Supporting Information

Carbazole-based Spiro[fluorene-9,9'-xanthene] as Efficient Hole-transporting Material for Perovskite Solar Cells

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Details for measurement and device fabrication

Electrochemical Measurement: Cyclic voltammetry was carried out on a PC-controlled CHI 620C electrochemical analyzer (CH instruments). Cyclic voltammetry experiments were performed at a scan rate of 100 mVs^{-1} using 0.1 M tetrabutylammoniumperchlorate (TBAP) as the supporting electrolyte in 1 mM solution of degassed dry dichloromethane. ~~Ag/Ag^+ was used as the reference electrode,~~ glassy carbon as the working electrode, and platinum wire as the counter electrode. The surface of working electrode was first polished with a 1 mm alumina slurry, and then with 0.3 mm an alumina slurry on a fine cloth. Next it was rinsed with deionized water and sonicated in water for 5 min. This polishing and ultrasonic treatment step were repeated twice.

Device Fabrication: The FTO (sahai VU glass) substrate was cleaned with detergent, purified water, and ultra-sonicated with ethyl alcohol in a water bath for 30 min. After solvent cleaning, the FTO substrates were cleaned in UV ozone chamber for 30 min. A bl-TiO_2 was deposited onto a cleaned FTO substrate by spray pyrolysis process using a 20mM titanium diisopropoxide bis(acetylacetonate) solution (Sigma-Aldrich) at 450 ˚C. Then, mp-TiO_2 films were deposited on bl-TiO_2 layer/FTO substrate using commercial TiO_2 paste (SC-HT040, ShareChem) by the spin coating method and were calcinated for 1 h at 500 ˚C in air atmosphere to remove the organic binder. The precursor solution for $(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$ perovskite was then spin-coated onto the mp-TiO_2/bl-TiO_2/FTO substrate by two consecutive steps at 1,000 r.p.m. for 5 s and then 5,000 r.p.m. for 20 s. During the second spin-coating (5,000 r.p.m.), 1 mL of ethyl ether was poured into the spinning precursor solution on the substrate. The precursor solution for $(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$ perovskite was prepared by dissolving 800 mg mL^{-1} of $FAPbI_3$, 30 mg mL^{-1} of $MAPbBr_3$ and 40 mg mL^{-1} of MACl in DMF/DMSO (8:2 v/v) mixed solvent. The intermediate phase substrate was placed on 150 ˚C hot plate for 10 min and 100 ˚C hot plate for 10 min. A p,p-Spiro OMeTAD solution was dissolved in chlorobenzene (CB) (91.4 mg mL^{-1}) with 35.65 µL4-tert-butylpyridine (tBP, 96%, Sigma-Aldrich), and 21.02 µL of lithium-bis(trifluoromethanesulfonyl) imide (Li-TFSi) solution in acetonitrile (ACN) (1.8 M), 9.14 µL of FK-209 solution in ACN (0.25 M). The Spiro-OMeTAD solution with additives was spin-coated onto the perovskite layer at 3000 r.p.m. for 30 s. Finally, Au metal electrode was deposited by thermal evaporation.

Measurement of solar cells: The current density-voltage (J-V) curves obtained using a solar simulator (Newport, Oriel Sol3A Class AAA) under illumination at AM 1.5 G with a source meter (Keithley 2420) at a size of 100 mA cm^{-2} and a calibrated Si-reference cell certified by NREL. The J-V curves of all devices were measured by masking the active area using a metal mask of 0.094 cm^2 and measured along the forward scan direction from -0.2 V to 1.5 V or the reverse scan direction from 1.5 V to -0.2 V. The scan speed and step voltage were fixed at 10mV and 100 mVs^{-1}, respectively. Measurement of external quantum efficiency (EQE) was performed using an IQE 200B system (ORIEL Instruments) under 100W xenon lamp irradiation. The light intensity in the EQE was calibrated by a silicon reference detector.

