

## Supporting Information

### **Spiro-*t*BuBED: A New Derivative of Spirobifluorene-Based Hole-Transporting Material for Efficient Perovskite Solar Cells**

Po-Han Lin,<sup>†</sup> Kun-Mu Lee,<sup>\*,‡</sup> Chang-Chieh Ting<sup>†</sup>  
and Ching-Yuan Liu<sup>\*,†</sup>

<sup>†</sup>Department of Chemical & Materials Engineering, National Central University,  
Jhongli District, Taoyuan 320, Taiwan (R.O.C) E-mail: [cyliu0312@ncu.edu.tw](mailto:cyliu0312@ncu.edu.tw)

<sup>‡</sup>Department of Chemical & Materials Engineering, Chang Gung University / Department of  
Pediatrics, Chang Gung Memorial Hospital, Linkou, Taoyuan 333, Taiwan (R.O.C)  
E-mail: [kmlee@mail.cgu.edu.tw](mailto:kmlee@mail.cgu.edu.tw)

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## General Information

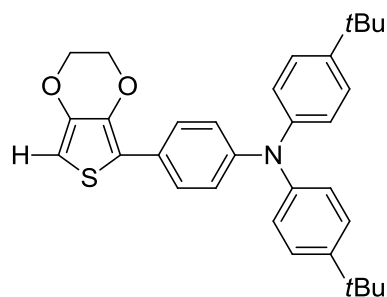
Unless otherwise noted, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen. Required chemicals such as Pd(OAc)<sub>2</sub>, P(Cy)<sub>3</sub>, P(*o*-tolyl)<sub>3</sub>, PivOH, and K<sub>2</sub>CO<sub>3</sub> are commercially available. Anhydrous or reagent-grade solvents such as dichloromethane, chloroform, and *N,N*-dimethylformamide (DMF) were purchased from Sigma-Aldrich, Acros, or Alfa Aesar and used directly without further purifications. Syringes used to transfer reagents and solvents were purged with nitrogen prior to use. Reactions were monitored by thin layer chromatography (TLC, aluminum plates coated with silica gel, Merck 60, F-254). The spots were visualized by UV light. Flash column chromatography was performed using silica gel (spherical, 63-210 μm or 40-75 μm). Melting points were measured on a Fargo MP-2D apparatus. NMR spectra were recorded on a Bruker Magnet System 300 or 500 MHz instrument. Chemical shifts were given relative to CDCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H NMR, 77.0 ppm for <sup>13</sup>C NMR). For the characterization of the observed signal multiplicities, the following abbreviations were applied: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), quint (quintet), m (multiplet), comp (complex), app (apparent), and br (broad). The mass spectra was recorded by Matrix-Assisted Laser Desorption/Ionization (MALDI) techniques operating with a Bruker autoflex speed. Absorption spectra (UV-Vis) were measured on a Hitachi U-4100 UV-Vis spectrophotometer. Photoluminescence spectra (PL) were measured on a Hitachi F-7000 fluorescence spectrophotometer. The optical band gap ( $E_g^{opt}$ ) of the synthesized hole-transporting material was calculated from the intersection of absorption and PL spectra. The experiments of cyclic voltammetry were carried out with an Autolab electrochemical analyzer using a Pt working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode. The measurements were conducted in dry THF solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as a supporting electrolyte under a scan rate of 100 mVs<sup>-1</sup>. The half-wave potential,  $E_{1/2}$ , was calculated by  $(E_{pa}+E_{pc})/2$ , where  $E_{pa}$  and  $E_{pc}$  are the potential energy of anodic and cathodic peaks, respectively. The HOMO energy level,  $E_{HOMO}$ , was calculated by  $-(E_{1/2} + 0.197 + 4.500 - 0.177)$  eV (vs. Ag/AgCl and NHE);  $E_{LUMO} = E_{HOMO} + E_g^{opt}$ . Thermogravimetric analysis (TGA) was run on a TA Instrument Q500. Differential scanning calorimetry (DSC) was run on a Netzsch Instrument LT-DSC (Netzsch 204 F1).

Device fabrication & characterization of perovskite solar cells (PSCs):

A TiO<sub>2</sub> compact layer (~30 nm in thickness) was deposited onto the FTO substrate surface by spin-coating a solution of titanium diisopropoxide bis(acetylacetonate) (75 wt.% of Ti(acac)<sub>2</sub>O*i*Pr<sub>2</sub> in isopropanol). A 150 nm-thick mesoporous TiO<sub>2</sub> film (TiO<sub>2</sub> particle size: ~20 nm, crystalline phase: anatase) was spin-coated onto the compact-TiO<sub>2</sub>/FTO substrate surface using home-made pastes and heated at 500 °C for 30 min. After sintering the TiO<sub>2</sub> layer, the films were cooled to room temperature and immersed in TiCl<sub>4</sub> solution (0.04 M in deionized water) at 70 °C for 30 min. The films were then rinsed by deionized water and then annealed at 500 °C for 30 min again. After cooling to room temperature, the substrate/films were transferred to a nitrogen-filled glove box. A solution consisting of PbI<sub>2</sub> (1.80 M) and CH<sub>3</sub>NH<sub>3</sub>I (1.80 M) in  $\gamma$ -butyrolactone (GBL) and DMSO (5/5, v/v) was coated onto the TiO<sub>2</sub> substrate by a two-step spin-coating process at 1000 and 5000 rpm for 10 and 20 sec, respectively. During the second spin-coating step, the substrate/films were treated with 50  $\mu$ L toluene by drop-casting. The substrate/films were dried on a hot plate at 100 °C for 10 min. **Spiro-*t*BuBED** or **Spiro-OMeTAD** (as reference cell) was dissolved in chlorobenzene (50 mg/mL), respectively. Each solution was heated to 80~90 °C for 20 min. Next on, 17.5  $\mu$ L of a solution of lithium bis(trifluoromethane)sulfonimide (Li-TFSI, 520 mg) in acetonitrile (1 mL) and 28.5  $\mu$ L 4-*tert*-butylpyridine (TBP) were added directly to the corresponding hole-transporting material (HTM) solutions from previous step. This as-prepared HTM solution was spin-coated onto the substrate/films at 2000 rpm for 30 sec. In certain cases, the MoO<sub>3</sub> was deposited by thermal evaporation (~10 nm). Finally, the Ag cathode layer was deposited by thermal evaporation (~100 nm). The active area of each cell was fixed at 0.16 cm<sup>2</sup> by a metal mask.

