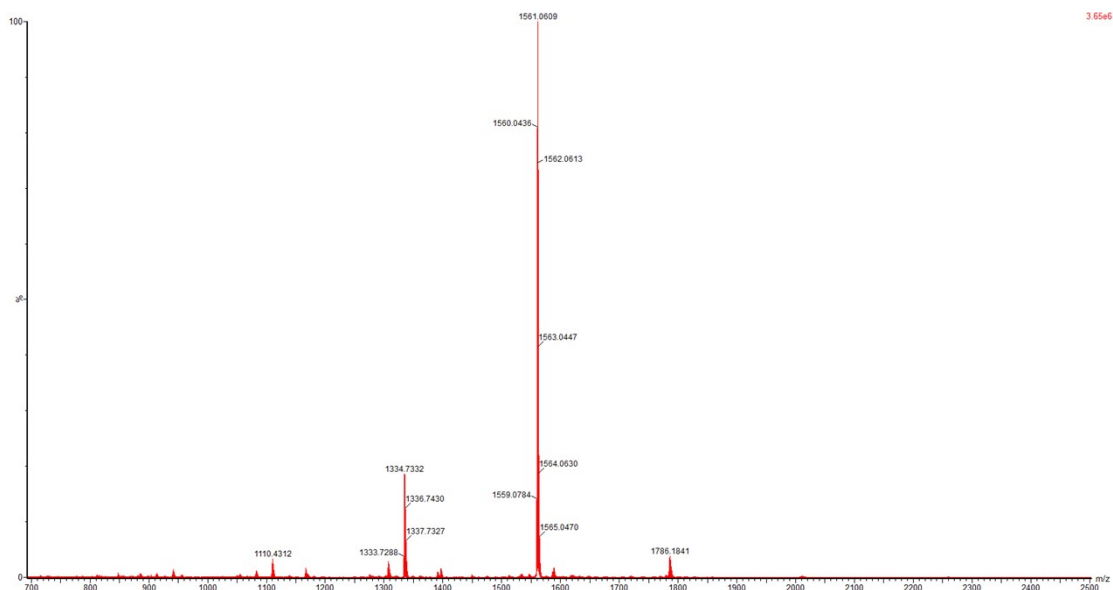


Figure S21. The high resolution mass spectrum (MALDI-TOF) of compound ABBT-BO.

