Supporting Information

Developing D-π-D hole-transport materials for perovskite solar cells: the effect of π-bridge on device performance

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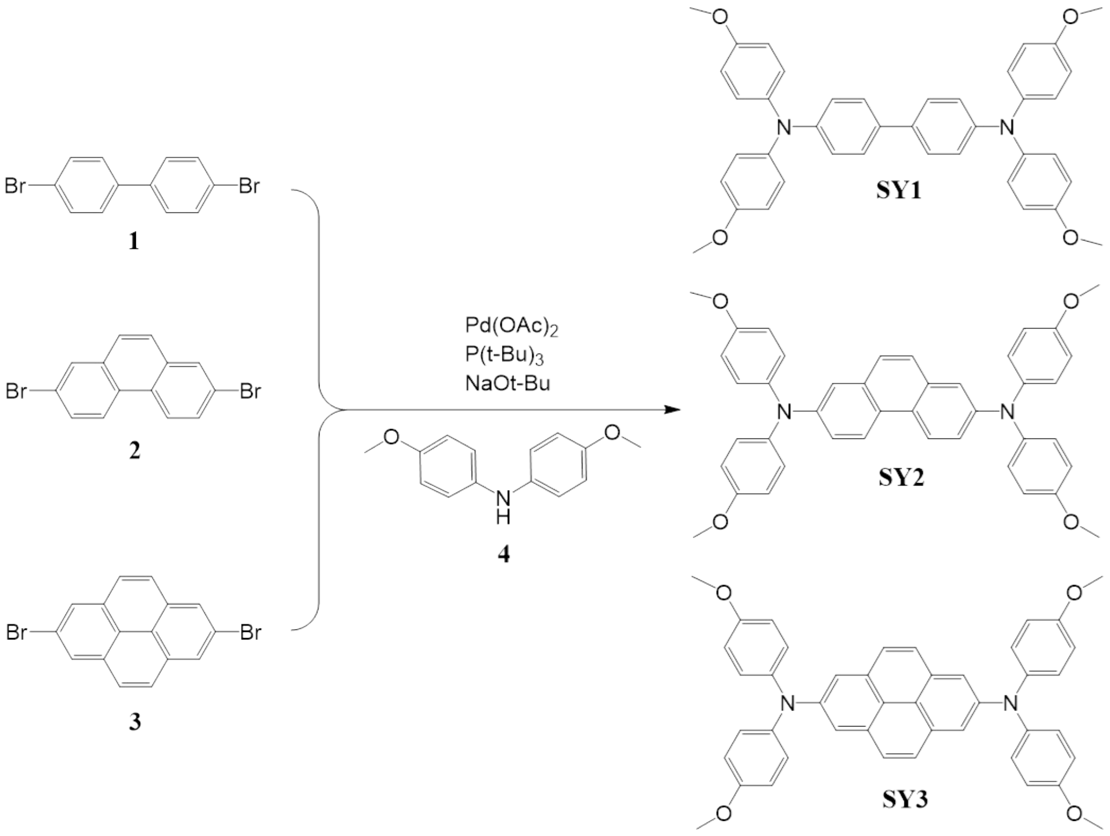
1. Experimental section

1.1. Materials and Methods

Materials were all available commercially and used without further purification if not mentioned specially. The synthetic routes of three HTMs are outlined in Scheme S1 and the details are depicted. ^{1}H NMR spectra were recorded using a Bruker Ultrashield 400 Plus NMR spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer.



Scheme S1. The synthesis route of SY1, SY2 and SY3.

1.1.1. Synthesis of SY1

In a 50 mL two-necked flask, a mixture of compound 1 (4,4'-dibromo-1,1'-biphenyl: 1 mmol, 310 mg), compound 4 (bis(4-methoxyphenyl)amine: 2.5 mmol, 573 mg) and sodium tert-butoxide (6 mmol, 576 mg) in anhydrous toluene (10 mL) was stirred for 30 minutes under N_2 atmosphere to remove oxygen. Then palladium(Ⅱ)acetate (0.02 mmol, 4.5 mg), tri-tert-butylphosphine (0.06 mmol, 12.2 mg) were 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 Mg_2SO_4 and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (hexane/EtOAc, v/v, 3:1) to give SY1 as a light yellow solid (yield 68%). 1H NMR (400 MHz, DMSO-d6), δ/ppm: 7.36-7.35 (d, 4H), 7.07-7.06 (d, 8H), 6.96-6.94 (d, 4H), 6.83-6.81 (d, 8H), 3.78 (s, 12H). MALDI-TOF-MS (m/z): calculated for [M-H] $C_{40}H_{36}N_2O_4$: 609.2709, found: 609.2738.

