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SUPPORTING INFORMATION

Dopant-Free 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT)-Based Hole Transporting Layer for Highly Stable Perovskite Solar Cells with Efficiency over 22%

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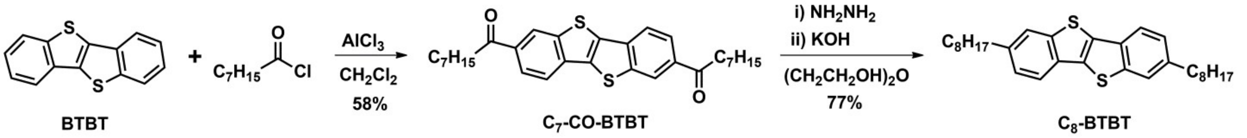
Materials and Methods

Air/moisture sensitive reactions were performed under N_2 atmosphere using a conventional Schlenk technique. Unless otherwise noted, all reagents were purchased from commercial sources and used without any purification. Column chromatography was carried out with 230-400 mesh silica gel. $^1H/^{13}C$ NMR spectroscopy characterizations were performed using a Bruker 400 spectrometer (^1H, 400 MHz; ^{13}C, 100 MHz). Elemental analyses were recorded on a LecoTruspec Micro model instrument. Mass spectrum was measured using an Advion Expression CMS L with an ionization method of atmospheric pressure chemical ionization (APCI).

Synthesis and Characterization



Scheme S1. Synthesis of 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT).

The starting compound [1]benzothieno[3,2-b][1]benzothiophene (BTBT) was prepared in accordance with the reported procedures.[1,2]

Synthesis of 2,7-bis(octan-1-one)[1]benzothieno[3,2-b][1]benzothiophene ***(C_7CO-BTBT)****:* [1]benzothieno[3,2-b][1]benzothiophene (BTBT) (1.3 g, 5.409 mmol) was dissolved in anhydrous dichloromethane (150 mL) under N_2 atmosphere and stirred at −10 °C for 5 min. Then, $AlCl_3$ (3.945 g, 29.587 mmol) was added into the reaction mixture. The resulting mixture was stirred at −10 °C for 30 min. Octanoyl chloride (4.399 g, 27.045 mmol) was subsequently added dropwise into the reaction mixture, and stirred for 1 h at the same temperature. Then, the mixture was allowed to warm to room temperature and stirred for 2 days. After completing the reaction, mixture was quenched with water to give a precipitate. Vacuum filtered precipitate was washed with water and methanol, respectively. The product was obtained as a pale yellow solid (1.55 g, 58% yield) and it was directly used in the following step without any further purification. Melting point: 265-266 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.59 (s, 1H), 8.09 (d, 1H, *J* = 8.0 Hz), 7.98 (d, 1H, *J* = 8.0 Hz), 3.08 (t, 2H, *J* = 12.0 Hz), 1.78-1.85 (m, 2H), 1.33-1.44 (m, 8H), 0.89 (t, 3H, *J* = 16.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 199.5, 142.8, 136.2, 135.8, 134.3, 124.9, 124.6, 121.9, 38.9, 31.7, 29.4, 29.2, 24.5, 22.6, 14.1.

