

Supporting Information

A₂-A₁-D-A₁-A₂ type non-fullerene acceptors based on methoxy substituted benzotriazole with three different end-capped groups for P3HT-based organic solar cells

Qianqian Zhang^{1,2#}, *Bo Xiao*^{2,3#}, *Mengzhen Du*^{1,2}, *Gongqiang Li*^{1*}, *Ailing Tang*², *Erjun Zhou*^{*2}

¹Key Laboratory of Flexible Electronic (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, P. R. China.

²CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology (NCNST), Beijing 100190, P. R. China.

³University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

*E-mail: zhouej@nanocr.cn or iamgqli@njtech.edu.cn

These two authors contributed equally to this work.

Materials and Methods.

Materials. All Chemicals and solvents were reagent grades and purchased from Alfa, Aldrich, TCI, Wako, Beijing Chemical Plant or other chemical companies and used without further purification. The BTA (monomer 1) and IDT (monomer 3) compounds were synthesized according to the procedures in the literatures¹⁻⁵.

1, 2-dimethoxy-4, 5-dinitrobenzene (1).

In a two neck round-bottom flask containing dichloromethane (300 mL), acetic acid (300 mL), and 1, 2-dimethoxybenzene (5.51 g, 40 mmol) cooled to 10 °C, 65% nitric

acid (60 mL) was dropped. The reaction was allowed to warm to room temperature and stirred for 1 hour. The mixture was again cooled to 10 °C and 100% nitric acid (120 mL) was dropped. The mixture was allowed to warm to room temperature and the mixture was stirred for 18 hours. After completion of the reaction, the reaction mixture was poured into ice-water and the dichloromethane layer separated. The water phase was extracted with dichloromethane. The combined organic phase was washed with water, sat. NaHCO₃ (aq), brine and dried over MgSO₄. Concentration in vacuum gave the crude product that was recrystallized from ethanol to obtain a yellow solid. Yield: 8.80 g (92%) ¹H NMR (400 MHz, CDCl₃) δ 7.34 (s, 2H), 4.02 (s, 6H).

4, 5-dimethoxybenzene-1, 2-diamine (2).

A mixture of 1,2-dimethoxy-4,5-dinitrobenzene (20 mmol, 4.56 g) and Sn(II)Cl₂ • 2H₂O (200 mmol, 45 g) in ethanol (100 ml) and conc. HCl (80 ml) was heated to 88 °C overnight. After cooling to room temperature, the product was filtered and washed with water and methanol. The reaction mixture was put into 1000 mL of erlenmeyer flask, and then 4 M NaOH was used to adjust the pH value to pH 10. Meanwhile, the reaction mixture was extracted three times quickly with dichloromethane. The organic layer was dried by MgSO₄ and then concentrated under reduced pressure quickly. As the product is unstable, it is directly transferred to the next step. The product was a light-yellow solid Yield: 3.0 g (90 %).

5, 6- dimethoxy-1H-benzo[d][1,2,3]triazole (3).

Compound 2 (10.9 g, 65 mmol) was dissolved in AcOH (8 mL) and 350 mL of water under nitrogen atmosphere and then stirred for half an hour at 90 °C. The reaction mixture was cooled, and a solution of NaNO₂ (4.3 g, 71.5 mmol) in 200 mL of water was dropped at 5 °C. It was stirred at room temperature overnight. The precipitate obtained after cooling was filtered off, dried in air, and column chromatography on silica gel (ethyl acetate as the eluent) was performed to obtain a red solid. Yield: 3.3 g (29%). ¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 2H), 3.98 (s, 6H).

5, 6-dimethoxy-2-octyl-2H-benzo[d][1,2,3]triazole (4).

Compound 3 (3.3 g, 18.5 mmol) were dissolved in N, N-dimethylformamide (40 mL). Under ice bath, sodium hydride (0.7 g, 27.6 mmol) was added in small portions in batches and then protected with nitrogen. After stirring for one hour, 1-bromooctane (5.3 g, 27.6 mmol) was dropped. The reaction mixture was stirred for 6 h and monitored by thin-layer chromatography. The reaction mixture was then poured into 100ml of water, extracted with CHCl₃, and washed with water twice. The organic extraction was dried over anhydrous MgSO₄, and the solvent was evaporated under reduced pressure. Column chromatography on silica gel (petroleum ether: dichloromethane = 1:1 as the eluent) was performed to obtain a light-yellow liquid. Yield: 3.0 g (55%). ¹H NMR (400 MHz, CDCl₃) δ 7.09 (s, 2H), 4.61 (t, J = 7.2 Hz, 2H), 3.96 (s, 6H), 2.05 (m, 2H), 1.30 (m, J = 31.2 Hz, 10H), 0.86 (t, J = 6.9 Hz, 3H).

4, 7-dibromo-5,6-dimethoxy-2-octyl-2H-benzo[d][1,2,3]triazole (5)

To a solution of 3 (1.16 g, 4.0 mmol) in a mixture of dichloromethane (140 mL) and acetic acid (60 mL) was added bromine (1.5 mL, 28.0 mmol), and the resulting mixture was stirred in the dark for ca. 48 h at room temperature. The mixture was then poured in water (300 mL), quenched with 1M Na₂SO₃ (aq), extracted with dichloromethane, sequentially washed with water, saturated NaHCO₃ (aq), and the solvents are evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether: dichloromethane = 2:1 as the eluent) to get the light-yellow liquid. Yield: 1.5 g (93 %). ¹H NMR (400 MHz, CDCl₃) δ 4.79 – 4.63 (t, 2H), 3.98 (s, 6H), 2.17 – 2.07 (m, 2H), 1.41 – 1.15 (m, 10H), 0.88 (t, 3H).

7-bromo-5, 6-dimethoxy-2-octyl-2H-benzo[d][1,2,3]triazole-4-carbaldehyde (6)

Compound 5 (5.03 g, 14.21 mmol) was dissolved in 300 mL of dry THF in a 500 mL flask. The mixture was deoxygenated with nitrogen for 30 min. Then 7.8 mL n-butyllithium (15.6 mmol, 2.0 mol • L⁻¹) was injected into the solution slowly at -78 °C and the solution was stirred for 1 hour at -78 °C. After that, DMF (4.15 g, 56.8 mmol) was added into the solution slowly, and then the mixture was stirred overnight at room

temperature. The reactant was quenched with 200 mL HCl (1 mol.L⁻¹), extracted with CHCl₃ and dried over anhydrous MgSO₄. Finally, the crude compound was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 5:1 as the eluent). Compound 6 was obtained as light-yellow liquid. Yield: 6.42 g (62%). ¹H NMR (400 MHz, CDCl₃) δ 10.61 (s, 1H), 4.86 – 4.71 (t, 2H), 4.12 (s, 3H), 4.00 (s, 3H), 2.11 (m, 2H), 1.31 (m, 10H), 0.86 (t, 3H).

