

Supporting Information

Li-TFSI Free Carbazole-based Hole Transport Material Enable Highly Stable Perovskite Solar Cells

Liangding Zheng^{a,#}, Yangmei Ou^{a,#}, Shihuai Wang^{*a}, Lin Xie^{*a} and Yong Hua^{*a}

Experimental Section

Materials

Carbazole, 4,4'-Dimethoxydiphenylamine, chlorobenzene (CB), and Ag-TFSI were obtained from Energy Chemical. Formamidinium iodide (FAI, 99%), methylammonium bromide (MABr, 99.5%) , and MAPbBr₃ were purchased from Greatcell Solar. Lead iodide (PbI₂, 99.99%) and Methylamine hydrochloride (MAHCl, 99.8%) were obtained from TCI. SnO₂ (15 wt% colloidal dispersion) purchased from Alfa. Other reagents are commercially available and used directly without further purification.

Device Fabrication

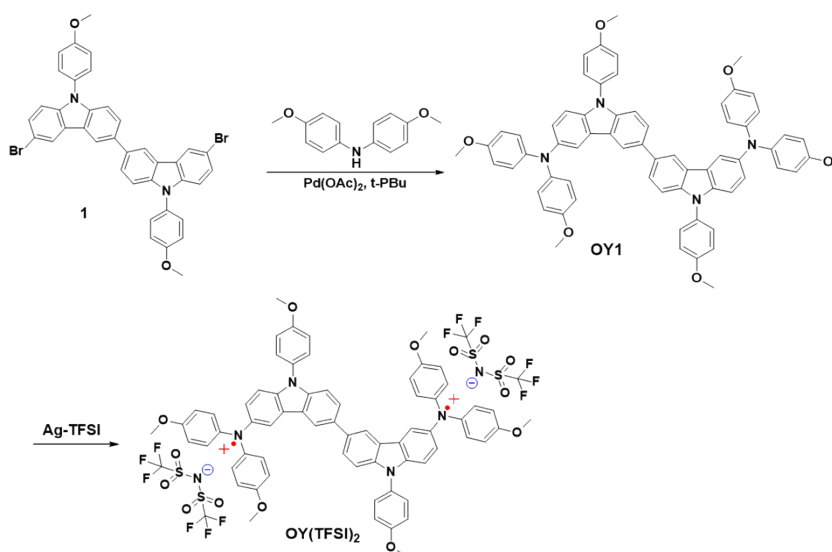
The ITO glass substrates were separately cleaned with detergent, deionized water, acetone and anhydrous ethanol each for 30 min. Then, the cleaned substrates were treated by ultraviolet ozone for 30 min to enhance the surface hydrophilic, 50 μL SnO₂ (2.67%, diluted by water) colloidal aqueous solution were deposited as prepared ITO substrates used as electron transport layer and further annealing treatment for 30 min at

150 °C. Before transferring into N₂-filled glovebox for fabricating perovskite function layer, the ITO covered with SnO₂ were treated with ultraviolet ozone for 15 min. 1.53 M PbI₂, 1.4 M FAI, 0.5 M MACl, 0.0122 M MAPbBr₃ in DMF: DMSO=8:1, and stirred overnight. Then, 40 μL of the perovskite precursor solution without and with additive was spin-coated on the substrates by a one-step coating process at 2000 rpm for 10 s and 6000 rpm for another 30 s. During the spinning process, 110 μL chlorobenzene (CB) used as anti-solvent dropped onto to the substrates at the last 15 s before the program end. After that, the prepared films were annealed at 120 °C for 1 h. Subsequently, HTMs solutions (Li-TFSI-doped OY1: 40mg OY1, 17 μL tBP, 22 μL Li-TFSI (260 mg Li-TFSI in 1 mL acetonitrile) dissolved in 1 mL CB; OY(TFSI)₂-doped OY1: 40mg OY1, 17 μL tBP, 8 mg OY(TFSI)₂ dissolved in 1 mL CB) is spin-coated onto the perovskite layer with a spin-coating process 3000rpm for 30s. Finally, 200 nm Ag electrode was thermally evaporated onto the hole transport layer under high vacuum to obtain complete devices.

