

Supporting Information

A low-cost asymmetric carbazole-based hole-transporting material for efficient perovskite solar cells

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Experimental

General

The structure of newly synthesized tri-substituted Cz-3OMeTAD was characterized by ^1H NMR and ^{13}C NMR spectra, elemental analysis (EA) and mass spectra (MS). It was recorded on instruments of Bruker 400 MHz NMR spectrometer, V FLASH EA 1112 Elemental Analyzer and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) Autoflex instrument from Bruker, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a STA 409 PC instrument at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere. UV-vis absorption spectra were recorded at room temperature using a Shimadzu UV-2006 ultraviolet-visible spectroscope. Photoluminescence (PL) and time-resolved PL (TRPL) spectra were recorded on Edinburgh Instruments FLS980. Cyclic voltammetry (CV) was performed using a CHI660E electrochemical workstation at a scan rate of 50 mV s^{-1} . All experiments were carried out in a three-electrode compartment cell with a Pt-sheet counter electrode, a glassy carbon working electrode, and a Pt-wire reference electrode. The supporting electrolyte used was 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution in dry acetonitrile. The cell containing the solution of the sample (1 mM) and supporting electrolyte was purged with a nitrogen gas thoroughly before scanning for its oxidation and reduction properties. Ferrocene was used for potential calibration in each measurement. All the

potential were reported relative to ferrocene-ferrocenium (Fc/Fc⁺) couple, whose oxidation potential was +0.13 V relative to the reference electrode. Density functional theory (DFT) calculations (B3LYP) were performed for the target compound with the 6-31 G (d,p) basis set by using the Gaussian 09 program. Atomic force microscopy (AFM) images were performed on Cypher S atomic force microscopy (AFM) to evaluate the surface morphology. Scanning electron microscopy (SEM) images were acquired by a Hitachi SU8010 scanning electron microscopy.

Synthesis and characterization

All chemicals were purchased from commercial sources and used directly without further purification or other treatment, except that toluene was dried over Na/benzophenone ketyl and freshly distilled prior to use. All air and water sensitive reactions were performed under a nitrogen atmosphere.

Synthesis of 1,3,6-trisbromocarbazole.

Carbazole (5.00 g, 29.94 mM) and 15 mL DMF were mixed in a 250 mL three-necked flask and stirred at 3 °C for 1 h under nitrogen atmosphere to prepared solution A. *N*-bromosuccinimide (15.90 g, 89.82 mM) and 100 mL DMF were mixed and stirred to form solution B. Then solution B was added dropwise into the solution A under 3 °C. The reaction mixture was kept at room temperature for 10 h. Then the mixture was added into 200 mL deionized water and a white precipitate was appeared. The

precipitate was filtered, washed by water and dried at 100 °C, and then the crude product was recrystallized by 50 mL CH₂Cl₂. A high purity of 1,3,6-trisbromocarbazole compound was obtained and the yield was 86%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.12 (d, *J* = 1.9 Hz, 1H), 8.08 (d, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.57 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H). Elemental analysis calcd (%) for C₁₂H₆Br₃N: C, 35.68; H, 1.50; found: C, 35.64; H, 1.52.

Synthesis of 9-ethyl-1,3,6-trisbromocarbazole.

1,3,6-Trisbromocarbazole (10.09 g, 25.00 mM) and NaH (12.00 g, 50.00 mM) were dissolved in 100 mL DMF, then the solution was added dropwise into bromoethane (10.00 g, 50.00 mM). The reaction mixture was stirred at 40 °C for 4 h under a nitrogen atmosphere. After cooled to room temperature, the mixture extracted with CH₂Cl₂ and the organic layer washed by water, and dried with anhydrous MgSO₄. Then the solvent was evaporated, the residue was recrystallization by CH₂Cl₂ and CH₃OH. A high purity of 9-ethyl-1,3,6-trisbromocarbazole compound was obtained and the yield was 98%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.12 (d, *J* = 1.9 Hz, 1H), 8.07 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 1.8 Hz, 1H), 7.59 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.31 (d, *J* = 8.8 Hz, 1H), 4.75 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). Elemental analysis calcd (%) for C₁₄H₁₀Br₃N: C, 38.93; H, 2.33; found: C, 38.88; H, 2.35.