Synthesis of compound 8

In a two-neck round-bottom flask, compound 6 (1.3 g, 3.3 mmol), compound 3 (1.98 g, 1.6 mmol) and toluene (60 mL) were added. The mixture was deoxygenated with nitrogen for 20 minutes, and then Pd(PPh₃)₄ (35 mg, 0.03 mmol) was added. The mixture was refluxed for 48 hours and then cooled to room temperature. 150 mL of KF saturated solution was added and stirred for 2 hours. The mixture was extracted with CH₂Cl₂ (3 × 100 mL). The organic phase was dried over anhydrous MgSO₄. After removing the solvent, the residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 7:1 as the eluent) and compound 8 was obtained as a bright red solid. Yield: 1.34 g (54%). ¹H NMR (400 MHz, CDCl₃) δ 10.58 (s, 2H), 8.79 (s, 2H), 7.59 (s, 2H), 7.29 (d, *J* = 8.2 Hz, 8H), 7.10 (d, *J* = 8.2 Hz, 8H), 4.77 (t, *J* = 7.1 Hz, 4H), 4.07 (m, 12H), 2.74 – 2.38 (m, 8H), 1.44 (m, 56H), 0.86 (t, 18H). ¹³C NMR (101 MHz, CDCl₃) ppm 187.24, 160.17, 156.31, 154.19, 147.17, 146.35, 141.88, 141.61, 139.13, 138.25, 136.54, 135.84, 128.44, 127.97, 124.97, 118.23, 116.09, 77.29, 77.03, 76.72, 63.12, 60.52, 56.87, 35.61, 31.74, 31.37, 30.04, 29.19, 29.10, 29.05, 26.56, 22.60, 14.08.

Synthesis of BTA100

A two-neck round-bottom flask was added compound 8 (193 mg, 0.125 mmol), 3-ethyl-1,3-thiazolidine-2,4-dione (113 mg, 0.78 mmol), chloroform (40 mL) and pyridine (2 mL). The mixture was deoxygenated with nitrogen for 10 minutes, and then refluxed for 48 hours. After cooling to room temperature, the mixture was poured into methanol (150 mL) and stirred for 30 minutes, then filtered. The residue was purified

by column chromatography on silica gel (chloroform as the eluent) and compound BTA100 was isolated as a red solid. Yield: 100 mg (45%). ¹H NMR (400 MHz, CDCl₃) δ 8.68 (s, 2H), 8.45 (s, 2H), 7.56 (s, 2H), 7.29 (d, J = 8.2 Hz, 8H), 7.10 (d, J = 8.2 Hz, 8H), 4.72 (t, J = 7.1 Hz, 4H), 3.99 (d, , 12H), 3.83 (q, J = 7.1 Hz, 4H), 2.67 – 2.47 (m, 8H), 2.21 – 2.07 (m, 4H), 1.68 – 1.52 (m, 8H), 1.31 (m, 50H), 0.86 (t, 18H). ¹³C NMR (101 MHz, CDCl₃) ppm 169.56, 142.05, 141.51, 128.31, 128.03, 77.29, 77.03, 76.71, 62.10, 56.74, 36.82, 35.61, 31.60, 29.79, 29.20, 29.07, 29.04, 14.09, 13.19, 1.03. Aromatic area signal of BTA100 responds weakly.

Synthesis of BTA101

A two-neck round-bottom flask was added compound 8 (772 mg, 0.5 mmol), 3-ethylrhodanine (644 mg, 4 mmol), chloroform (40 mL) and pyridine (2 mL). The mixture was deoxygenated with nitrogen for 10 minutes, and then refluxed for 12 hours. After cooling to room temperature, the mixture was poured into methanol (150 mL) and stirred for 30 minutes, then filtered. The residue was purified by column chromatography on silica gel (petroleum ether: chloroform = 1:2 as the eluent) and compound BTA100 was isolated as a purple black solid. Yield: 220 mg (24%). ¹H NMR (400 MHz, CDCl₃) δ 8.70 (s, 2H), 8.34 (s, 2H), 7.56 (s, 2H), 7.29 (d, J = 8.1 Hz, 8H), 7.10 (d, J = 8.1 Hz, 8H), 4.74 (t, J = 7.1 Hz, 4H), 4.28 – 4.15 (t, 4H), 3.99 (d, 12H), 2.69 – 2.49 (m, 8H), 2.16 (t, 4H), 1.68 – 1.50 (m, 8H), 1.45 – 1.10 (m, 50H), 0.86 (t, 18H). ¹³C NMR (101 MHz, CDCl₃) ppm 195.80, 168.10, 156.28, 154.41, 154.09, 148.05, 145.68, 141.97, 141.53, 139.41, 138.61, 137.03, 135.80, 128.33, 128.00, 127.58, 125.24, 124.98, 121.28, 118.06, 113.79, 77.29, 77.02, 76.71, 63.05, 62.28, 60.46, 56.76, 39.76, 35.61, 31.75, 31.37, 29.77, 29.20, 29.08, 29.06, 26.54, 22.60, 14.09, 12.34.

Synthesis of BTA103

A two-neck round-bottom flask was added compound 8 (200 mg, 0.13 mmol), 2-(3-ethyl-4-oxothiazolidin-2-ylidene)malononitrile (151 mg, 0.78 mmol), chloroform (40 mL) and pyridine (2 mL). The mixture was deoxygenated with nitrogen for 10 minutes,

