

A Novel AIE Molecule as Hole Transport Layer Enables Efficient and Stable Perovskite Solar Cells

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Materials and characterization

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. All film samples were spin-cast on quartz slice substrates. For the PL measurement, the TPE-CZ samples were prepared on quartz substrates or in a quartz cuvette. The excitation wavelength is 352 nm. For the PL and TRPL measurements of the perovskite, the samples were also deposited on quartz substrates and tested at a excitation wavelength of 532 nm. PL and TRPL measurements were carried out by a Fluorescence Spectrometer (Edinburgh Instrument, FLS 920). The high-resolution scanning electron microscopy (SEM) cross-section image of the prepared PeSCs was observed using an FEI Nova Nano-SEM 450 system.

For the hole-only devices, a polymer hole transport layer PEDOT:PSS (4083) was coated on the precleaned ITO substrates at 4000 r for 40 s. The substrates were then annealed at 135 °C for 10 min. Subsequently, the perovskite absorber layer ($\text{CH}_3\text{NH}_3\text{PbI}_3$) was deposited on the substrates. The detailed procedure is mentioned below. Then TPE-CZ or Spiro-OMeTAD was spin-coated on top of the perovskite film. Finally, Ag was evaporated through the vacuum evaporation system as top electrode. Current-voltage characteristics were measured by a Keithley 2400 in the dark. The hole mobility of the devices were obtained by the space-charge-limited current (SCLC) method, which can be described by the following equation:

$$J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$$

where J is the current density, μ is the hole mobility, ε_0 is the vacuum permittivity (8.85×10^{-12} F/m), ε_r is the dielectric constant of the material (normally taken to approach 3 for organic semiconductors), V is the applied bias, and d is the film thickness.

Electrochemical characterizations

Cyclic voltammetry (CV) was performed by a Zahner IM6e electrochemical workstation, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. TPE-CZ or Spiro-OMeTAD was drop-cast onto the electrode from CB solutions to form thin films. 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the supporting electrolyte. The scan rate was 0.05 V s⁻¹. The E_{HOMO} of TPE-CZ and Spiro-OMeTAD are calculated as refer to the eqs

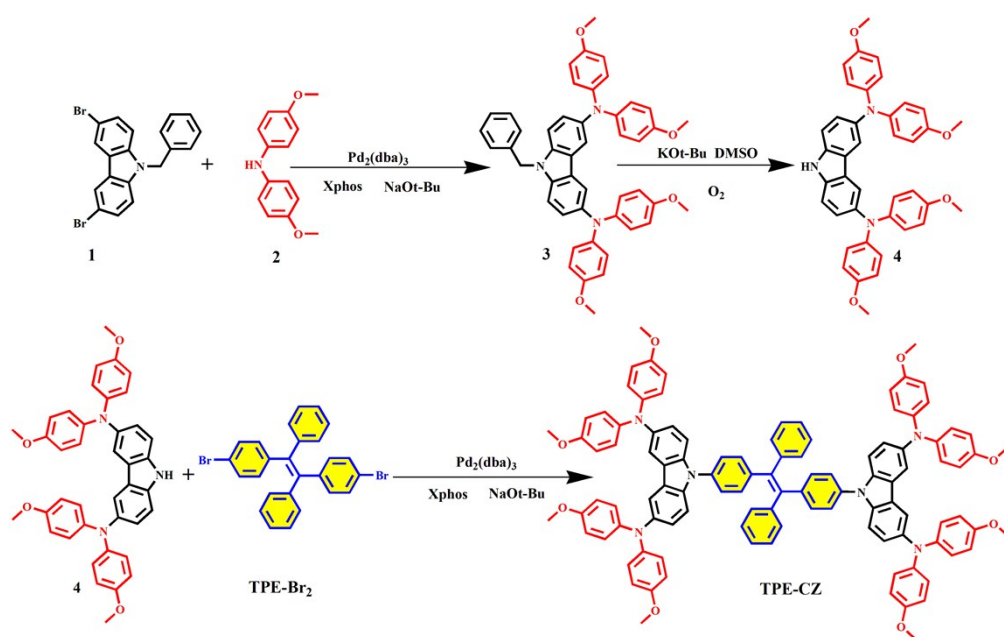
$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.7) \text{ eV}$$

