# Electronic Supplementary Information

# Dithieno[3,2-b:2′,3′-d]pyrrole-based Hole Transport Materials for Perovskite Solar Cells with Efficiencies over 18%

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## EXPERIMENTAL SECTION

### 1. Materials and instruments

FAI, MABr, mesoporous $TiO_2$ (30NRD) and FK209 were purchased from Dyesol. $PbI_2$, $PbBr_2$ and CsI were ordered from TCI. Fluorine doped tin dioxide (FTO) coated glass substrates were obtained from Hartford Glass Company. Spiro-MeOTAD was purchased from the p-OLED (China). Lithium bis-(trifluoromethylsulfonyl)imide obtained from Sigma Aldrich.

### 2. Characterization

#### 2.1 UV-Vis and CV measurements.

The absorption spectra of the solution of HTMs (dissolve in DCM) were measured using a SHIMADZU UV-2600 spectrophotometer. Fluorescence measurements were recorded by a HITACHI F–4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) of these samples containing 0.1 M of tetrabutylammoniun hexafluorophosphate (n-$Bu_4NPF_6$) was performed on a CHI660D electrochemical workstation in conjunction with a three-electrode electrochemical cell composed of a platinum electrode (counter electrode), Ag/AgCl electrode (reference electrode) and a glassy carbon disk (working electrode) at a scan rate of 10 mV $s^{-1}$. All potentials were reported against the ferrocene/ferrocenium (Fc/Fc+) reference.

#### 2.2 Conductivity Measurements

Two-contact electrical conductivity set-up was used for measuring conductivities of the three HTMs. Samples were prepared using glass substrates cleaned via sonication

in soap water, DI-water, Acetone, then Isopropanol for 25 min, respectively. Thin layers of three HTMs were prepared by spin coating at 1000 rpm for 1 min from solutions with the same concentrations used for fabricating the devices. Finally, a 80 nm thick Ag back contact was deposited by thermal evaporation. The conductivity (σ) was determined by using eq.1 [1].

$$\sigma = L / Rwd \quad \text{(eq. 1)}$$

Here $L$ is the channel length (0.05 mm), $w$ is the channel width (0.2 μm), $d$ is the thickness of HTM film. Thicknesses of the prepared films were measured with a DekTak profilometer, and $R$ is the resistance.

**2.3 Mobility Measurements**

Hole mobility of the studied HTMs were recorded by space-charge-limited currents (SCLCs) according to previous literature [2, 3]. Devices for mobility measurements are similar to those devices for *J-V* curves, but the $TiO_2$ layer was replaced by PEDOT: PSS. First, PEDOT: PSS was spin coated onto the substrates and then annealed on a hotplate at 120 °C for 30 min, forming a thin layer (< 100 nm). After that, HTMs were deposited via spin coating at 2000 rpm for 30 s. Finally, a 150 nm thick Ag back contact was deposited onto the HTM layer. The thicknesses of the HTMs were measured by using a Dektak profilometer. The current density of devices was measured with a Keithley 2400 Source-Measure unit. Hole mobility was calculated by the equations (2)

$$J = \frac{9}{8} \mu \varepsilon_o \varepsilon_r \frac{v^2}{d^3} \quad (2)$$

where $J$ is the current density, $\mu$ is the hole mobility, $\varepsilon_o$ is the vacuum permittivity ($8.85\times10^{-12}$ F/m), $\varepsilon_r$ is the dielectric constant of the material (approach 3), $V$ is the applied bias, and $d$ is the film thickness.

**2.4 Topography and CS-AFM**

Topography and current sensing atomic force microscopy (CS-AFM) of thin films of the HTMs were measured using Agilent SPM 5500 atomic force microscope equipped with MAC III controller (three lock-in amplifiers). A tip with resonance frequency of 67 kHz was used for measuring topography in non-contact mode. CS-AFM is a technique for the nanoscale electrical characterization of materials with high spatial resolution for measuring surface current using conducting Pt/Ir coated Si tip. The conducting tip scaned the film in contact mode and measured the variation in current across the surface with fixed bias. Carriers were injected from the conducting tip into the HTM and collected at the grounded FTO electrode. An in-built preamplifier with 1 $nAV^{-1}$ sensitivity was used for measuring the current. The images were taken at 1 V bias to avoid oxidation/reduction of the tip and impurities on the surface of the film.

**2.5 Transient Measurements**

A Nitrogen Laser and a dye laser (Model 1011) were coupled resulting in a pump laser as the excitation source (pulse duration < 1 ns) for measuring transient of the fabricated devices. The pulse width was measured by oscilloscope through the response of the photodiode (spectral range 280 - 1100 nm). Charge transport time and

charge carrier lifetime obtained from transient photocurrent (TPC) and transient photovoltage (TPV). TPC was measured under short circuit conditions (by a very low resistor at 50 Ω) while TPV was measured under open circuit condition (by a huge resistor at 1 MΩ). Charge transport time and charge carrier lifetime were obtained by fitting the decay function with mono-exponential equation $Aexp(-t/\tau)$ where $\tau$ is the charge carrier life time. The obtained data were fitted with a mono-exponential decaying function to calculate charge transport time of the devices.

**3. Device Fabrication**

Perovskite solar cells were fabricated on fluorine-doped tin dioxide (FTO) coated substrates (1.5 cm × 1.5 cm). FTO substrates were etched by diluted HCl solution (1 ml HCl in 10 ml DI water) and Zinc powder. The etched substrates were then cleaned via sonication in soap water, DI-water, acetone and isopropanol for 25 min, respectively, followed by treatment with oxygen plasma.

A thin layer of compact $TiO_2$ (0.15 M titanium diisopropoxide in ethanol) was spin coated at 4500 rpm for 45 sec followed by annealing at 200 $^oC$ for 10 min. A thin layer of mesoporous $TiO_2$ scaffolds was deposited by spin coating at 5000 rpm for 30 sec using a commercial $TiO_2$ paste (30 NRD, Dyesol) diluted in ethanol at a weight ratio of 1: 6 followed by annealing at 450 $^oC$ for 30 min. Substrates coated with $TiO_2$ are immersed in 25 mM $TiCl_4$ aqueous solution and annealed at 70 $^oC$ for 30 min followed by washing via DI water and ethanol, which was then annealed at 450 $^oC$ for 30 min.

