

Supplementary Information

Peripheral substituent regulation of bias structured azulene-based hole transport materials for perovskite solar cells

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1. Experimental section

1.1 Calculation of HOMO and LUMO energy levels

The HOMO energy levels of HTMs were tested by cyclic voltammetry (CV) measurement, which were carried out in THF solution with [TBA] PF₆ (0.1 M) as electrolyte and ferrocene/ferrocenium (Fc/Fc⁺) as an external reference.

$$E_{\text{HOMO}} = 4.44 + [0.67 + (E^{1/2}_{\text{ox}} - E^{1/2}_{\text{Fc/Fc}^+})] \quad (1)$$

where $E^{1/2}_{\text{ox}}$ and $E^{1/2}_{\text{Fc/Fc}^+}$ are 1/2 of the first redox potential of HTM material and ferrocene, respectively.

The LUMO energy levels of HTMs were calculated according to the equation:

$$E_{\text{LUMO}} = - (| E_{\text{HOMO}} | - E_g) \quad (2)$$

where E_g was estimated from the cross point of the absorption and emission spectra of material.

1.2 Hole mobility and hole conductivity measurements

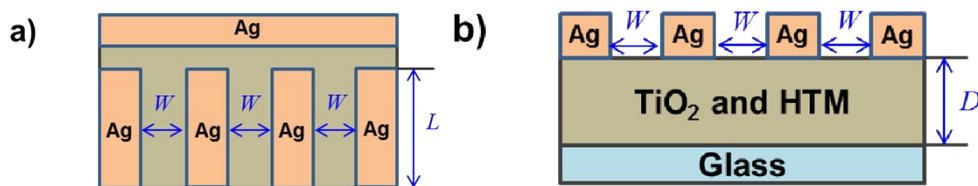
Hole mobility was measured by using the space-charge-limited current (SCLC) method with the device structure of FTO/PEDOT:PSS/HTM/Au. Two devices (eight groups of data) are tested and the data shown in Figure is an average data. Space-charge-limited current can be described by equation below:

$$J = \frac{9}{8} \mu \varepsilon_0 \varepsilon_r \frac{V^2}{D^3} \quad (3)$$

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.

$$\sigma = \frac{W}{R L D} \quad (4)$$

where L is the channel length 10 mm, W is the channel width 2 mm, D is the film thickness of the TiO₂ and HTM, and R is the film resistance calculated from the gradients of the curves.



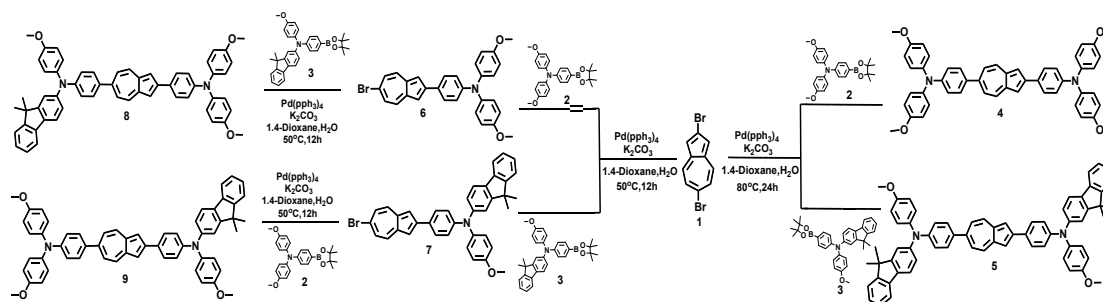
Scheme S1 Schematic illustrations of the conductivity device: (a) top-sectional view, (b) cross-sectional view.

1.3 Materials

The raw materials and palladium catalysts used to synthesize the HTMs were purchased from Energy Chemicals, China. Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI), 4-tert-butylpyridine (TBP) were purchased from Xi'an Polymer Light Technology Corp., Spiro-OMeTAD, Methylamine hydrochloride (MACI), formamidinium iodide (FAI) were purchased from Advanced Election Technology Co., Ltd., anhydrous solvents of chlorobenzene (CB), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), were purchased from Sigma-Aldrich, Lead (II) iodide (PbI_2) were purchased from TCI (Shanghai) Development Co., Ltd.. All of the used solvents and reagents were analytical grade and used without further purification.

1.4 Synthesis of HTMs

2,6-dibromoazulene (**1**) were synthesized according to the reported procedures.²⁴ The detailed synthesis of other compounds are shown below, and all materials were well characterized by ^1H NMR, ^{13}C NMR (see Figure S1-S6)



Scheme S2 Synthetic routes of azulene based hole transport materials.