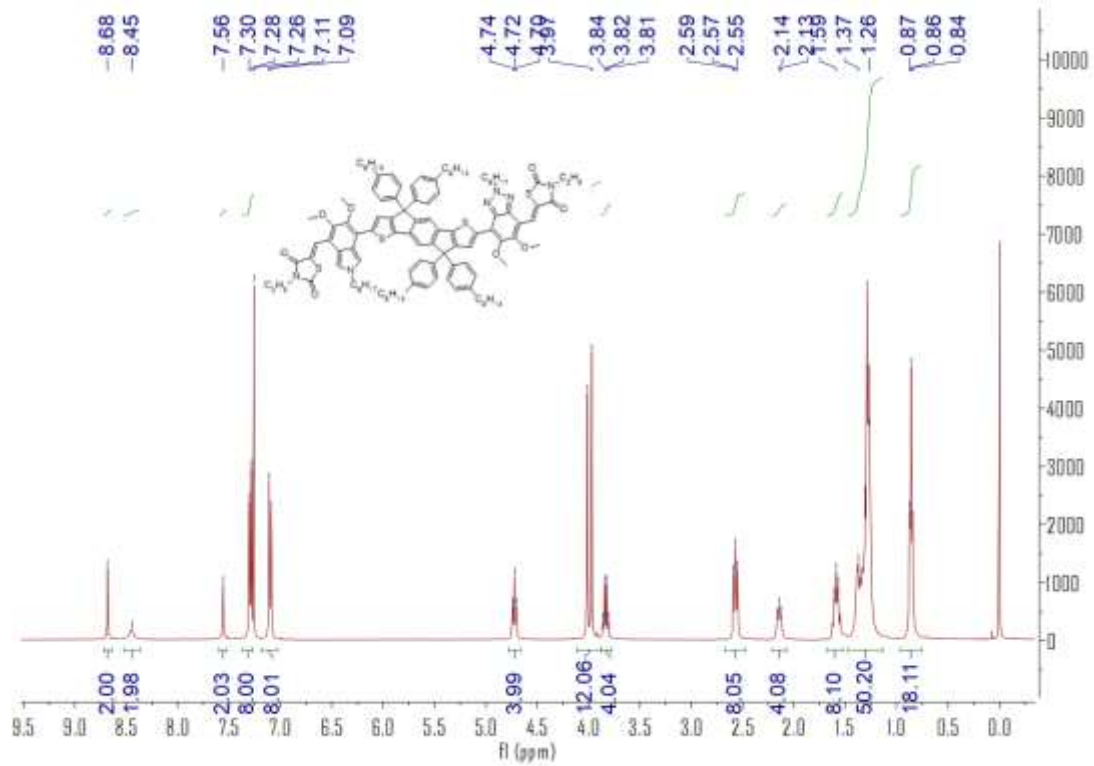
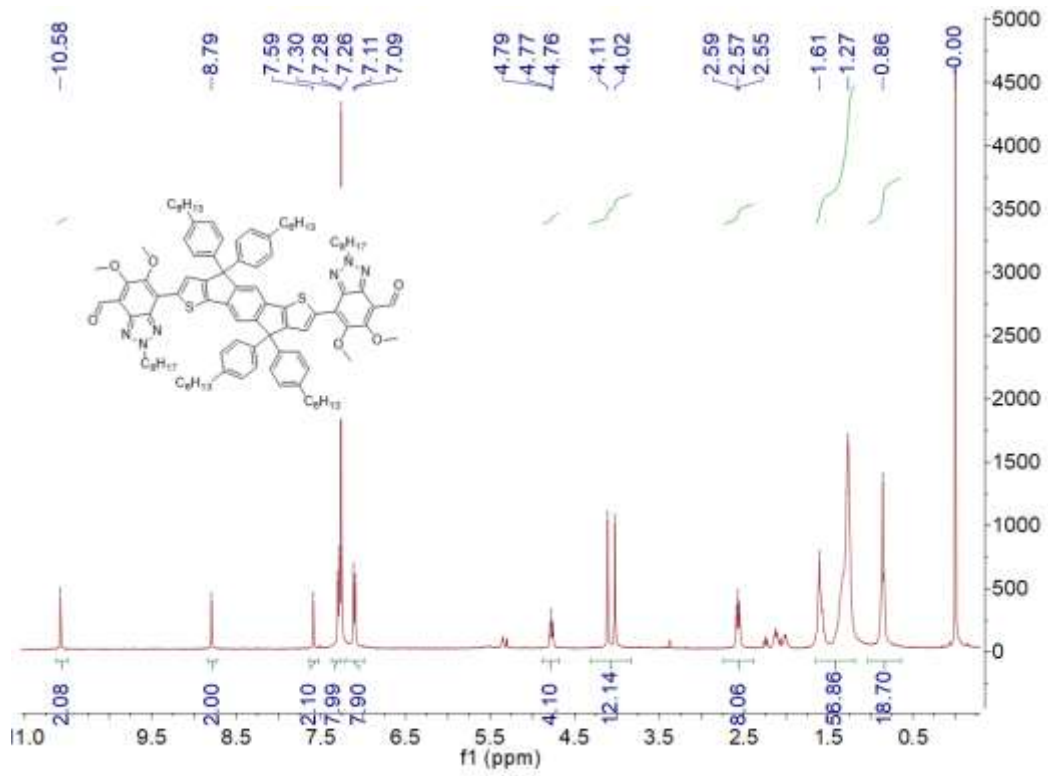
and then refluxed for 20 minutes. After cooling to room temperature, the mixture was poured into methanol (150 mL) and stirred for 30 minutes, then filtered. The residue was purified by column chromatography on silica gel (chloroform as the eluent) and compound BTA100 was isolated as a red solid. Yield: 190 mg (77%). ^1H NMR (400 MHz, CDCl_3) δ 8.72 (s, 2H), 8.51 (s, 2H), 7.57 (s, 2H), 7.29 (d, $J = 8.2$ Hz, 8H), 7.10 (d, $J = 8.2$ Hz, 8H), 4.75 (t, $J = 7.0$ Hz, 4H), 4.34 (q, $J = 7.0$ Hz, 4H), 4.02 (d, 12H), 2.71 – 2.46 (m, 8H), 2.25 – 2.10 (m, 4H), 1.69 – 1.53 (m, 8H), 1.54 – 0.98 (m, 50H), 0.85 (d, $J = 6.8$ Hz, 18H). ^{13}C NMR (101 MHz, CDCl_3) ppm 187.24, 160.17, 156.31, 154.19, 147.17, 146.35, 141.88, 141.61, 139.13, 138.25, 136.54, 135.84, 128.44, 127.97, 124.97, 118.23, 116.09, 77.29, 77.03, 76.72, 63.12, 60.52, 56.87, 35.61, 31.74, 31.37, 30.04, 29.19, 29.10, 29.05, 26.56, 22.60, 14.08.

Methods. ^1H NMR spectrum was obtained by a Bruker Advance III 400 (400 MHz) nuclear magnetic resonance (NMR) spectroscope. UV-vis absorption spectra was tested on Lambda950 (Perkin Elmer Instruments Co. Ltd, USA). Photoluminescence spectra was tested on Perkin Elmer Instruments (shanghai) Co. Ltd, USA. Thermogravimetric analysis (TGA) was recorded on Diamond TG/DTA under the protection of nitrogen at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Cyclic voltammetry (CV) was done on a electrochemical workstation with working electrode Pt plate, counter electrode Pt wire and standard calomel electrode (SCE) as reference electrode. The CV curves were recorded versus the potential of SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc^+) redox couple, which absolute energy level is 4.8 eV below vacuum. The height and phase images of blend films were obtained on a Veeco Dimension 3100 atomic force microscopy (AFM) in the tapping-mode using an etched silicon cantilever. XRD measurements were carried out in the reflection mode at room temperature using a 12-Kw D/MAX-TTRIII (CBO) X-ray diffraction system. 2D-GIWAXS were conducted on a Xeuss SAXS/WAXS system with X-ray wavelength of 1.5418 \AA . The film samples were irradiated at a fixed angle of 0.2° .