Synthesis of 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene ***(C8-BTBT)****:* A mixture of 2,7-bis(octan-1-one)[1]benzothieno[3,2-b][1]benzothiophene (C_7CO-BTBT) (400 mg, 0.812 mmol), hydrazine hydrate (663 mg, 20.706 mmol) and potassium hydroxide (251 mg, 4.466 mmol) was dissolved in diethylene glycol (20 mL) under N_2 atmosphere, and stirred at 110 °C for 1 hour. After stirring at 210 °C for 5 hours, the mixture was allowed to cool down to room temperature. During this cooling process a white precipitate is formed. Then, the vacuum filtered precipitate was washed with water and methanol to give a crude product. The crude was then purified through column chromatography on silica gel using hexane as the mobile phase, which afforded the final product as a white solid (290 mg, 77% yield). Melting point: 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.76 (d, 1H, *J* = 8.0 Hz), 7.71 (s, 1H), 7.27 (d, 1H, *J* = 8.0 Hz), 2.76 (t, 2H, *J* = 16.0 Hz), 1.69-1.72 (m, 2H), 1.28-1.35 (m, 10H), 0.87 (t, 3H, *J* = 12.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 142.4, 140.1, 132.5, 131.2, 125.8, 123.3, 121.1, 36.1, 31.9, 31.7, 29.5, 29.3, 29.2, 22.7, 14.1. MS (APCI) *m/z* [M$^+$]; calcd for $C_{30}H_{40}S_2$: 464.26; found: 465.26 [M+H]$^+$, 352.72 [M-C_8H_{17}]$^+$. Elemental analysis (%) calcd for $C_{30}H_{40}S_2$: C, 77.53; H, 8.67; found: C, 77.71; H, 8.89.

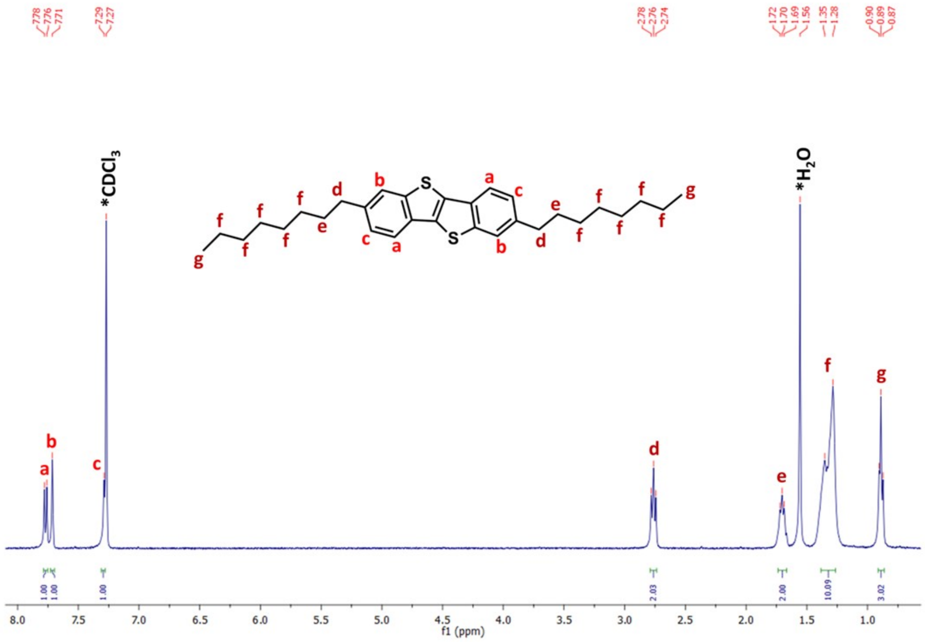


Figure S1. ^{1}H NMR spectra of **C8-BTBT** in $CDCl_3$ at room temperature with the corresponding aromatic/aliphatic proton assignments.