Characterization

Gaussian 09 ab initio quantum chemical software package was used to perform the gas phase DFT calculations. DFT method was employed to obtain the ground state properties. The geometry optimization was performed under the UB3LYP/6-31G (d, p) level for OY1. The resulted optimized geometries were further used as input to obtain frontier molecular orbitals. The UV-Vis absorption spectra were measured by a U4100 spectrophotometer (Hitachi). The time-resolved PL spectra were measured using a FLS1000 Edinburgh Instruments spectrofluorimeter equipped with the integrating sphere. Incident photon-to-current conversion efficiency (IPCE) spectra were obtained by a Newport QE measurement fit consisting of a Xenon light source (Spectral Products ASB-XE-175). The space charge limited current (SCLC) was obtained by Qinglang 150 W solar simulator with model Sirius-ss150A and Oriel IV Test Station software in a dark environment, under bias from 0 V to 10 V and current limit at 200mA. The current density-voltage (J-V) characteristics were measured by a Newport solar simulator (model 91160) and a Keithley 2400 source/meter under 100 mW cm⁻² (AM

1.5 G illumination). In this work, the mask area of the measured device is 0.0625 cm².



Scheme S1. The detailed synthetic routes of OY1 and OY(TFSI)₂.

Synthesis of OY1 and OY(TFSI)₂

OY1: Compound 1 (702 mg, 1.0 mmol), and bis(4-methoxyphenyl)amine (572 mg, 2.5 mmol) in toluene (15 mL) were degassed with nitrogen for 10 min. Pd(OAc)₂ (100 mg), t-Bu₃P (50 μ L), and t-BuOK (250 mg) were added to the mixture and refluxed for 24 h in the absence of light. The reaction mixture was then extracted with CH₂Cl₂, the organic layer was dried over anhydrous MgSO₄, and concentrated by rotary evaporation. The mixture was purified by chromatography (SiO₂, hexane/ CH₂Cl₂, 1/1 [v/v]) to afford a yellow powder (89%, OY1). ¹H NMR (600 MHz, *d*-DMSO) δ 8.55 (s, 2H), 8.00 (s, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 4.0 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 4.0 Hz, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 4.0 Hz, 8H), 6.84 (d, *J* = 4.0 Hz, 8H), 3.86 (s, 8H), 3.70 (s, 16H). HRMS (OY1) calculated (found) for C₆₆H₅₄N₄O₆ 998.4051 (998.4042).

OY(TFSI)₂: OY1 (200 mg, 0.2 mmol) and silver bis(trifluoromethanesulfonyl)imide (AgTFSI) (156 mg, 0.4 mmol) were mixed into 20 mL dichloromethane. The solution was purged and backfilled with nitrogen for 10 min and then stirred at room temperature for 24 h under dark. The resultant silver precipitation was removed by filtration and the solution was dried by rotary evaporation under vacuum to give a dark-purple powder. The final powder was recrystallized from DCM/methanol and dried under vacuum

overnight. Elemental analysis calcd (%) for $C_{70}H_{54}F_{12}N_6O_{14}S_4$: C, 53.91; H, 3.49; N, 5.39; S, 8.22. Found: C, 53.86; H, 3.52; N, 5.32; S, 8.28.