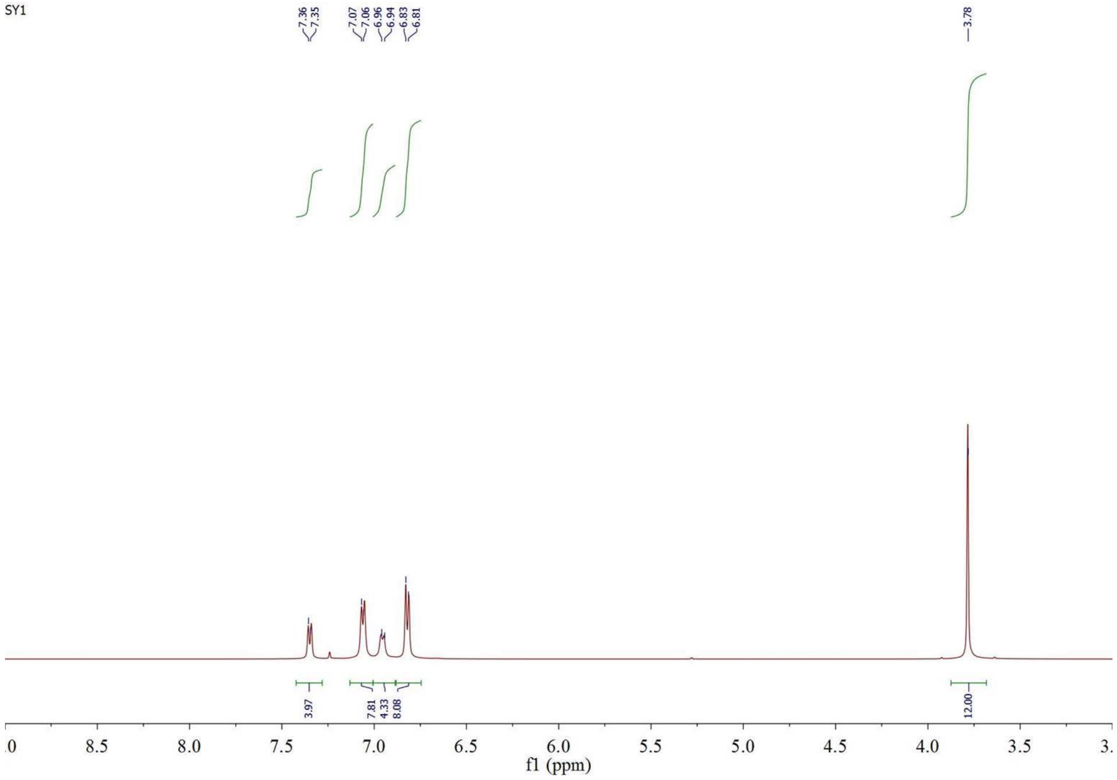


Figure S1. ^{1}H NMR spectra of SY1.