Perovskite solar cells fabrication and characterization:

The perovskite solar cells were fabricated on F-doped indium oxide (FTO) pattern glass substrates (Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Sheet resistance $<15 \Omega$) with the following device configuration: FTO/c-TiO₂/mp-TiO₂/CH₃NH₃PbI₃/Hole transport layer (HTL)/Ag. First, the FTO glass substrates were cleaned by sequential ultrasonic treatment in detergent, acetone, deionized water, and isopropyl alcohol for 15 min and then dried with a nitrogen stream. The precleaned FTO glass substrates were treated by ultraviolet (UV)-ozone for 20 min in UV chamber. A 30 nm thick TiO₂ blocking layer was sequentially spin coated from a solution containing 0.3 M in n-butyl alcohol. The mesoporous TiO₂ layer was spin coated from a solution containing 1 g 18NRT Dyesol paste in 3.5 ml of ethyl alcohol at 5000 rpm for 30 s and then annealed the substrates at 500 °C for 30 min. The obtained meso-TiO₂ films were infiltrated with PbI₂ (Sigma-Aldrich, 99%) by spin-coating at 3500 rpm for 30 s. The PbI₂ films were dipped into CH₃NH₃I (10 mg/mL) (TCI, 99%) solution in isopropanol (Sigma-Aldrich) for 3 min and then annealed at 105 °C for 10 min. The HTL solution was prepared by mixing Spiro-OMeTAD or TPE-CZ (the concentration of Spiro-OMeTAD is 75 mg ml⁻¹ as the reported work⁽¹⁾ and the TPE-CZ concentration optimization process is achieved by trying different concentration of 70 mg ml⁻¹, 75 mg ml⁻¹ and 80 mg ml⁻¹), 28 μl tert-butylpyridine and 17 μl of bis(trifluoromethane) sulfonamide lithium salt (Li-TFSI) solution (520 mg in 1 ml acetonitrile) in 1 ml chlorobenzene. The HTL solution was spin-coated onto the perovskite film at 3000 rpm for 30 s. Finally, a 100 nm thick Ag anode (thermal deposition rate of 1.0 Å/s) was deposited on the substrate through a shadow mask to give a device area of 0.06 cm² under a vacuum level of 10⁻⁶ Pa. The *J-V* characteristic of the as-prepared PeSCs were tested with a Keithley 2400 under 100 mW cm⁻² simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000) in a N₂-filled glove box. The scan rate for *J-V* characteristics was 20 mV s⁻¹. The external quantum efficiency spectra (EQE) of the devices was measured by on an IPCE measuring system (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp).

The synthetic route of TPE-CZ.

Solvents and other chemicals are also commercial available and used as received unless specially stated. NMR spectra were recorded on a Bruker 400 MHz spectrometer and the MALDI-TOF/MS spectrometer was performed by SHIMADZU of AXIMA Assurance. The procedure for synthesis of TPE-CZ: the monomer 3 and 4 were obtained according to the reported literature.⁽²⁾



Scheme 1. The synthetic routes of TPE-CZ.

TPE- Br_2 (490 mg, 1 mmol), 4 (1.27 g, 2.04 mmol), $\text{Pd}_2(\text{dba})_3$ (39 mg, 0.04 mmol) and Xphos (29 mg, 0.06 mmol) were dissolved in dry toluene (15 mL). The mixture was purged with nitrogen for 30 minutes at room temperature. After that, sodium tert-butoxide (358 mg, 3.72 mmol) was added. The reaction was heated at reflux (110 °C) for 4 hours under nitrogen atmosphere. The mixture was quenched by adding water and extracted with CH_2Cl_2 . The combined organic extracts were dried over M_2SO_4 . After removal the solvent under reduced pressure, the crude product was purified by chromatography petroleum ether/ethyl acetate (2:1) to afford 1.18 g of TPE-CZ with yield 75 %. The ^1H NMR of the compound was shown in Fig S1a. To better identify the the hydrogen on the aromatic rings, DMSO- d_6 was used as a deuterated reagent. The ^{13}C NMR (CDCl_3) spectrum was also provided in Fig. S1b. The NMR and MALDI-

TOF-MS (an isotopic cluster peaking at m/z of 1570.24, calculating for M^+) synergistically confirmed its chemical structure.