Synthesis of 1,3,6-tris(N,N-p-dimethoxyphenylamino)-9-ethyl-carbazole (Cz-3OMeTAD).

9-Ethyl-1,3,6-tribromocarbazole (0.43 g, 1.00 mM), 4,4'-dimethoxydiphenylamine (0.92 g, 4.00 mM), tris(dibenzylideneacetone)dipalladium (0.037 g, 0.04 mM), tritertbutylphosphine (0.012 g, 0.06 mM) and NaO^tBu (0.57 g, 6.00 mM) were mixed in a 50 mL two-necked flask, and added to 20 mL of dry toluene under nitrogen atmosphere. The reaction mixture was stirred at 110 °C for 36 h under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂ and the organic layer washed by water, and dried with anhydrous MgSO₄. Then the solvent was evaporated, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10/1). A high purity of 1,3,6-tris(*N,N*-*p*-dimethoxyphenylamino)-9-ethyl-carbazole (Cz-3OMeTAD) compound was obtained and the yield was 80%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.93 (s, 3H), 6.91 (s, 3H), 6.86 (s, 3H), 6.84 (s, 3H), 6.73 (s, 3H), 6.72 (s, 3H), 3.77 (s, 8H), 3.76 (s, 8H), 3.74 (s, 8H), 2.05 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 5H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 135.953, 130.623, 123.862, 121.841, 112.129, 104.807. Elemental analysis calcd (%) for C₅₆H₅₂O₆N₄: C, 76.62; H, 5.92; found: C, 76.58; H, 5.94. MS (MALDI-TOF) *m/z*: Calc. 877.0524; Found: 877.0551.

Fabrication and characterization of solar cells

FTO (fluorine-doped tin oxide) substrate was sequentially rinsed by liquid detergent, deionized water, acetone and ethanol in an ultrasonic cleaner, and alcohol and finally treated under oxygen plasma for 15 min. The TiO₂ thin layers were deposited by spin-

coating 0.15 M titanium diisopropoxide bis(acetylacetonate) solution at 2000 rpm for 20 s, then repeated twice on clean FTO substrates, followed by sintering at 500 °C for 30 min in the air. Subsequently, the perovskite precursor solution was prepared by mixing 922 mg PbI₂ (99.99%) and 349.8 mg CH₃NH₃I dissolved in the cosolvent of DMF (Aladdin) and DMSO (Aladdin) with PbI₂:CH₃NH₃I molar ratio of 1:1.1. The mixture solution was spin-coated on the TiO₂ layer at 6000 rpm, after 7 s of delay time. Then, the perovskite films were transferred on a hot plate, first annealed in ambient air (real-time humidity of 30%-50%) at 100 °C for 40 min, and then annealed in DMSO atmosphere at 100 °C for 15 min. For the DMSO atmosphere, a sufficient amount of DMSO solvent was dropped into a small ceramic crucible, and then a glass Petri dish was used to cover the samples and crucible. Finally, HTM solution (spiro-OMeTAD or Cz-3OMeTAD) was employed with 73 mg HTM (spiro-OMeTAD or Cz-3OMeTAD), 18 μL of lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (520 mg Li-TFSI in 1 mL acetonitrile) and 30 μL of 4-tert-butyl pyridine in 1 mL of chlorobenzene) were deposited on the perovskite film by spinning at 4000 rpm for 30 s. The masked active area of the device is 0.04 cm². The current-voltage (*J-V*) characteristics were performed on a CHI660D electrochemical workstation (ShangHai, China). All the cells were measured under a 100 mW cm⁻² (AM1.5 simulated irradiation) illumination with a standard ABET Sun 2000 Solar Simulator.