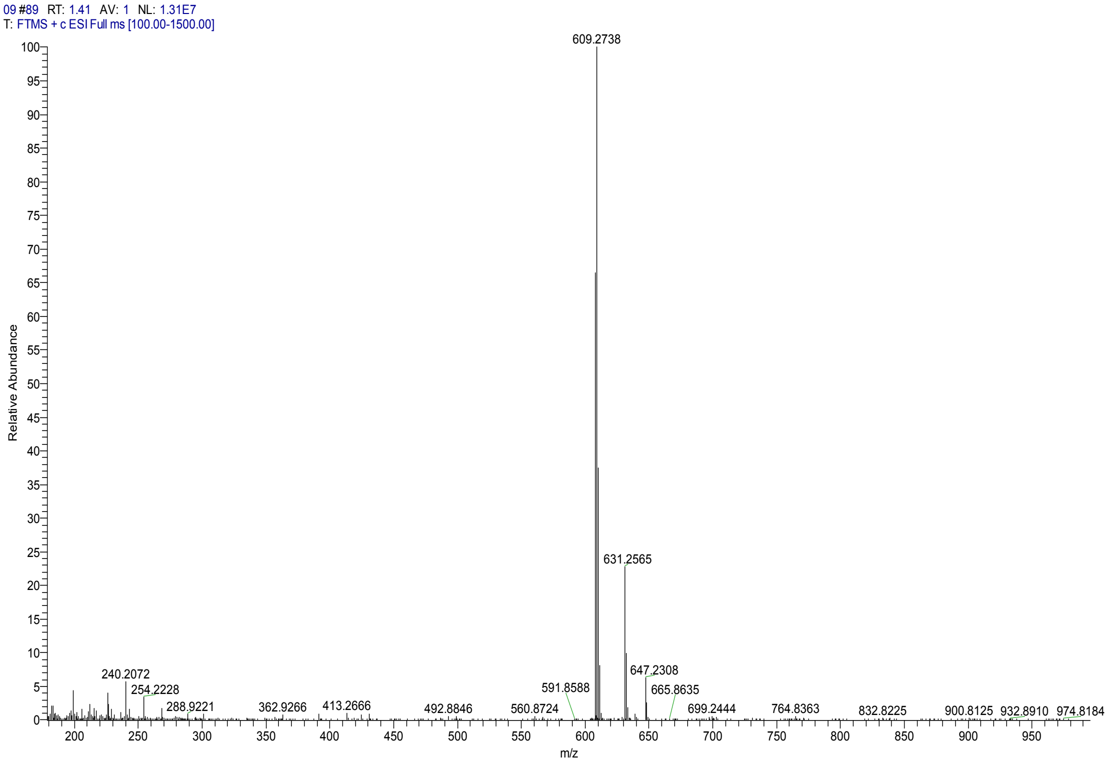


Figure S2. Mass spectrum of SY1.

1.1.2. Synthesis of SY2

The general procedure for preparation of SY2 is similar with SY1 above. A mixture of compound 2 (2,7-dibromo-phenanthrene: 1 mmol, 333 mg), compound 4 (2.5 mmol, 573 mg), sodium tert-butoxide (6 mmol, 576 mg), palladium(Ⅱ)acetate (0.02 mmol, 4.5 mg), tri-tert-butylphosphine (0.06 mmol, 12.2 mg), and anhydrous toluene (10 mL) was heated to 110 °C and stirred for 12 h under a N_2 atmosphere with a reflux condenser, SY2 was prepared by silica gel column chromatography, get a yellow solid. Yield (63%). 1H NMR (400 MHz, DMSO-d6), δ/ppm: 8.37-8.36 (d, 2H), 8.11-8.09 (d, 2H), 7.96 (s, 2H), 7.51-7.50 (d, 2H), 7.10-7.09 (d, 8H), 6.94-6.93 (d, 8H), 3.76 (s, 12H).