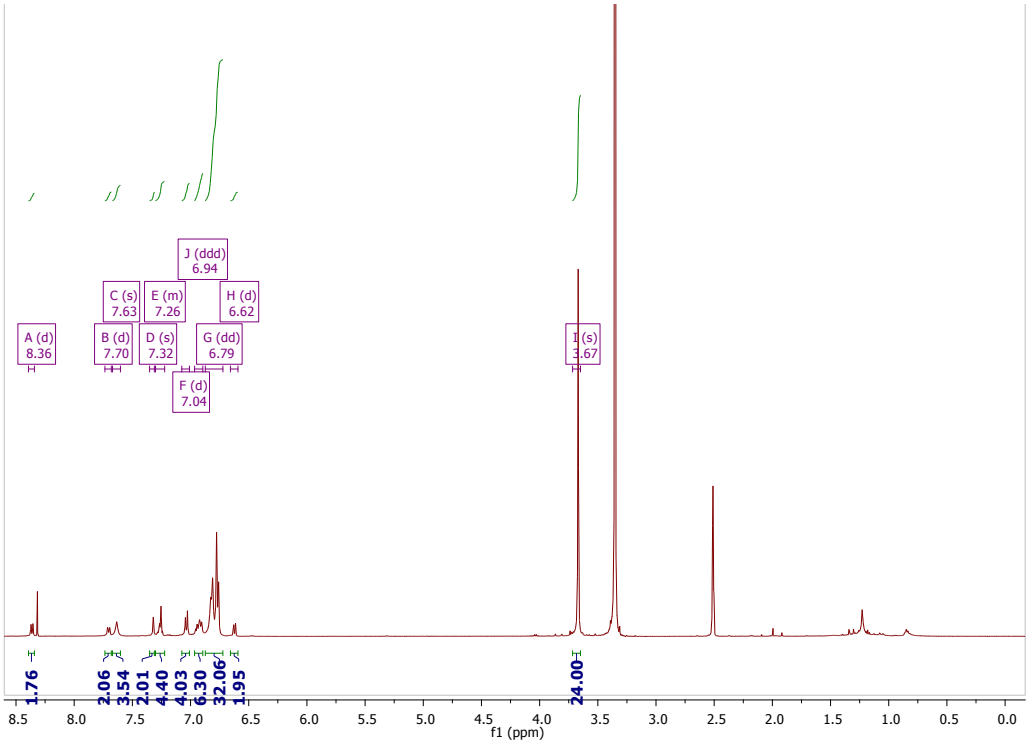

Figure S1. ^{1}H-NMR of SFXDAnCBZ.

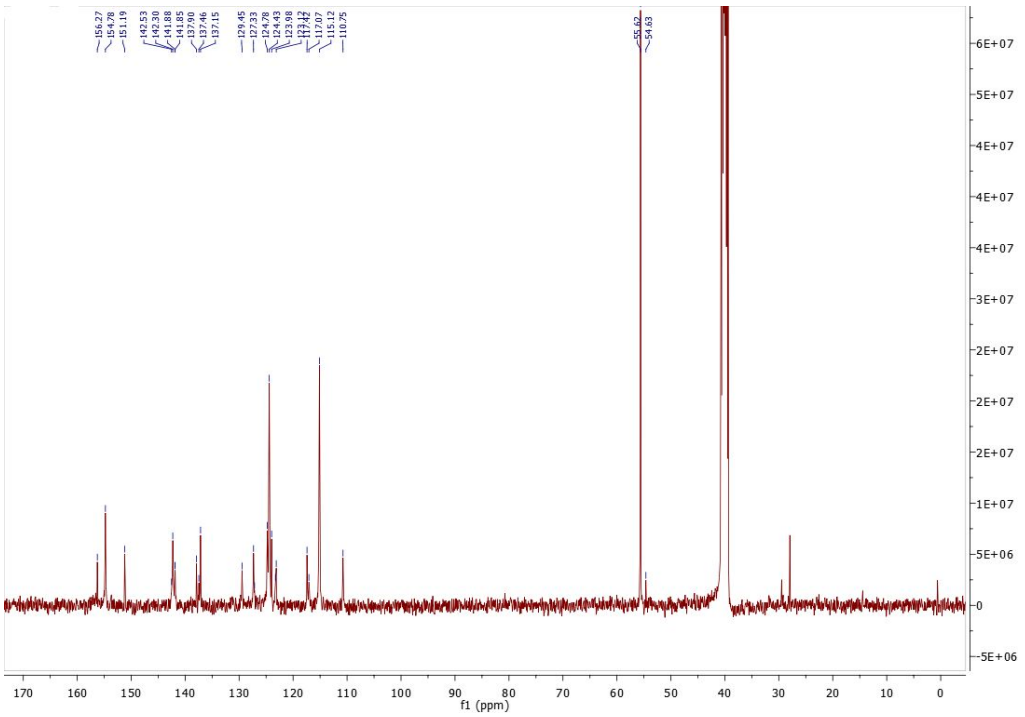

Figure S2. ^{13}C-NMR of SFXDAnCBZ.