Synthesis of 4,4'-(azulene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (AzudiT) (**4**)

Add **1** (572 mg, 2 mmol), **2** (1.725 g, 5 mmol), Tetratriphenylphosphine palladium and Saturated potassium carbonate solution (20 mL) to a clean two necked flask. Use 1,4-

dioxane as the reaction solvent. Heat to reflux and react under nitrogen atmosphere for 24 hours. Extract three times with water (30 mL) and ethyl acetate (60 mL). Collect the organic layer and evaporate under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 7:1 volume/volume). The product was obtained in 74% yield (2.37 g, 16.9 mmol) as red solid. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 9.6 Hz, 2H), 8.07 (s, 1H), 7.51 (d, *J* = 9.7 Hz, 1H), 7.49 – 7.44 (m, 4H), 7.20 – 7.13 (m, 7H), 7.10 – 7.01 (m, 7H), 6.92 – 6.86 (m, 8H), 3.84 (s, 12H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 156.13, 149.10, 148.65, 140.61, 139.91, 134.06, 129.03, 128.10, 126.91, 123.69, 120.36, 119.97, 114.78, 114.74, 113.33, 54.85.

Synthesis of N,N'-(azulene-2,6-diyl bis(4,1-phenylene))bis(N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine) (Azu-diF) (5)

The synthesis step refers to 4, and 2 is replaced with 3. The product is red powder, and the yield is 70%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.26 (d, *J* = 10.4 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.78 – 7.72 (m, 4H), 7.69 – 7.60 (m, 4H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 10.4 Hz, 2H), 7.30 (ddt, *J* = 13.3, 10.8, 7.1 Hz, 6H), 7.19 – 7.13 (m, 4H), 7.00 (ddd, *J* = 9.3, 6.0, 3.3 Hz, 10H), 3.78 (s, 6H), 1.41 – 1.34 (m, 12H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.47, 154.61, 153.60, 149.11, 148.72, 148.37, 147.15, 140.51, 140.07, 139.02, 137.87, 134.30, 134.02, 129.65, 129.18, 128.26, 127.56, 127.03, 126.46, 123.82, 122.99, 122.50, 122.22, 121.80, 120.67, 119.43, 118.16, 114.96, 114.01, 54.69, 46.88, 26.80.

Synthesis of 4-(6-bromoazulen-2-yl)-N,N-bis(4-methoxyphenyl)aniline (6)

Dissolve 1 (286 mg, 1 mmol), 2 (345 mg, 1 mmol), Tetratriphenylphosphine palladium (25 mg, 0.02 mmol) and Saturated potassium carbonate solution (5 mL) with 1,4 dioxane (20 mL). Under a nitrogen atmosphere, the reaction solution is heated to 50 °C. After 12 h of the reaction, it was extracted three times with water (30 mL) and ethyl acetate (60 mL). The organic layer is collected and evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 7:1 volume/volume). The product is a red powder with a yield of 84%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.38 (d, *J* = 10.4 Hz, 2H), 7.58 (dd, *J* = 19.2, 9.6 Hz,

4H), 7.39 (s, 2H), 7.17 – 7.10 (m, 4H), 7.01 – 6.95 (m, 4H), 6.84 (d, $J = 8.6$ Hz, 2H), 3.77 (s, 6H).

N-(4-(6-bromoazulen-2-yl)phenyl)-N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine(7)

The synthesis step refers to 6, and 2 is replaced with 3. The product is red powder, and the yield is 85%. ^1H NMR (400 MHz, DMSO-*d*6) δ 8.37 (d, $J = 10.4$ Hz, 2H), 7.74 (t, $J = 7.9$ Hz, 2H), 7.64 (d, $J = 8.7$ Hz, 2H), 7.57 (d, $J = 10.4$ Hz, 2H), 7.50 (d, $J = 7.4$ Hz, 1H), 7.38 (s, 2H), 7.34 – 7.23 (m, 3H), 7.18 – 7.13 (m, 2H), 7.01 (ddd, $J = 15.1, 8.6, 2.1$ Hz, 5H), 3.77 (s, 3H), 1.37 (s, 6H).

N-(4-(2-(4-(bis(4-methoxyphenyl)amino)phenyl)azulen-6-yl)phenyl)-N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (Azu-2T6F) (8)

The synthesis step is the same as 6, where 1 is replaced by 6, and 2 is replaced with 3. The product is a red powder with a yield of 91%. ^1H NMR (400 MHz, DMSO-*d*6) δ 8.21 (d, $J = 10.4$ Hz, 2H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.72 (dd, $J = 7.8, 4.6$ Hz, 2H), 7.63 – 7.57 (m, 4H), 7.49 (d, $J = 7.3$ Hz, 1H), 7.38 (d, $J = 10.3$ Hz, 2H), 7.33 – 7.22 (m, 3H), 7.16 – 7.12 (m, 2H), 7.10 – 7.04 (m, 4H), 7.02 – 6.91 (m, 9H), 6.81 (d, $J = 8.5$ Hz, 2H), 3.75 (d, $J = 8.5$ Hz, 9H), 1.37 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.06, 155.06, 154.92, 152.27, 147.94, 146.48, 140.58, 139.98, 134.43, 129.11, 128.12, 127.50, 126.97, 126.38, 123.75, 122.87, 122.46, 120.59, 120.30, 119.92, 119.39, 118.14, 114.81, 114.73, 113.78, 113.37, 113.07, 55.00, 46.17, 25.97.