Table S1 Materials quantities and cost for the synthesis of 9-ethyl-1,3,6-

trisbromocarbazole

	Weight reagent (g)	Weight solvent (g)	Weight workup (g)	Price of Chemical (\$/Kg)	Material Cost (\$/g product)	Cost per step (\$/step)
Carbazole	1.57			476.54	0.75	8.38
N,N-Dimethyl formamide		4.47		170.46	0.76	
N- Bromosuccinimi de	5			197.18	0.99	
N,N-Dimethyl formamide		29.78		170.46	5.08	
Water			62.88	-	-	
CH ₂ Cl ₂			15.71	50.89	0.8	
NaH	0.96			3696.11	3.55	13.23
N,N-Dimethyl formamide		7.57		170.46	1.29	
Bromoethane	0.8			2110.92	1.69	
Water		150		-	-	
CH ₂ Cl ₂			125.88	50.89	6.41	
Na ₂ SO ₄			1	165.88	0.17	
Methanol			3.96	31.07	0.12	
Total						21.61

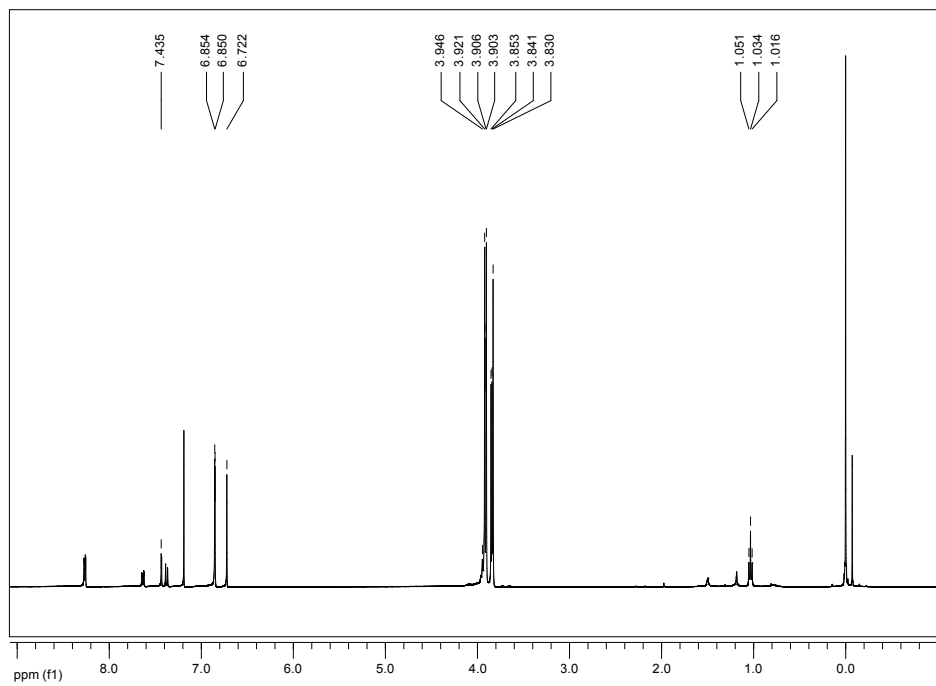


Fig. S1 ^1H NMR spectrum of Cz-3OMeTAD.