An IPCE spectrometer (EQE-R-3011, ENLI Technology Co. Ltd., Taiwan) calibrated with a single-crystal silicon reference cell was used for the incident monochromatic photon-to-current conversion efficiency (IPCE) measurements. An AM 1.5G solar simulator (Yamashita Denso Corporation, YSS-50A) was used as the irradiation light source for the characteristic current density-voltage (J-V) measurements. The intensity of the simulated sunlight was calibrated to 100 mW/cm<sup>2</sup>. The J-V characteristics of the cell under an illumination of AM 1.5G simulated sunlight were obtained by applying the external potential bias to the cell and measuring the photocurrent output with a Keithley model 2400 digital source meter (Keithley, USA).

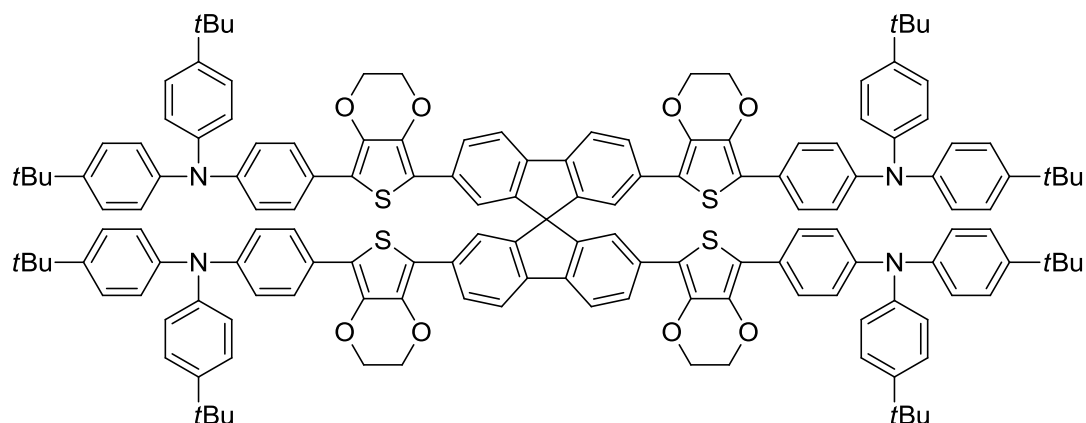
## First C-H Arylation Reaction: Synthesis of the End-Group



### 4-(*tert*-Butyl)-*N*-(4-(*tert*-butyl)phenyl)-*N*-(4-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)phenyl)aniline<sup>[1]</sup> (**5**):

To a solution of Pd(OAc)<sub>2</sub> (12 mg, 0.05 mmol), P(Cy)<sub>3</sub> (28 mg, 0.10 mmol), PivOH (31 mg, 0.30 mmol), and K<sub>2</sub>CO<sub>3</sub> (207 mg, 1.50 mmol) in DMF (3 mL) in a flame-dried Schlenk tube were added 4-bromo-*N,N*-bis(4-(*t*-butyl)phenyl)aniline (436 mg, 1.00 mmol) and ethylenedioxythiophene (EDOT) (426 mg, 3.00 mmol) under N<sub>2</sub>. The reaction mixture was then heated at 100 °C under N<sub>2</sub> for 6 h. After the reaction mixture had cooled to room temperature, water (10 mL) was added. The mixture was extracted with ethyl acetate (2 × 20 mL), and the combined organic layers were washed with brine (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. Purification by flash chromatography (dichloromethane : hexanes = 60 : 40) gave the desired product **5** (353 mg, 71%). Yellow solid; m.p.: 198.6-199.7 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 7.62 (d, *J* = 8.7 Hz, 2 H), 7.31 (d, *J* = 8.6 Hz, 4 H), 7.07-7.13 (comp, 6 H), 6.27 (s, 1 H), 4.26-4.31 (comp, 2 H), 4.21-4.26 (comp, 2 H), 1.38 (s, 18 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 146.6, 145.5, 144.8, 142.1, 137.2, 126.7, 126.6, 125.9, 123.9, 123.0, 117.6, 96.5, 64.6, 64.3, 34.2, 31.4.

