**Supporting information**
For Journal of Material Chemistry A

**Spiro-thiophene derivative as hole-transport materials for perovskite solar cells**

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**Experimental Section**

Scheme S1 shows the synthetic procedures for compound BiT-SCPDT.

All commercially available chemicals were used as received without further purification. 5-octyl-2,2'-bithiophene 1, trimethyl(5'-octyl-[2,2'-bithiophen]-5-yl) stannane 2, SCPDT, and 4Br-SCPDT were prepared as described in the literatures.1,2
Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) that was conducted on plates precoated with silica gel Si 60-F254(Merck, Germany). Column chromatography was carried out on silica gel SI 60 (Merck, Germany), mesh size 0.063 – 0.200 mm (normal) or 0.040-0.063 mm (flash). 1H NMR and 13C NMR were recorded on a Bruker Avance 600 spectrometer. ESI mass spectra were obtained with an ICR-FTMS APEX II (Bruker Daltonics) mass spectrometer. Elemental analyses were carried out by the analysis and test center.

4Br-SCPDT (B) (164 mg, 0.2 mM), trimethyl(5'-octyl-[2,2'-bithiophen]-5-yl)stannane (A) (768 mg, 1.0 mM), tetrakis(triphenylphosphine) palladium (0) (47 mg, 0.04 mM) and toluene (20 mL) was heated at 110 °C under N₂ for three days. Then the resulting mixture was extracted with toluene (20 mL×3) and the organic layers were washed with brine, dried over Na₂SO₄. After concentrated under vacuum to remove the solvent, the crude product was purified by column chromatography (toluene/hexane=1:2) to give the desired compound as a dark red solid (360 mg, 54%).

1HNMR (400 MHz, CDCl₃, δ): 6.92-6.88 (m, 3H), 6.65 (s, 1H), 6.63 (d, 1H), 2.76 (s, 2H), 2.64 (m, 2H), 1.26 (m, 10H), 0.80 (t, 3H). High-resolution mass spectrometry (HRMS) (electron-ionization (EI)) mass-to-charge ratio (m/z) : M+ calculated for C₈₁H₈₈S₁₂, 1444.35; found 1444.41. Anal. Calcd for C₈₁H₈₈S₁₂: C 67.26, H 6.13, S 26.60. Found: C 67.53, H 6.28, S 26.85.

Figure S1 and S2 present the 1H NMR and Mass Spectrum of SCPDT-BiT.
**Figure S1** $^1$H NMR Spectroscopy of SCPDT-BiT.

**Figure S2** Mass Spectroscopy of SCPDT-BiT.
**Equipment.** All commercially available chemicals were used as received without further purification. Solvents were purified by standard methods and dried if necessary. Reactions were monitored by thin layer chromatography (TLC) that was conducted on plates precoated with silica gel Si 60-F254 (Merck, Germany). Column chromatography was carried out on silica gel SI 60 (Merck, Germany), mesh size 0.063-0.200 mm (normal) or 0.040-0.063 mm (flash). $^1$H NMR and $^{13}$C NMR were recorded on a Bruker Avance 600 spectrometer. ESI mass spectra were obtained with an ICR-FTMS APEX II (Bruker Daltonics) mass spectrometer. Cyclic voltammetry measurements were carried out on a CHI600 electrochemical workstation, using a concentration of a few mM in dichloromethane containing tetrabutylammonium hexafluorophosphate, Bu₄N⁺PF₆⁻ (ca., 0.01 M as a supporting electrolyte) in a three-electrode cell, where the Ag/AgCl electrode was used as the reference electrode and platinum wire as the working electrode. The scanning rate was set at 100 mV s⁻¹. The absorption spectra of SCPDT-BiT was measured using a UV/Vis spectrometer (SHIMADZU, UV-3600 UV/Vis/NIR Spectrophotometer). Differential scanning calorimetry (DSC) was run on a TA Instrument Q10.