Fabrication and characterization of photovoltaic cells

Organic solar cells were fabricated with the structure of ITO/PEDOT:PSS/active layer/Ca/Al. The patterned indium tin oxide (ITO) glass with a sheet resistance of $10 \Omega \text{ sq}^{-1}$ was cleaned by ultrasonication sequentially in detergent, water, acetone and 2-propanol. After drying, the substrates were treated in an ultraviolet ozone chamber (Ultraviolet Ozone cleaner, Jelight Company, USA) for 15 min. A thin layer of poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) was spin-coated onto the ITO glass and baked at $150 \text{ }^\circ\text{C}$ for 15 min. The substrates were then transferred into a glove-box with nitrogen atmosphere and thin films of active layer were spin-coated from a solution of **P3HT:BTA100**, **P3HT:BTA101** or **P3HT:BTA103** (15 mg mL^{-1} in total) in different solvents. The calcium layer (ca. 20 nm) and the aluminum layer (ca. 80 nm) were then evaporated onto the surface of the photosensitive layer under vacuum (ca 4×10^{-6} torr) to form the negative electrode. The active area of the device was 4 mm^2 . PSCs based on the thicknesses of the active layer were detected by Alpha-atepD-120 stylus profilometer, Kla-Tencor.

The J-V curve was measured using a Keithley 2400 source-measure unit. Photocurrent was measured under AM 1.5 G illumination at 100 mW.cm^2 using a Newport Thermal Oriel 91159A solar simulator. Light intensity is calibrated with a Newport oriel PN 91150V Si-based solar cell. The EQE spectrum was measured using an Oriel Newport system (Model 66902). The mobility of hole-only or electron-only of the OSCs device was achieved by fabricated the architecture ITO/PEDOT:PSS/active layer/Au for holes or ITO/Titanium (diisopropoxide) bis (2, 4-pentanedionate), 75% in isopropanol liquid (TIPD)/active layer/Al for electrons. The mobility was extracted by fitting the current density-voltage curves using the Mott-Gurney relationship (SCLC). The active layer and electrodes were prepared the same as the solar cells' condition. Au (80 nm) and Al (80 nm) cathodes were thermal evaporated in glove box at a chamber pressure of $\sim 1.0 \times 10^{-6}$ torr.