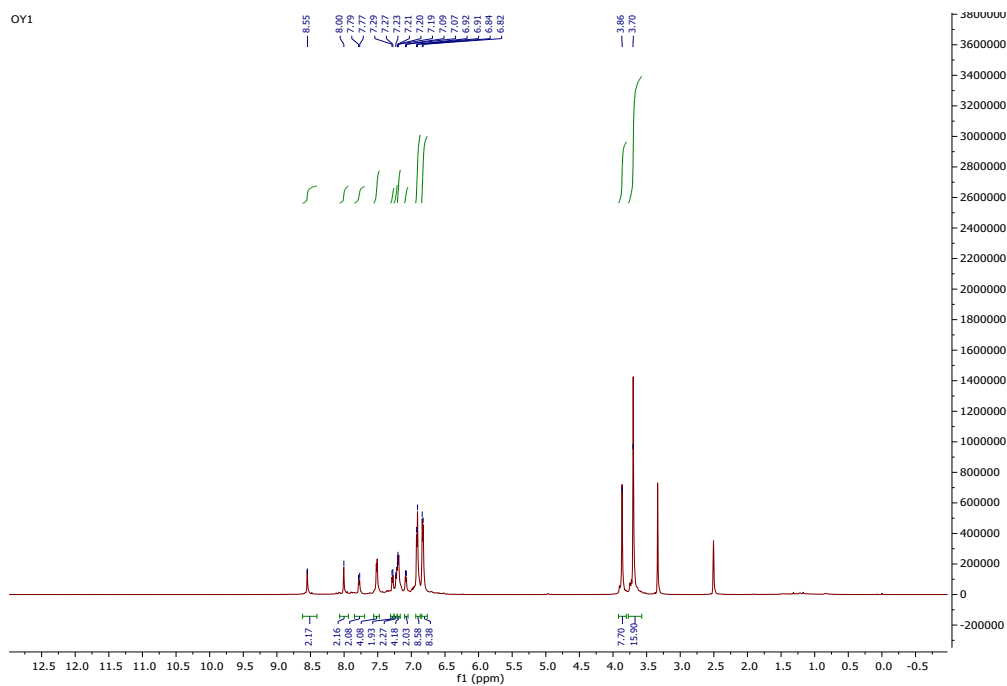


Fig S1. 1H NMR spectra of OY1.

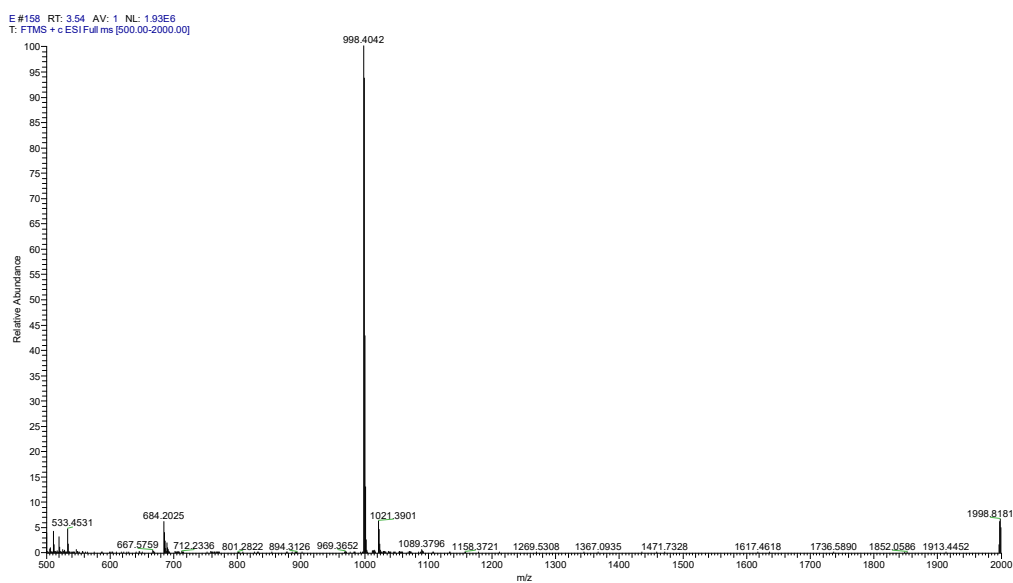


Fig S2. HRMS spectra of OY1.

