Supporting Information

Importance of Terminated Groups in 9,9-bis(4-methoxyphenyl)-substituted Fluorene-based Hole Transport Materials for Highly Efficient Organic-inorganic Hybrid and All-inorganic Perovskite Solar Cells

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Experimental Section

Materials and Reagents

The **YT2** was synthesized according to our previous work. ^[1] Other chemicals and solvents were commercial available for use without further purification. NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer. High-resolution MALDI spectra were collected with a Fourier transform-ion cyclotron resonance mass spectrometer instrument (Varian 7.0TFTICR-MS). **YT1** and **YT3** were fully characterized by NMR and mass spectral data. The synthetic routs of the three HTMs are outlined in **Scheme S1** and the details are depicted below.



Scheme S1. The synthesis route of YT1, YT2 and YT3.

9,9-bis(4-methoxyphenyl)-*N*²,*N*²,*N*⁷,*N*⁷-tetraphenyl-9H-fluorene-2,7-diamine (YT1)

A mixture of 2,7-dibromo-9,9-bis(4-methoxyphenyl)-9H-fluorene **1** (1mmol) and diphenylamine (2.25mmol), and sodium *tert*-butoxide (360 mg, 3.75 mmol) in toluene was stirred for 30 minutes under N_2 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 then followed by product extraction with ethyl acetate. The organic layer was dried over

anhydrous Mg₂SO₄ and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (hexane/EtOAc, v/v, 3:1) to give **YT1** as a white solid (yield 96%). ¹H NMR (400 MHz, CDCl₃, δ): 7.48 (d, J = 4.0 Hz, 2H), 7.19 (t, J = 4.0 Hz, 8H), 7.12 (s, 2H), 7.06 (d, J = 8.0 Hz, 8H), 7.01 (d, J = 8.0 Hz, 4H), 6.96-6.94 (t, J = 4.0 Hz, 4H), 6.70 (d, J = 8.0 Hz, 4H), 3.76 (s, 6H). ¹³C NMR (400 MHz, CDCl₃, δ): 158.17, 152.84, 147.70, 146.71, 137.94, 134.54, 129.24, 129.12, 124.16, 124.03, 123.34, 122.62, 120.55, 113.44, 113.37, 55.25. HR-MS (ESI) m/z: [M+1]⁺ calcd for 713.3163; found, 713.3160.

9,9-bis(4-methoxyphenyl)-*N*²,*N*²,*N*⁷,*N*⁷-tetrakis(4-(9-(4-methoxyphenyl)-9H-fluoren-9yl)phenyl)-9H-fluorene-2,7-diamine (YT3)

A mixture of compound **YT1** (1 mmol) and 9-(4-methoxyphenyl)-9H-fluoren-9-ol **2** (5mmol) was dissolved in dichloromethane at room temperature. Then a solution of boron trifluoride diethyl ether complex (0.1mL) in dichloromethane was added dropwise to the mixture and stirred for 2h at room temperature. Then the reaction was quenched with water and extracted with dichloromethane. The organic layer was dried over anhydrous Mg₂SO₄ and evaporated under vacuum. The remaining crude product was purified by chromatography (SiO₂, hexane/EtOAc, v/v, 2:1) to give YT3 as a light yellow solid (yield 90%). ¹H NMR (400 MHz, DMSO-*d*, δ): 7.87 (d, J = 4.0 Hz, 8H), 7.57 (t, J = 4.0 Hz, 2H), 7.33-7.37 (m, 16H), 7.23-7.26 (m, 8H), 6.95-6.97 (m, 16H), 6.90-6.91 (m, 2H), 6.74-6.80 (m, 22H), 6.61 (d, J = 4.0 Hz, 4H), 3.66 (s, 12H), 3.58 (s, 6H). ¹³C NMR (400 MHz, DMSO-*d*, δ): 163.15, 163.04, 157.56, 157.52, 156.26, 156.19, 155.99, 151.27, 150.91, 150.53, 145.10, 142.82, 142.65, 142.26, 139.27, 134.03, 133.85, 133.80, 132.95, 132.72, 132.67, 131.20, 128.54, 128.28, 128.21, 126.75, 126.75, 126.64, 125.91, 125.65, 118.93, 118.84, 118.64, 68.96, 60.18. HR-MS (ESI): m/z: [M+1]⁺ calcd for 1793.7341; found, 1793.7396.



Figure S1.¹ H NMR (CDCl₃) spectrum of YT1.



Figure S2. ¹³C NMR (CDCl₃) spectrum of YT1.



Figure S3. HR-MS spectra of YT1.



Figure S4.¹ H NMR (DMSO-*d*) spectrum of YT3.



Figure S5. ¹³C NMR (DMSO-*d*) spectrum of YT3.