## Second C-H Arylation Reaction: Gram-Scale Synthesis of Spiro-*t*BuBED



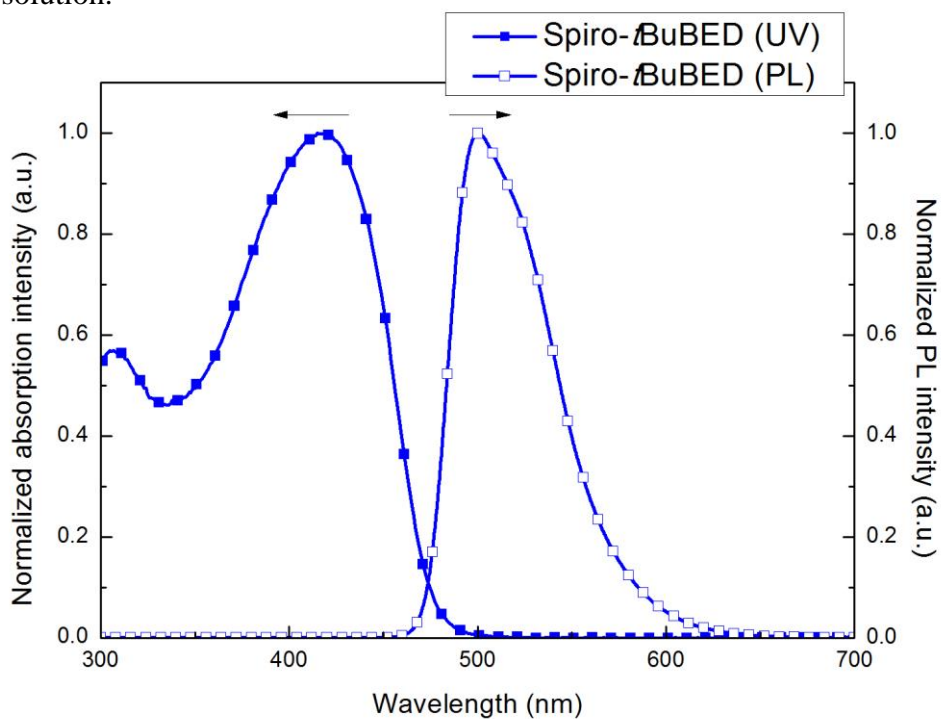
### Spiro-*t*BuBED:

To a solution of Pd(OAc)<sub>2</sub> (23 mg, 0.10 mmol), P(*o*-tolyl)<sub>3</sub> (61 mg, 0.20 mmol), PivOH (62 mg, 0.60 mmol), and K<sub>2</sub>CO<sub>3</sub> (621 mg, 4.50 mmol) in DMF (9 mL) in a flame-dried Schlenk flask were added 2,2',7,7'-tetrabromo-9,9'-spirobi[fluorene] (632 mg, 1.00 mmol) and **5** (2087 mg, 4.20 mmol) under N<sub>2</sub>. The reaction mixture was then heated at 100 °C under N<sub>2</sub> for 48 h. After the reaction mixture had cooled to room temperature, water (20 mL) was added. The mixture was extracted with dichloromethane (2 × 60 mL), and the combined organic layers were washed with brine (100 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in *vacuo*. Purification by flash chromatography (dichloromethane : hexanes = 45 : 55) gave the desired product **Spiro-*t*BuBED** (1.41 g, 61%). Bright yellow solid; m.p.: 293.0-294.3 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, ppm): δ 7.76-7.87 (comp, 8 H), 7.49 (d, *J* = 8.3 Hz, 8 H), 7.23 (d, *J* = 8.5 Hz, 16 H), 6.95-7.07 (comp, 28 H), 4.22 (app s, 16 H), 1.30 (s, 72 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, ppm): δ 149.4, 146.5, 145.5, 144.8, 139.8, 138.5, 137.6, 132.6, 126.7, 126.4, 125.9, 123.8, 123.1, 122.9, 121.1, 120.1, 115.5, 114.7, 64.4, 34.2, 31.4; HRMS (MALDI): calcd. for C<sub>153</sub>H<sub>148</sub>N<sub>4</sub>O<sub>8</sub>S<sub>4</sub>: 2298.0207, found: 2298.0231 ([M+H]<sup>+</sup>).

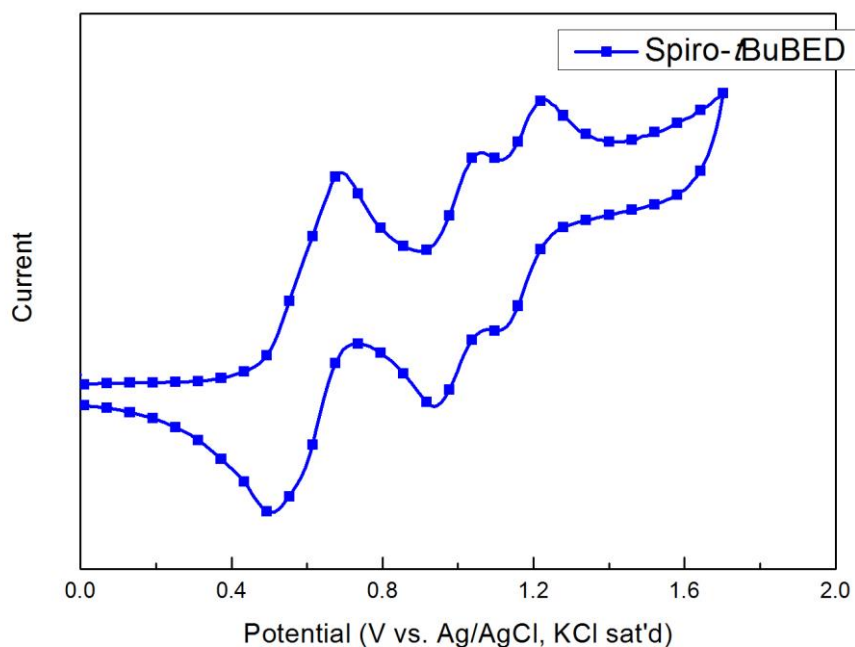
### References:

- [1] Chang, Y.-C.; Lee, K.-M.; Lai, C.-H.; Liu, C.-Y. *Chem. Asian J.* **2018**, *13*, 1510–1515.

