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Cyclopenta[*hi*]aceanthrylene-Based Dopant-Free Hole-Transport Material for Organic-inorganic Hybrid and All-inorganic Perovskite Solar Cells

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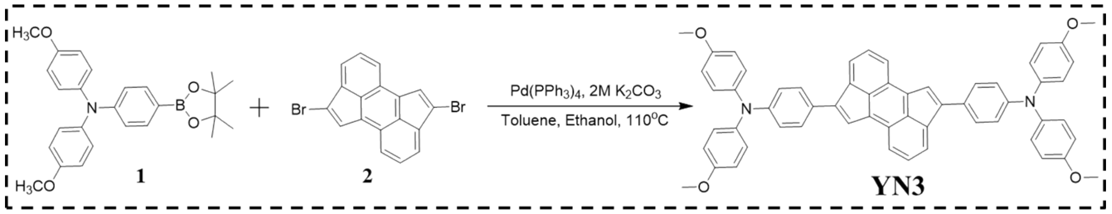
Experimental Section

Materials and Reagents

The key intermediates 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**1**) [1] and 2,7-Dibromocyclopenta[hi]-aceanthrylene (**2**) [2] were synthesized according to previous literatures. Other chemicals and solvents were commercial available for use without further purification. ^{1}H NMR and ^{13}C NMR spectra for **YN3** were recorded on a Bruker AVANCE 400 MHz spectrometer. The synthetic rout of **YN3** is outlined in Scheme S1 and the details are depicted below.



Scheme S1. The synthesis route of **YN3**

The synthesis route of **YN3**

The mixture of 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (1) (2.25 mmol), 2,7-Dibromocyclopenta[hi]-aceanthrylene (2) (1 mmol), $Pd(PPh_3)_4$ (100 mg, 0.016 mmol) and 2 M aqueous solution of K_2CO_3 (2 mL) in toluene (10 mL) and ethanol (2 mL) under N_2 atmosphere was heated to reflux for 24 h. Then the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:1 mixture of hexane and CH_2Cl_2 as eluent to afford the target compound. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.15 (d, J = 4.0 Hz, 2H), 7.97 (d, J = 4.0 Hz, 2H), 7.62 (d, J =

4.0 Hz, 4H), 7.44 (d, J = 4.0 Hz, 2H), 7.18 (s, 2H), 7.10 (d, J = 4.0 Hz, 8H), 6.96 (d, J = 4.0 Hz, 4H), 6.82 (d, J = 4.0 Hz, 8H), 3.74 (s, 12H). ^{13}C NMR (400 MHz, CDCl$_3$, δ): 156.15, 148.30, 142.02, 140.79, 140.00, 137.31, 128.90, 128.51, 128.31, 126.77, 126.38, 125.87, 124.24, 121.61, 121.16, 120.60, 114.82, 55.19. HRMS (MALDI-TOF): m/z: [M+1] calcd for 833.3341; found, 833.3355.