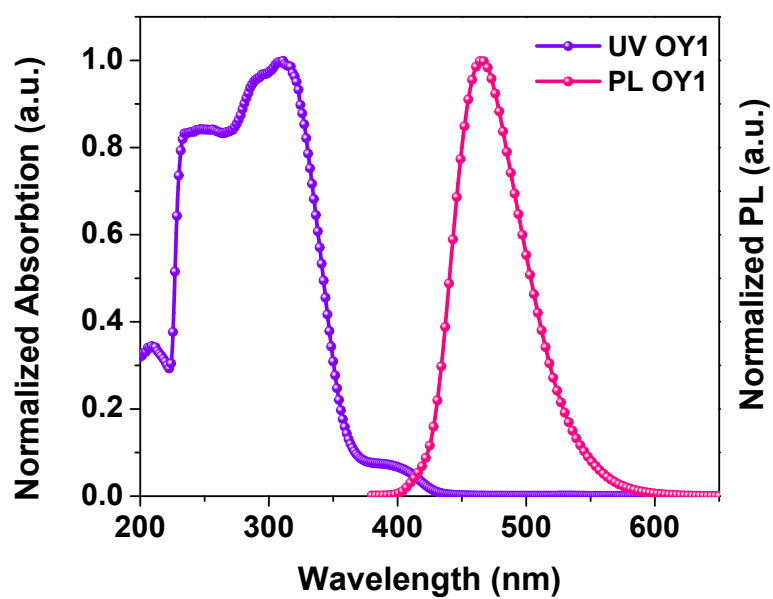


Fig. S3 UV-vis absorption and PL spectra of OY1.

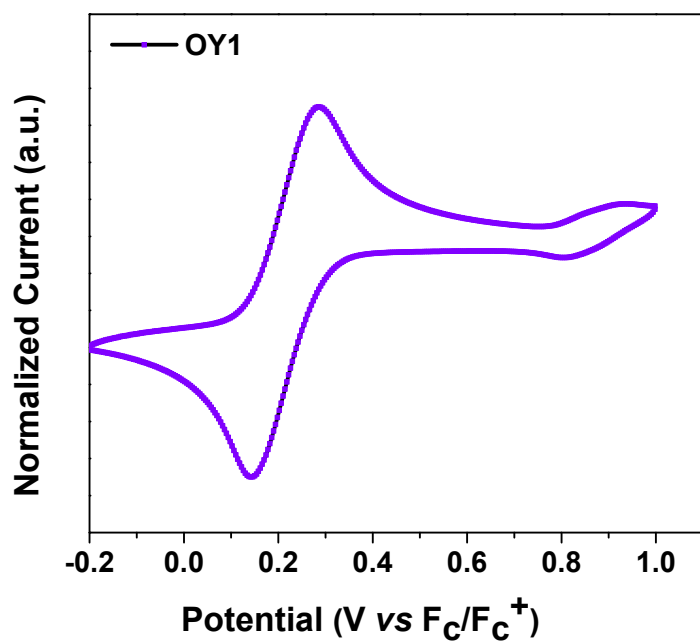


Fig. S4 CV spectra of OY1.

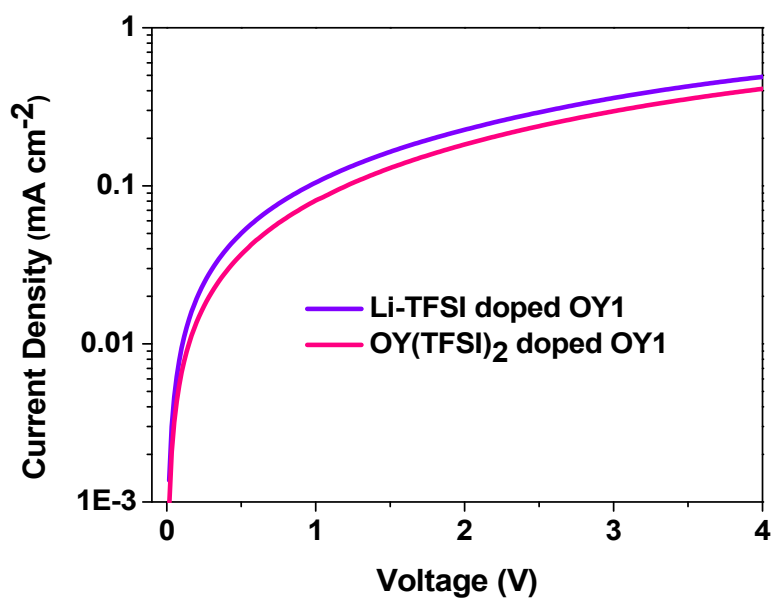


Fig. S5 J-V curves of the OY1 doped with Li-TFSI and OY(TFSI)₂ under dark.