Perovskite film was prepared according to the method reported by a previously work [4]. The mixed perovskite precursor solutions contain FAI/$PbI_2$/MABr/$PbBr_2$ (mole ratio is 1/1.1/0.2/0.2) in anhydrous DMF/DMSO (v/v = 4/1). To improve the quality of perovskite film, CsI (1.5 M) was added to the above solution. The volume ratio of FAI/$PbI_2$/MABr/$PbBr_2$ and CsI is 5 / 95.

The mixed solution was stirred under 60 degree for an half of hour. A two-step program at 1000 and 6000 rpm for 10 and 30 s respectively was employed for spinning. During the second spinning process, a 100 $\mu L$ chlorobenzene was dripped on the substrate 15s before the coating is completed. Films with Cs-containing perovskite turned dark immediately after spin coating. The substrates were then annealed (usually at 100 °C) for 1 h in a nitrogen filled glove box.

After the perovskite annealing, the substrates were cooled down for few minutes and a Spiro-OMeTAD solution (70 nm in chlorobenzene) was spin coated at 4000 rpm for 20 s. Spiro-OMeTAD was doped with Li-TFSi and FK209 and TBP. The Spiro-OMeTAD additive molar ratios were 0.5, 0.03 and 3.3 for Li-TFSI, FK209 and TBP, respectively. Note that, the concentration of H16 and H18 is the same as that of Spiro-OMeTAD used. Samples were then transferred to the evaporator for Au deposition (80 nm) as the top electrode.

**4. Photovoltaic Performance Characterizations**

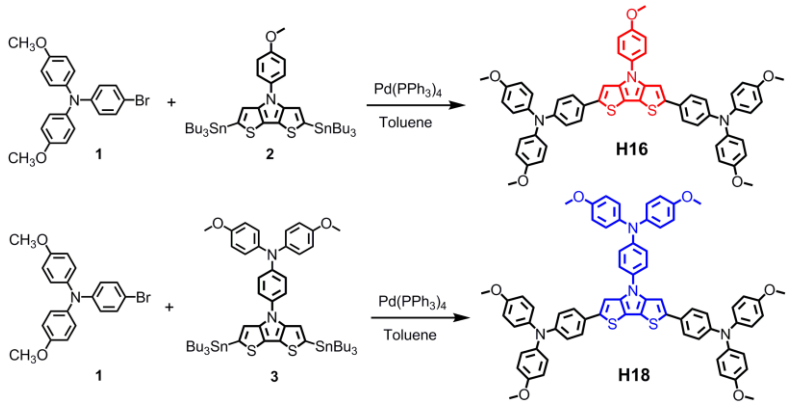
The current density−voltage ($J-V$) characterization of the devices was carried out by using a standard xenon-lamp-based solar simulator (Oriel Sol 3A, USA) under simulated AM 1.5 irradiation (100 $mW \cdot cm^{-2}$) with a digital source meter (Keithley

2400). The $J-V$ measurement was carried out under reverse scan with a scan rate of 0.1 V/s. At the same time, a measurement under forward scan was also performed for the devices to check the hysteresis of the $J-V$ curve. A NREL certified silicon reference cell (Oriel P/N 91150 V, with KG-5 visible color filter) was used as reference cell. All tests were carried out in air, and a mask with well defined area size of 14.0 $mm^2$ was attached onto the cell during test. Dozens of devices were fabricated and measured independently to obtain the statistical histograms of PCE devices. External quantum efficiency (EQE) was carried out with an ORIEL Intelligent Quantum Efficiency (IQE) 200 Measurement system established with the tunable light source.

**5. Synthesis**

$^{1}H$ NMR and $^{13}C$ NMR spectra were measured using Bruker AM–300/400 spectrometer. The chemical shifts were referenced from TMS. The mass spectra having high resolution were recorded using a Micromass GCT–TOF mass spectrometer. The synthetic routes for the H16 and H18 are shown in Scheme S1.

4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (MPDTP) and N-(4-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)phenyl)-4-methoxy-N-(4-methoxyphenyl) aniline (TPDTP) were synthesized according to our previously work [5]. All other solvents and chemicals used in this work were used as received from commercial suppliers without further purification.




**Scheme S1**. Synthetic routes to organic hole-transporting materials H16/H18.

**Synthesis of Compound H16/H18**

In a dried Schlenk tube was dissolved compound 4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (MPDTP) or N-(4-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)phenyl)-4-methoxy-N-(4-methoxyphenyl) aniline (TPDTP) (1 mmol) in anhydrous THF (10 mL), n-BuLi (0.88 mL, 2.5 mol/L) was added dropwise at -78 °C under argon atmosphere. The resulted mixture was stirred at the same temperature for one hour before $Sn(But)_3Cl$ (780 mg, 2.2 mmol) was added. The remaining mixture was slowly warmed to room temperature and stirred overnight. The reaction was terminated by adding ice water, and the mixture was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. After the solvent was evaporated, the crude product **2/3** was obtained and used to synthesize compound H16/H18 without further purification.

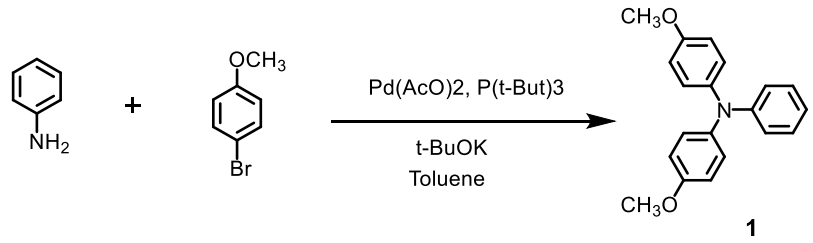
To a 100 mL two-neck round-bottom flask, a mixture of compound **2/3**, compound **1** (845 mg, 2.2 mmol), $Pd(PPh_3)_4$ (57 mg, 0.05 mmol) and toluene (10 mL) was added and heated at reflux for 8 hours under argon atmosphere. After evaporating the solvent

under reduced pressure, the remaining crude product was purified by column chromatography on silica gel eluented with DCM:PE = 1:15~2:1 (v/v) to afford the desired product H16/H18.