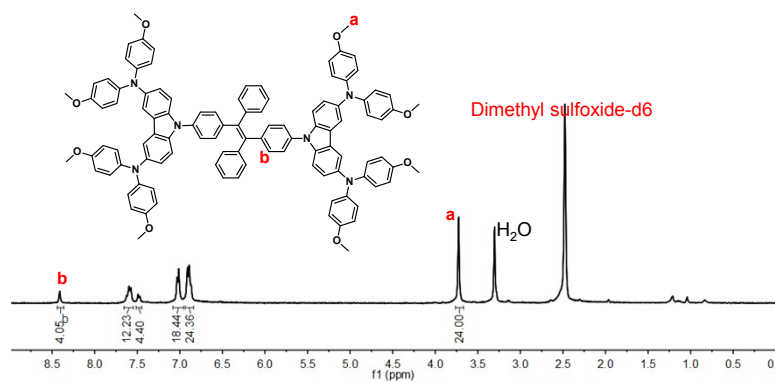


Fig. S1a The ^1H NMR(d_6 -DMSO) spectrum of TPE-CZ

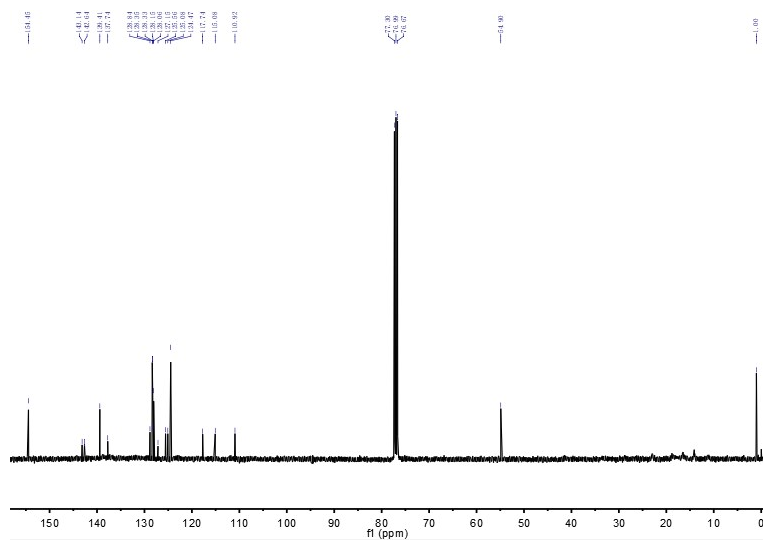


Fig. S1b The ^{13}C NMR (CDCl_3) spectrum of TPE-CZ.

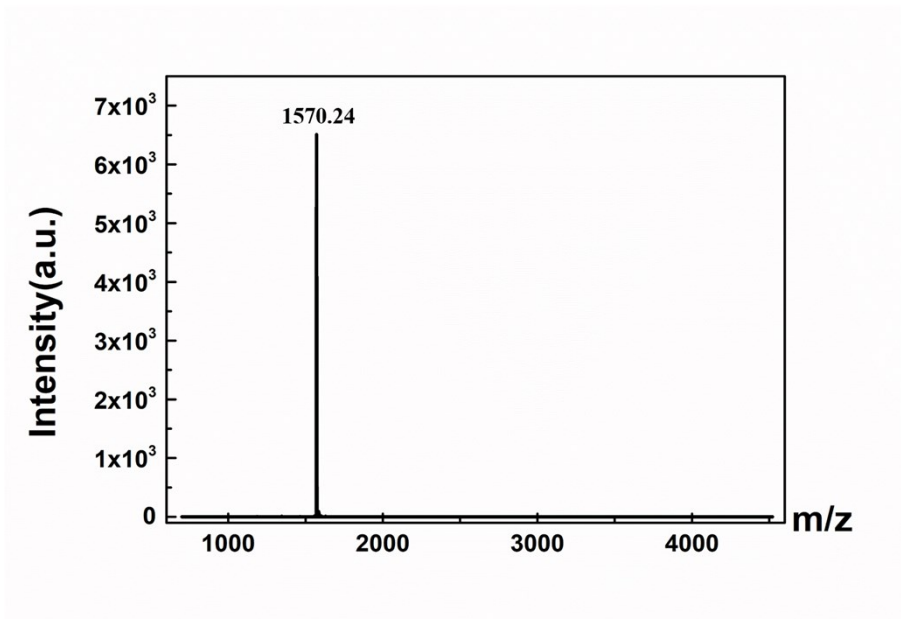


Fig. S1c The MALDI-TOF-MS spectrum of TPE-CZ.