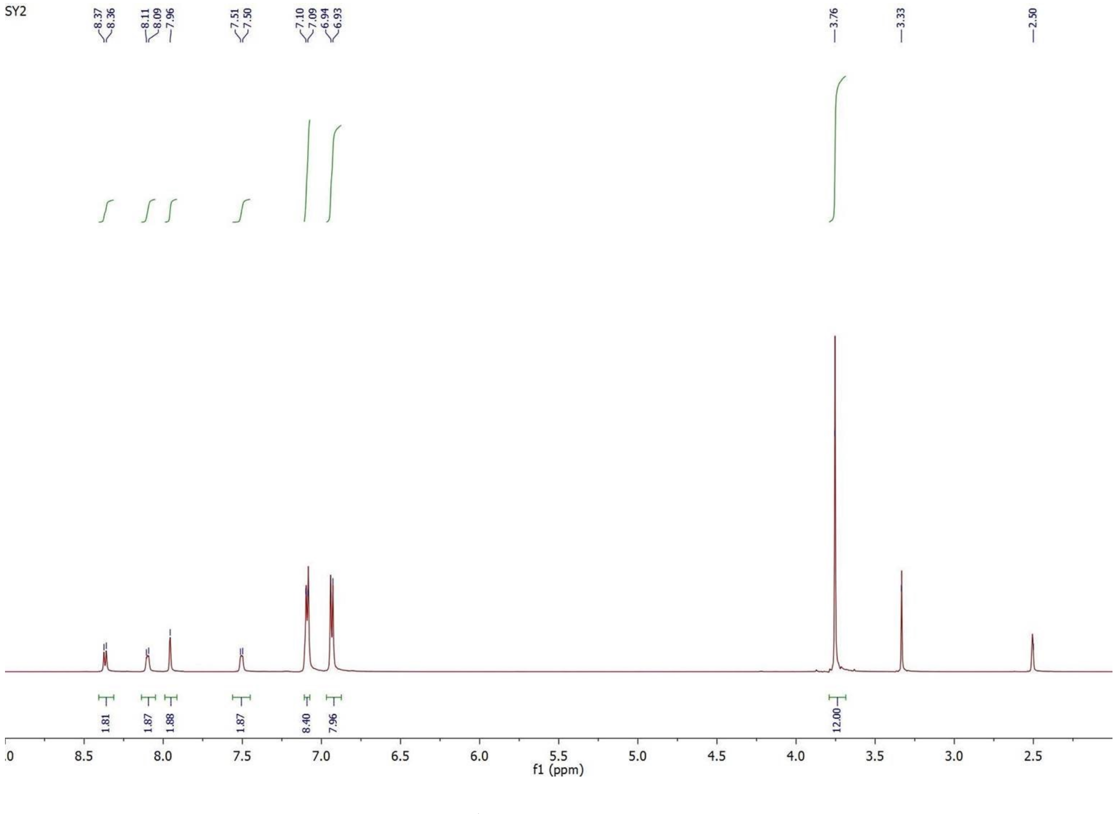


Figure S3. ^{1}H NMR spectra of SY2.

1.1.3. Synthesis of SY3

The general procedure for preparation of SY3 is similar with SY1 above. A mixture of compound 3 (2,7-dibromo-pyrene: 1 mmol, 357 mg), compound 4 (2.5 mmol, 573 mg), sodium tert-butoxide (6 mmol, 576 mg), palladium(Ⅱ)acetate (0.02 mmol, 4.5 mg), tri-tert-butylphosphine (0.06 mmol, 12.2 mg), and anhydrous toluene (10 mL) was heated to 110 °C and stirred for 12 h under a N_2 atmosphere with a reflux condenser, SY3 was prepared by silica gel column chromatography, get a yellow solid. Yield (60%). 1H NMR (400 MHz, $CDCl_3$), δ/ppm: 7.69-7.67 (d, 8H), 7.16-7.14 (d, 8H), 6.87-6.85 (d, 8H), 3.82 (s, 12H). MALDI-TOF-MS (m/z): calculated for [M-H] $C_{44}H_{36}N_2O_4$: 657.2709, found: 657.2741.