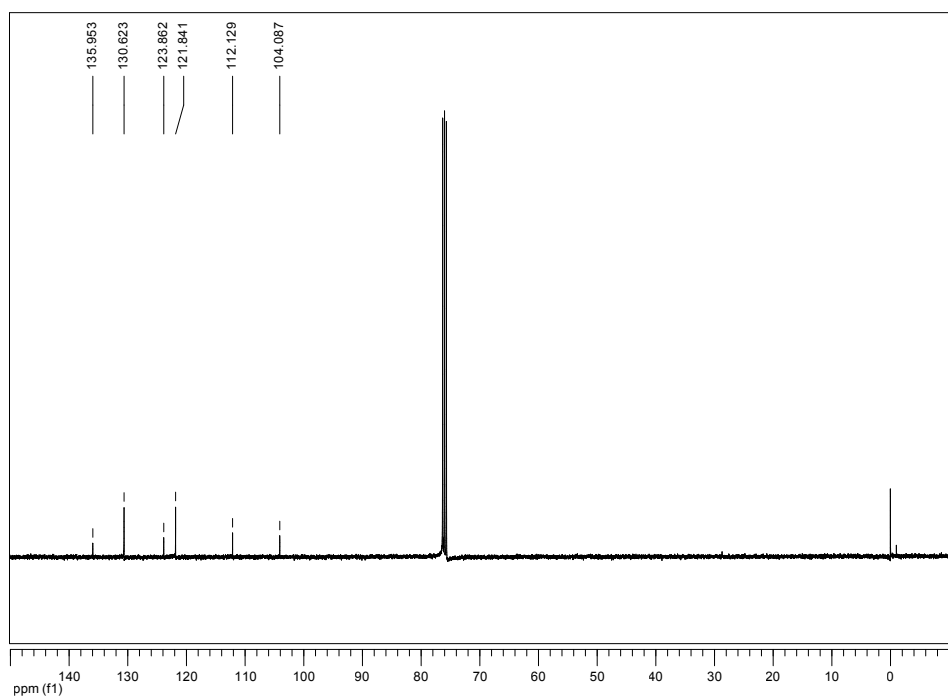


Fig. S2 ^{13}C NMR spectrum of Cz-3OMeTAD.

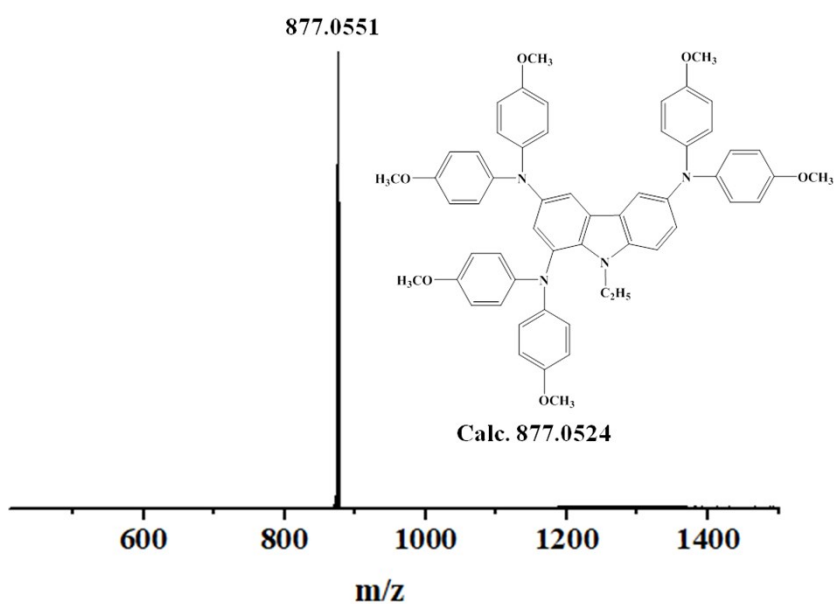


Fig. S3 MS spectrum of Cz-3OMeTAD.