H16: Yellow solid, 65% yield for two steps. MP: 134-136 °C. $^{1}$H NMR (400 MHz, $(CD_3)_2CO$): δ 7.58 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 4H), 7.35 (s, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 8H), 6.89 (d, *J* = 8.8 Hz, 8H), 6.83 (d, *J* = 8.4 Hz, 4H), 3.87 (s, 3H), 3.77 (s, 12H). $^{13}$C NMR (100 MHz, $(CD_3)_2CO$): δ 159.9, 158.1, 149.9, 145.9, 143.9, 142.1, 134.1, 129.0, 128.4, 127.5, 126.1, 121.8, 116.6, 116.4, 116.3, 108.4, 56.7, 56.5. HRMS (ESI) calcd for $C_{55}H_{46}N_3O_5S_2$ ($M+H^+$): 892.2879, found: 892.2783.

H18: Yellow solid, 65% yield for two steps. MP: 158-160 °C. White solid, 58% yield for two steps. $^{1}$H NMR (400 MHz, $(CD_3)_2CO$): δ 7.43-7.39 (m, 6H), 7.33 (s, 2H), 7.08 (d, *J* = 8.8 Hz, 4H), 7.01 (d, *J* = 8.8 Hz, 8H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.90-6.86 (m, 12H), 6.80 (d, *J* = 8.4 Hz, 4H), 3.76-3.75 (m, 18H). $^{13}$C NMR (100 MHz, $(CD_3)_2CO$): δ 158.2, 158.0, 149.8, 149.0, 142.2, 142.1, 133.5, 130.5, 129.8, 129.1, 128.6, 128.4, 127.5, 125.2, 122.1, 121.8, 116.5, 116.4, 108.6, 56.5. HRMS (ESI) calcd for $C_{68}H_{57}N_4O_6S_2$ ($M+H^+$): 1089.3719, found: 1089.3785.

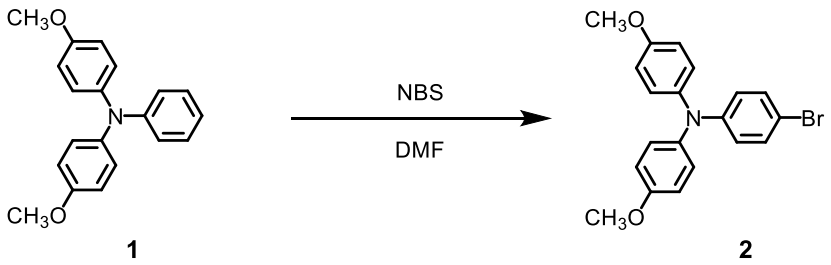
**The synthetic cost of H16**.




**1**

To a 100 mL two-neck round-bottom flask, a mixture of Aniline (2.3 g, 24.7 mmol), 4-Bromoanisole (10.2 g, 54.4 mmol), $Pd(AcO)_2$ (111 mg, 0.494 mmol), P(*t*-But)$_3$ (10% in Toluene, 2 g, 0.988 mmol), Potassium tert-butanolate (6.92 g, 61.75mmol) and toluene (35 mL) was added and refluxed overnight under argon atmosphere. After evaporating the solvent, the remaining crude product was purified by column chromatography on silica gel eluented with dichloromethane (DCM): petroleum ether (PE) = 1:15~1:5 (v/v) to afford the desired product **1** as an off-white solid (6.864 g, 91% yield).

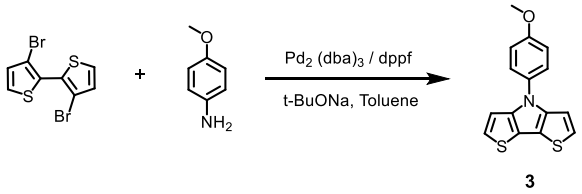
| **Regent** | **Amount / g** | **Amount / mL** | **Price / g or mL** | **Total price / RMB** |
|---|---|---|---|---|
| Aniline | 2.3 | | 0.17 | 0.39 |
| 4-Bromoanisole | 10.2 | | 0.6 | 6.12 |
| $Pd(AcO)_2$ | 0.111 | | 170 | 18.87 |
| P(t-But)$_3$ / 10% in Toluene | 2.0 | | 7.5 | 15 |
| *t*-BuOK | 6.92 | | 0.53 | 3.67 |
| Toluene | | 35 | 0.1 | 3.5 |
| Silica gel | 200 | | 0.036 | 7.2 |
| Petroleum ether 60-90 °C | | 1000 | 0.022 | 22 |
| dichloromethane | | 150 | 0.02 | 3 |
| **Total cost** | 79.15 RMB | | | |
| Amount intermediate **1** | 6.864 g | | | |
| **COST** for intermediate **1** | 11.53 RMB/g | | | |




**1** **2**

N-Bromo-succinimide (1.96 g, 11 mmol) was added in small portions to a solution of **1** (3.05 g, 10 mmol) in DMF (20 mL) and the obtained mixture was stirred for 2 h at room temperature. The reaction mixture was then poured into water and the obtained solid was filtered, washed with water and dried under vacuum. The collected crude product was purified by column chromatography on silica gel eluented with DCM: PE = 1:10~1:5 (v/v) to afford the desired product **2** as an off-white solid (3.639 g, 95% yield).