N-(4-(6-(4-(bis(4-methoxyphenyl)amino)phenyl)azulen-2-yl)phenyl)-N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (Azu-2F6T) (9)

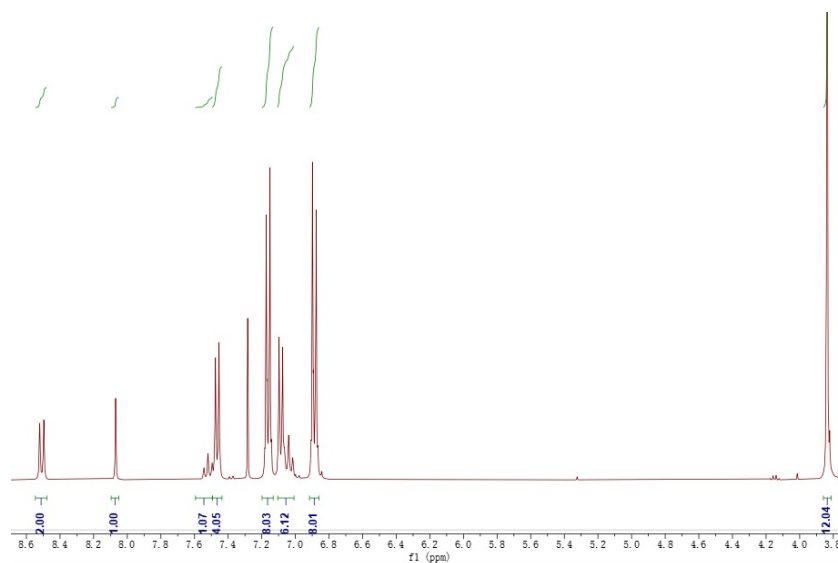
The synthesis step is the same as 6, replace 1 with 7. Its product is a red powder with a yield of 90%. ^1H NMR (400 MHz, DMSO-*d*6) δ 8.23 (d, $J = 10.4$ Hz, 2H), 7.89 (d, $J = 8.6$ Hz, 2H), 7.73 (dd, $J = 7.8, 4.3$ Hz, 2H), 7.64 (s, 2H), 7.55 (d, $J = 8.7$ Hz, 2H), 7.50 (d, $J = 7.1$ Hz, 1H), 7.37 (d, $J = 10.6$ Hz, 2H), 7.27 – 7.24 (m, 2H), 7.15 – 7.07 (m, 8H), 6.99 – 6.93 (m, 8H), 6.83 (d, $J = 8.7$ Hz, 2H), 3.76 (d, $J = 9.0$ Hz, 9H), 1.37 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 156.15, 155.04, 153.53, 148.88, 148.72, 148.33, 147.14, 140.52, 139.91, 139.01, 136.68, 134.29, 133.91, 129.05, 128.17, 127.43, 126.96, 126.86, 126.40, 123.73, 122.79, 122.46, 122.18, 120.56, 119.93, 119.38,

118.06, 114.82, 113.86, 56.13, 46.83, 26.58.

1.5 Device Fabrication

Preparation of n-i-p type perovskite solar cells: The laser-etched conductive glass FTO (fluorine-doped tin dioxide) was cut into a glass substrate of 90 mm × 30 mm size. Washed the FTO substrate sequentially with deionized water, ethanol, and acetone for 15 min each time. By spray pyrolysis method, 20 M ethanol and 2 M acetyl acetone isopropanol solution were sprayed on the FTO glass substrate and heated to 500 °C to form a dense oxide layer and cut into 15 nm × 15 nm glass. Ultraviolet ozone machine was used for 30 min, 30 μL titanium dioxide (mass ratio 6:1) ethanol solution was rotated onto the tight layer at a speed of 5000 rpm/s for 30 s. Mesoporous TiO₂ was prepared by annealing at 100 °C for 30 min, and then by secondary annealing at 500 °C.