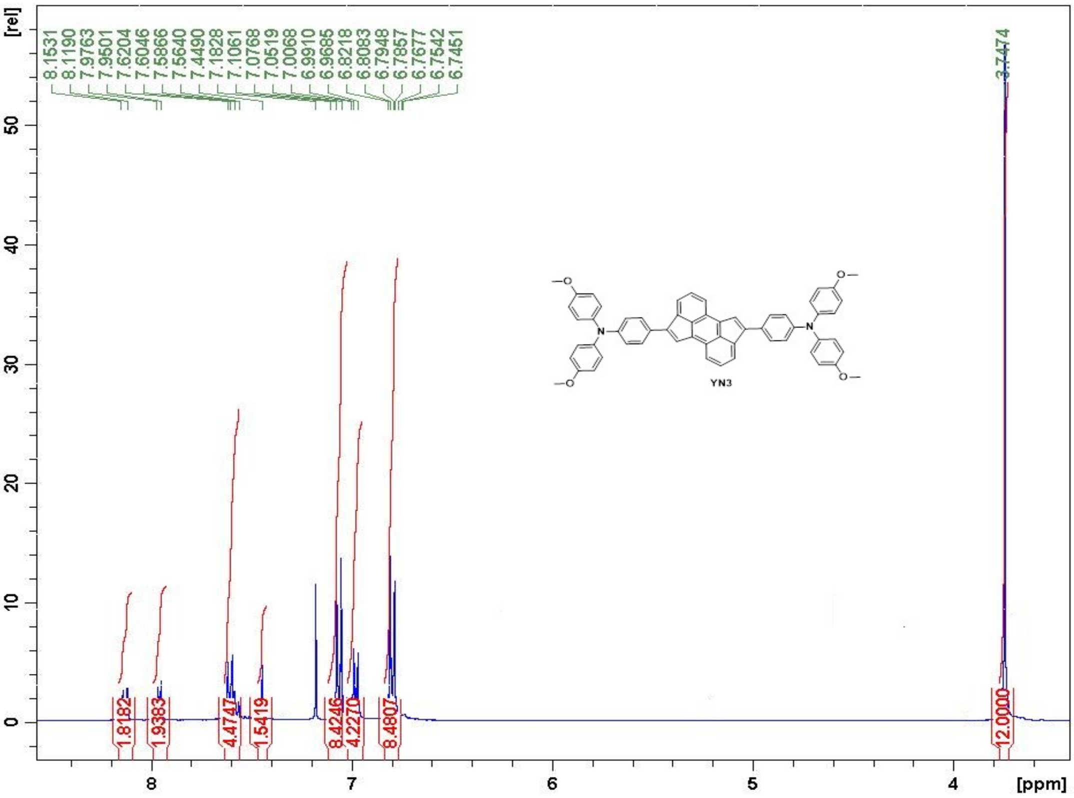


Figure S1. ^{1}H NMR (CDCl$_3$) spectrum of **YN3.**

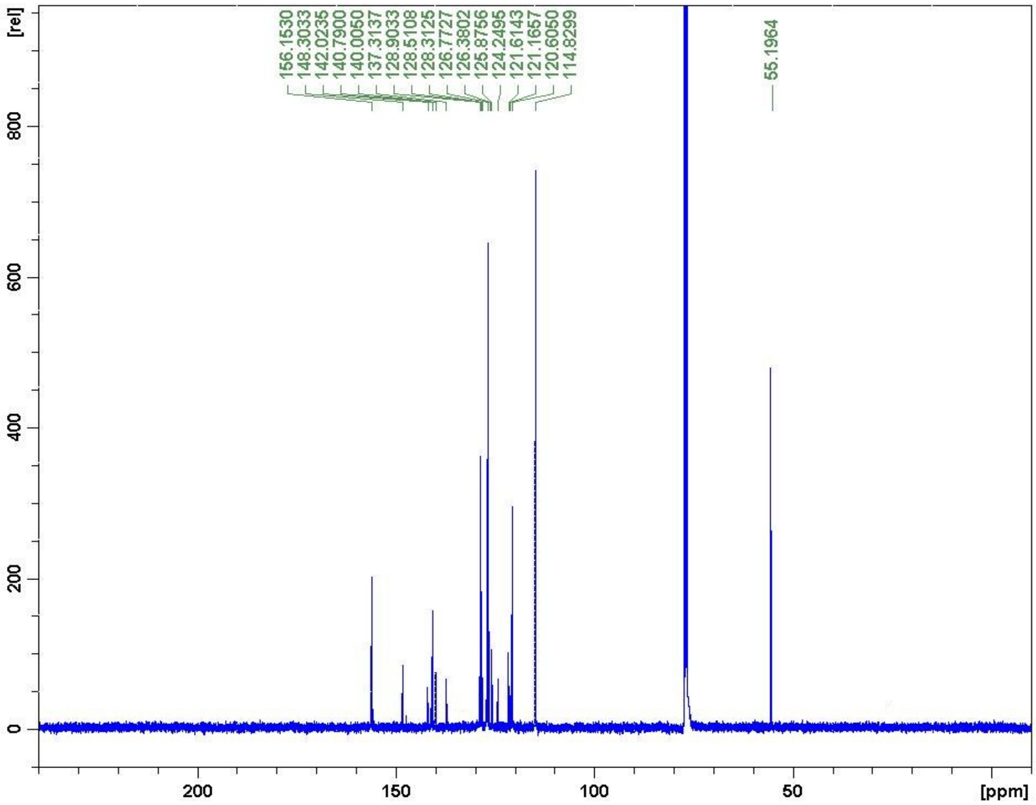


Figure S2. ^{13}C NMR (CDCl$_3$) spectrum of **YN3.**