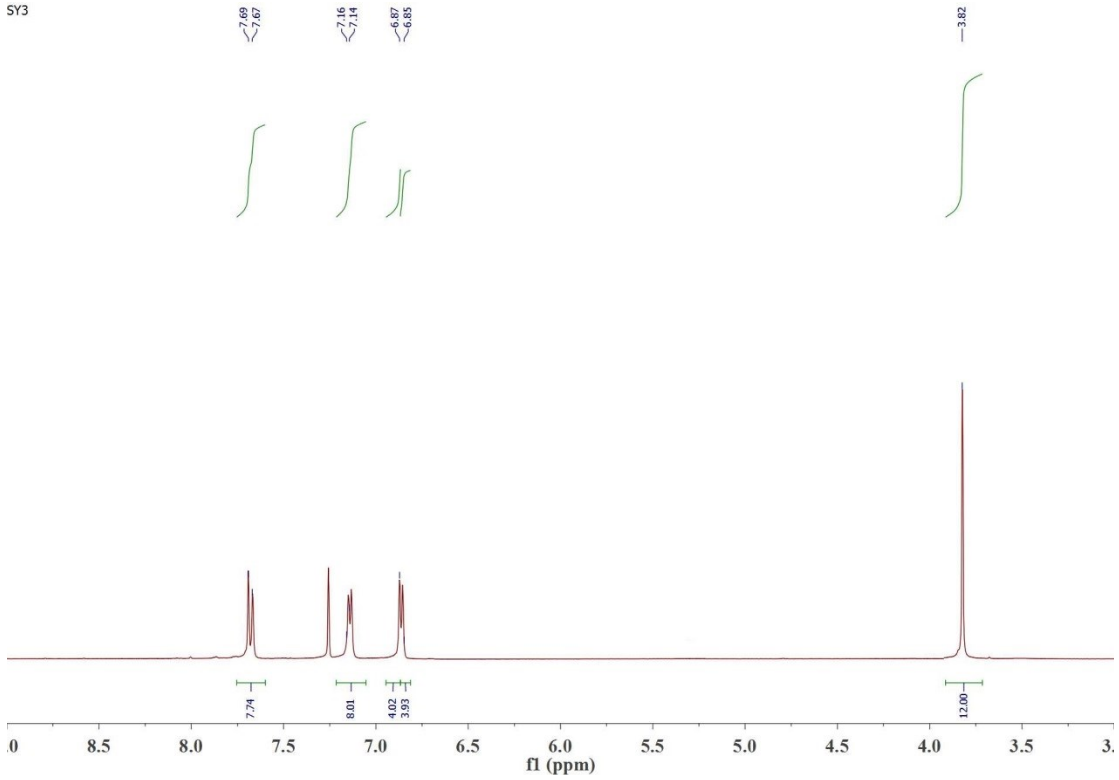


Figure S4. ^{1}H NMR spectra of SY3.

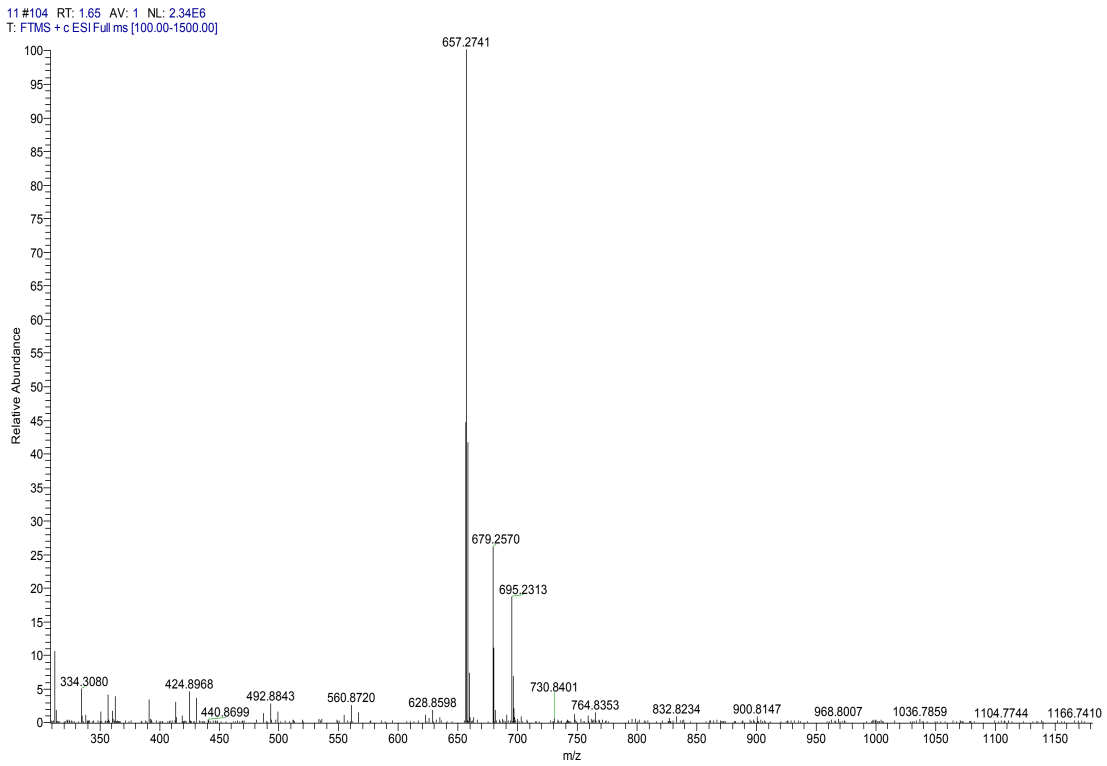


Figure S5. Mass spectrum of SY3.

2. 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 3 mm) was used as the working electrode, a platinum wire as the counter electrode, Ag/AgCl as the reference electrode and 0.1 M of tetrabutylammoniunhexafluorophosphate (n-Bu$_4$NPF$_6$) in dichloromethane solution as supporting electrolyte. The cyclovoltammetric scan rates were 50 Mv s^{-1}.

3. 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.

4. Mobility Measurements

Indium Tin Oxide (ITO) coated glass substrates (Pilkington TEC15) were patterned by etching with zinc powder and 2 M hydrochloric acid. The 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. The HTMs were dissolved in anhydrous chlorobenzene. *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.

