

## Supporting Information

### **Efficient Perovskite Solar Cells Enabled by Large Dimensional Structured Hole Transporting Material**

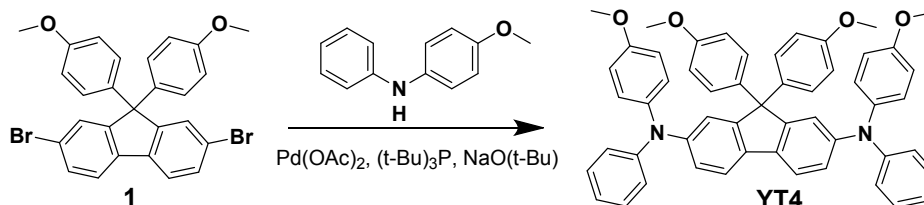
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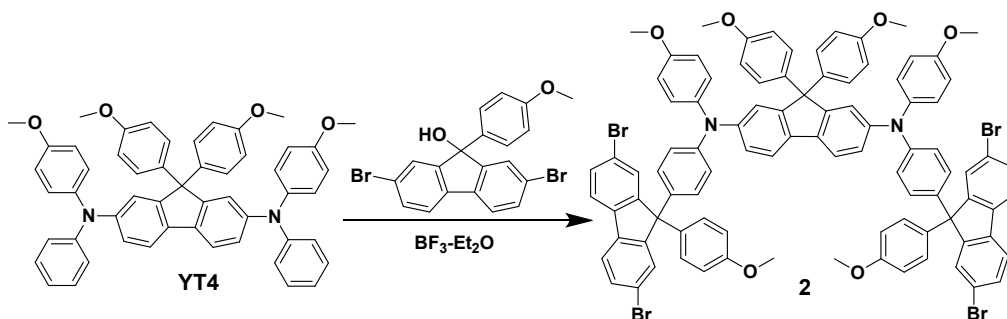
## Experimental Section

Commercially available reagents were purchased from Sigma-Aldrich, Energy, and used without further purification. Toluene was freshly distilled before use. Other solvents were used directly. NMR spectra were recorded on a Bruker AVANCEIIIHD600 MHz spectrometer. High-resolution mass spectra were collected with a Fourier transform-ion cyclotron resonance mass spectrometer instrument (Thermo Fisher LTQOrbitrapXL). F1 was characterized by NMR and mass spectral data. The synthetic routes of F1 are outlined in followed schemes and the details are depicted below.



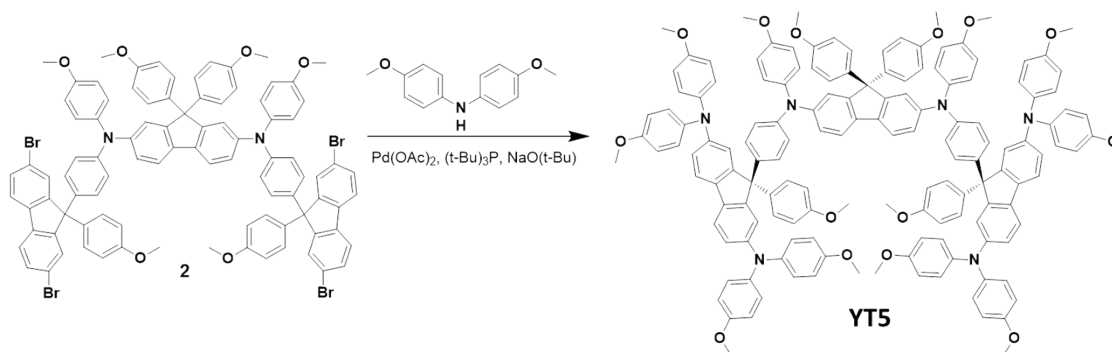
**Scheme S1.** The synthesis route of **YT4**.