Preparation of perovskite solution (in the glove box): Dissolved PbI₂, FAI and MAcl in a mixture solvent of N,N-dimethylformamide and dimethyl sulfoxide (4:1 by volume) in a molar ratio of 1.1 : 1 : 0.4. Stirred overnight at room temperature and proceed to the next step on the rotary coater. 30 μL of prepared perovskite solution was rotated onto the mesoporous TiO₂ for 10 s at a rotational speed of 1000 rpm/s, then increased to 5000 rpm/s for 30s, and then dropped 200 μL of anti-solvent chlorobenzene onto the perovskite layer at the last 15 s. Then the treated perovskite film was transferred to the heating table at 150 °C and annealed for 30 minutes. Then, the HTMs solution (40 mg HTMs, 30 mM LiTFSI and 200 mM TBP dissolved in 1 mL chlorobenzene) was rotated onto the surface of the perovskite film by spin-coating method. The rotation number was adjusted to 5000 rpm/s and the spin-coating time was 30 s. Finally, 100 nm Au was deposited onto the device film by vacuum evaporation.



2. NMR spectra

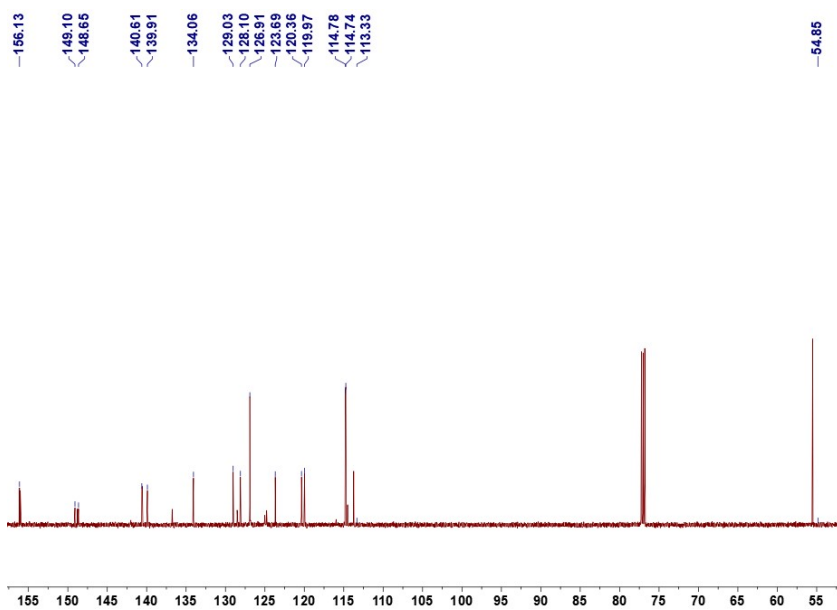


Figure S1 ¹H NMR and ¹³C NMR spectra of Azu-diT recorded in Chloroform-*d*.