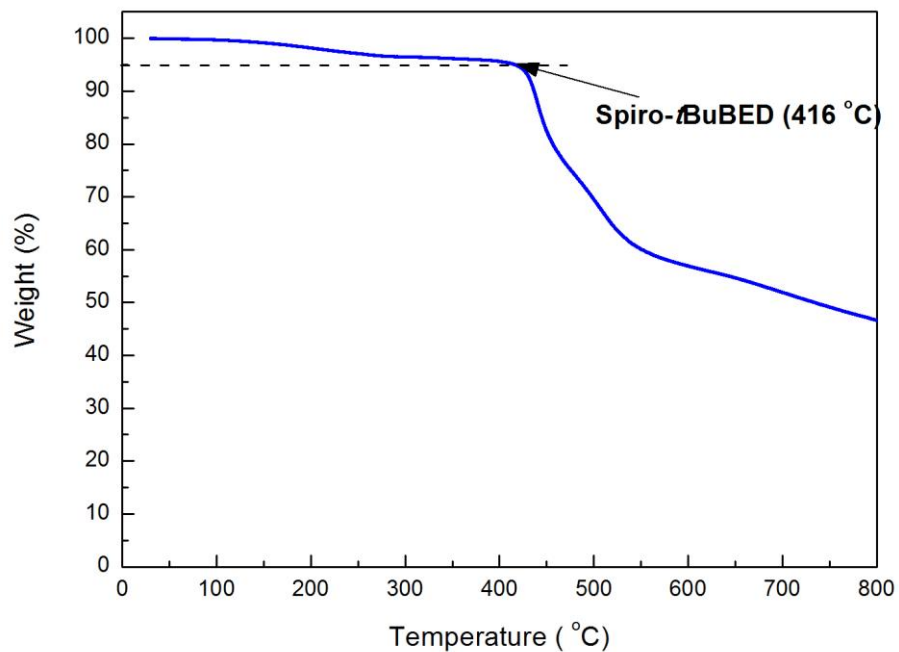
**Figure S1.** The UV-Vis absorption and photoluminescence spectra of **Spiro-*t*BuBED** in THF solution.



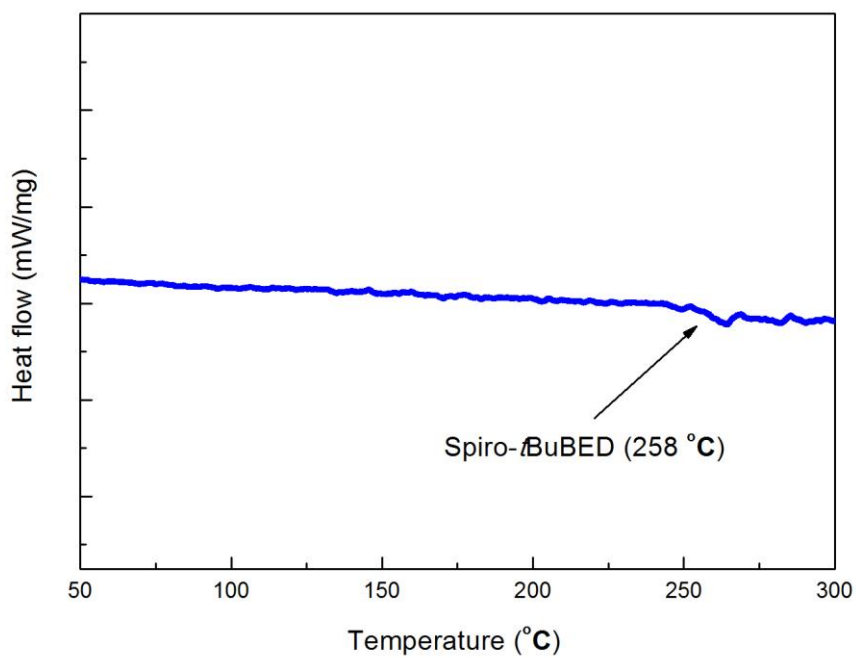
**Figure S2.** Cyclic voltammety spectra of **Spiro-*t*BuBED** in THF solution.



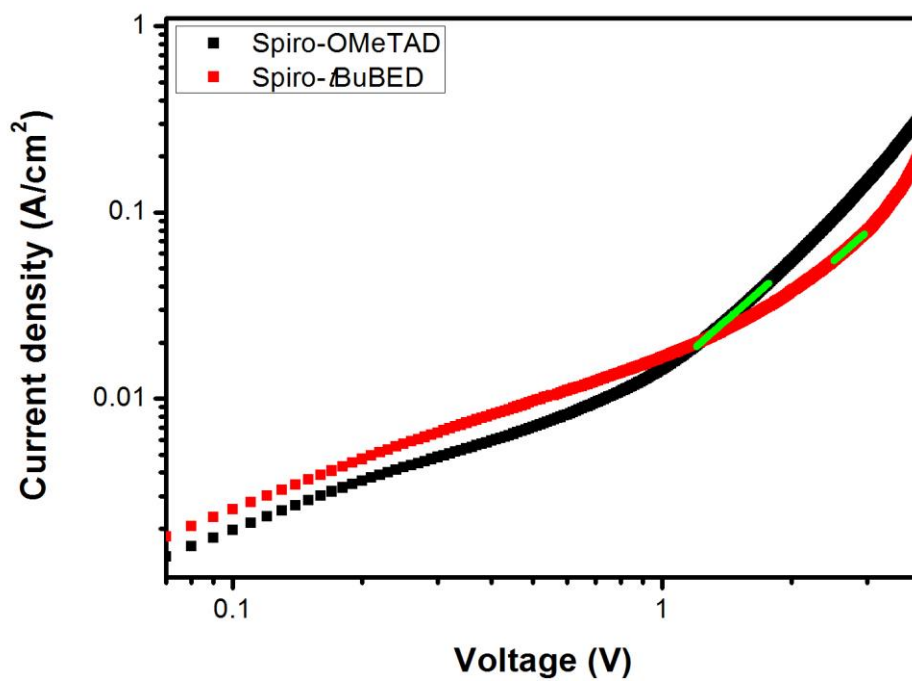
**Figure S3.** Thermogravimetric analysis curves of **Spiro-*t*BuBED**.