*Synthesis of N<sup>2</sup>,N<sup>7</sup>,9,9-tetrakis(4-methoxyphenyl)-N<sup>2</sup>,N<sup>7</sup>-diphenyl-9H-fluorene-2,7-diamine (YT4).* A mixture of **1** (1 mmol), 4-Methoxydiphenylamine (2.25 mmol), and sodium tert-butoxide (360 mg, 3.75 mmol) in toluene was stirred for 30 minutes under N<sub>2</sub> atmosphere to remove oxygen. Then palladium acetate (5 % mmol), tri-tert-butyl phosphine (5 % mmol) was added. And the mixture was stirred overnight at 110 °C until the reaction was complete by TLC analysis. After cooling, the reaction was quenched by water, and extracted by ethyl acetate three times. The organic layer was dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (SiO<sub>2</sub>, hexane/EtOAc, v/v, 3:1) to give **YT4** as a white solid. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.21 (t, *J* = 7.9 Hz, 4H), 6.99 (t, *J* = 8.9 Hz, 4H), 6.95 – 6.91 (m, 4H), 6.91 – 6.88 (m, 8H), 6.87 – 6.83 (m, 6H), 6.78 (d, *J* = 8.9 Hz, 4H), 3.73 (s, 6H), 3.69 (s, 6H). HR-MS (ESI) *m/z*: [M]<sup>+</sup> calcd for 772.9332; found, 772.9322.



**Scheme S2.** The synthesis route of **2**.

*Synthesis of  $N^2,N^7$ -bis(4-(2,7-dibromo-9-(4-methoxyphenyl)-9H-fluoren-9-yl)phenyl)- $N^2,N^7,9,9$ -tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (**2**).* A mixture of compound **YT4** (1 mmol) and compound 2,7-dibromo-9-(4-methoxyphenyl)-9H-fluoren-9-ol (2 mmol) was dissolved in dichloromethane at room temperature. Then a solution of boron trifluoride diethyl ether complex (0.2 mL) in dichloromethane was added dropwise to the mixture and stirred overnight at room temperature. Then the reaction was quenched by water and extracted by dichloromethane three times. The organic layer was dried over anhydrous  $Mg_2SO_4$  and evaporated under vacuum. The remaining crude product was purified by chromatography ( $SiO_2$ , hexane/EtOAc, v/v, 2:1) to give **2** as a white solid (yield 70 %).  $^1H$  NMR (600 MHz,  $DMSO-d_6$ )  $\delta$  7.82 (d,  $J = 8.1$  Hz, 4H), 7.53 – 7.49 (m, 6H), 7.44 (d,  $J = 1.6$  Hz, 4H), 6.93 (d,  $J = 8.9$  Hz, 4H), 6.90 (d,  $J = 8.8$  Hz, 4H), 6.83 (d,  $J = 8.6$  Hz, 6H), 6.80 (s, 3H), 6.78 – 6.77 (m, 4H), 6.76 (d,  $J = 3.5$  Hz, 4H), 6.75 (s, 3H), 6.65 – 6.61 (m, 8H), 3.63 (s, 6H), 3.62 (s, 6H), 3.53 (s, 6H).



**Scheme S3.** The synthesis route of **YT5**.

*Synthesis of YT5.* A mixture of **3** (1 mmol), 4,4'-dimethoxy-4-biphenylamin (6 mmol), and sodium tert-butoxide (360 mg, 3.75 mmol) in toluene was stirred for 30 minutes under N<sub>2</sub> atmosphere to remove oxygen. Then palladium acetate (5 % mmol), tri-tert-butyl phosphine (5 % mmol) was added. And the mixture was stirred overnight at 110 °C until the reaction was complete by TLC analysis. After cooling, the reaction was quenched by water, and extracted by ethyl acetate three times. The organic layer was dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (SiO<sub>2</sub>, hexane/EtOAc, v/v, 2:1) to give **YT5** as a grey white solid (yield 60 %). <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) δ 7.50 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 7.7 Hz, 4H), 6.69 – 6.85 (m, 4H), 6.79-6.83 (m, 16H), 6.63-6.79 (m, 16H), 6.71 – 6.77 (m, 22H), 6.59-6.70 (m, 16H), 6.51 (d, J = 2.2 Hz, 4H), 3.61 (s, 6H), 3.60 (s, 6H), 3.58 (s, 24H), 3.43 (s, 6H). HR-MS (ESI) *m/z*: [M]<sup>+</sup> calcd for 2222.9332; found, 2222.9224.

### Computational Details

In the simulation, Optimization and single point energy calculations are performed using the cam-B3LYP and the 6-31G\*\* basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09.