Table S1: Materials costs for the synthesis of TPE-CZ.

	Chemical	Price of Chemical	Chemical cost	Cost per step
Step 1	Monomer 1	23000.8 \$/1 kg	29.90 \$(1.3 g)	37.80 \$ (1.3 g)
	Monomer 2	3659.7 \$/1 kg	4.43 \$(1.21 g)	
	Pd ₂ (dba) ₃	10000.1 \$/1 kg	1.50 \$(0.15 g)	
	Xphos	1626.7 \$/1 kg	0.12 \$(0.076 g)	
	NaOtBu	309.19 \$/25 kg	0.007 \$(0.576 g)	
	petroleum ether	60.66 \$/20 L	0.30 \$(0.1 L)	
	ethyl acetate	90.19 \$/20 L	1.00 \$(0.02 L)	
	MgSO ₄	46.2 \$/1 kg	0.023 \$(0.5 g)	
	Silica gel	58.7 \$/1 kg	0.35 \$(6.0g)	
Step 2	t-BuOK	500.18 \$/25 kg	0.038 \$(1.74 g)	2.20 \$ (1.27 g)
	DMSO	27.75 \$/2 L	0.28 \$(0.02 mL)	
	MgSO ₄	46.2 \$/1 kg	0.023 \$(0.5 g)	
	Silica gel	58.7 \$/1 kg	0.32 \$(5.5g)	
	petroleum ether	60.66 \$/20 L	0.30 \$(0.1 L)	
	ethyl acetate	90.19 \$/20 L	1.00 \$(0.02 L)	
Step 3	TPE-Br ₂	30912 \$/ kg	15.15 \$(490 mg)	27.26 \$ (1.18 g)
	Pd ₂ (dba) ₃	10000.1 \$/1 kg	0.40 \$(39 mg)	
	Xphos	1626.7 \$/1 kg	0.05 \$(29 mg)	
	NaOtBu	70.07 \$/5 kg	0.005 \$(358 mg)	
	petroleum ether	60.66 \$/20 L	6.17 \$(0.2 L)	
	ethyl acetate	90.19 \$/20 L	5.00 \$(0.1 L)	
	MgSO ₄	46.2 \$/1 kg	0.04 \$(1.00 g)	
	Silica gel	58.7 \$/1 kg	0.32 \$(5.5g)	
	CH ₂ Cl ₂	70 \$/20 L	0.10 \$(0.03L)	
	Toluene	30 \$/20 L	0.02 \$(0.015 L)	
Total cost				67.26 \$ (1.18 g)

The synthetic cost for spiro-MeOTAD has been widely reported as 92-108 \$/g⁽³⁾, which is much higher than the TPE-CZ.