5. Device fabrication

5.1. Fabrication of $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ solar cells

The fluorine-doped SnO_2 (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 TiO_2, intended to block the recombination current at the FTO support, was prepared on cleaned FTO substrate by spray pyrolysis of solution (0.2 M titanium isopropoxide and 2 M 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), PbI_2 (1.1 M), MABr (0.2 M) and $PbBr_2$ (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 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. Here, the SY1, SY2, SY3 and Spiro-OMe TAD/chlorobenzene 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. Current-voltage characteristics were measured under 100 mW cm^{-2} (AM 1.5 G illumination) using a Newport solar simulator (model 91160) and a Keithley 2400 source/meter. A certifiedreference solar cell (Fraunhofer ISE) was used to calibrate the light source for an intensity of 100 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 (Lab Jack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE). Electron lifetime measurements were performed using a white LED (Luxeon Star 1 W) 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 10 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 0.09 cm^2 and reducing the influence of the scattered light.

5.2. Fabrication of $CsPbI_2Br$ solar cells

Glass/ITO substrates (1.5 cm*1.5 cm) were cleaned by sonication in deionized water, detergent, deionized water and ethanol and then dried in an oven. Glass/ITO substrates were treated under oxygen plasma for 10 min before use. 30 nm SnO_2 nanoparticles were spun coated onto ITO substrates at 4000 rpm for 30 s. The 10 nm ZnO nanoparticles were spun coated onto ITO/SnO_2 substrates at 5500 rpm for 30 s, followed by thermal annealing in air at 150 °C for 30 min. 1 M PbI_2 and 1 M 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 6000 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. The HTM was spun on the perovskite film at 4000 rpm for 20 s. Finally, a 12 nm MoO_3 and 100 nm silver (Ag) were thermally evaporated under vacuum, respectively. Current-voltage characteristics were measured under 100 mW cm^{-2} (AM 1.5 G 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^{-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 (Lab Jack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE). Electron lifetime measurements were performed using a white LED (Luxeon Star 1 W) 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 10 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 0.09 cm^2 and reducing the influence of the scattered light.

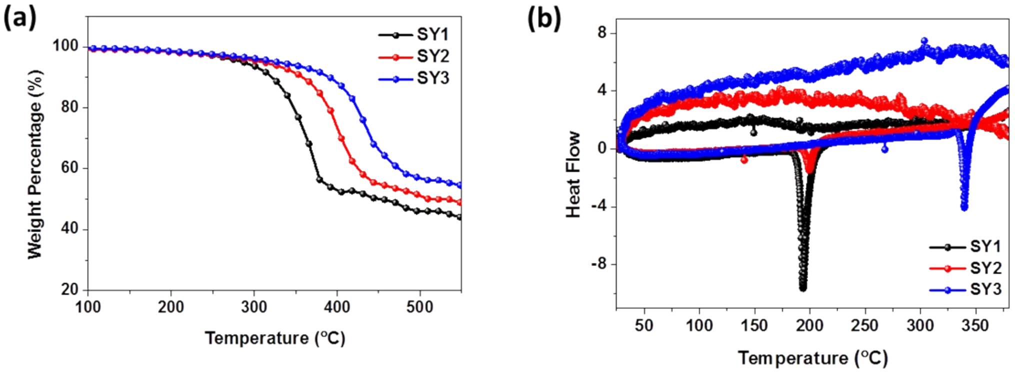


Figure S6. (a) Thermogravimetric analysis (TGA) of **SY1**, **SY2**, and **SY3**. (b) Differential scanning calorimetry results (DSC) of **SY1**, **SY2**, and **SY3**.