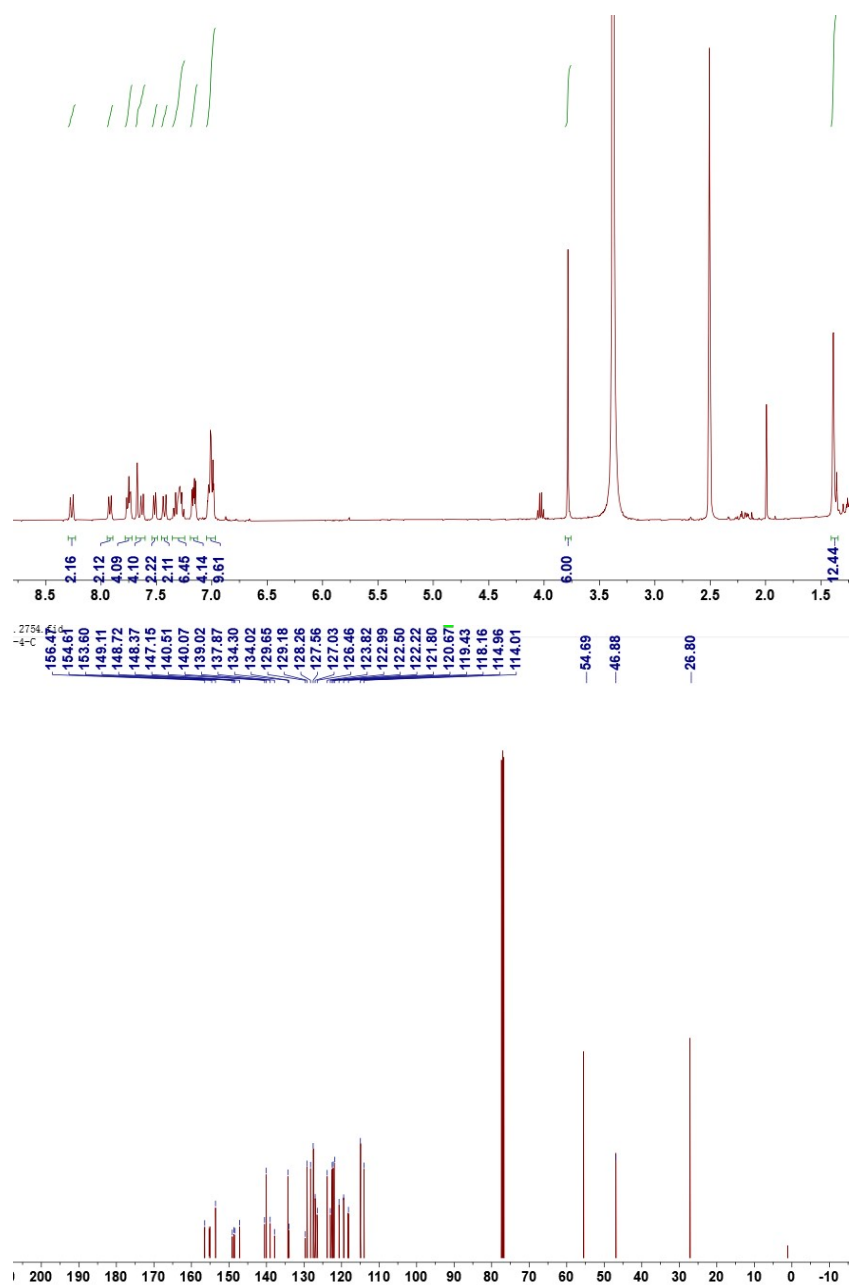


Figure S2 ^1H NMR recorded in d_6 -DMSO and ^{13}C NMR spectra of Azu-diF recorded in Chloroform- d .

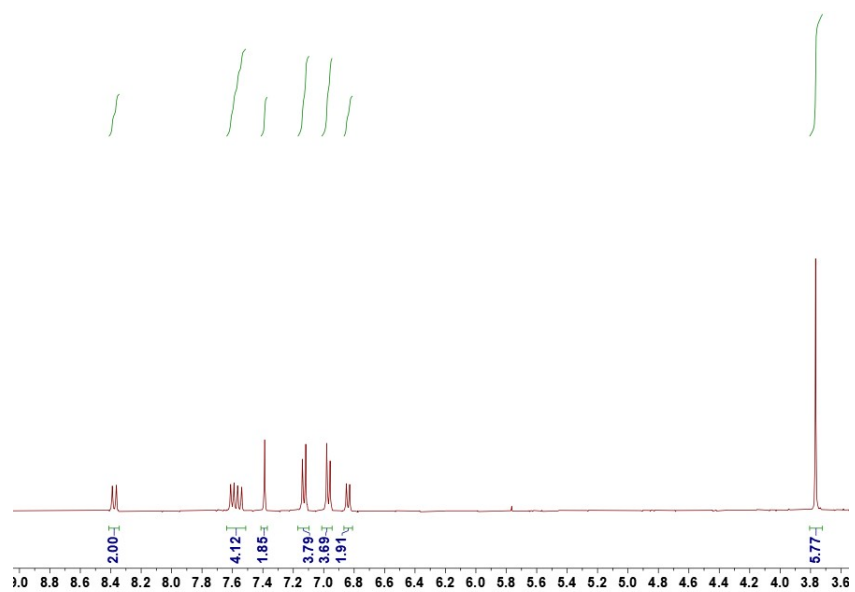


Figure S3 ^1H NMR spectra of 4-(6-bromoazulen-2-yl)-N,N-bis(4-methoxyphenyl)aniline recorded in d_6 -DMSO.

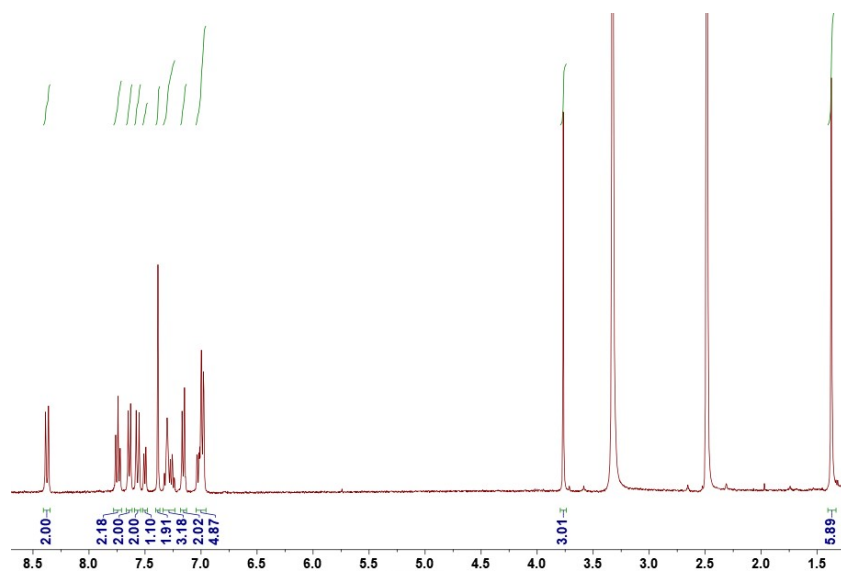


Figure S4 ^1H NMR spectra of N-(4-(6-bromoazulen-2-yl)phenyl)-N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine recorded in d_6 -DMSO.