### Mobility Measurements

Due to the low mobility of charge carriers in organic semiconductors, the injected carrier forms a space charge. This space charge creates a field that opposes the applied bias and thus decreases the voltage drop across junction; as a result, space charge limited currents (SCLCs) have been proposed as the dominant conduction mechanism in organic semiconductors by researchers. The andohmic conduction can be described by equations (2):

$$J = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{d^3} \quad (2)$$

where *J* is the current density, *μ* is the hole mobility, *ε<sub>o</sub>* is the vacuum permittivity (8.85×10<sup>-12</sup> F/m), *ε<sub>r</sub>* is the dielectric constant of the material (normally taken to approach 3 for OSs), *V* is the applied bias, and *d* is the film thickness. The FTO substrates were

carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol successively. The remaining organic residues were removed with 10 min by airbrush. A 40 nm thick PEDOT: PSS layer was spin-coated onto the substrates, which were then annealed at 120 °C for 30 min in air. The substrates were then transferred into a glovebox for further fabrication steps. Here the concentration of YT4 and YT5 is 70 mg mL<sup>-1</sup> and 50 mg mL<sup>-1</sup> in chlorobenzene, respectively, with addition of 18 μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile) and 29 μL tert-butylpyridine (*t*BP). This HTMs solution was spin-coated at 4000 rpm to yield films. The thicknesses of the films are measured by using a Dektak 6M profilometer. 80 nm of gold was then evaporated onto the active layer under high vacuum (less than 10<sup>-6</sup> mbar). *J-V* characteristics of the devices have been measured with a Keithley 2400 Source-Measure unit, interfaced with a computer. Device characterization was carried out in air.

### **Conductivity Measurement**

The electrical conductivities of the HTMs films were determined by using two-probe electrical conductivity measurements. The conductivity devices were fabricated as following. Glass substrates without conductive layer were carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol successively. A thin layer of nanoporous TiO<sub>2</sub> was coated on the glass substrates by spin-coating with a diluted TiO<sub>2</sub> paste (Dyesol DSL 18NR-T) with terpineol (1:3, mass ratio). The thickness of the film is ca. 500 nm, as measured with a DekTak profilometer. After sintering the TiO<sub>2</sub> film on a hotplate at 500 °C for 30 min, the film was cooled to room temperature. A solution of HTMs in chlorobenzene was subsequently deposited by spin-coating. Here the concentration of of doped YT4 and YT5 is 70 mg mL<sup>-1</sup> and 50 in mg mL<sup>-1</sup>, respectively, in chlorobenzene with addition of 18 μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile) and 29 μL tert-butylpyridine (*t*BP). Subsequently, a 80 nm thick Au back contact was deposited onto the organic semiconductor by thermal evaporation in a vacuum chamber with a base pressure of about 10<sup>-6</sup> bar, to complete the device fabrication. *J-V* characteristics were recorded on a Keithley 2400 semiconductor characterization system.

## Fabrication of Hybrid Perovskite Solar Cells

The etched fluorine-doped SnO<sub>2</sub> (FTO, 7 Ω) substrates were cleaned in an ultrasonic bath for half an hour in the following order: deionized water, acetone and ethanol. The precursor solution of SnO<sub>2</sub> QD was spin-coated onto the substrate at a speed of 1000 rpm for 3 s and then 3400 rpm for 25 s. The SnO<sub>2</sub> QD electron transporting layer films were annealed under ambient atmosphere at 170 °C for 1 h. The (CsPbI<sub>3</sub>)<sub>0.05</sub>(FA<sub>0.85</sub>MA<sub>0.15</sub>Pb(I<sub>0.85</sub>Br<sub>0.15</sub>)<sub>3</sub>)<sub>0.95</sub> perovskite precursor solution was prepared into the DMSO/DMF (1:5 v:v) mixture. The perovskite solution was spin-coated in a two-step program; first at 1000 for 10 s and then at 6000 rpm for 30 s. During the second step, 100 μL of chlorobenzene were poured on the spinning substrate 15 s prior to the end of the program. The substrates were then annealed at 100 °C for 1 h in a nitrogen filled glove box. 5mg mL<sup>-1</sup> PEAI isopropanol solution was spin-coated on the top of the perovskite film at 5000 rpm for 30s and then annealed at 100 °C for 10min. Subsequently, the concentration of doped YT4 and YT5 is 70 mg mL<sup>-1</sup> and 50 in mg mL<sup>-1</sup>, respectively, in chlorobenzene with addition of 18 μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile) and 29 μL tert-butylpyridine (*t*BP). The spiro-OMeTAD in chlorobenzene (80 mg/mL) solution was prepared with addition of 18 μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile) and 29 μL tert-butylpyridine (*t*BP). As a last step 80 nm of gold top electrode were thermally evaporated under high vacuum. Current-voltage characteristics were measured under 100 mW/cm<sup>2</sup> (AM 1.5G illumination) using a Newport solar simulator (model 91160) and a Keithley 2400 source/meter. A certified reference solar cell (Fraunhofer ISE) was used to calibrate the light source for an intensity of 100 mW/cm<sup>2</sup>. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using a computer-controlled setup consisting of a Xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectra Products CM110), and a potentiostat (LabJack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE). The voltage scan rate was 10 mV s<sup>-1</sup> and no device preconditioning was applied before starting the measurement, such as light soaking or forward voltage bias applied for long time. The cells were masked with a black metal mask limiting the active area to 0.0625 cm<sup>2</sup> and reducing the influence of the scattered light.