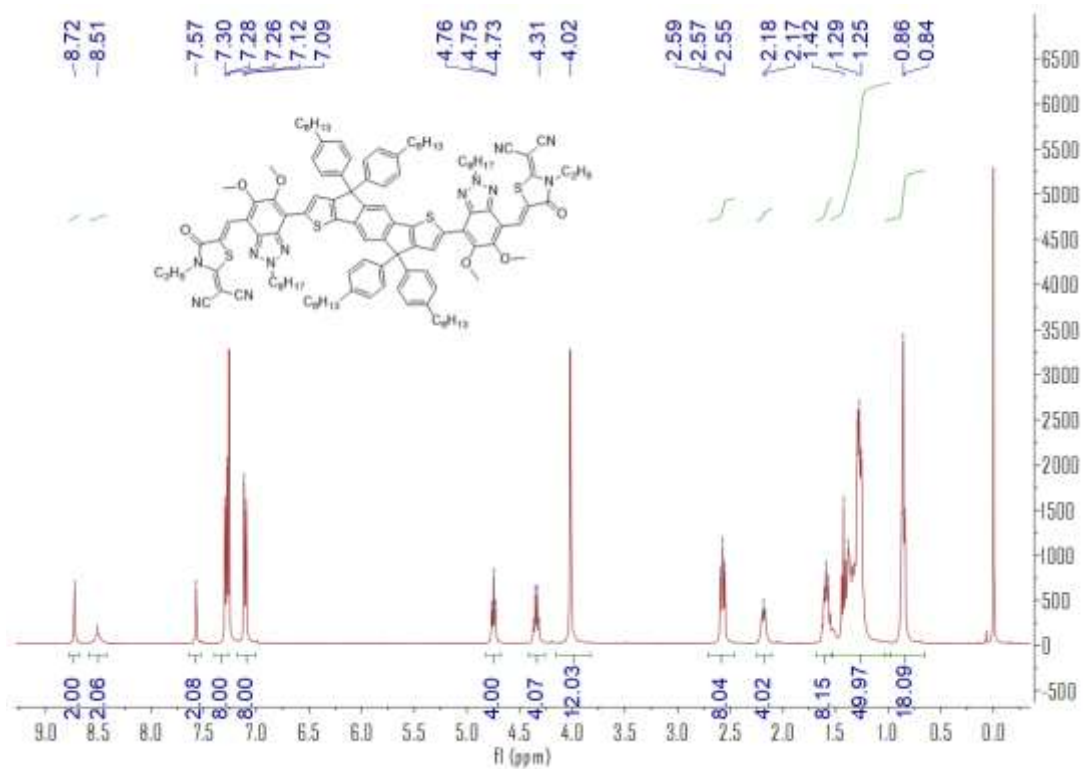
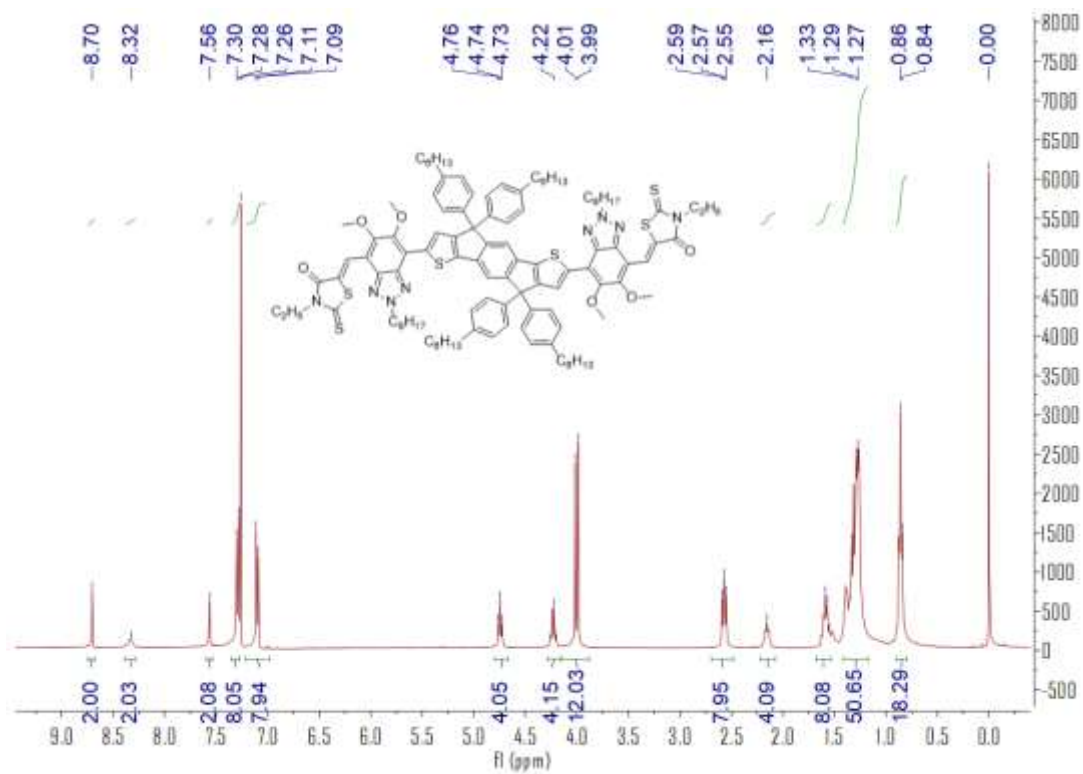
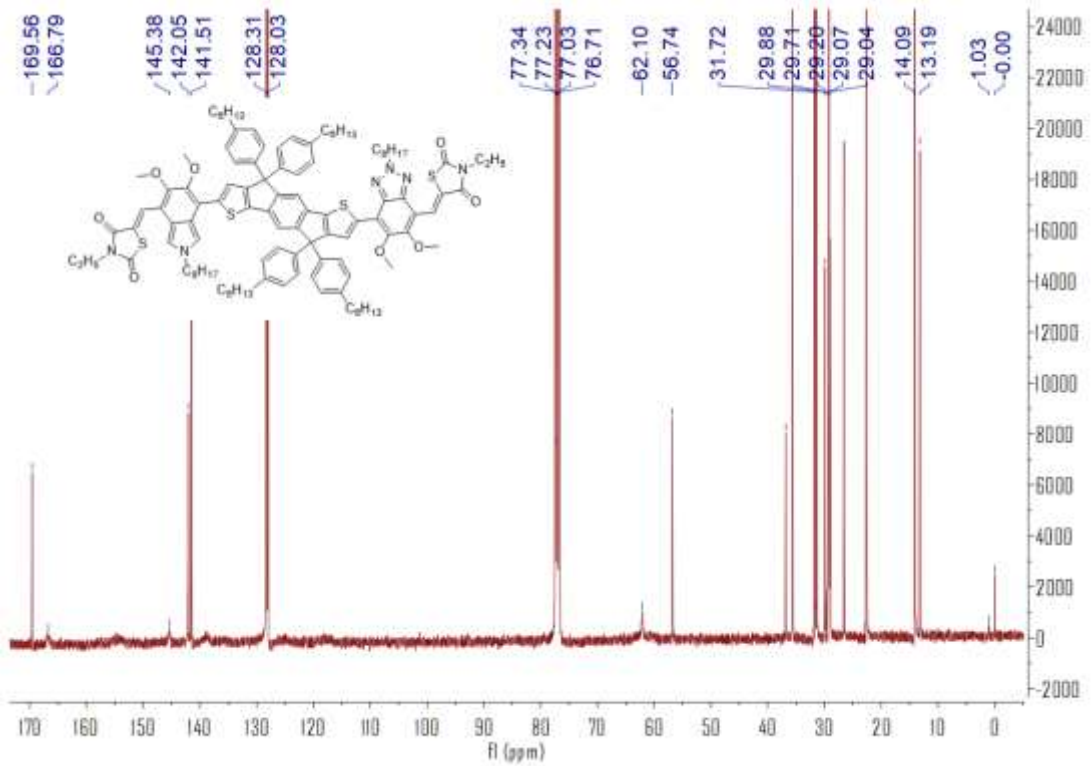
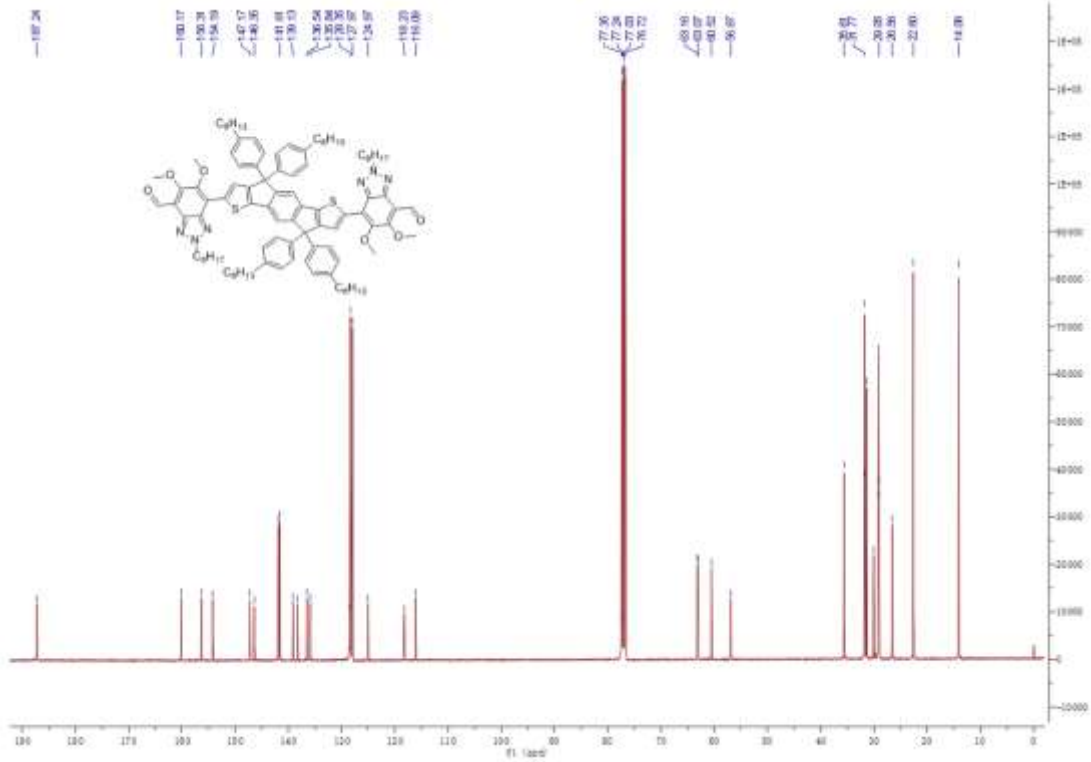