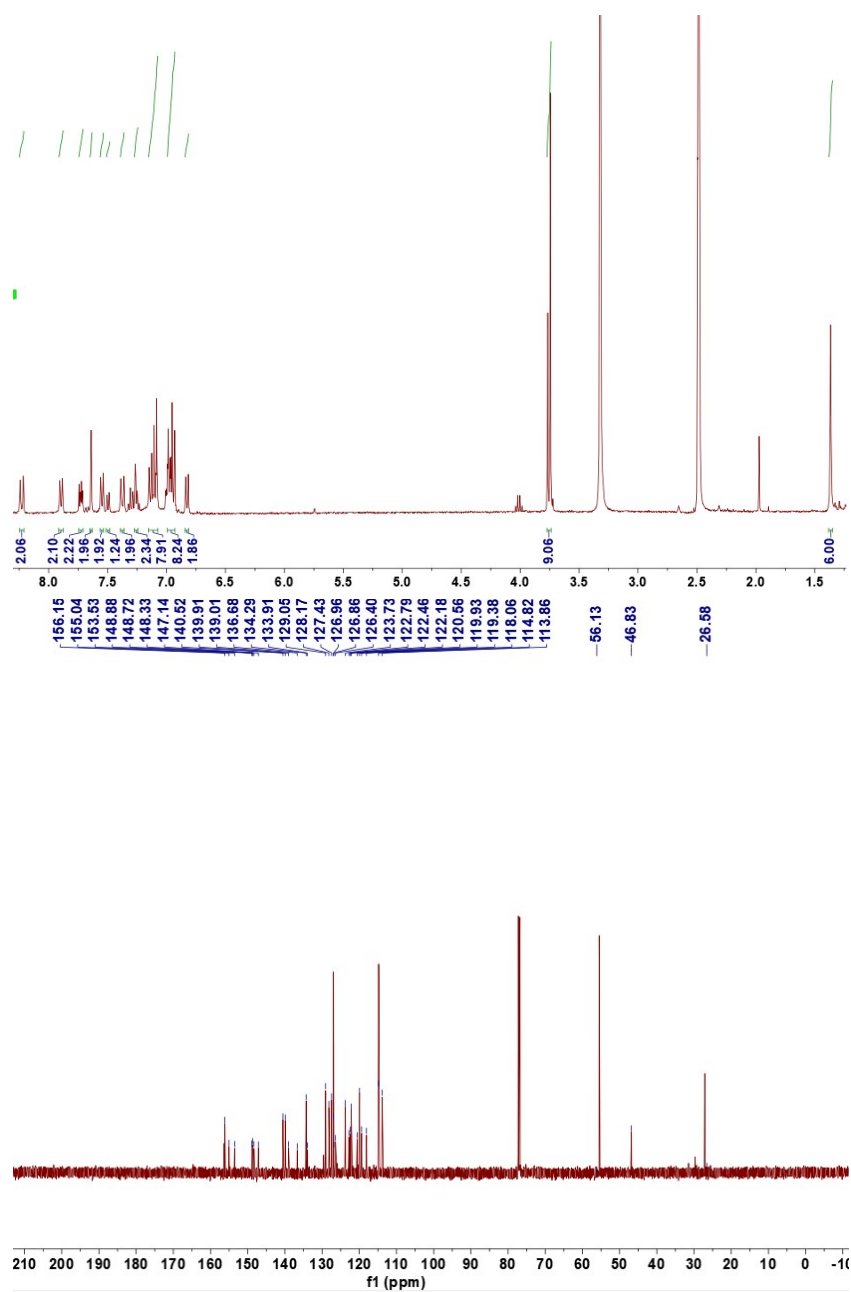


Figure S5 ^1H NMR recorded in d_6 -DMSO and ^{13}C NMR spectra of Azu-2T6F recorded in Chloroform- d .