**Figure S4.** Differential scanning calorimetry curves of **Spiro-*t*BuBED**.



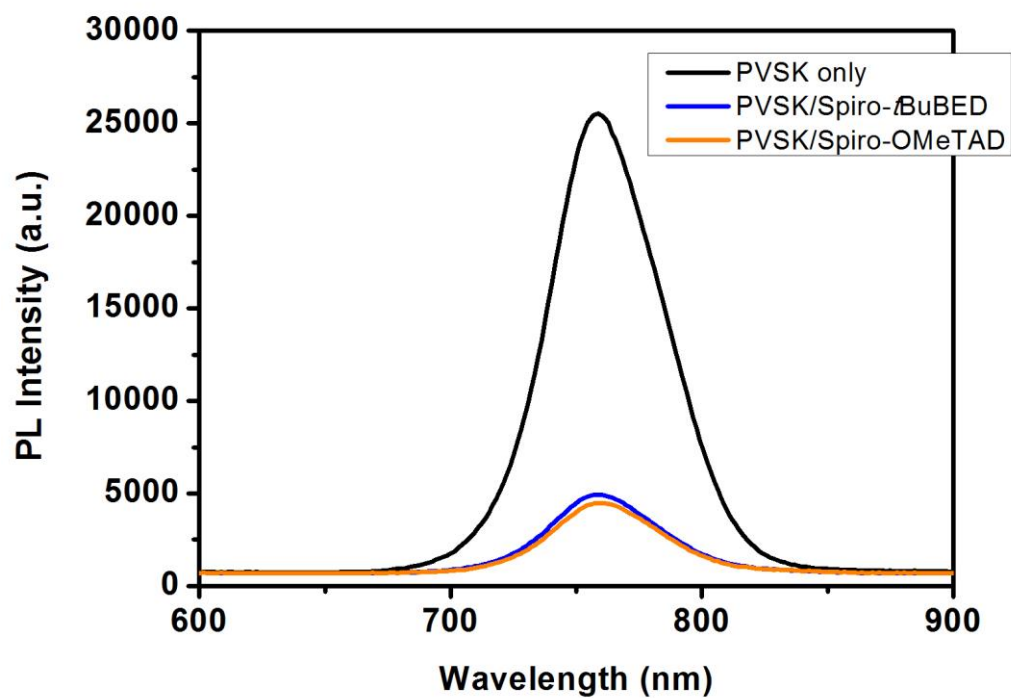
**Figure S5.** J-V curves for the determination of the hole mobility of HTMs in the space-charge limited current (SCLC) region.



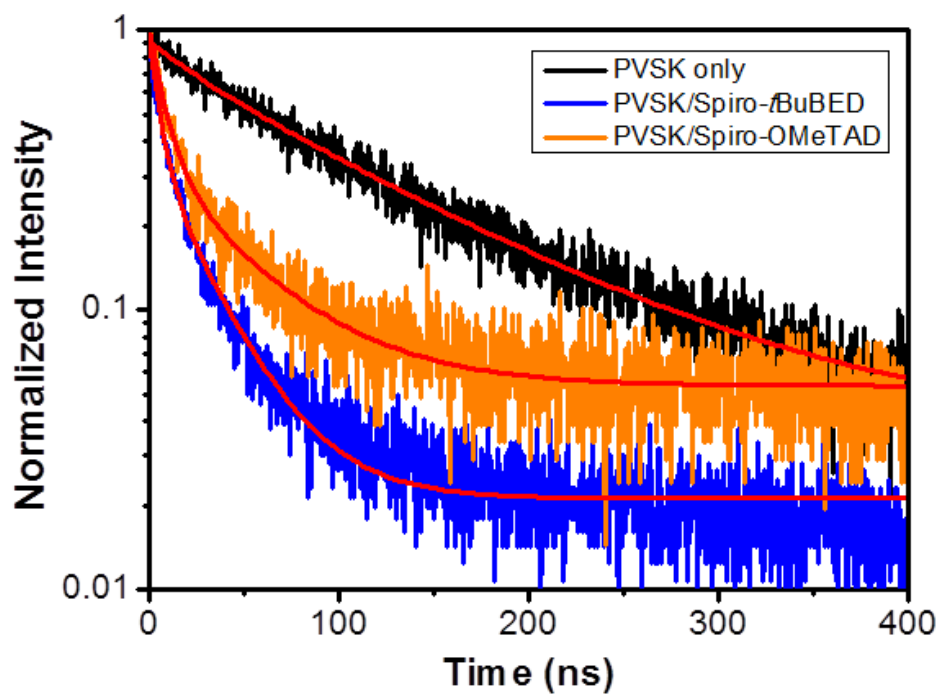
	<b>spiro-<i>t</i>BuBED</b>	<b>spiro-OMeTAD</b>
Hole mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	2.29 × 10 <sup>-4</sup>	3.53 × 10 <sup>-4</sup>