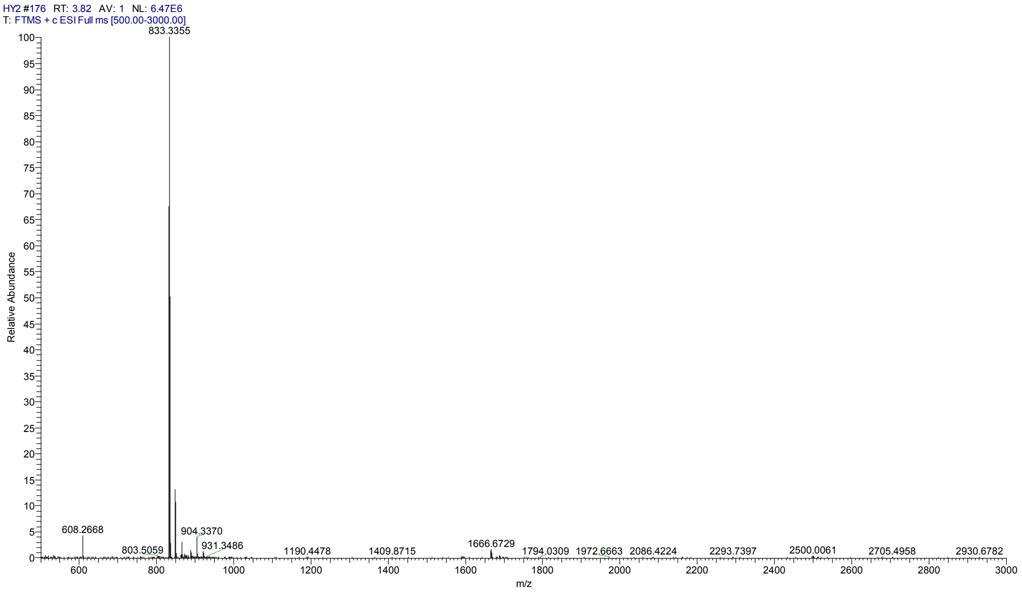


Figure S3. HR-MS spectra of **YN3.**

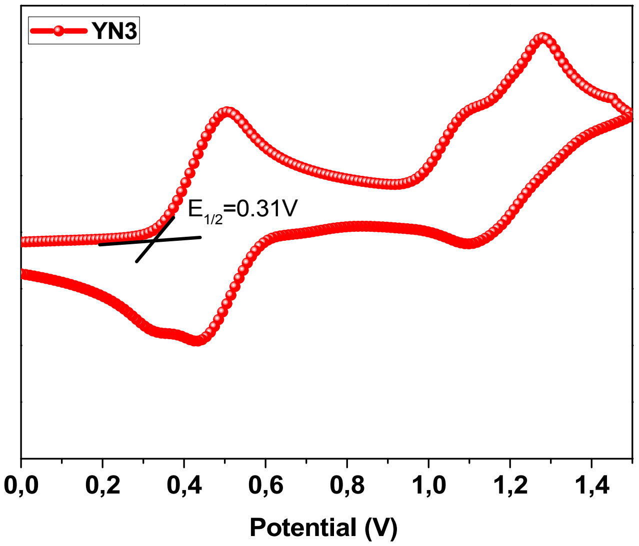


Figure S4. CV curve of **YN3**.