## Fabrication of All-Inorganic Perovskite Solar Cells

The etched ITO substrates ( $7 \Omega$ ) were cleaned with water, ethanol, acetone, and in an ultrasonic bath, and subsequently treated in a UV-ozone cleaner for 15 min. The compact  $\text{SnO}_2$  layer was deposited onto the UV-treated ITO substrate by spin-coating  $70 \mu\text{L}$  of dilute  $\text{SnO}_2$  dispersion ( $v(\text{SnO}_2 \text{ dispersion}): v(\text{H}_2\text{O}): v(\text{isopropyl alcohol}) = 1: 3: 3$ ) at 3000 r.p.m. for 15 s, followed by baking at  $150^\circ\text{C}$  for 15 min in ambient air. 312 mg CsI, 277 mg  $\text{PbI}_2$  and 220 mg  $\text{PbBr}_2$  were added in 1 mL DMSO, and then heated at  $60^\circ\text{C}$  for overnight in  $\text{N}_2$ . The  $\text{CsPbI}_2\text{Br}$  precursor solution ( $75 \mu\text{L}$ ) was dropped onto the  $\text{SnO}_2$  substrate and spin-coated via a two-step process, the first step is 1000 rpm for 10 s, and the second step is 2500 rpm for 100 s, respectively. Then the coated films were annealed on hot plates in two steps: (1)  $40^\circ\text{C}$  for 2 min; (2)  $160^\circ\text{C}$  for 30 min. Subsequently, the concentration of YT5 is  $50 \text{ mg mL}^{-1}$  in chlorobenzene with addition of  $18 \mu\text{L}$  Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile) and  $29 \mu\text{L}$  tert-butylpyridine (*t*BP). The spiro-OMeTAD in chlorobenzene ( $80 \text{ mg/mL}$ ) solution was prepared with addition of  $18 \mu\text{L}$  Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile) and  $29 \mu\text{L}$  tert-butylpyridine (*t*BP). Finally, 80 nm of Au was thermally evaporated as a top electrode to finish the device fabrication. Current-voltage characteristics were measured under  $100 \text{ mW/cm}^2$  (AM 1.5G illumination) using a Newport solar simulator (model 91160) and a Keithley 2400 source/meter. A certified reference solar cell (Fraunhofer ISE) was used to calibrate the light source for an intensity of  $100 \text{ mW/cm}^2$ . Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using a computer-controlled setup consisting of a Xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectra Products CM110), and a potentiostat (LabJack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE). The voltage scan rate was  $10 \text{ mV s}^{-1}$  and no device preconditioning was applied before starting the measurement, such as light soaking or forward voltage bias applied for long time. The cells were masked with a black metal mask limiting the active area to  $0.0625 \text{ cm}^2$  and reducing the influence of the scattered light.