**Figure S6.** Steady-state PL spectra of the devices fabricated as FTO/perovskite/HTMs.

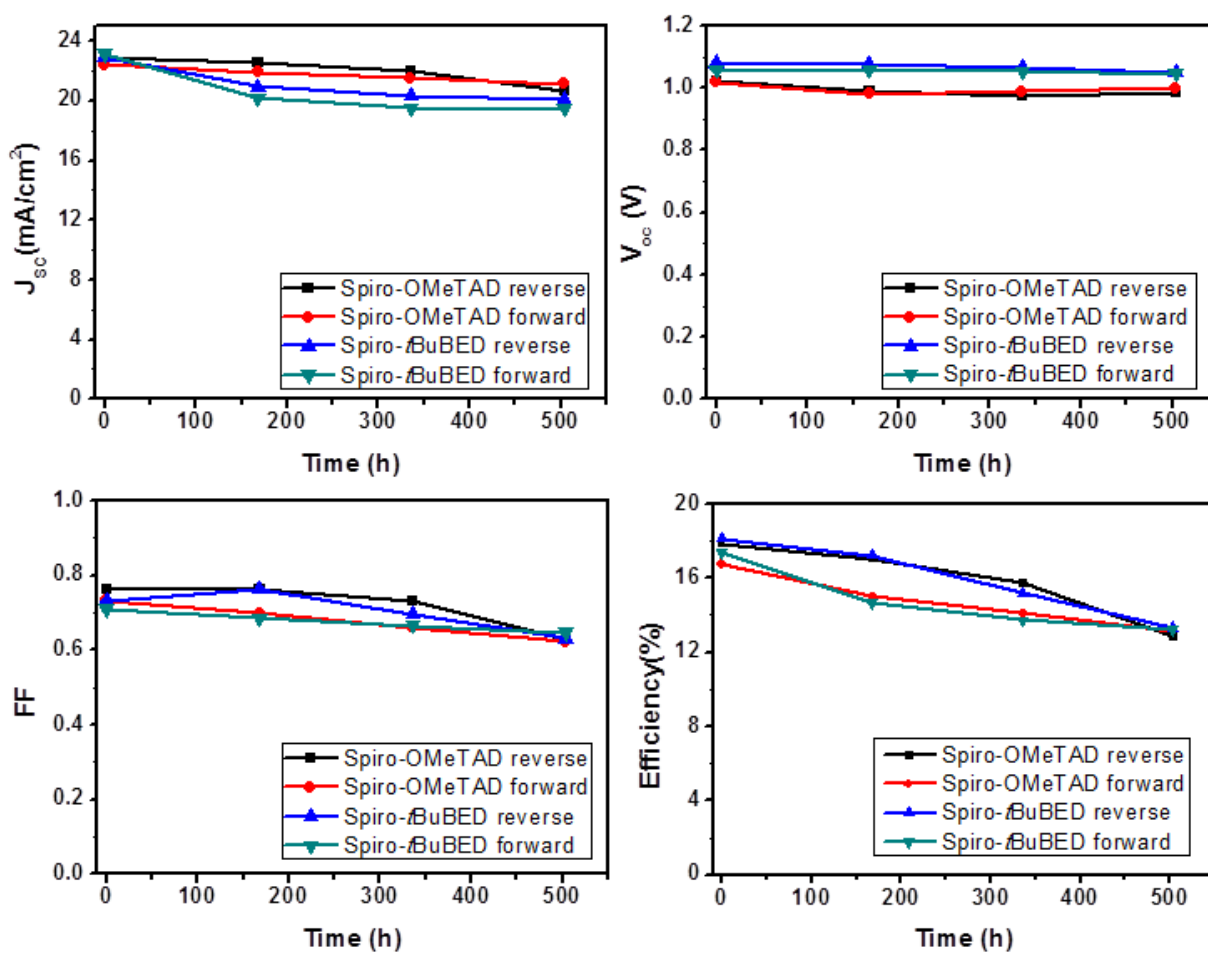


**Figure S7.** Time-resolved PL spectra of the devices fabricated as FTO/perovskite/HTMs.

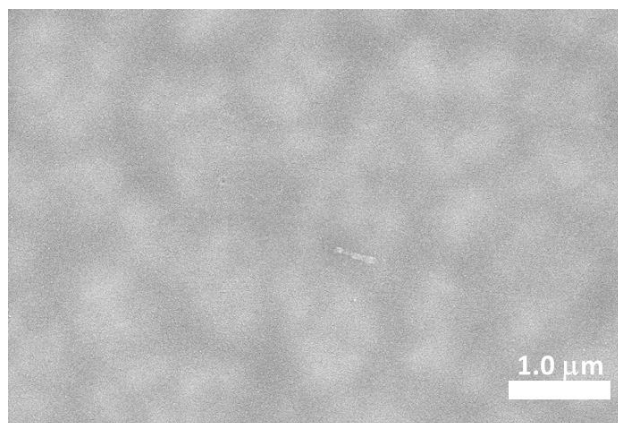


Sample	$A_1$	$\tau_1$ (ns)	$A_2$	$\tau_2$ (ns)	avg. $\tau$ (ns)
PVSK only	0.84	114.51	0.16	30.92	<b>101.13</b>
PVSK/Spiro- <i>t</i> BuBED	0.62	5.59	0.38	29.01	<b>14.49</b>
PVSK/Spiro-OMeTAD	0.69	8.18	0.31	48.27	<b>20.60</b>

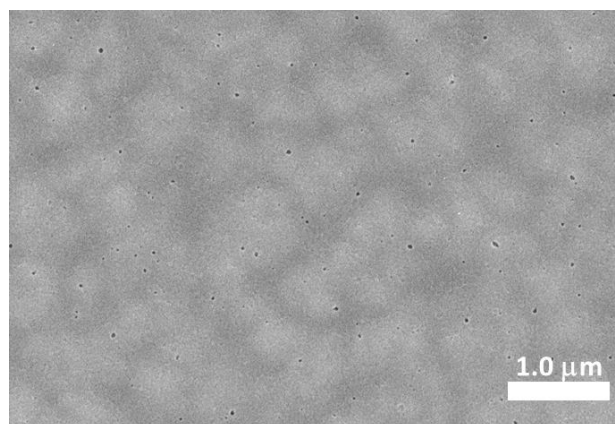
**Figure S8.** Stability test of the PSCs based on **spiro-*t*BuBED** (the devices have been stored in the box under 30% RH at 25-28°C for 4 weeks).