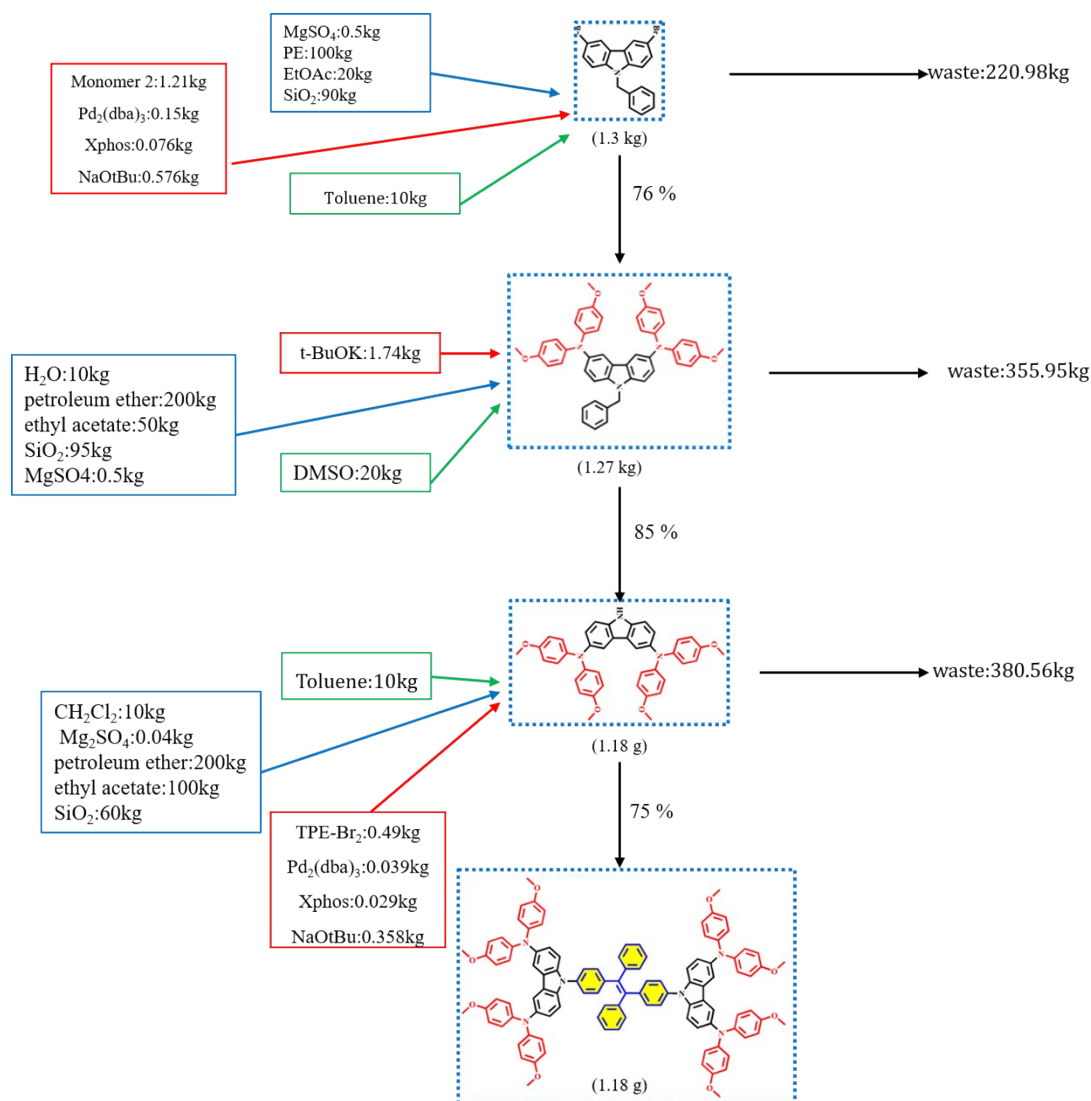


Fig. S2 Flowchart describing the synthesis of 1.1 kg of TPE-CZ. The requisite quantities of reagent (red arrow), solvents (green arrow) and work-up materials (blue arrow) as indicated for each step.

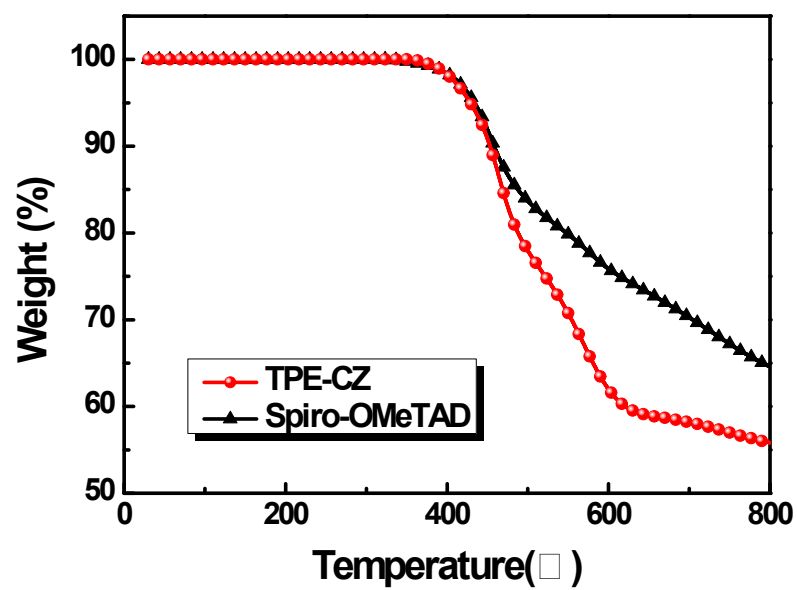


Fig. S3 TGA curves of TPE-CZ and Spiro-OMeTAD.