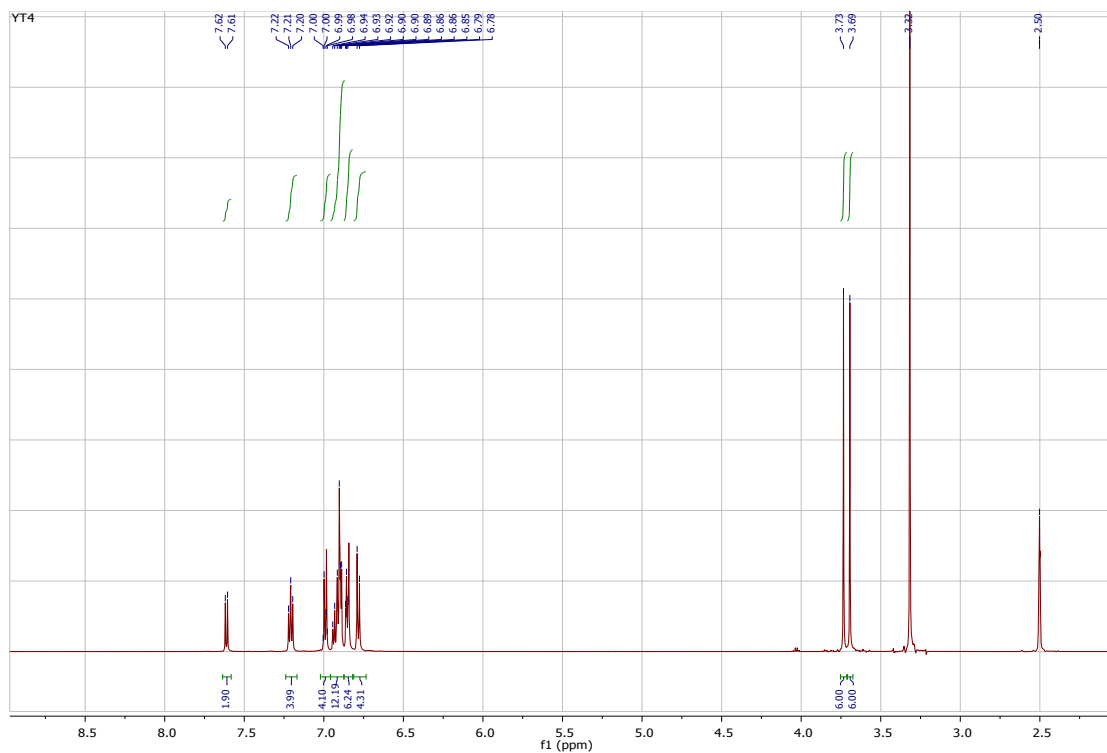


Figure S4.  $^1\text{H}$  NMR spectrum of YT4.

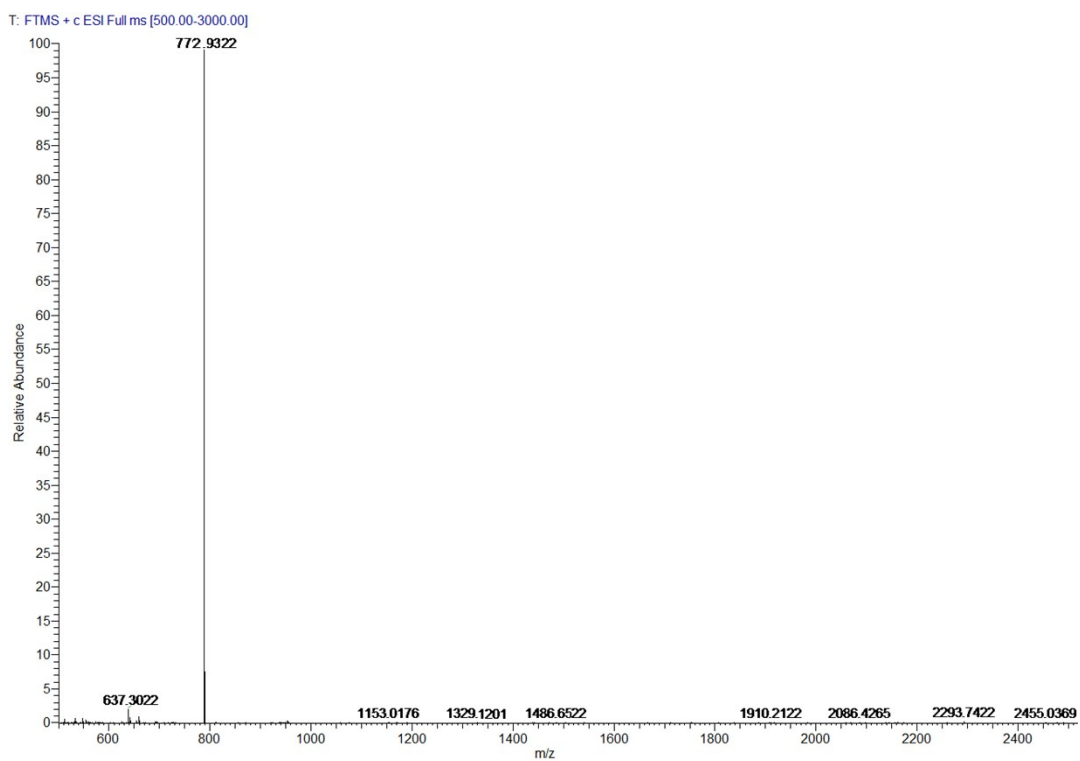


Figure S5. HR-MS spectra of YT4.