**Figure S9.** Top-view picture of the HTM layer from SEM.

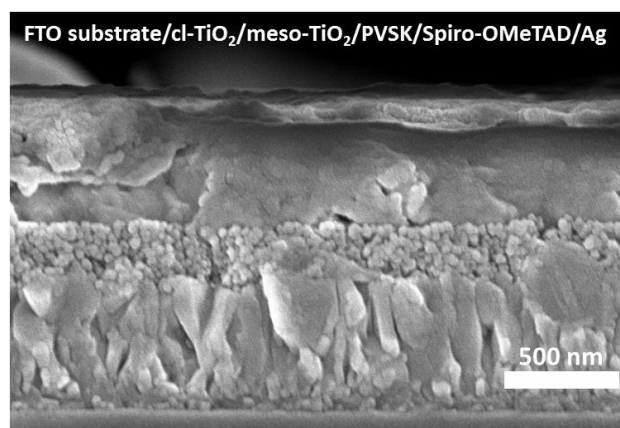
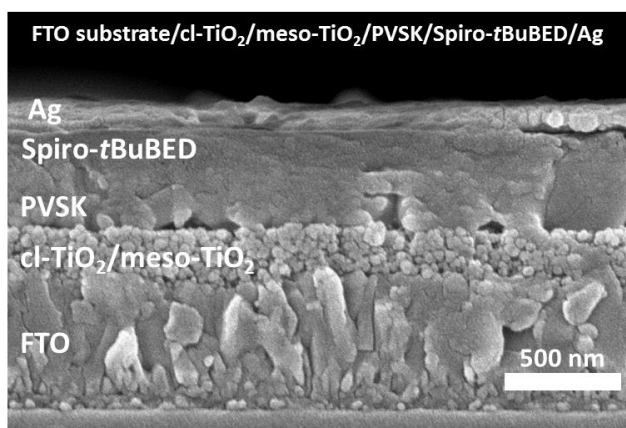