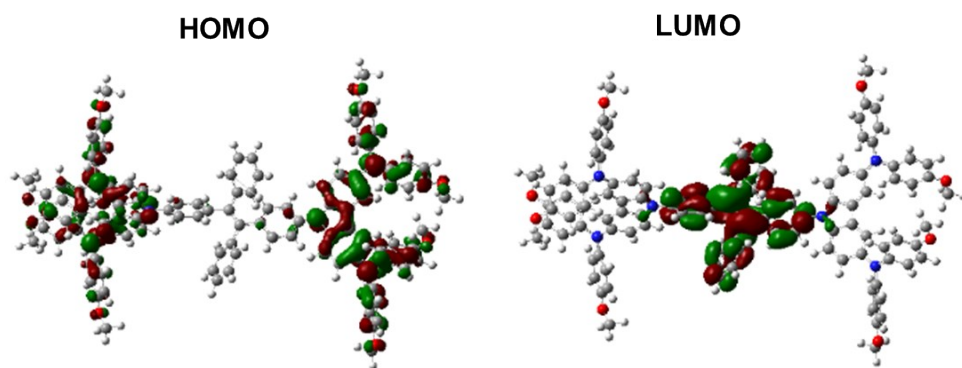


Fig. S4 Optimized molecular geometries and frontier molecular orbitals of TPE-CZ using DFT evaluated at the B3LYP/6-31G(d) level.

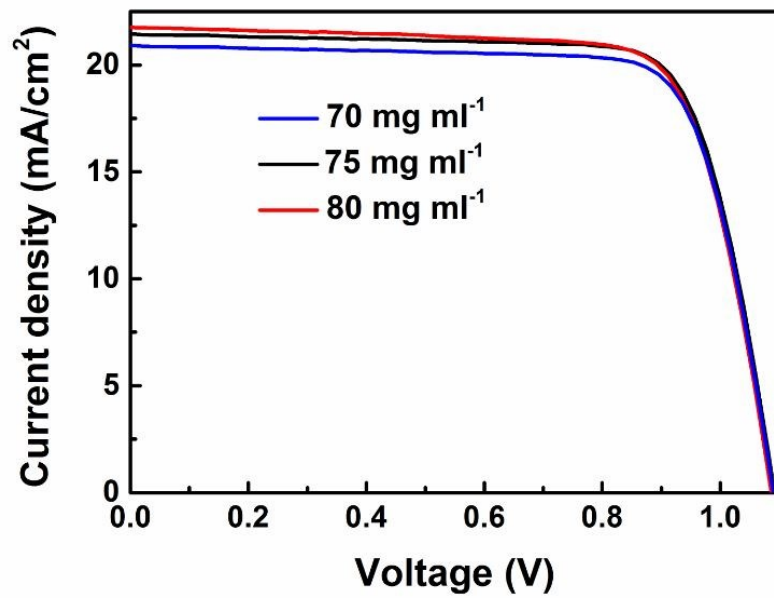


Fig. S5 J - V characteristics of PeSCs based TPE-CZ with various mass concentrations.

Table S2. The device parameters based on TPE-CZ HTL with different concentrations.

Concentration (mg ml ⁻¹)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
80	21.71	1.08	75.4	17.7
75	21.47	1.08	77.5	18.0
70	20.86	1.08	76.7	17.3