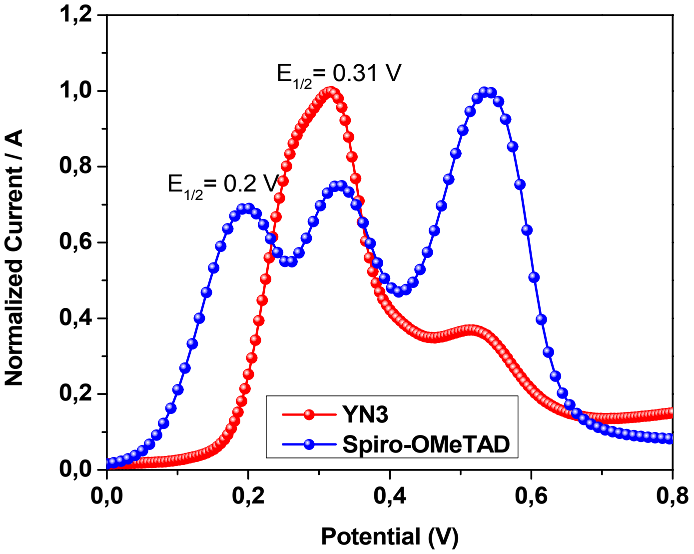
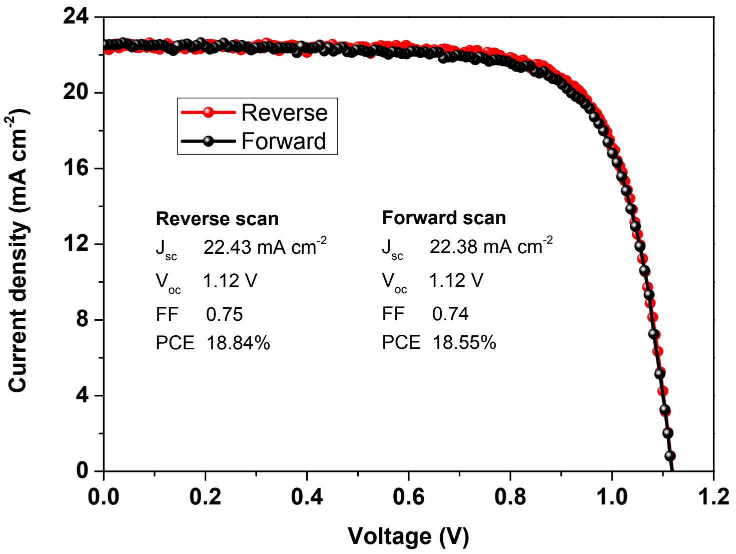
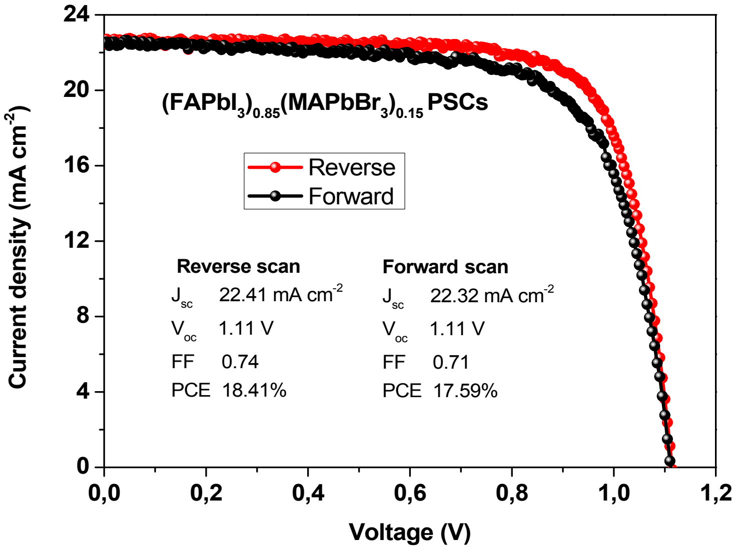


Figure S5. Normalized differential pulsed voltammetry (DPV) of **YN3**.


Current density (mA cm^{-2})
Voltage (V)
24
20
16
12
8
4
0
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Reverse
Forward
Reverse scan
J_{sc} 22.43 mA cm^{-2}
V_{oc} 1.12 V
FF 0.75
PCE 18.84%
Forward scan
J_{sc} 22.38 mA cm^{-2}
V_{oc} 1.12 V
FF 0.74
PCE 18.55%


$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ PSCs
Current density (mA cm^{-2})
Voltage (V)
24
20
16
12
8
4
0
0,0
0,2
0,4
0,6
0,8
1,0
1,2
Reverse
Forward
Reverse scan
J_{sc} 22.41 mA cm^{-2}
V_{oc} 1.11 V
FF 0.74
PCE 18.41%
Forward scan
J_{sc} 22.32 mA cm^{-2}
V_{oc} 1.11 V
FF 0.71
PCE 17.59%