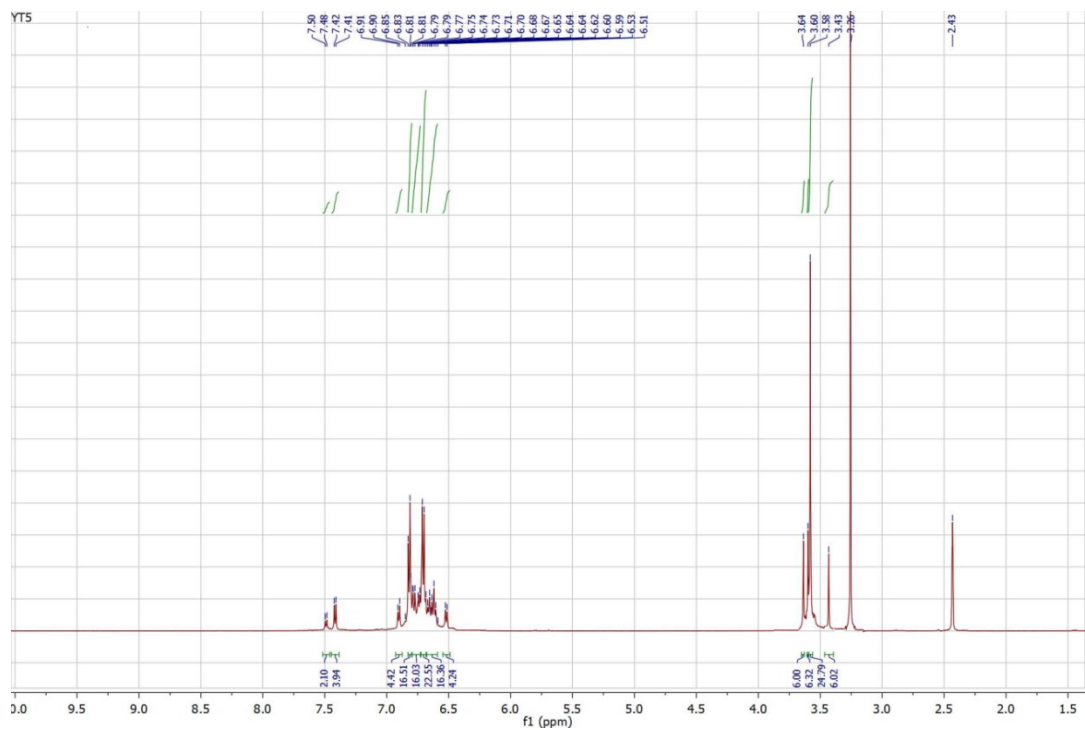


Figure S6. <sup>1</sup>H NMR spectrum of YT5.