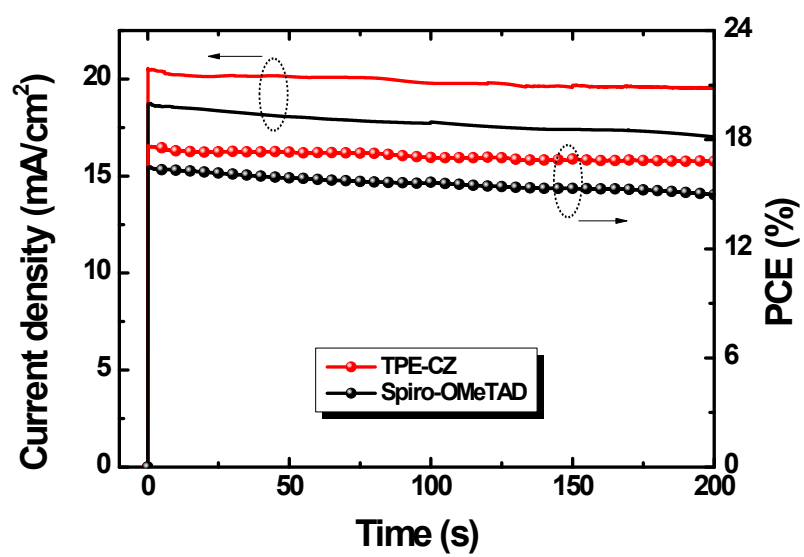


Fig. S6 Stabilized power output of the PeSCs based on TPE-CZ and Spiro-OMeTAD HTLs, respectively.

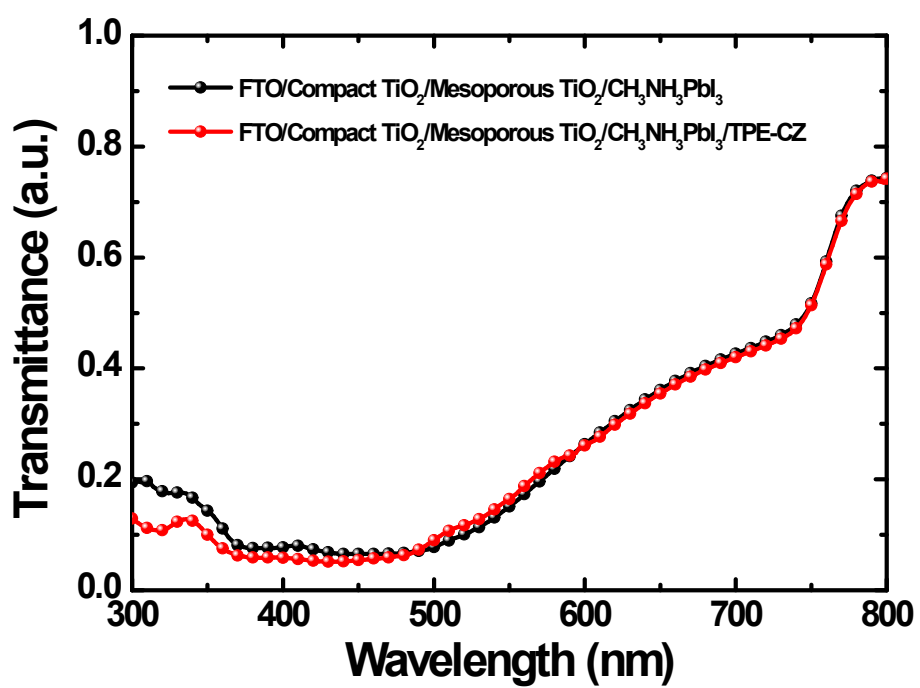


Fig. S7 Transmittance spectra of the sample FTO/Compact TiO₂/Mesoporous TiO₂/CH₃NH₃PbI₃ with or without TPE-CZ layer.

Table S3. The PL lifetime for the related device.

Samples	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	τ_{ave} (ns)
CH ₃ NH ₃ PbI ₃	1.8	19.4	31.9	80.6	26.1
CH ₃ NH ₃ PbI ₃ /TPE-CZ	1.1	80.8	12.4	19.2	3.3
CH ₃ NH ₃ PbI ₃ /Spiro-OMeTAD	1.3	74.6	14.9	25.4	4.7