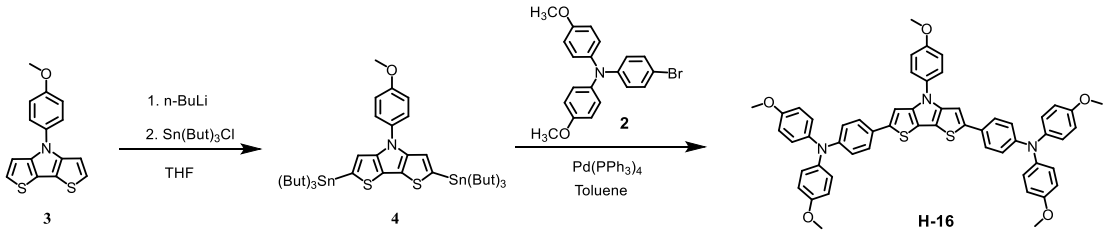
| **Regent** | **Amount / g** | **Amount / mL** | **Price / g or mL** | **Total price / RMB** |
|---|---|---|---|---|
| 1 | 3.05 | | 11.53 | 35.17 |
| NBS | 1.96 | | 0.65 | 1.27 |
| DMF | | 20 | 0.1 | 2 |
| Silica gel | 100 | | 0.036 | 3.6 |
| Petroleum ether 60-90 °C | | 300 | 0.022 | 6.6 |
| dichloromethane | | 60 | 0.02 | 1.2 |
| **Total cost** | 49.84 RMB | | | |
| Amount intermediate **2** | 3.639 g | | | |
| **COST** for intermediate **2** | 13.7 RMB/g | | | |




**3**

To a 100 mL two-neck round-bottom flask, a mixture of 3,3'-Dibromo-2,2'-bithiophene (1.62 g, 5 mmol), sodium *tert*-butoxide (1.92 g, 20 mmol), $Pd_2(dba)_3$ (46 mg, 0.05 mmol), dppf (112 mg, 0.2 mmol) and anhydrous toluene (20 mL) was added and stirred at room temperature for 5 minutes under argon atmosphere. Then, p-Anisidine (0.8 g, 6.5 mmol) was added, the resulting mixture was heated at reflux overnight. After evaporating the solvent, the remaining crude product was purified by column chromatography on silica gel eluented with DCM: PE = 1:25~1:10 (v/v) to afford the desired product **3** as a light yellow solid (1.144 g, 80% yield).

| **Regent** | **Amount / g** | **Amount / mL** | **Price / g or mL** | **Total price / RMB** |
|---|---|---|---|---|
| 3,3'-Dibromo-2,2'-bithiophene | 1.62 | | 68.5 | 110.97 |
| p-Anisidine | 0.8 | | 0.436 | 0.35 |
| $Pd_2(dba)_3$ | 0.046 | | 90 | 4.14 |
| dppf | 0.112 | | 4.85 | 5.43 |
| *t*-BuONa | 1.92 | | 0.4 | 0.77 |
| Toluene | | 20 | 0.1 | 2 |
| Silica gel | 100 | | 0.036 | 3.6 |
| Petroleum ether 60-90 °C | | 300 | 0.022 | 6.6 |
| dichloromethane | | 20 | 0.02 | 0.4 |
| **Total cost** | 134.26 RMB | | | |
| Amount intermediate **3** | 1.144 g | | | |
| **COST** for intermediate **3** | 117.36 RMB/g | | | |




In a dried Schlenk tube was dissolved compound **3** (286 mg, 1 mmol) in anhydrous THF (10 mL), n-BuLi (0.88 mL, 2.5 mol/L) was added dropwise at -78 °C under argon atmosphere. The resulting mixture was stirred at the same temperature for one hour before $Sn(But)_3Cl$ (780 mg, 2.2 mmol) was added. The remaining mixture was slowly warmed to room temperature and stirred overnight. The reaction was terminated by adding ice water, and the mixture was extracted with ethyl acetate and dried with anhydrous $MgSO_4$. After the solvent was evaporated, the crude product **4** was obtained and used to synthesize H16 without further purification.

To a 100 mL two-neck round-bottom flask, a mixture of compound **4**, compound **2** (845 mg, 2.2 mmol), $Pd(PPh_3)_4$ (57 mg, 0.05 mmol) and toluene (15 mL) was added and heated at reflux for 8 hours under argon atmosphere. After evaporating the solvent under reduced pressure, the remaining crude product was purified by column chromatography on silica gel eluented with DCM: PE = 1:15~2:1 (v/v) to afford the desired product H16 as a yellow solid (0.581 g, 91% yield for two steps).

| **Regent** | **Amount / g** | **Amount / mL** | **Price / g or mL** | **Total price / RMB** |
|---|---|---|---|---|
| **3** | 0.286 | | 117.36 | 33.56 |
| n-BuLi (2.5mol / L) | | 0.88 | 0.4 | 0.352 |
| $Sn(But)_3Cl$ | 0.781 | | 1.69 | 1.32 |
| THF | | 10 | 0.6 | 6 |

| | | | | |
|---|---|---|---|---|
| **2** | 0.845 | | 13.7 | 11.58 |
| $Pd(PPh_3)_4$ | 0.057 | | 44 | 2.51 |
| Toluene | | 15 | 0.1 | 1.5 |
| Silica gel | 200 | | 0.036 | 7.2 |
| Petroleum ether 60-90 °C | | 1000 | 0.022 | 22 |
| dichloromethane | | 1000 | 0.02 | 20 |
| **Total cost** | 106.02 RMB | | | |
| Amount H16 | 0.581 g | | | |
| **COST** for H16 | 182.48 RMB/g | | | |

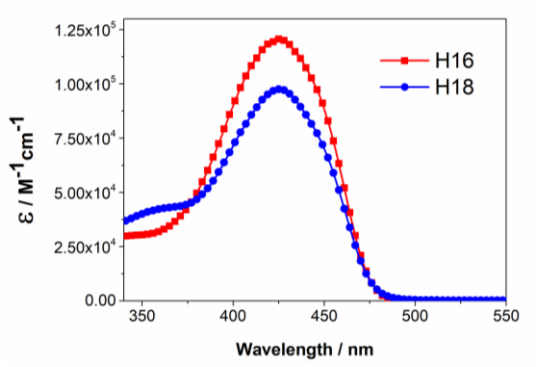



**Figure S1**. The absorption coefficients for H16 (12.1× $10^4$ $M^{-1}$ $cm^{-1}$) and H18 (9.8× $10^4$ $M^{-1}$ $cm^{-1}$).