Figure S1. ¹H NMR spectra of compound **8**, BTA100, BTA101 and BTA103 in CDCl₃



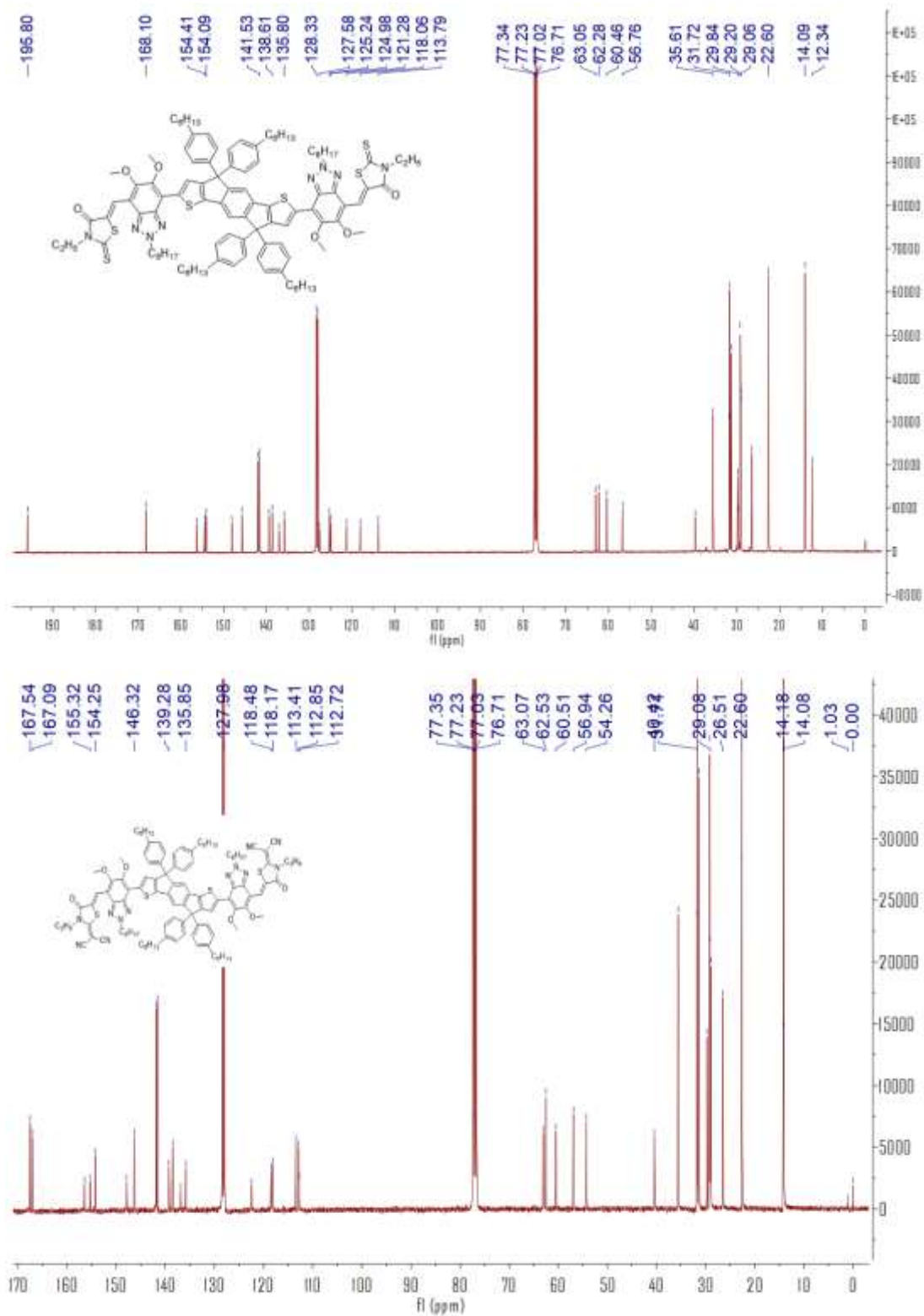
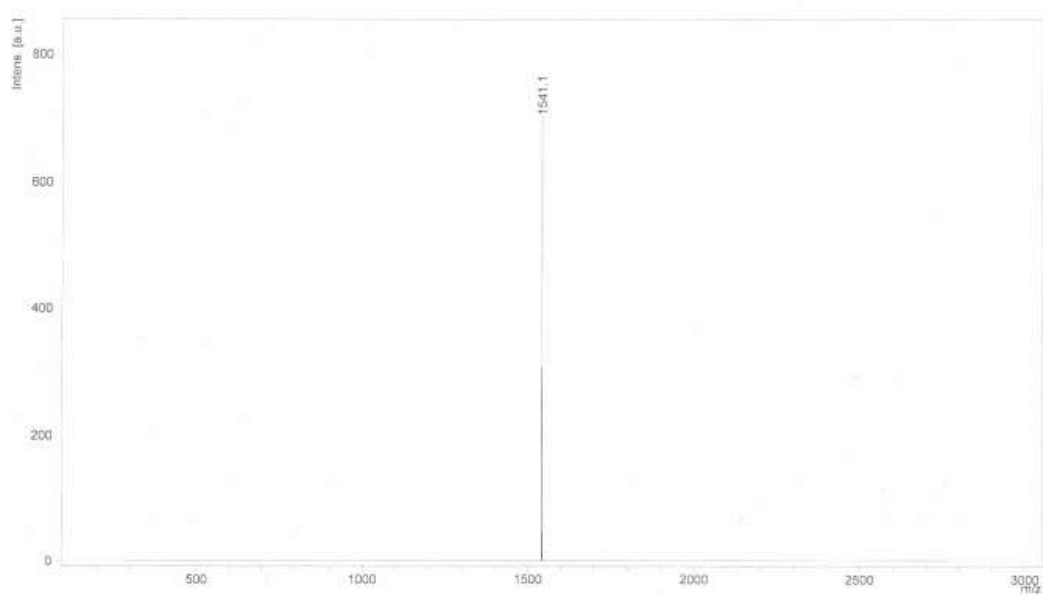


Figure S2. ^{13}C NMR spectra of compound **8**, **BTA100**, **BTA101** and **BTA103** in CDCl_3 , and aromatic area signal of BTA100 responds weakly.