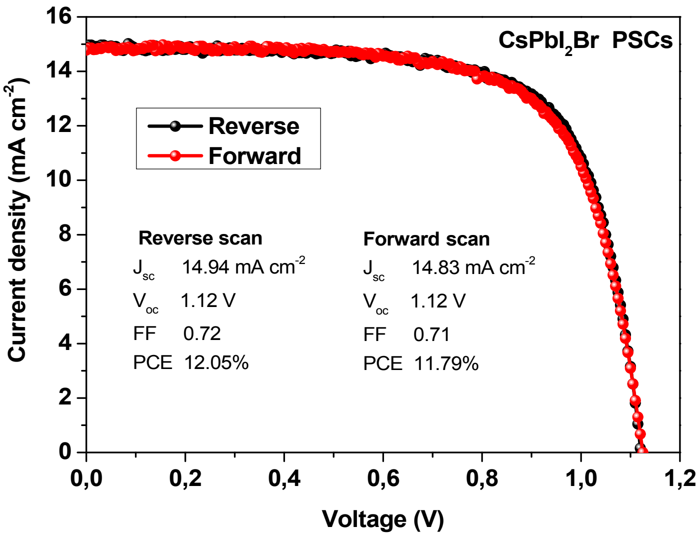


Figure S6. Reverse and forward *J-V* curves of PSCs.

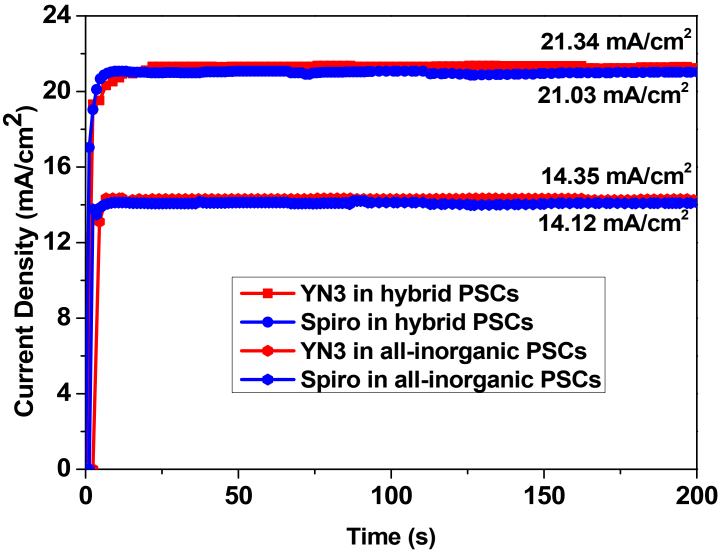


Figure S7. Stability of the J_{SC} maintaining the PSCs at the maximum power point at **YN3** and **Spiro-OMeTAD.**

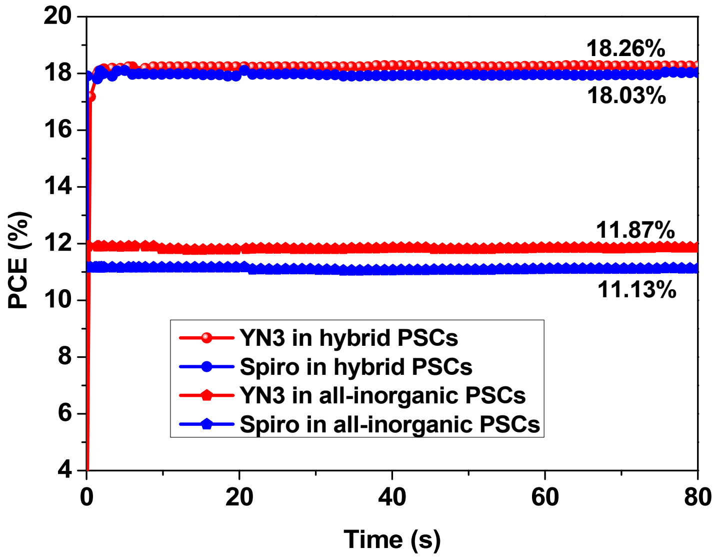


Figure S8. Stabilized power output for the different PSCs devices based on **YN3** and **Spiro-OMeTAD**.