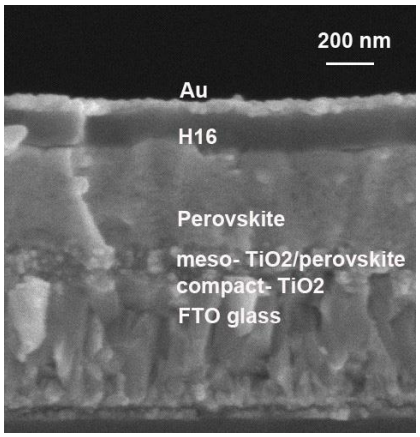



**Figure S2**. The cross-section view of the device based on H16.

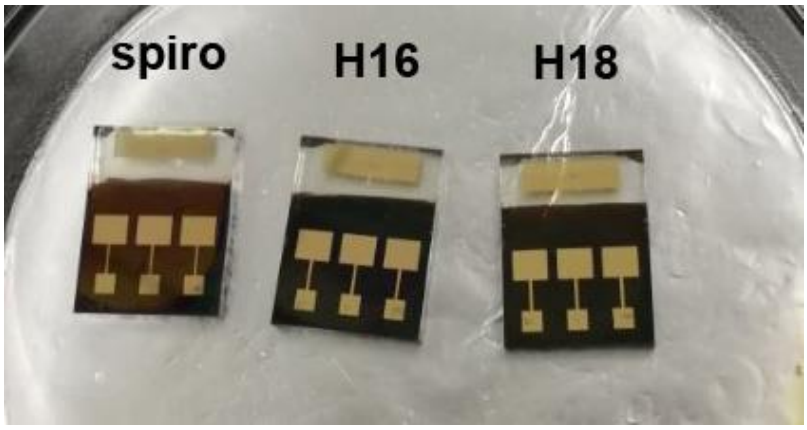



**Figure S3**. The champion cells based on H16, H18 and spiro-OMeTAD.

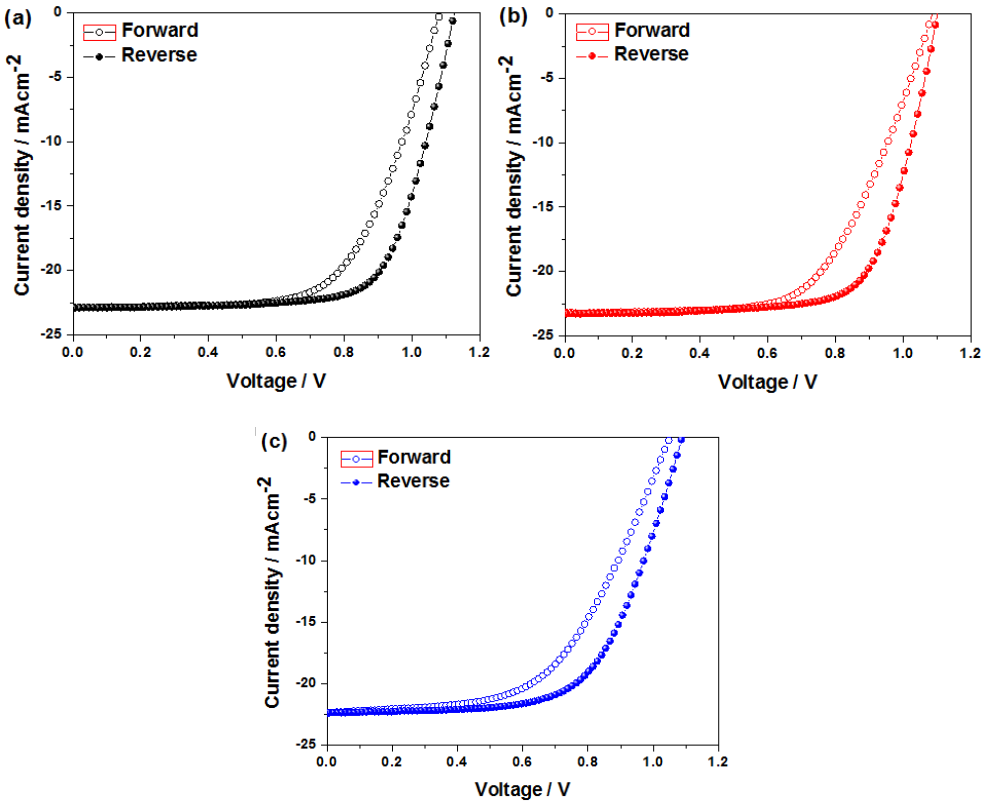



**Figure S4.** Forward and reverse *J-V* characteristics of Spiro-OMeTAD (a), H16 (b) and H18 (c) based PSCs.

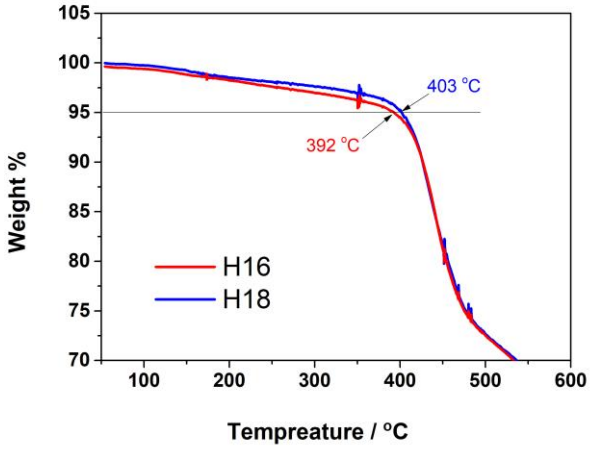