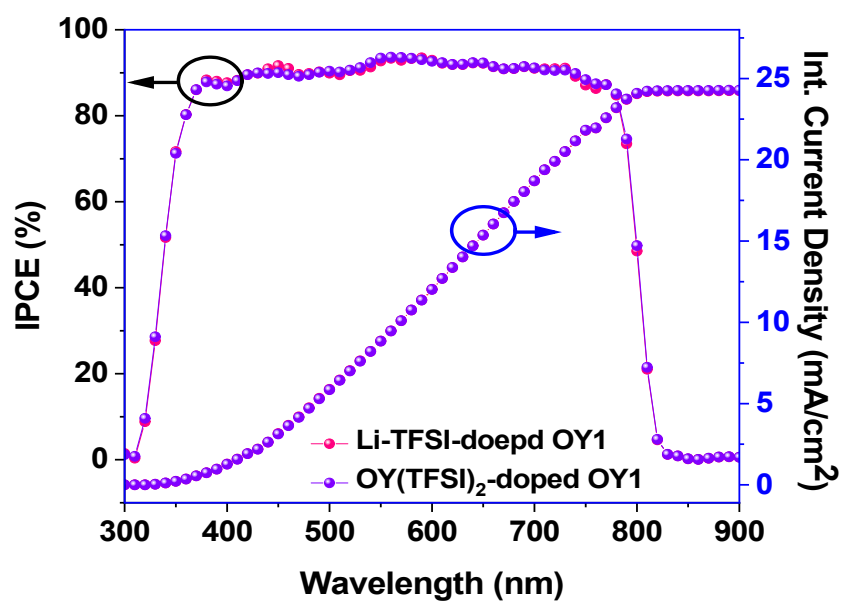


Fig. S6 IPCE and integral J_{sc} curves of these devices.

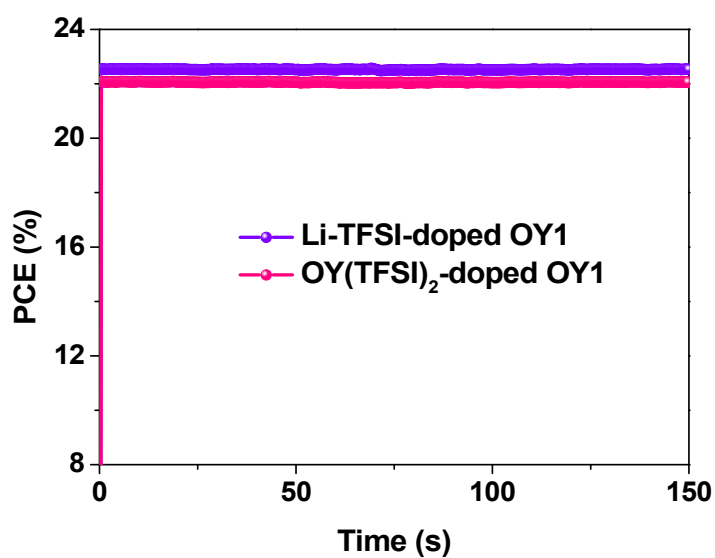


Fig. S7 Steady PCE of devices at the maximum power point within 150s.

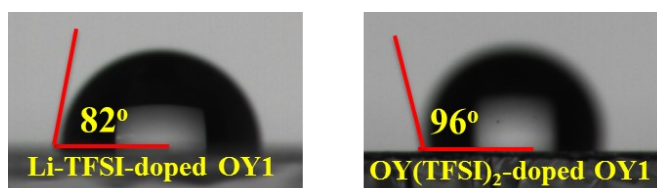


Fig. S8 Water contact angle measurements of HTL films.

Table S1. Photophysical and electrochemical data of OY1.

HTM	λ_{inter} (nm)	E_g (eV)	E_{HOMO}^c (eV)	E_{LUMO}^d (eV)
OY1	410	3.02	-5.14	-2.12