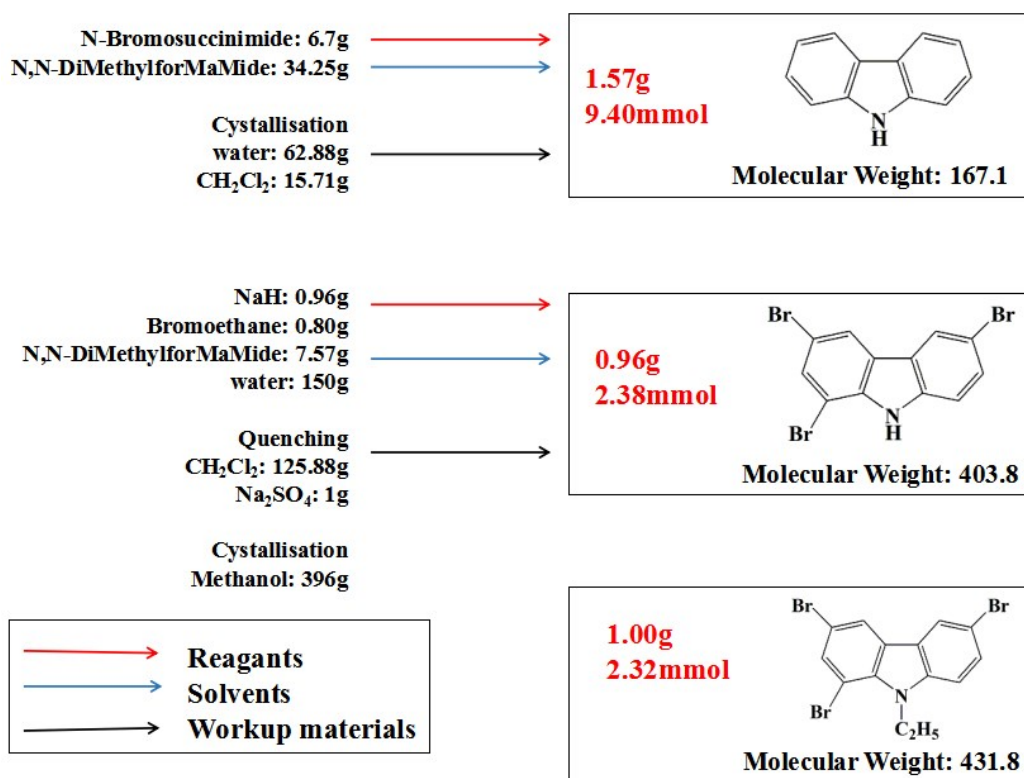


Fig. S4 Synthetic route of 1 gram Cz-3OMeTAD.

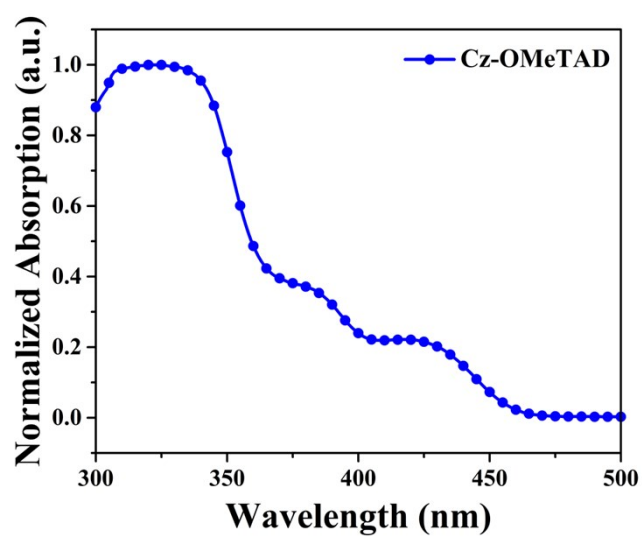


Fig. S5 UV-visible absorption spectra of Cz-OMeTAD tested in CH_2Cl_2 solution.