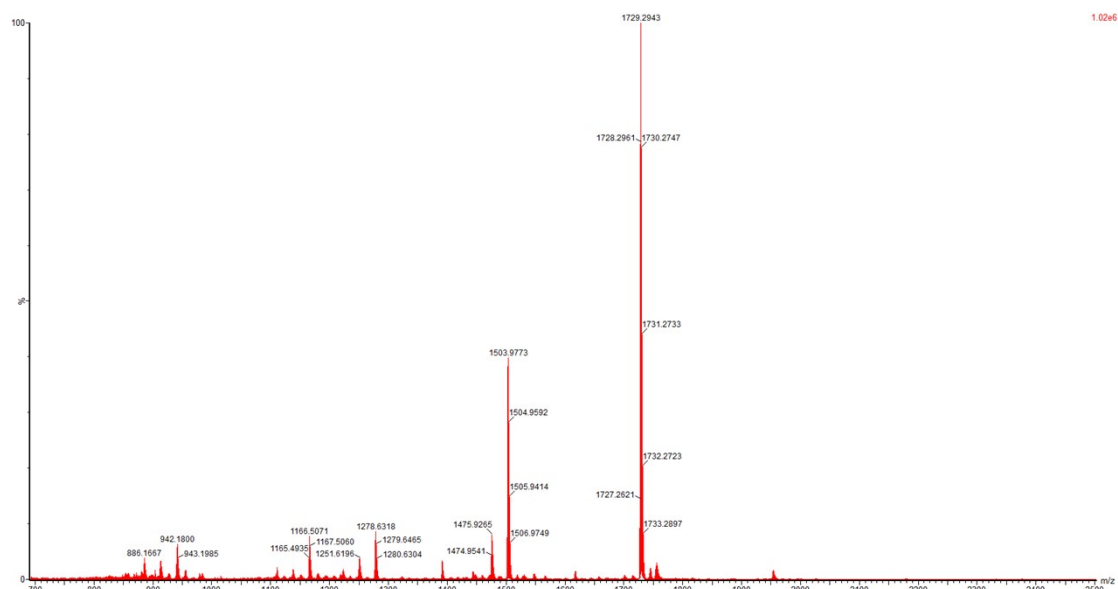


Figure S22. The high resolution mass spectrum (MALDI-TOF) of compound ABBT-DT.

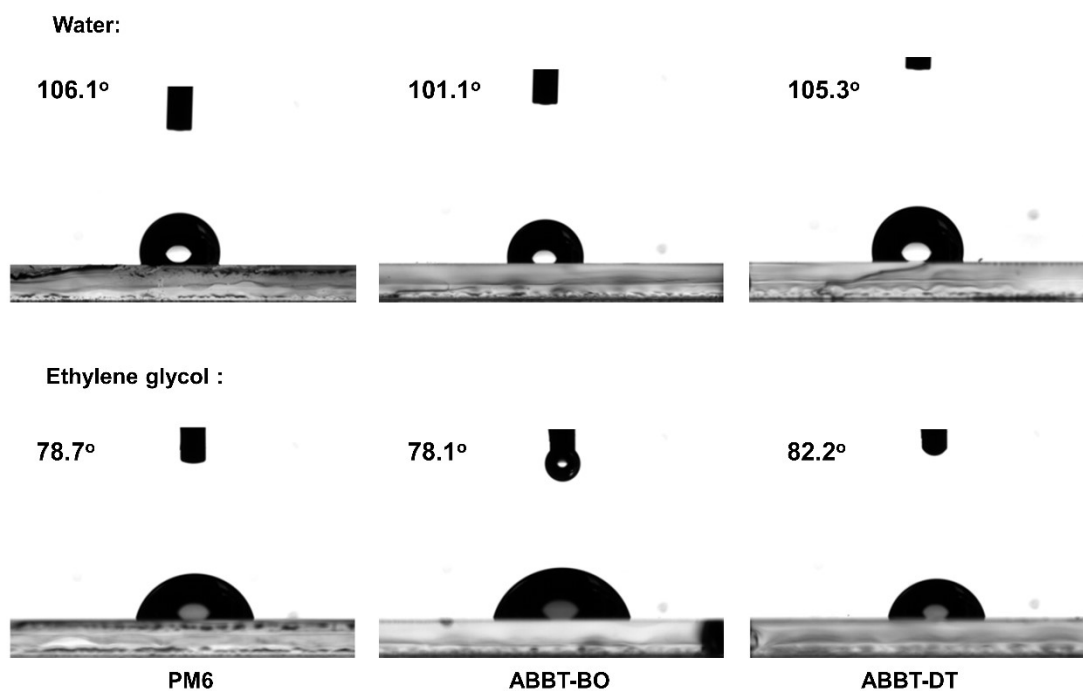


Figure S23. Photographs of water and ethylene glycol droplets on the top surfaces of PM6, ABBT-BO, and ABBT-DT film.

Table S3. Surface energy for pure films calculated from water and ethylene glycol contact angle.

Film	Contact angle[°]		γ_s^d [mJ m ⁻²]	γ_s^p [mJ m ⁻²]	γ_s [mJ m ⁻²]
	Water	Ethylene glycol			
PM6	106.1	78.7	21.77	2.36	24.13
ABBT-BO	101.1	78.1	14.08	6.98	21.06
ABBT-DT	105.3	82.2	12.16	7.07	19.13

γ_s^d is the dispersion component of surface free energy. γ_s^p is the polar component of surface free energy. γ_s is surface free energy.

References

- [1] Y. Zhang, G. Cai, Y. Li, Z. Zhang, T. Li, X. Zuo, X. Lu, Y. Lin, *Adv. Mater.* **2021**, *33*, 2008134.