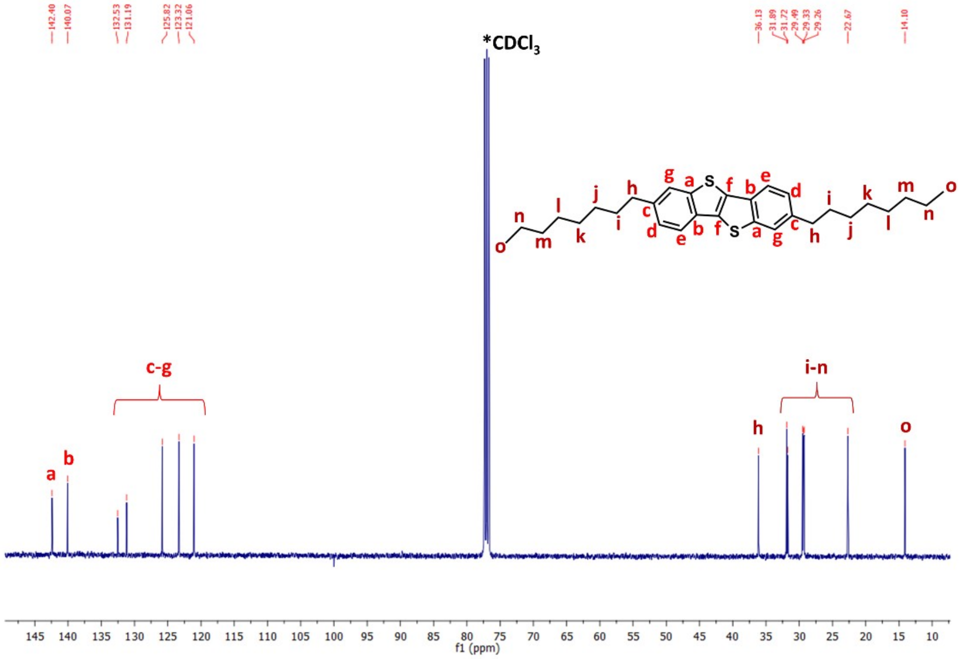


Figure S2. ^{13}C NMR spectra of **C8-BTBT** in $CDCl_3$ at room temperature with the corresponding aromatic/aliphatic carbon assignments.