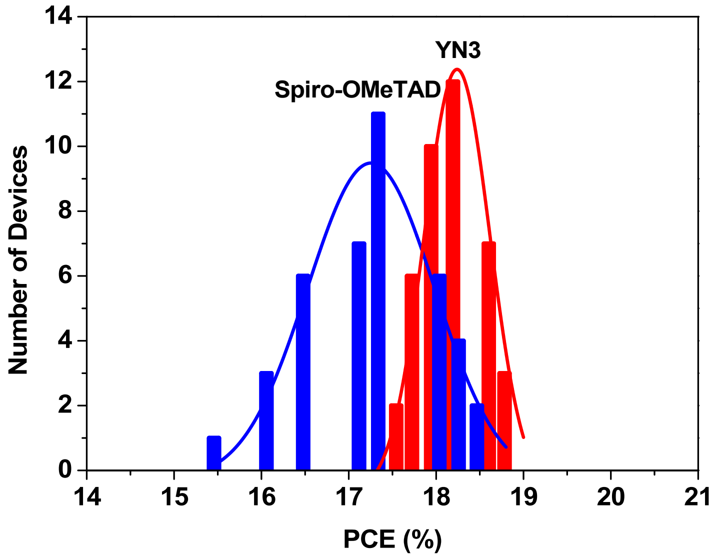


Figure S9. Statistical efficiencies for $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ PSCs based on **YN3** and **Spiro-OMeTAD** (40 devices).

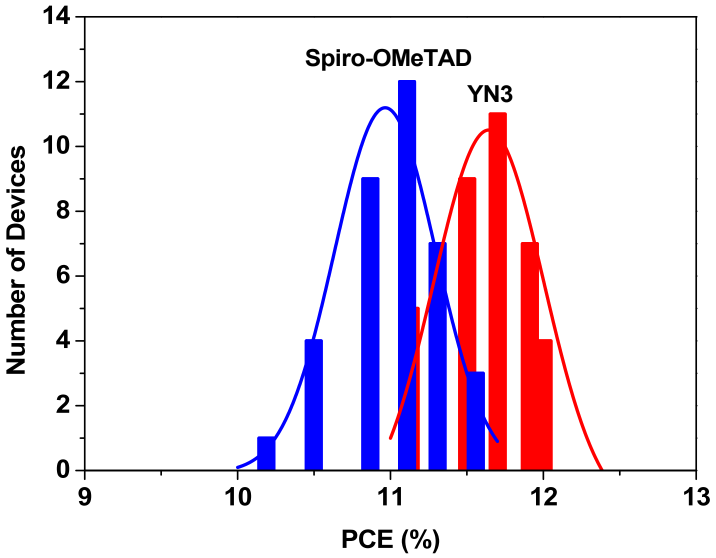


Figure S10. Statistical efficiencies for **$CsPbI_2Br$ PSCs** based on **YN3** and **Spiro-OMeTAD (36 devices).**

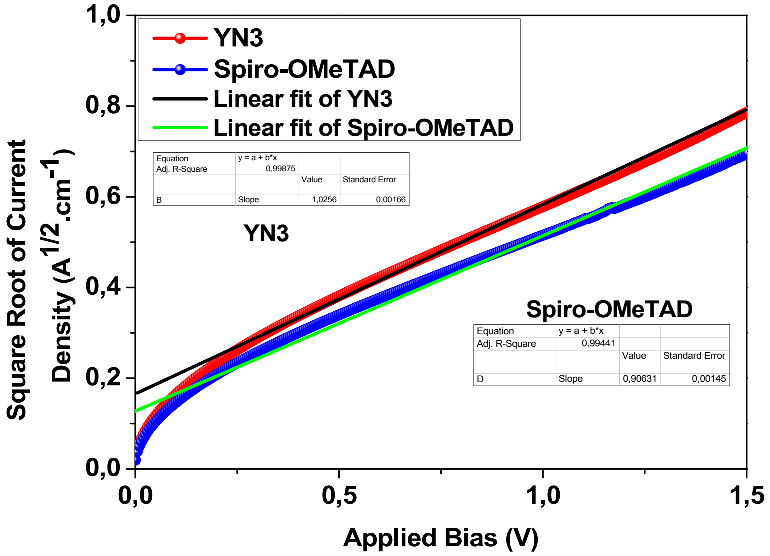


Figure S11. Plots of the square root of current density vs. applied voltage for **YN3** and **Spiro-OMeTAD** film. Linear regression fits to the plot were used to calculate the hole-mobility.