**spiro-*t*BuBED**

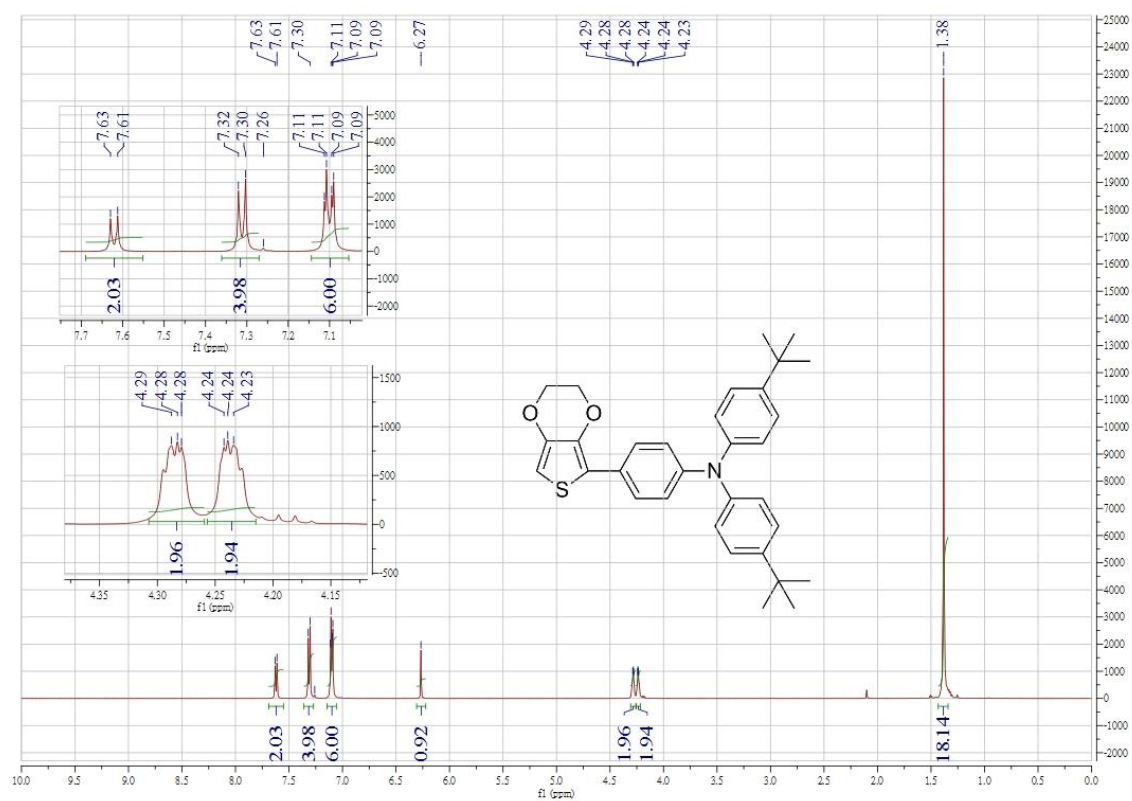


**spiro-OMeTAD**

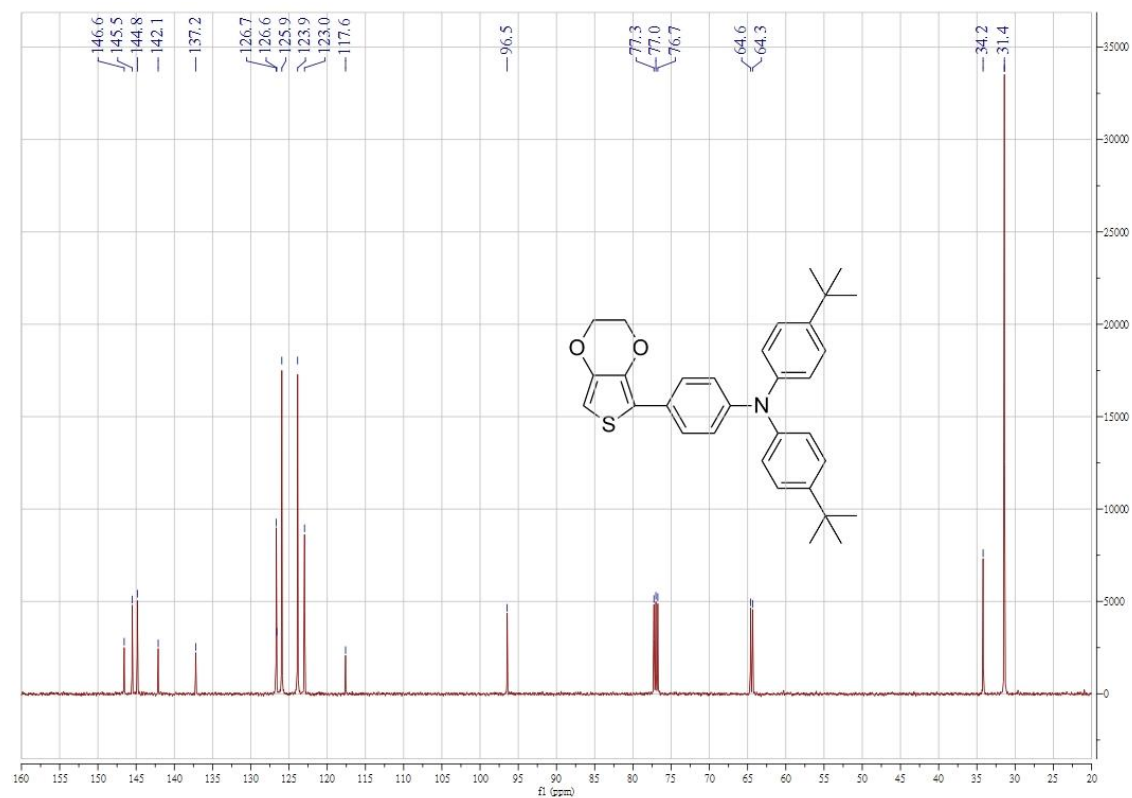
**Figure S10.** Cross-section picture of the PSC device from SEM.



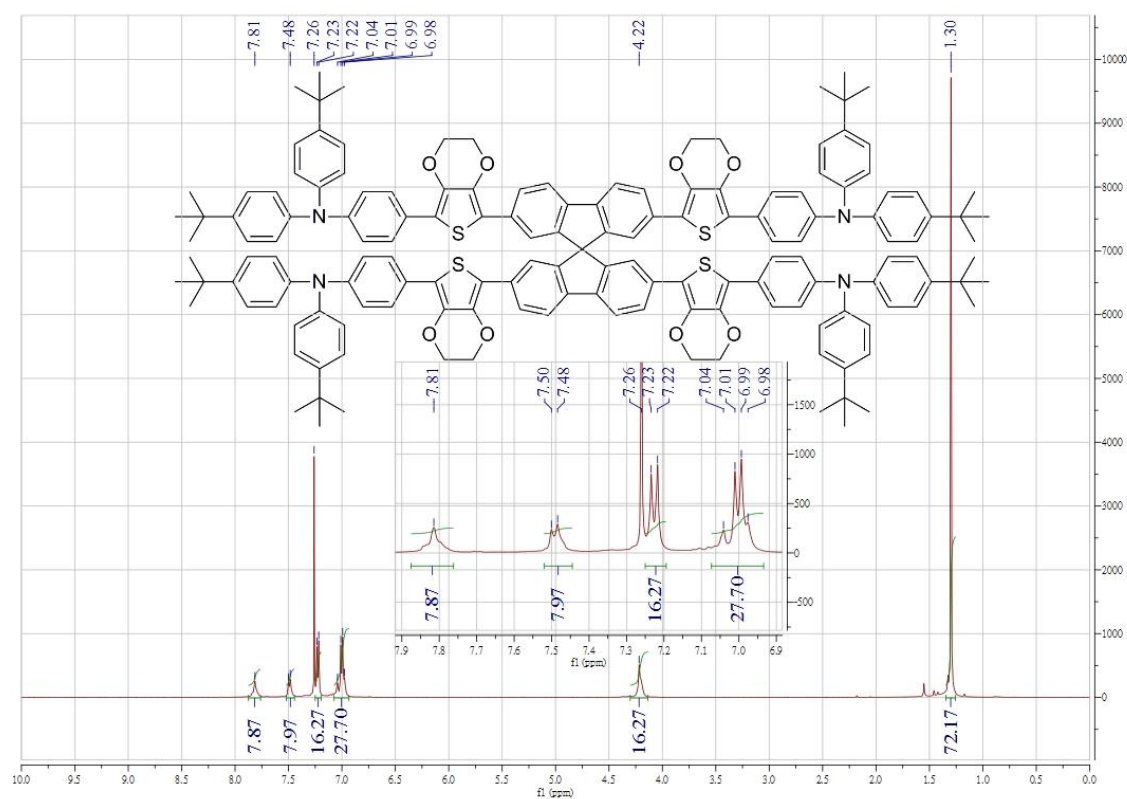
**Figure S11.**  $^1\text{H}$  NMR spectrum of **5** (500 MHz,  $\text{CDCl}_3$ )



**Figure S12.**  $^{13}\text{C}$  NMR spectrum of **5** (125 MHz,  $\text{CDCl}_3$ )



**Figure S13.**  $^1\text{H}$  NMR spectrum of **spiro-*t*BuBED** (500 MHz,  $\text{CDCl}_3$ )



**Figure S14.**  $^{13}\text{C}$  NMR spectrum of **spiro-*t*BuBED** (125 MHz,  $\text{CDCl}_3$ )