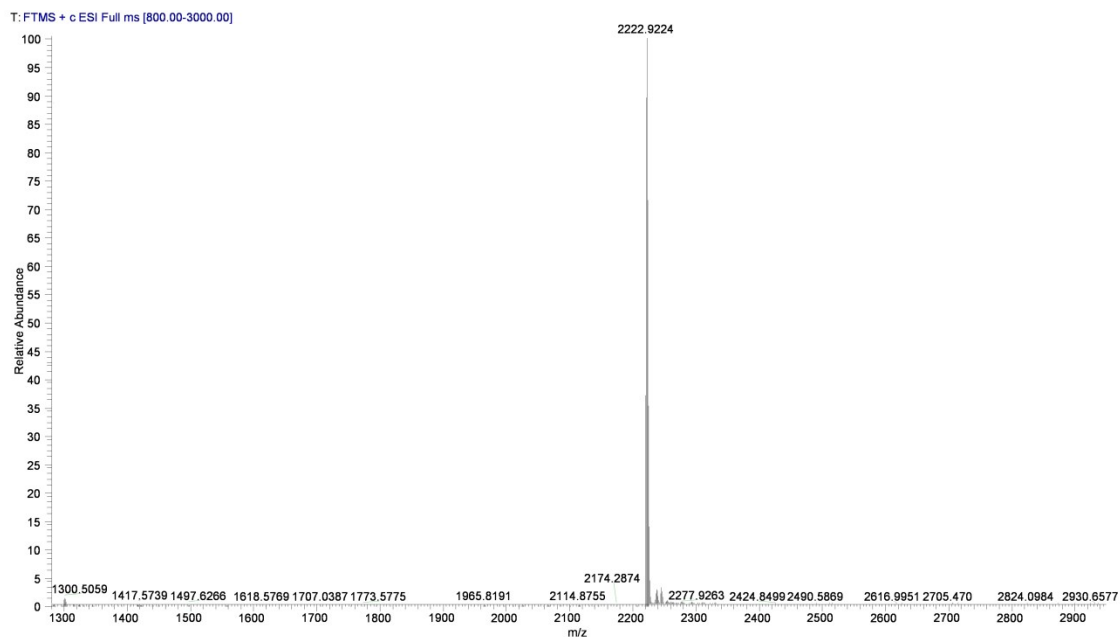
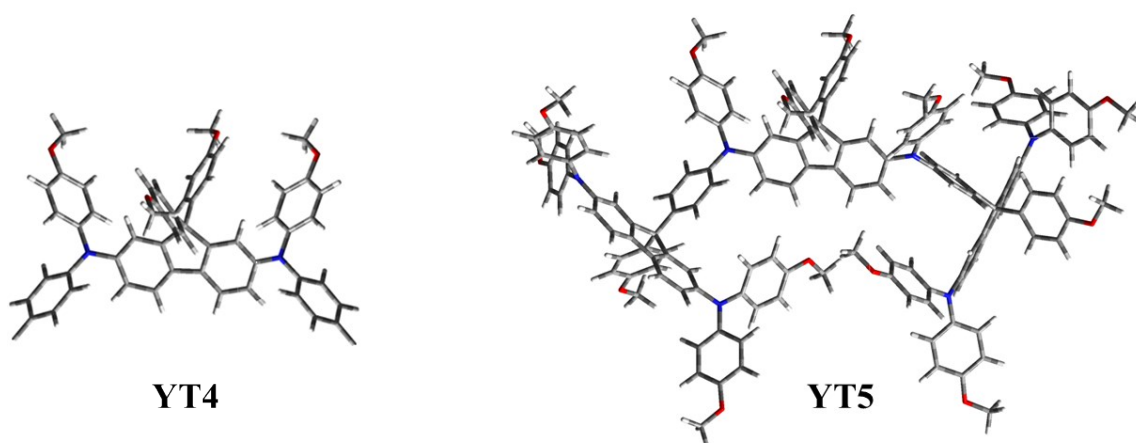
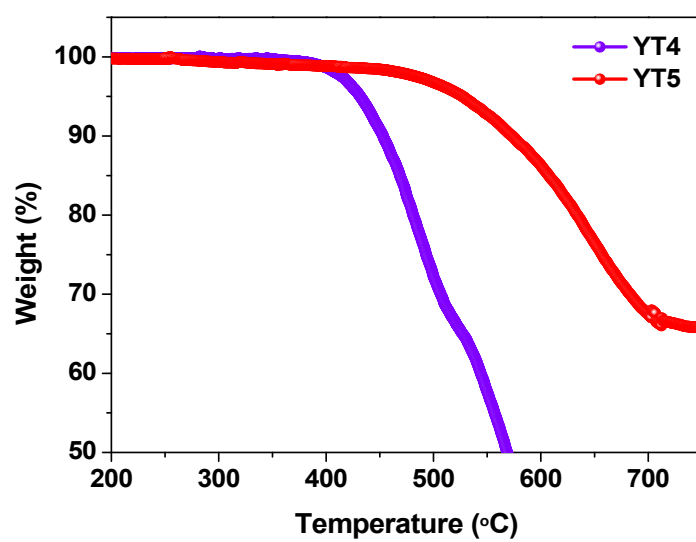