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, Ag/AgCl as the reference electrode and 0.1 M of tetrabutylammoniunhexafluorophosphate (n-Bu_4NPF_6) 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. $E_{HOMO} = -5.1 - (E_{1/2} - E_{1/2}{}^{Fc})$.

Computational Details

In the simulation, Optimization and single point energy calculations are performed using the cam-B3LYP [3] and the 6-31G** basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09.[3]

Conductivity Measurement

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_2 was coated on the glass substrates by spin-coating with a diluted TiO_2 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_2 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 **YN3** is 20 mg mL^{-1} in chlorobenzene. The doped Spiro-OMeTAD/chlorobenzene (20 mg/mL) solution was prepared with addition of 5 μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), and 8 μL tert-butylpyridine (*t*BP). Subsequently, a 200 nm thick Ag back contact was deposited onto the organic semiconductor by thermal evaporation in a vacuum chamber with a base pressure of about 10^{-6} bar, to complete the device fabrication. *J*-*V* characteristics were recorded on a Keithley 2400 semiconductor characterization system.

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. Here the concentration of **YN3** is 20 mg mL^{-1} in chlorobenzene. The doped Spiro-OMeTAD/chlorobenzene (20 mg/mL) solution was prepared with addition of 5 μL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), and 8 μL tert-butylpyridine (*t*BP). This HTMs solution was spin-coated at 2000 rpm to yield films. The thicknesses of the films are measured by using a Dektak 6M profilometer. 200 nm of silver was then evaporated onto the active layer under high vacuum (less than

10^{-6} 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.

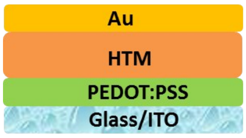


Figure S12. Schematic illustratuions of the mobility device.

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

The fluorine-doped SnO_2 (FTO, 15 Ω-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 (0.2M titanium isopropoxide and 2M acetylacetone in isopropoanal). 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 concentration of **YN3** is 20 mg mL^{-1} in chlorobenzene. The doped 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 (*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^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 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). 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 cm^2 and reducing the influence of the scattered light.

Fabrication of $CsPbI_2Br$ perovskite solar cells

The fluorine-doped SnO_2 (FTO, 15 Ω-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 (0.2M titanium isopropoxide and 2M acetylacetone in isopropenal). 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 PbI_2 (1M) and CsBr (1M) in anhydrous DMF: DMSO =1:9 (v/v). The perovskite solution was spin-coated in a two-step program; first at 1500 rpm for 15 s and then at 5000 rpm for 30 s. The substrates were then annealed by a two-step process at 55°C for 60 s and 240°C for 60 s in a nitrogen filled glove box. Here the concentration of **YN3** is 20 mg mL^{-1} in chlorobenzene. The doped 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 (*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^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 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). 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 cm^2 and reducing the influence of the scattered light.

[1] Y. Hua, L. T. L. Lee, C. S. Zhang, J. Z. Zhao, T. Chen, W. Y. Wong, W. K. Wong, X. J. Zhu, *J. Mater. Chem. A*, **2015**, *3*, 13848-13855.

[2] J. D. Wood, J. L. Jellison, A. D. Finke, L. Wang, K. N. Plunkett, *J. Am. Chem. Soc*. **2012**, *134*, 15783–15789.

[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. M. a, G. A. Petersson, H. Nakatsuji, M. Caricato, X. L. and, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. H. a. M. E. a. K. T. a. R. F. a. J. H. a. M. I. a. T. N. a. Y. H. a. O. K. and H. Nakai and T. Vreven and Montgomery, {Jr.}, J. A. and J. E. Peralta and F. Ogliaro and M. Bearpark and J. J. Heyd and E. Brothers and K. N. Kudin and V. N. Staroverov and R. Kobayashi and J. Normand and K. Raghavachari and A. Rendell and J. C. Burant and S. S. Iyengar and J. Tomasi and M. Cossi and N. Rega and J. M. Millam and M. Klene and J. E. Knox and J. B. Cross and V. Bakken and C. Adamo and J. Jaramillo and R. Gomperts and R. E. Stratmann and O, Gaussian Inc. Wallingford CT **2009**.