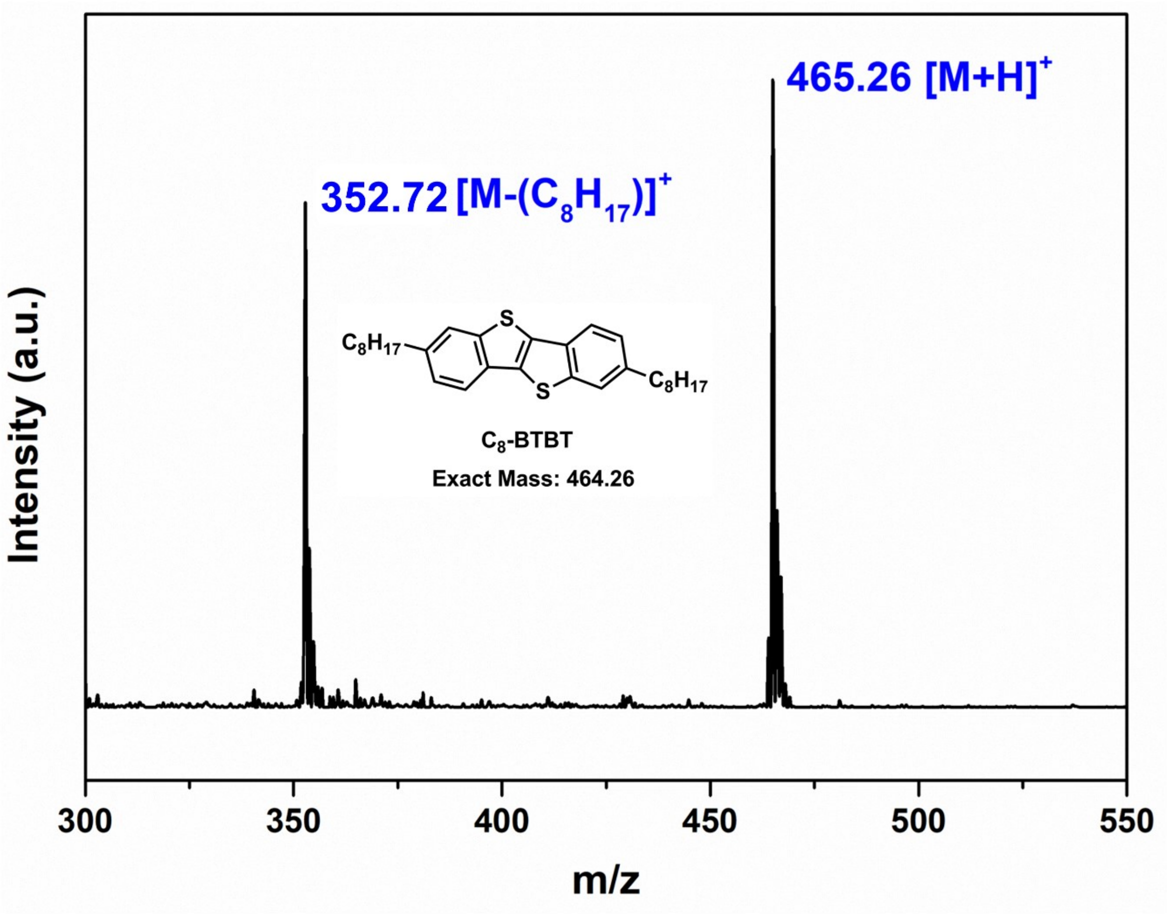


Figure S3. Positive ion mode mass spectrum of **C8-BTBT** recorded using atmospheric pressure chemical ionization (APCI) technique with an atmospheric solids analysis probe (ASAP).

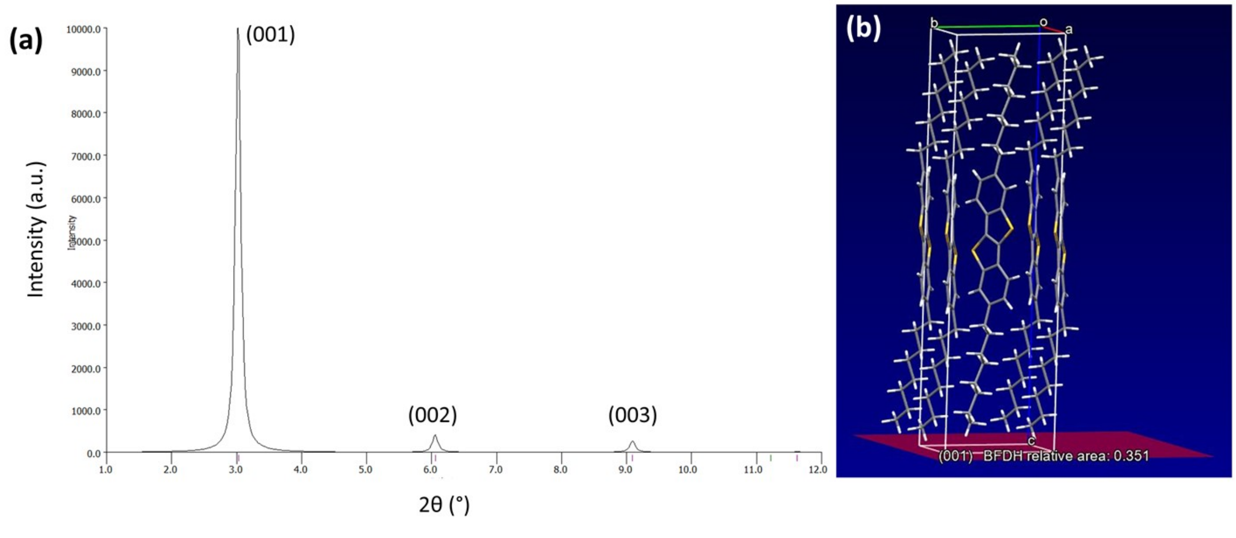


Figure S4. (a) Simulated powder XRD pattern of C8-BTBT based on the reported single-crystal structure (CCDC Deposition number: 679293) showing low angle (2θ = 1-12°) diffraction planes of (001), (002), and (003). (b) The corresponding unit cell molecular orientation and packing for (001) crystalline plane.