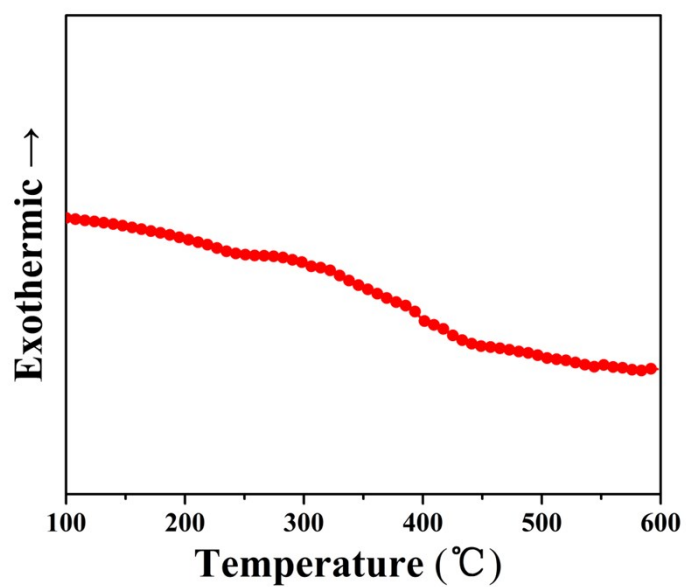


Fig. S6 DSC curves of Cz-3OMeTAD with a scan rate of 10°C .

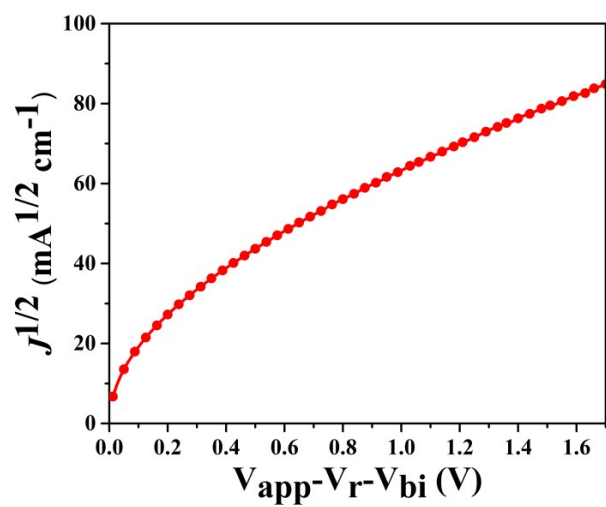


Fig. S7 Dark $J^{1/2}$ - V characteristic of hole-only device.

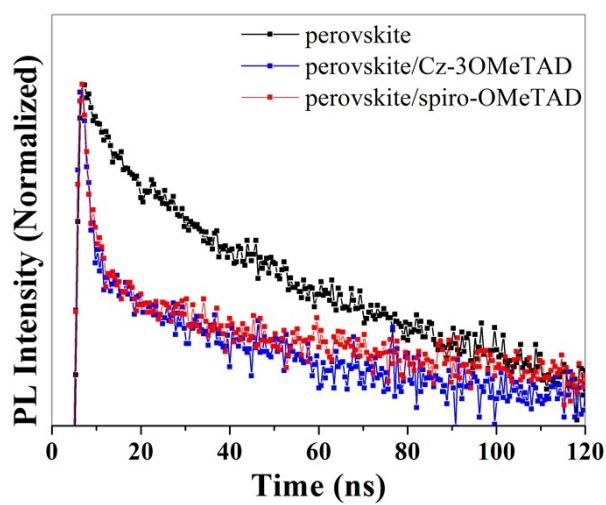


Fig. S8 Time-resolved PL spectra of pristine perovskite films, perovskite films coated with doped Cz-3OMeTAD and doped spiro-OMeTAD.