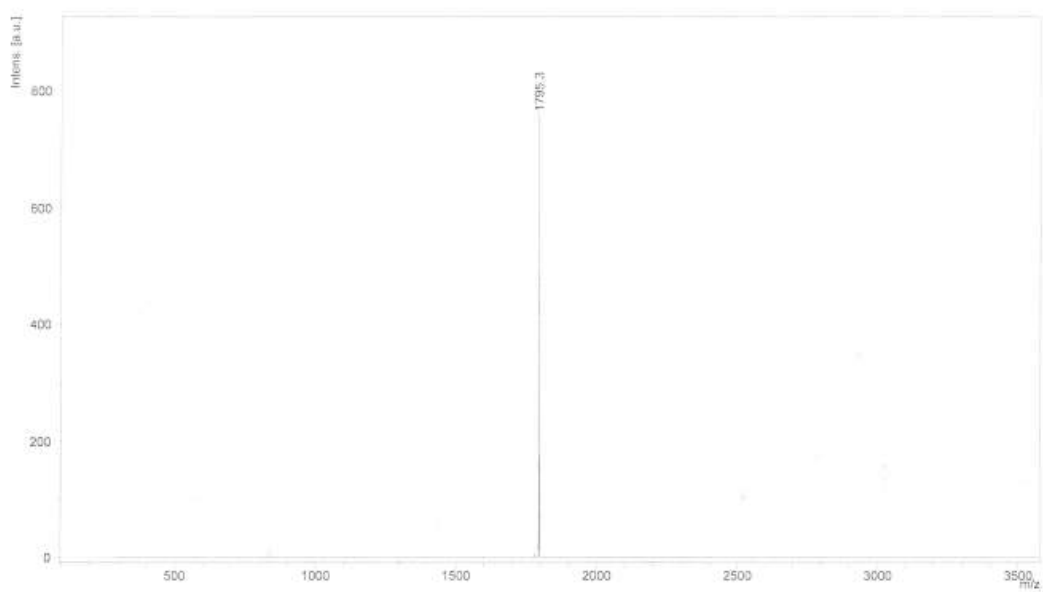
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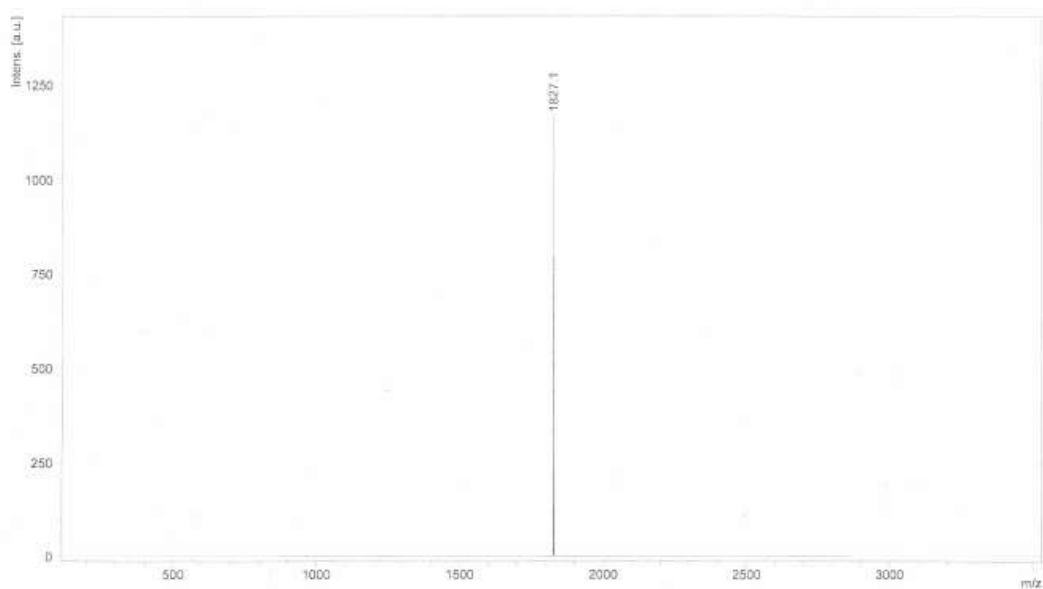
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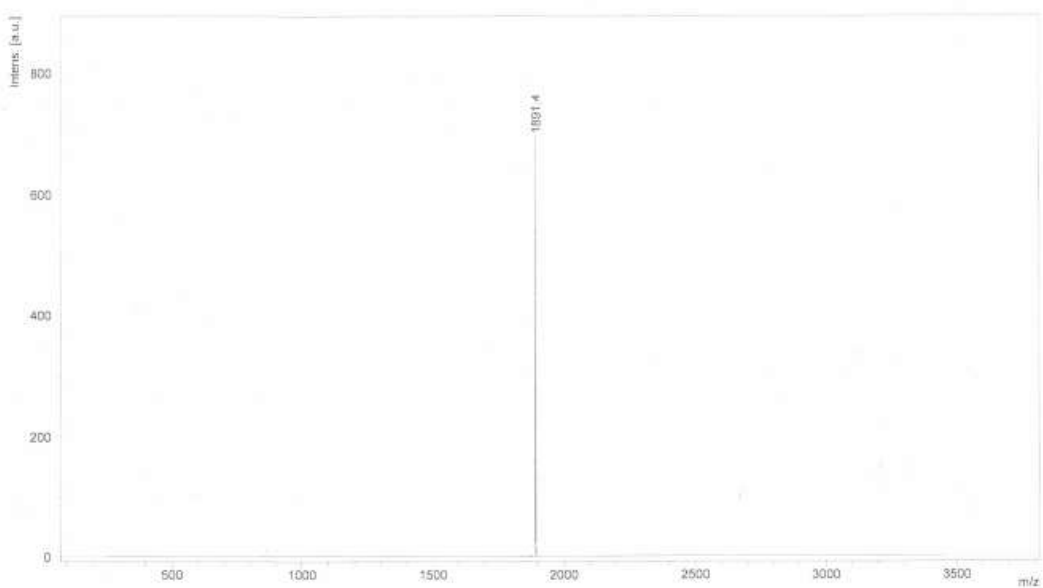


Figure S3. MALDI-TOF MS spectra of compound **8**, **BTA100**, **BTA101** and **BTA103**

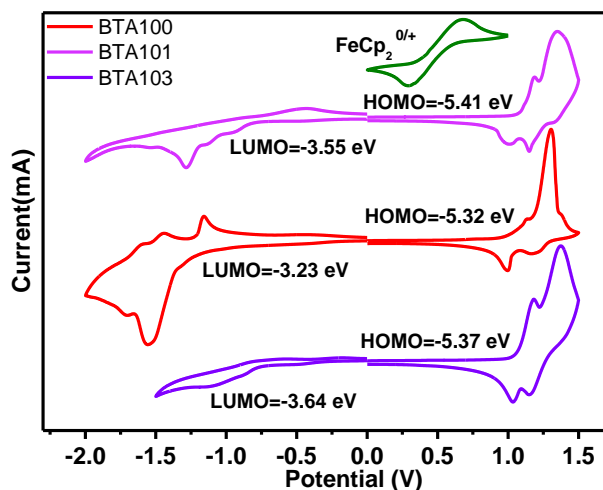
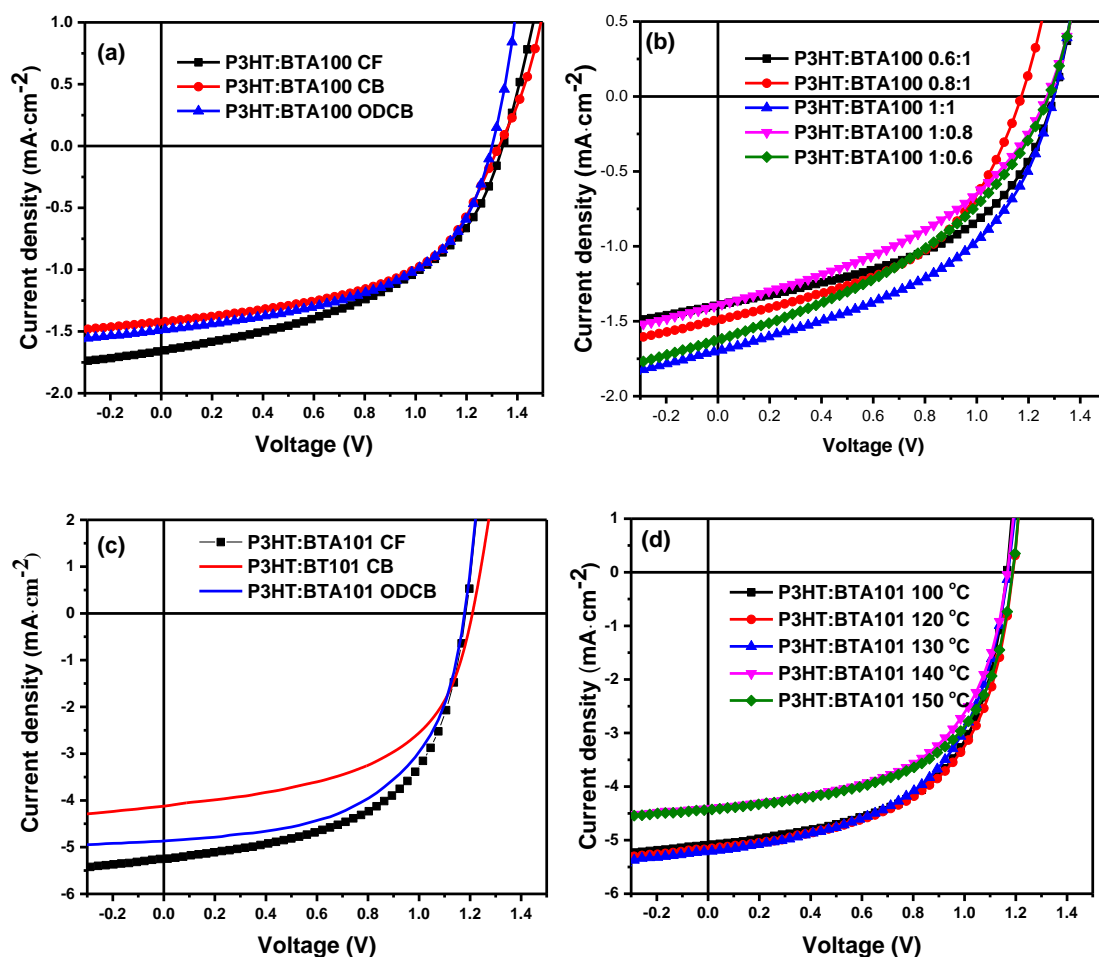