Device fabrication

Fluorine-doped tin oxide (FTO) glass substrates (NSG, 10 Ω/sq) were cleaned by sonication in a detergent solution (2% Hellmanex in de-ionized water), de-ionized water, acetone, ethanol, and treated with UV-ozone, respectively, after etching with zinc powder and 2 M HCl solution. The SnO_2 ETL was deposited from a commercial SnO_2 colloidal dispersion (Alfa Aesar, 15% in H_2O) diluted with water (1:5, volume ratio). The dispersion was spin coated onto clean substrates at 4000 rpm for 15 s, and then annealed on a hot plate at 150 °C for 30 min. The perovskite films were deposited on SnO_2 film by spin coating a precursor solution containing, 0.05 M CsI, 0.90 M FAI, 0.10 M MABr, 0.90 M PbI_2, and 0.10 M $PbBr_2$ in dimethylformamide/dimethylsulphoxide (4:1, volume ratio) using a two-step program (2000 rpm for 10 s followed by 6000 rpm for 20 s). During the second step, 200 µL of chlorobenzene was poured on the spinning substrate 8−10 s prior to the end of the spinning to get rid of co-solvents and enable perovskite crystallization. The substrates were then heated at 100 °C for 1 h on a hot plate. After films were cooled to room temperature, C8-BTBT dissolved in various concentrations (1 to 20 mg/mL) in chlorobenzene was spin-coated onto the perovskite film at 4000 rpm for 20 s, and then heated 40 °C for 5 min on a hot plate. For comparison, ~73 mM of spiro-OMeTAD solution in chlorobenzene with 200 mM tert-butylpyridine and 30 mM of lithium bis(triuoromethanesulfonyl)imide (Li-TFSI) was deposited on the perovskite film by spin coating at 4000 rpm for 20 s. The devices were completed by thermal evaporation of 100 nm Au electrode.

Characterizations

The microstructural features and the thickness of the layers were investigated using Hitachi model field emission scanning electron microscopy (FE-SEM). Contact angle measurements were carried out with Krüss DSA100 drop shape analyzer at ambient conditions. The morphology and microstructure of the organic HTL films were characterized with atomic force microscopy (Veeco-Bruker, Multimode 8) and X-ray diffraction (Malvern Panalytical, Empyrean X-Ray Diffractometer), respectively. The θ-2θ out-of-plane X-ray diffraction (XRD) measurements performed in this study uses the Bragg-Brentano parafocusing geometry having the incident angle (between the X-ray source and the sample) always the ½ of the detector angle 2θ. The current density–voltage (J–V) curves were recorded using Keithley 4200 semiconductor characterization system using OAI Class AAA solar simulator under AM 1.5 G illumination of 100 mW/cm^2 as the light source. The J–V curves were recorded between −0.2 and 1.2 V with 0.02 V steps. The incident photon-to-electron conversion efficiency (IPCE) of the cells was recorded using a 150 W xenon light source EQE system (Enli-Tech) in the DC mode without any voltage bias. The J–V and IPCE curves of all cells were measured through a non-reflective metal mask with an aperture area of 0.16 cm^2. Steady-state photoluminescence (PL) spectra of perovskite films were recorded with a spectrofluorometer (Fluorolog 322) by exciting the samples at a fixed wavelength of 460 nm and scanning the emission monochromator. Time-resolved PL (TRPL) spectra were recorded on a spectrofluorometer Fluorolog 322 working in a single-photon counting mode by exciting the samples with picosecond pulsed diode laser head NanoLED-405LH (Horiba) which emit <200 ps duration pulses at 405 nm with repetition rate of 1 MHz and pulse energy about 11 pJ was used as an excitation source. Shelf-life stability tests have been carried out in similar experimental conditions, such as relative humidity level (40–

45 %) without encapsulation at room temperature during a period of 120 days. For the thermal stability experiments, devices were aged at 60 °C and 85 °C in ambient atmosphere (~40-45% RH) using a hot plate and the J-V curve of the cells were measured periodically.