**Figure S5.** Thermogravimetric heating curves of H16 and H18 (heating rate 12 °C $min^{-1}$ in $N_2$ atmosphere).

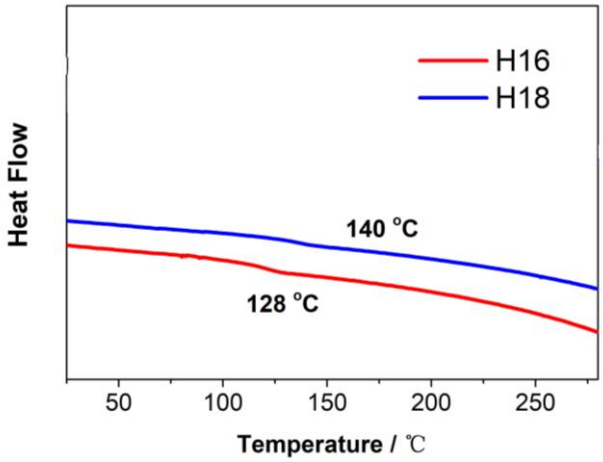
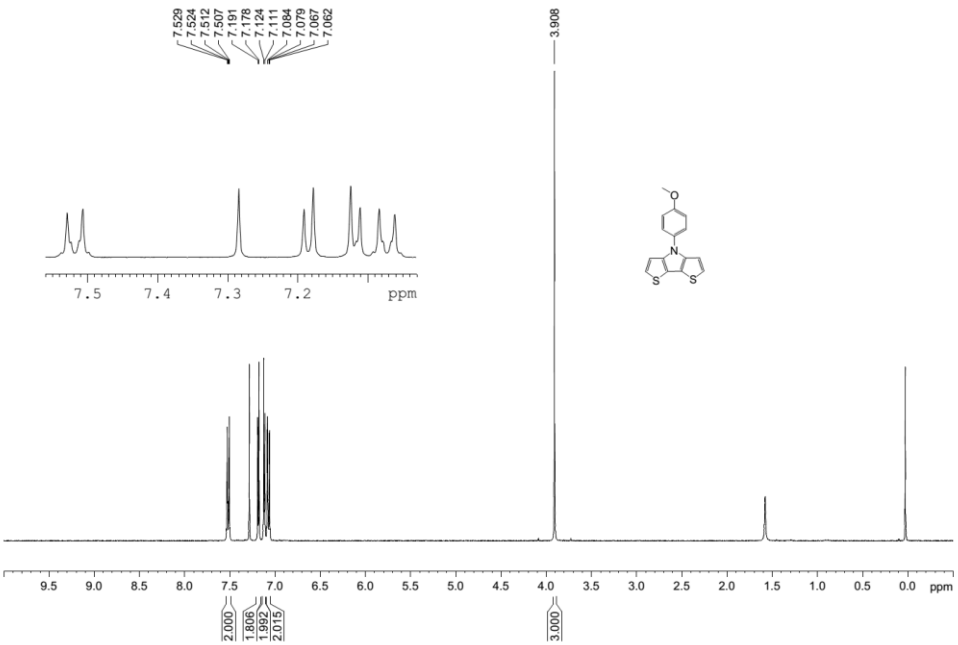
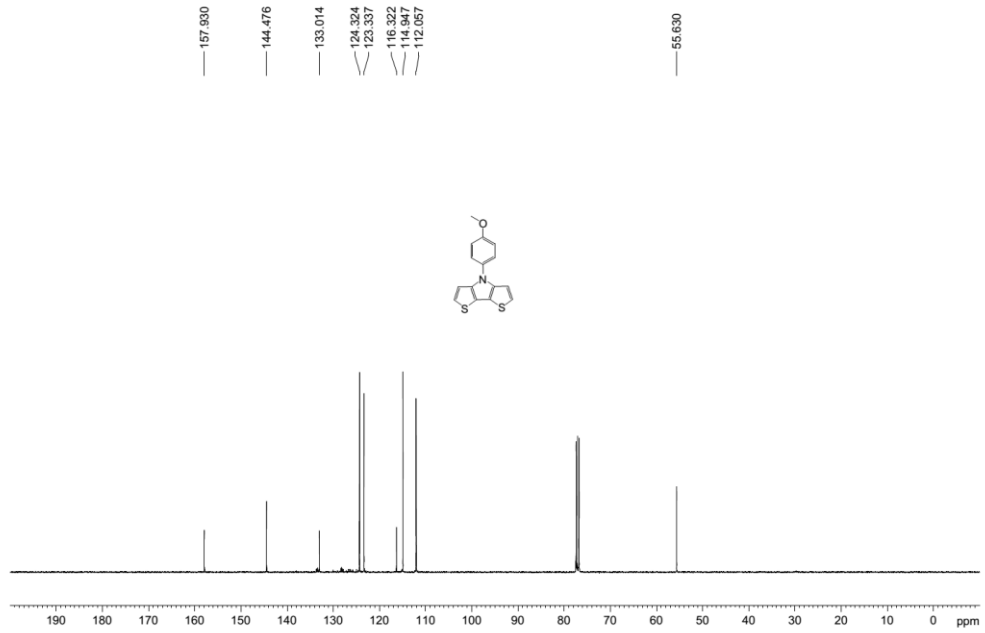



**Figure S6.** Differential scanning calorimetry (DSC) curves of H16 and H18. The $T_g$ of H16 and H18 was determined to be 128 °C and 140 °C.

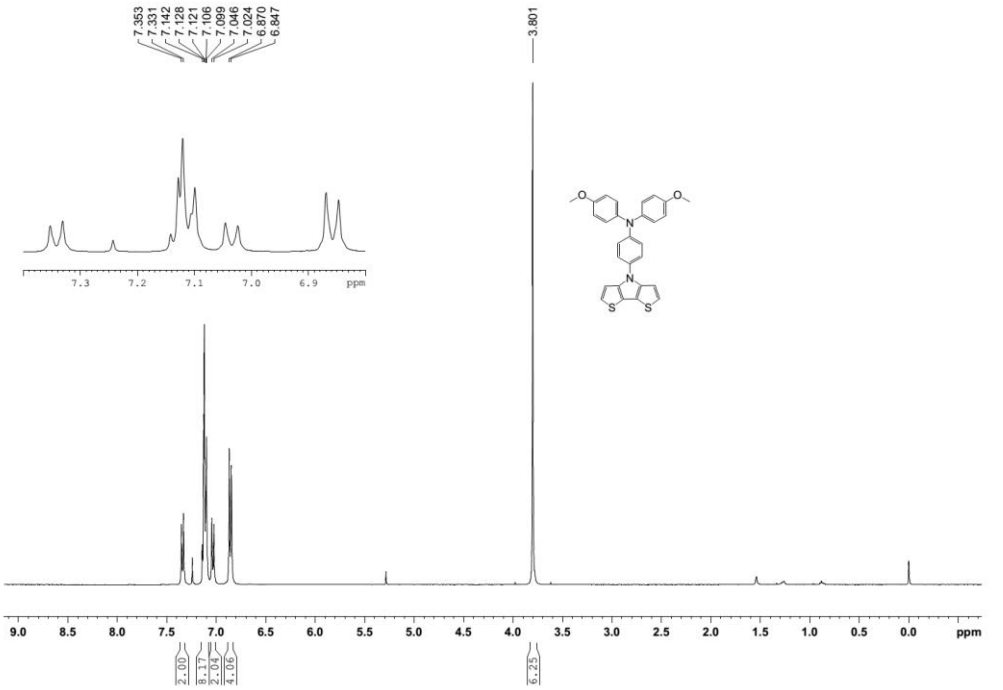
$^{1}H$ and $^{13}C$ NMR ($CDCl_3$) spectra of compound