All the data are fitted with a biexponential decay model,

$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$ and the τ_{ave} is calculated by the formula

$$\tau_{ave} = \frac{\sum_i A_i \tau_i}{\sum_i A_i}$$

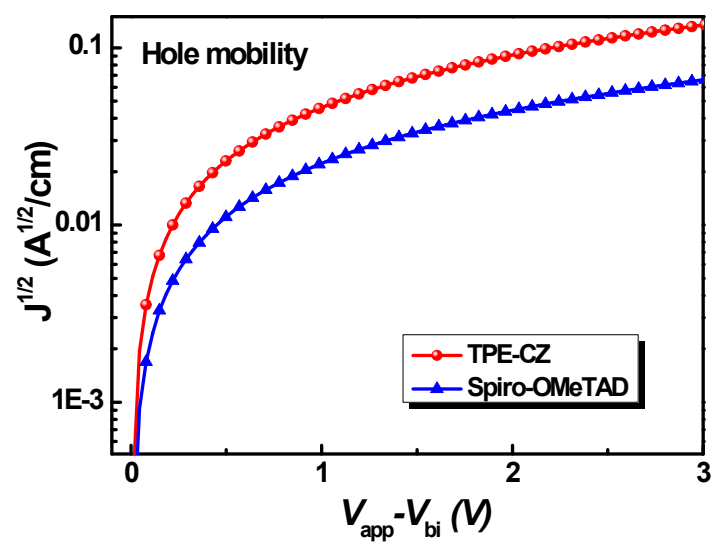


Fig. S8 J - V characteristics in the dark of hole-only devices with a structure of ITO/PEDOT:PSS/ $CH_3NH_3PbI_3$ /TPE-CZ or Spiro-OMeTAD/Ag.

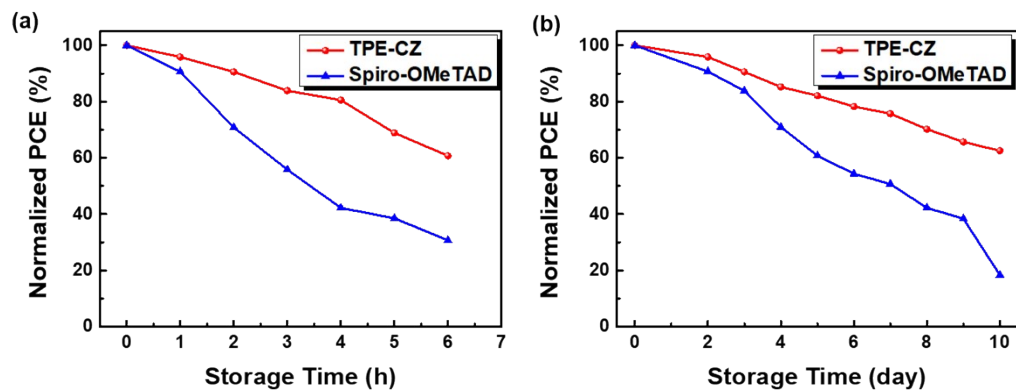


Fig. S9 (a) Normalized PCE decay of the PeSCs without encapsulation stored in a N_2 -filled glove box under UV light illumination. (b) Normalized PCE decay of the PeSCs without encapsulation stored in a petri dish wrapped with tin foil in ambient.

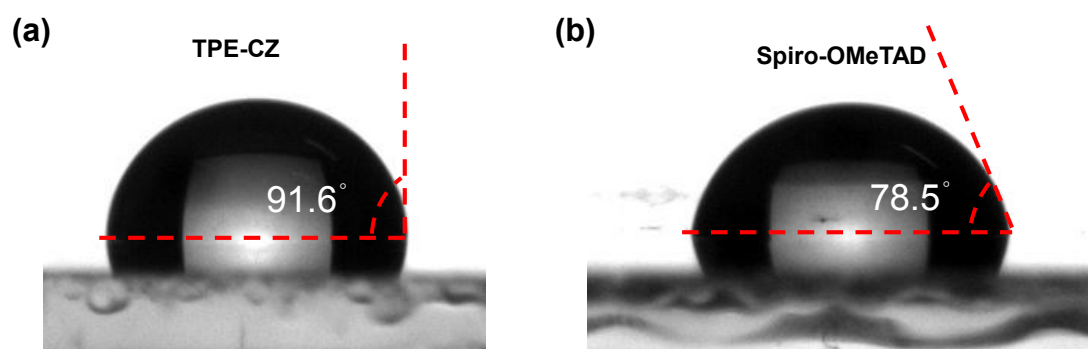


Fig. S10 Contact angle to deionized water of (a) TPE-CZ and (b) Spiro-OMeTAD.

References

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