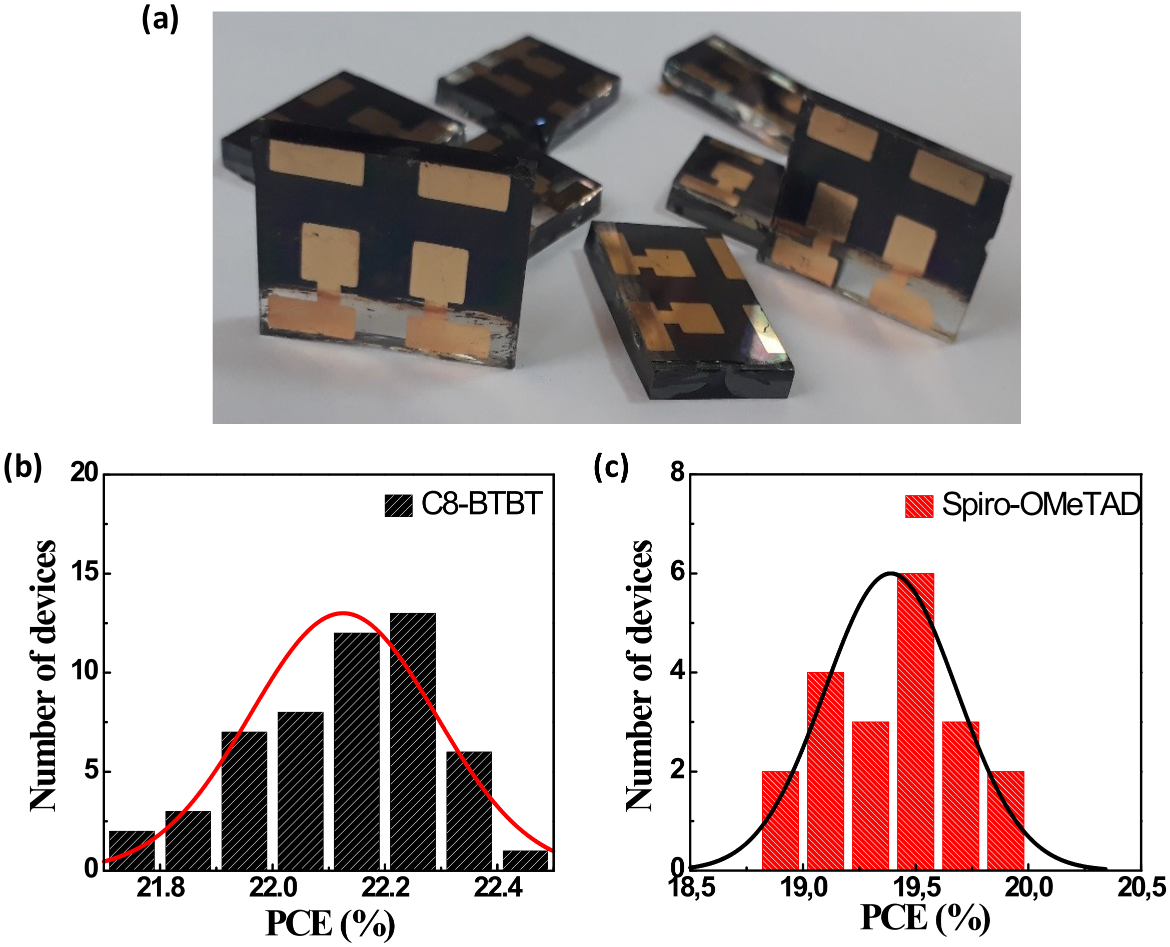


Figure S5. Digital photographs of cells (a) PCE histogram charts of the C8-BTBT based cells (a) and the spiro-OMeTAD based cells (b).

References

[1] B. Košata, V. Kozmik, J. Svoboda, V. Novotná, P. Vaněk, M. Glogarová, *Liq. Cryst.* **2003**, *30*, 603.

[2] H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, T. Yui, *J. Am. Chem. Soc.* **2007**, *129*, 15732.