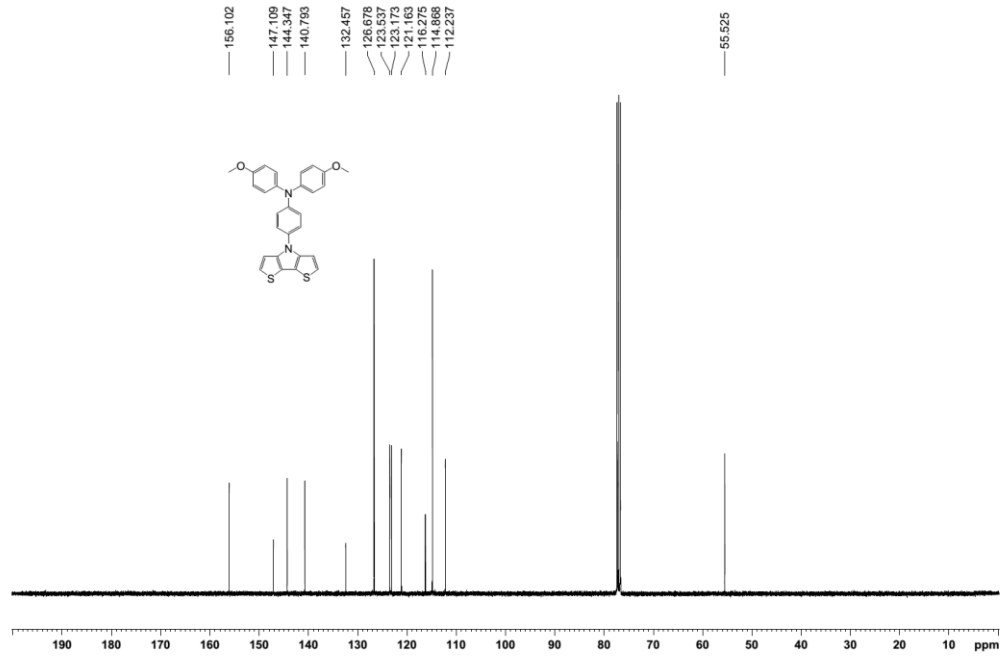
4-(4-methoxyphenyl)-4H-dithieno[3,2-b:2',3'-d]yrrole (MPDTP)