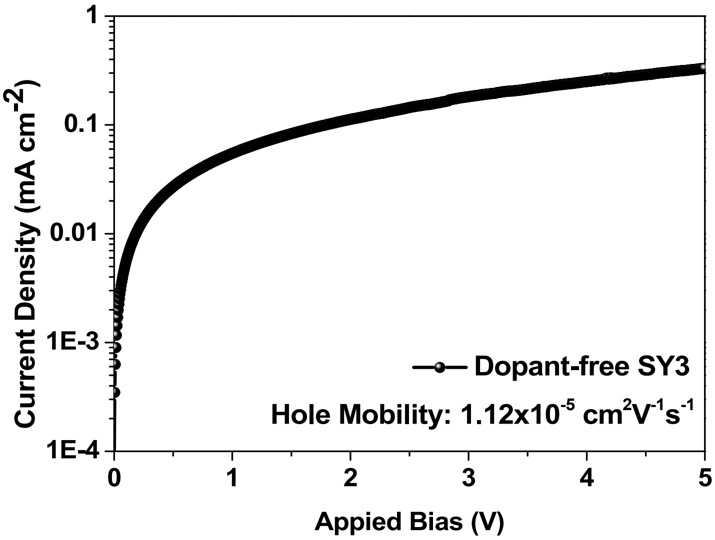


Figure S7. *J*–*V* curves obtained from the hole-only ITO/PEDOT:PSS/SY3/Au device

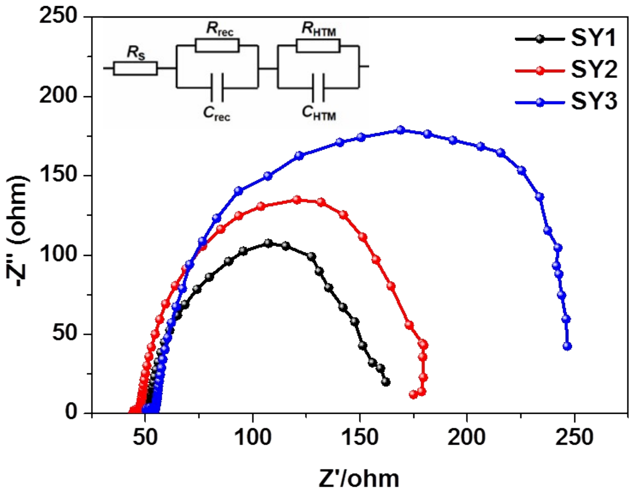


Figure **S8**. (a) Nyquist ESI spectra of PSCs based on the SY1, SY2 and Spiro-OMeTAD.

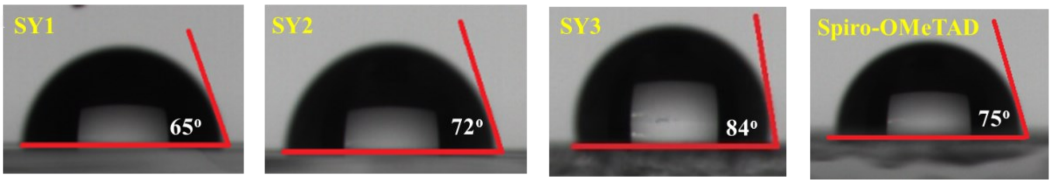


Figure S9. The water contact angles of SY1, SY2, SY3 and Spiro-OMeTAD-based films.

Table S1. Time constants of the time-resolved photoluminescence (TRPL) spectra.

HTM	**τ1 (ns)**	**τ2 (ns)**
Perovskite/**SY1**	9.95	55.53
Perovskite/**SY2**	7.03	33.75
Perovskite/**SY3**	6.84	25.24
Perovskite/**Spiro-OMeTAD**	6.56	24.37

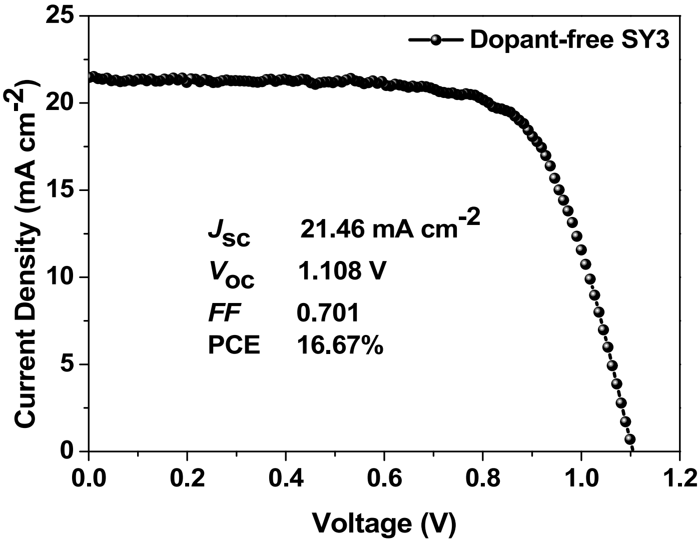


Figure S10. (a) *J*-*V* characteristics of $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ solar cells based on dopant-free SY3.