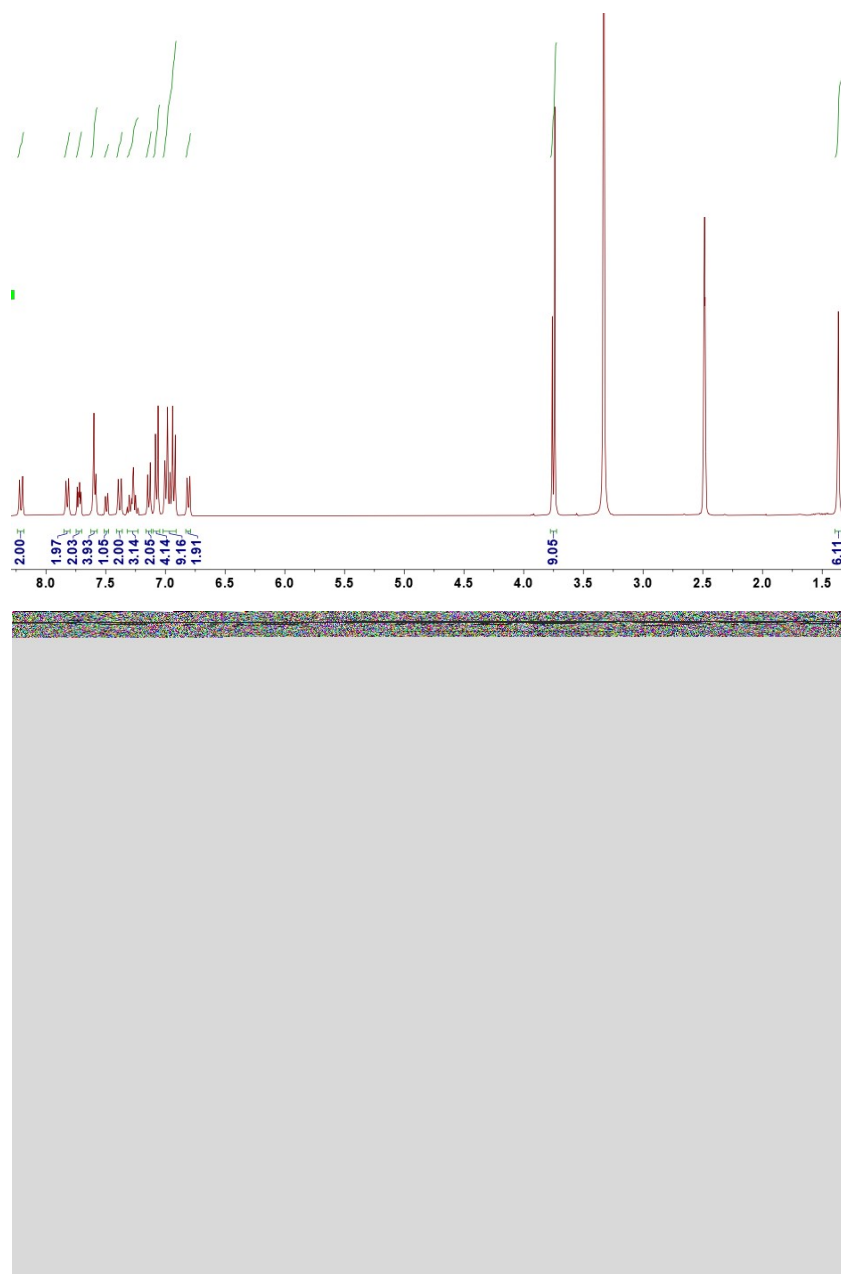


Figure S6 ^1H NMR recorded in d_6 -DMSO and ^{13}C NMR spectra of Azu-2F6T recorded in Chloroform- d .

3. Additional data and spectra

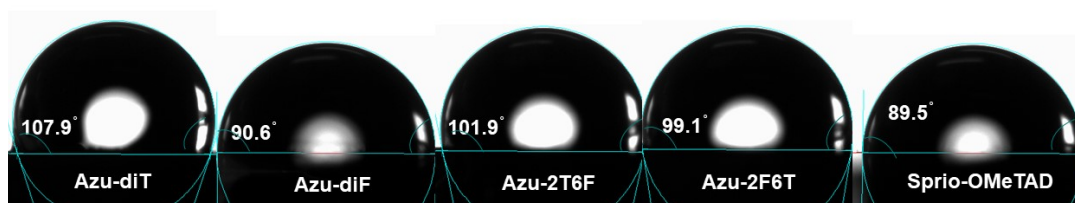


Figure S7 Contact angle of HTMs.