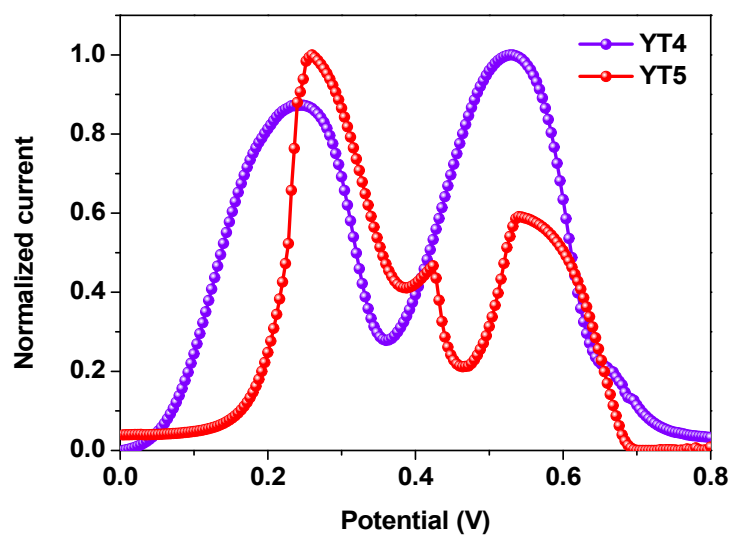
Figure S7. HR-MS spectra of YT5.



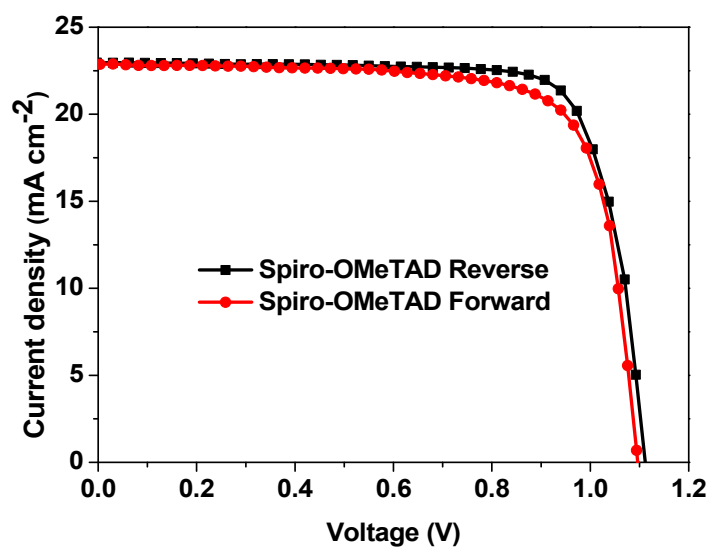
**Figure S8.** Molecular Geometry of **YT4** and **YT5**.



**Figure S9.** Thermal gravimetric analysis of **YT4** and **YT5**.



**Figure S10.** Normalized differential pulsed voltammetry (DPV) results of YT4 and YT5.



**Figure S11.**  $J$ - $V$  curves of hybrid PSCs based on Spiro-OMeTAD.

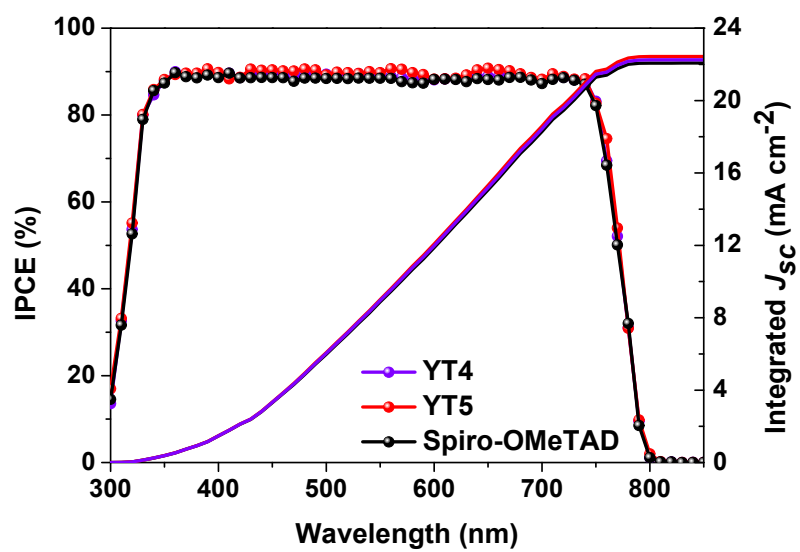


Figure S12. IPCE curves of PSCs based on the YT4, YT5 and Spiro-OMeTAD.