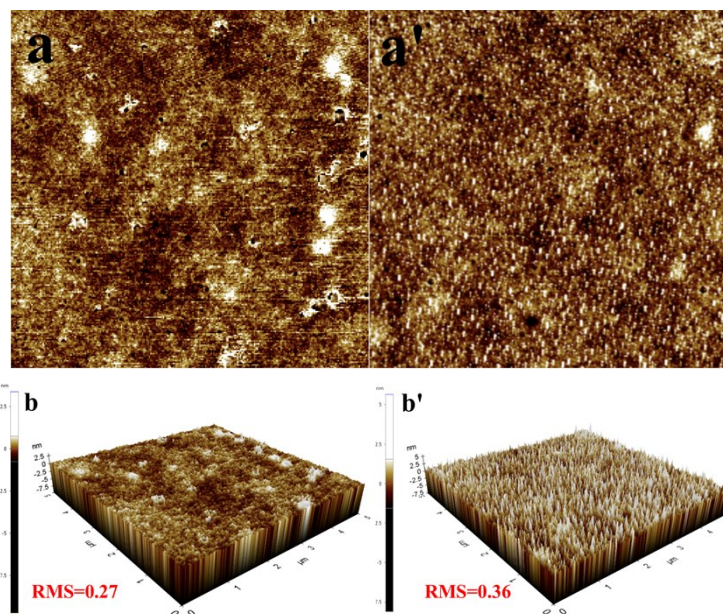


Fig. S9 AFM height and phase images of Cz-3OMeTAD (a, b) and (a', b') spiro-OMeTAD.

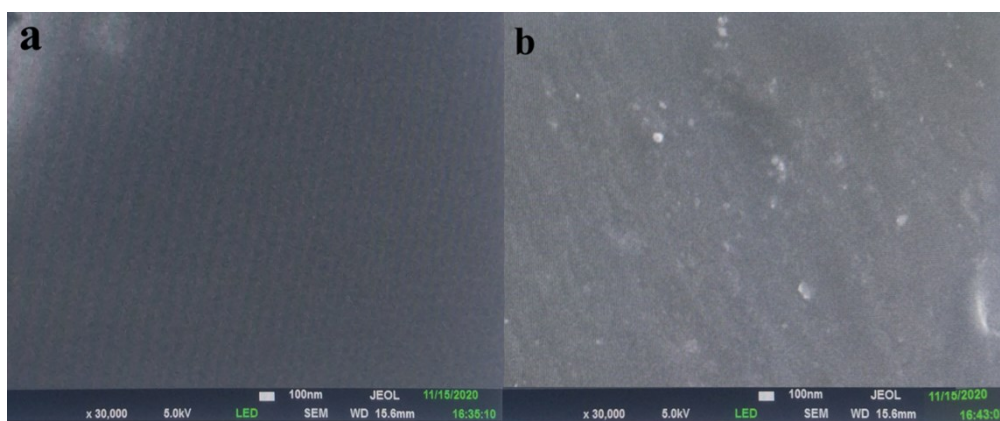


Fig. S10 SEM images of (a) Cz-3OMeTAD and (b) spiro-OMeTAD.

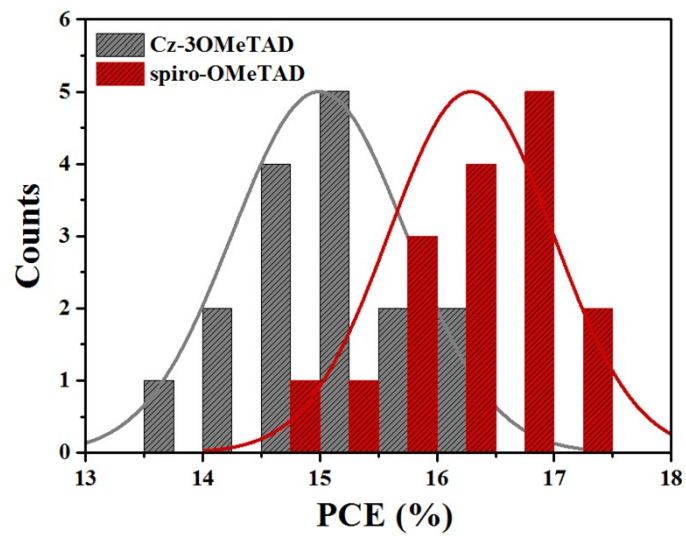


Fig. S11 Histograms of PCEs measured for 16 PSC devices using Cz-3OMeTAD and spiro-OMeTAD.