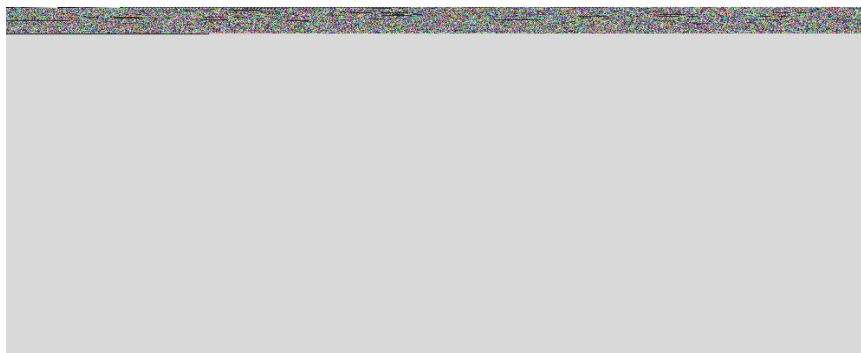


Figure S8 (a) TGA and (b) DSC results of Azulene-based HTMs.

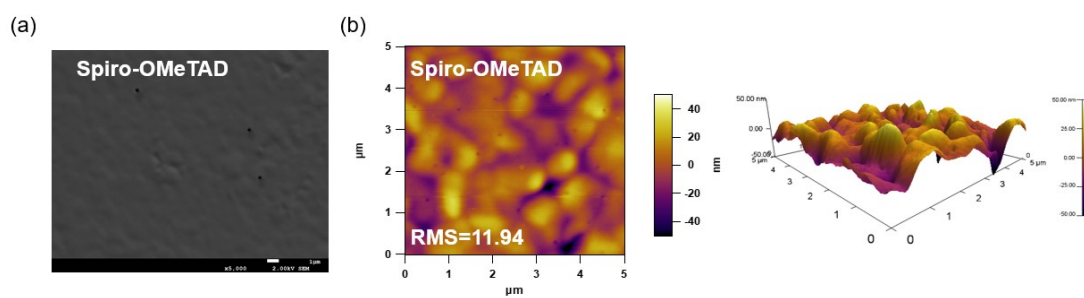


Figure S9 (a) SEM and (b) AFM images of Spiro-OMeTAD.

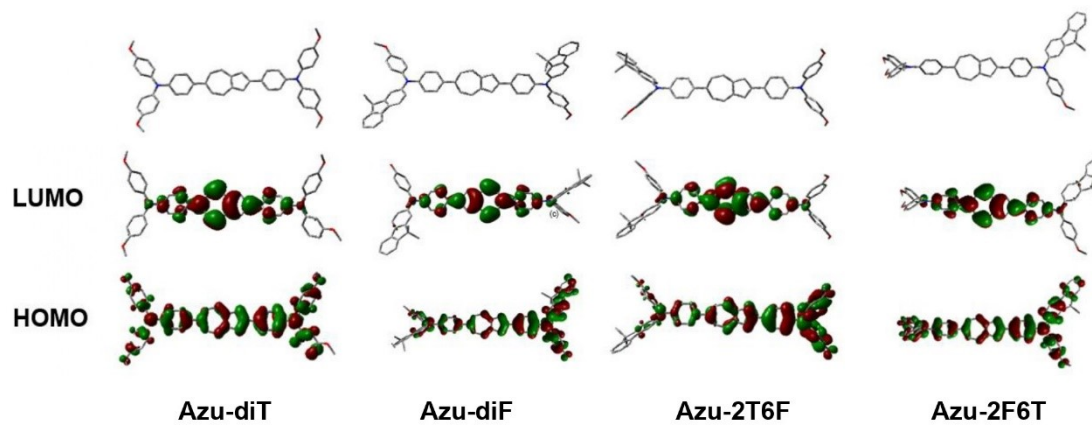


Figure S10 The calculated HOMO and LUMO profiles.

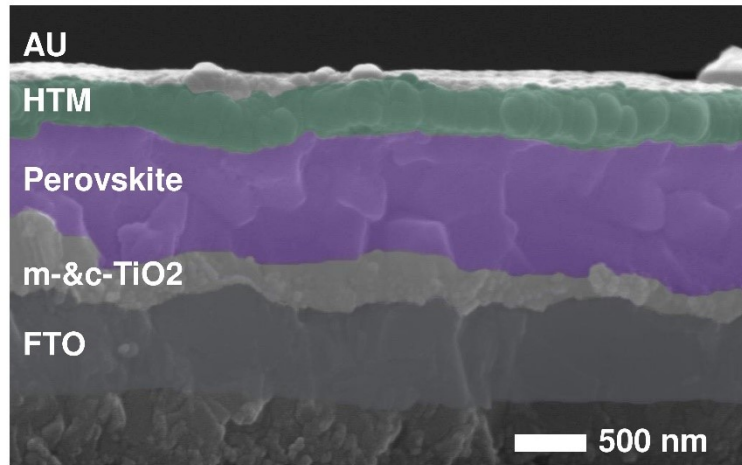


Figure S11 The cross-sectional SEM image of Azu-2T6F based PSC device. (Thickness for each layer: Au 80 nm, HTL 150 nm, PVK 750 nm, m-&C-TiO₂ 500 nm)