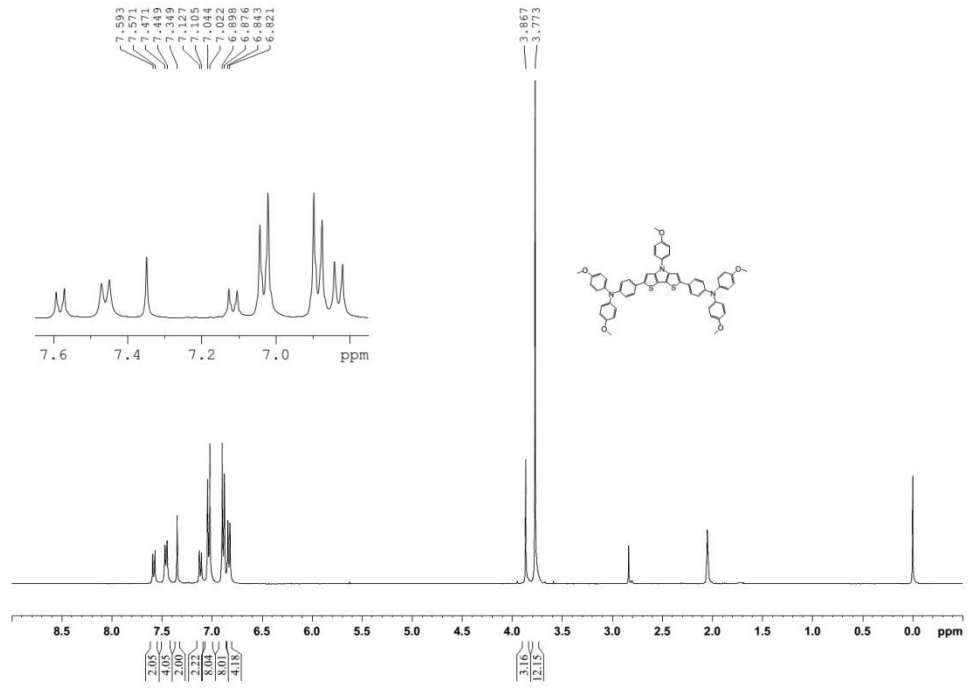



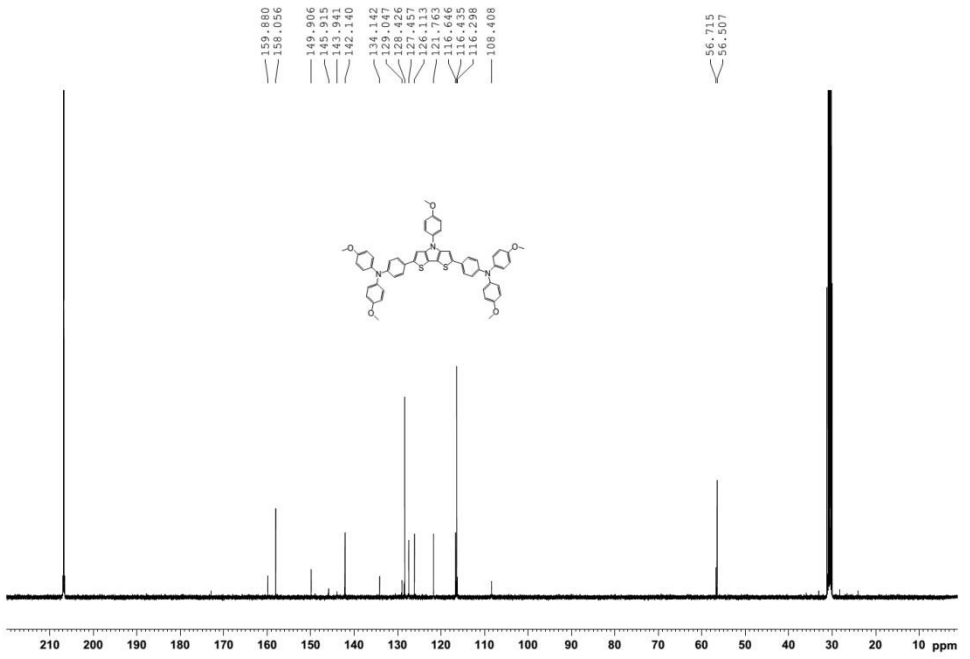
$^{1}H$ and $^{13}C$ NMR ($CDCl_3$) spectra of compound N-(4-(4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl)phenyl)-4-methoxy-N-(4-methoxyphenyl)aniline (TPDTP)



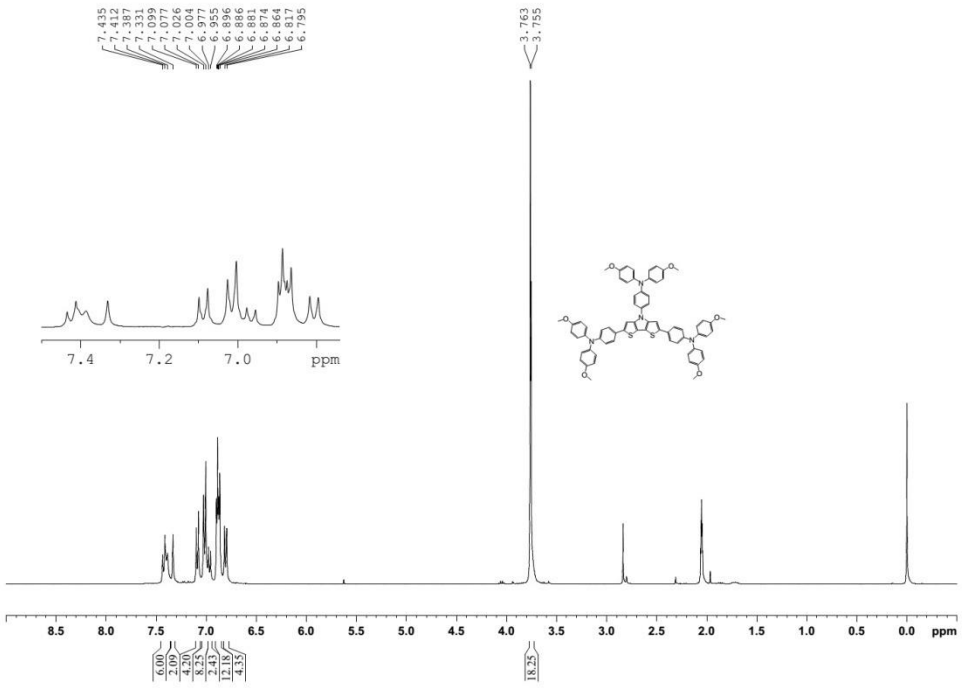



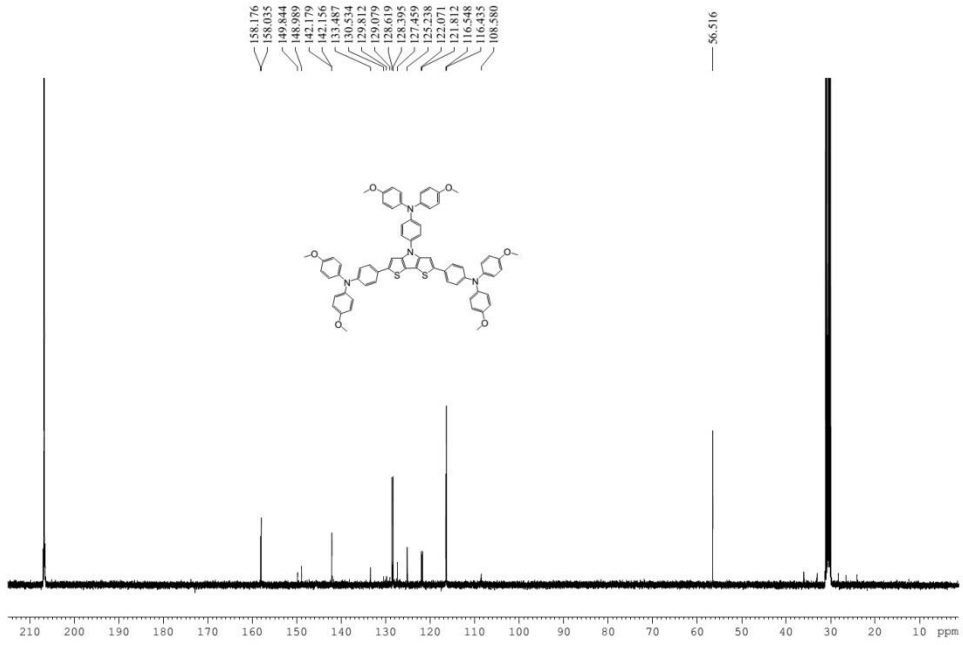
$^{1}H$ and $^{13}C$ NMR ($d_6$-Acetone) spectra of compound H16



$^{1}$H and $^{13}$C NMR ($d_6$-Acetone) spectra of compound H18



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