Figure S4. Cyclic voltammograms of **BTA100**, **BTA101** and **BTA103** films on a platinum electrode measured in $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ acetonitrile solutions.



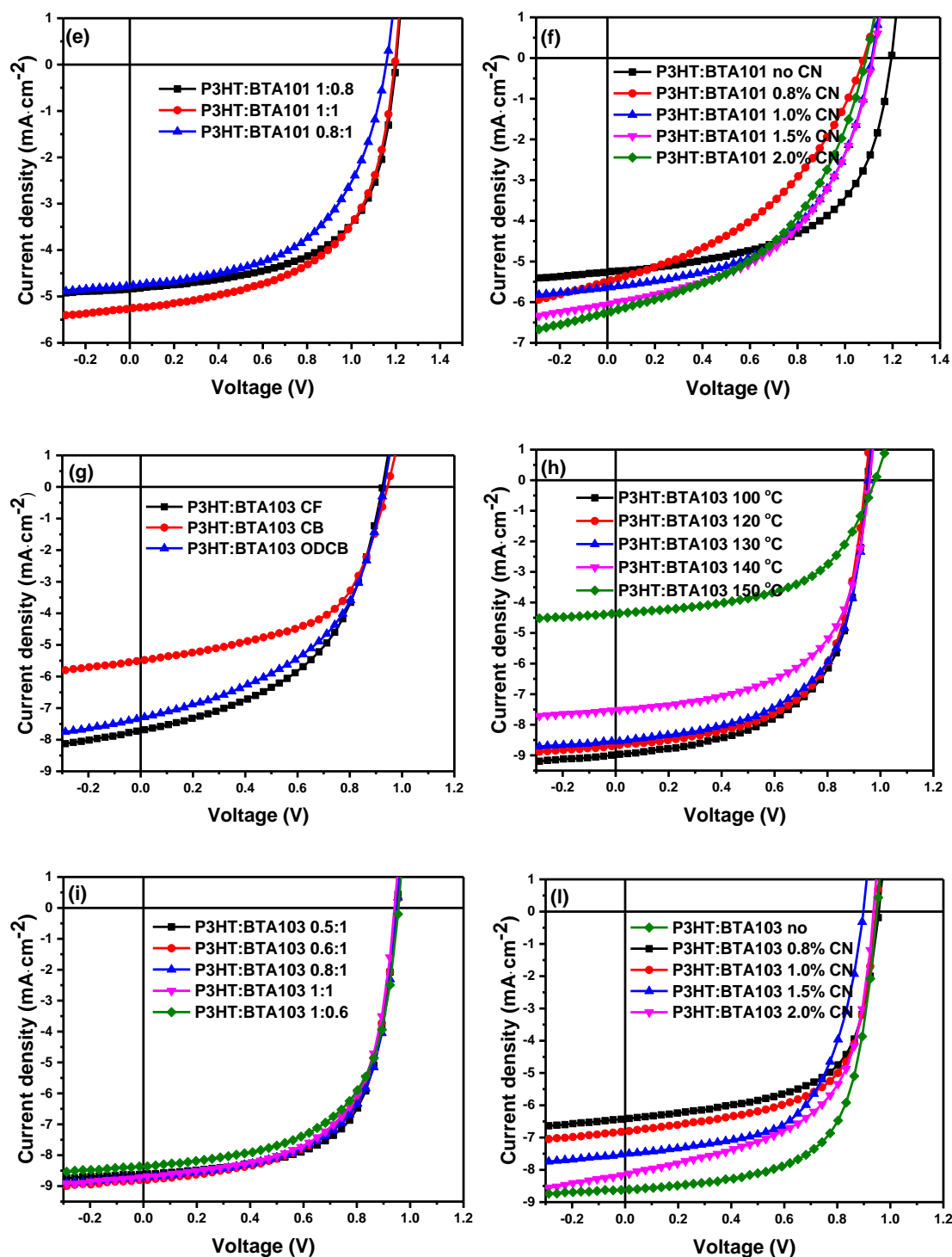


Figure S5. The J-V curves for optimization of devices: (a) (c) (g) The solvent optimization of the OSCs devices at the D/A ratio of 1:1 with 100 °C; (d) (h) temperatures of annealing for P3HT:BTA101 and P3HT:BTA103 in CF as solvent at the D/A ratio of 1:1 and 1:1, respectively; (b) (e) (i) D/A ratio for P3HT:BT100, P3HT:BT101 and P3HT:BTA103 in CF solvent with 100 °C, 120 °C and 120 °C annealing, respectively; (f) (l) CN as additive for P3HT:BT101 and P3HT:BTA103 in CF as solvent at the D/A ratio of 1:1 and 1:2 with 120 °C and 120 °C annealing, respectively.

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