Computational Details

In the simulation, Optimization and single point energy calculations are performed at B3LYP/6-31G(d) level using Gaussian 09 program basis set for all atoms, without any symmetry constraints.



Figure S7. Frontier orbitals of YT1, YT2 and YT3.



Figure S8. The cross-section image of the device architecture.



Figure S9. Hysteresis curve of these HTMs in (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}-based PSCs.



Figure S10. Hysteresis curve of YT3 and Spiro-OMeTAD in CsPbI₂Br-based PSCs.



Figure S11. Dark *J-V* curves of the devices with YT1, YT2 and YT3.

Electrochemical Measurements

Electrochemical experiments were performed with a CH Instruments electrochemical workstation (model 660A) using a conventional three-electrode electrochemical cell. A glassy carbon electrode (diameter 3mm) was used as the working electrode, a platinum wire as the counter electrode, a Ag/AgCl as the reference electrode and 0.1 M of

tetrabutylammoniunhexafluorophosphate (*n*-Bu₄NPF₆) in dichloromethane solution as supporting electrolyte. The cyclovoltammetric scan rates were 50 mV/s. Each measurement was calibrated with Fc. $E_{1/2}$ ^{Fc} = 0.20 V. E_{HOMO} = -5.1– ($E_{1/2}$ - $E_{1/2}$ ^{Fc}).

Fabrication of (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15} perovskite solar cells

The fluorine-doped SnO₂ (FTO, 15Ω -square) substrates were etched with zinc powder and HCl acid (concentration 4 M) to form the desired electrode pattern. The substrates were cleaned in an ultrasonic bath for half an hour in the following order: deionized water, acetone and ethanol. A compact layer of TiO₂, intended to block the recombination current at the FTO support, was prepared on cleaned FTO substrate by spray pyrolysis of solution (0.2M titanium isopropoxide and 2M acetylacetone in isoproponal). Afterwards, a layer of mesoporous TiO_2 particles were spin-coated on the FTO glass with a thickness of 200 nm. The perovskite films were deposited from a precursor solution containing FAI (1 M), PbI₂ (1.1 M), MABr (0.2 M) and PbBr₂ (0.2 M) in anhydrous DMF: DMSO=4:1 (v/v). The perovskite solution was spin-coated in a two-step program; first at 1000 rpm for 10 s and then at 4000 rpm for 30 s. During the second step, 100 μ L 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. Here, the **YT1**, YT2, YT3 and Spiro-OMeTAD/chlorobenzene (80 mg/mL) solution was prepared with addition of 20 µL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), and 30 µL tert-butylpyridine (tBP). As a last step 80 nm of gold top electrode were thermally evaporated under high vacuum. Currentvoltage characteristics were measured under 100 mW/cm² (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/cm². 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). Electron lifetime measurements were performed using a white LED (Luxeon Star 1W) as the light source. The photocurrent decay was determined by monitoring photocurrent transients by applying a small square-wave modulation to the base light intensity. The voltage scan rate was 10mV 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 0.09 cm² and reducing the influence of the scattered light.

Fabrication of CsPbI₂Br perovskite solar cells

Glass/ITO substrates (2.5 cm*1.5 cm) were cleaned by sonication in deionized water, detergent, deionized water and isopropanol (IPA) and then dried in an oven. Glass/ITO substrates were treated under oxygen plasma for 15 min before use. 30 nm SnO₂ nanoparticles were spun coated onto ITO substrates at 4000 rpm for 30 s. The 10 nm ZnO nanoparticles were spun coated onto ITO/SnO₂ substrates at 5500 rpm for 30 s, followed by thermal annealing in air at 150°C for 30 min. 1M PbI₂ and 1M CsBr were dissolved in a mixture of DMF and DMSO (1:9 v/v), and stirred overnight in a glovebox. The perovskite precursor solution was spun coated onto ITO/ETL substrates via a two-step temperature-control procedure at 1500 rpm and 5000 rpm for 15 s and 30 s, respectively. Subsequently, the substrates were thermally annealed by a two-step process at 55°C for 60 s and 240°C for 60 s. Here, the **YT1**, **YT2**, **YT3** and **Spiro-OMeTAD**/chlorobenzene (80 mg/ml) solution was prepared with addition of 20 μ L Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), and 30 μ L tert-butylpyridine (*t*BP). Finally, a 12 nm MoO₃ and 100 nm silver (Ag) were thermally evaporated under vacuum, respectively. The cells

were masked with a black metal mask limiting the active area to 0.09 cm^2 and reducing the influence of the scattered light. Current-voltage characteristics were measured under 100 mW/cm² (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/cm². 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). Electron lifetime measurements were performed using a white LED (Luxeon Star 1W) as the light source. The photocurrent decay was determined by monitoring photocurrent transients by applying a small square-wave modulation to the base light intensity. The voltage scan rate was 10mV 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 0.09 cm² and reducing the influence of the scattered light.