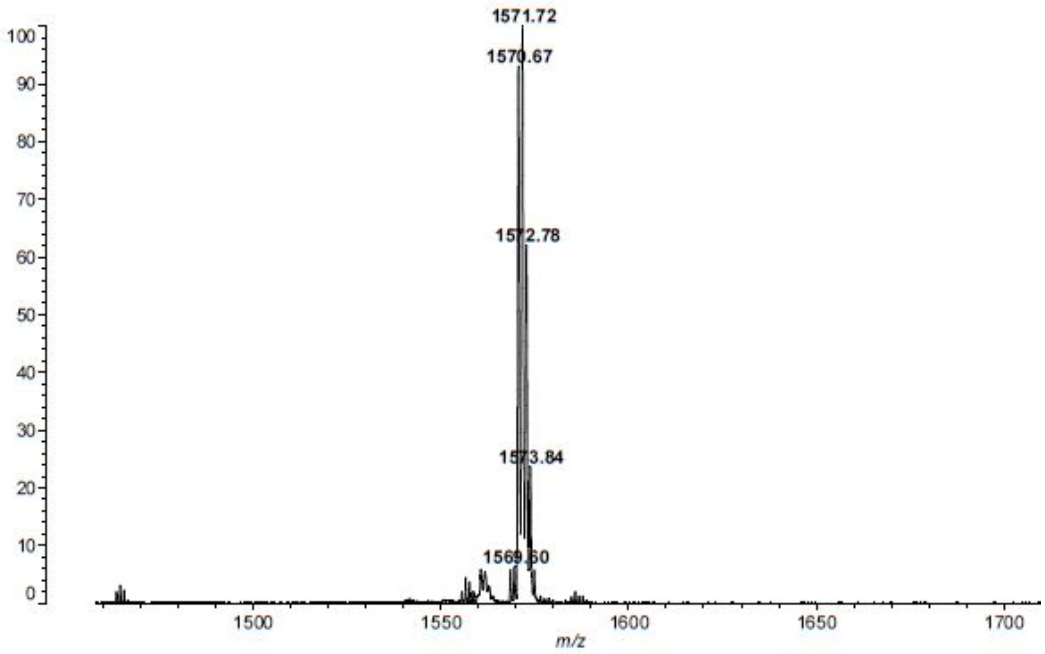

Figure S3. MALDI-TOF Mass spectrum of SFXDAnCBZ.

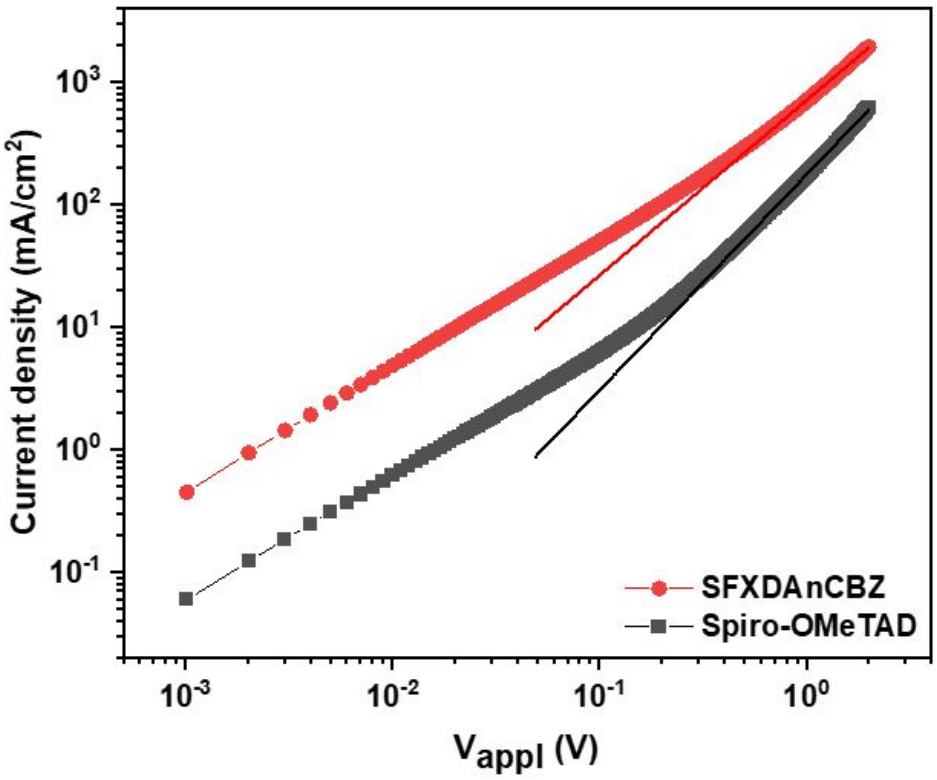

Figure S4. The space-charge-limited-current (SCLC) of hole-only devices with the configuration of FTO/PEDOT:PSS/Spiro-OMeTAd or SFXDAnCBZ (with Li-bis(trifluoromethanesulfonyl)imide) (Li-TFSi) and 4-*tert*-butylpyridine (*t*BP) as additives)/Au.

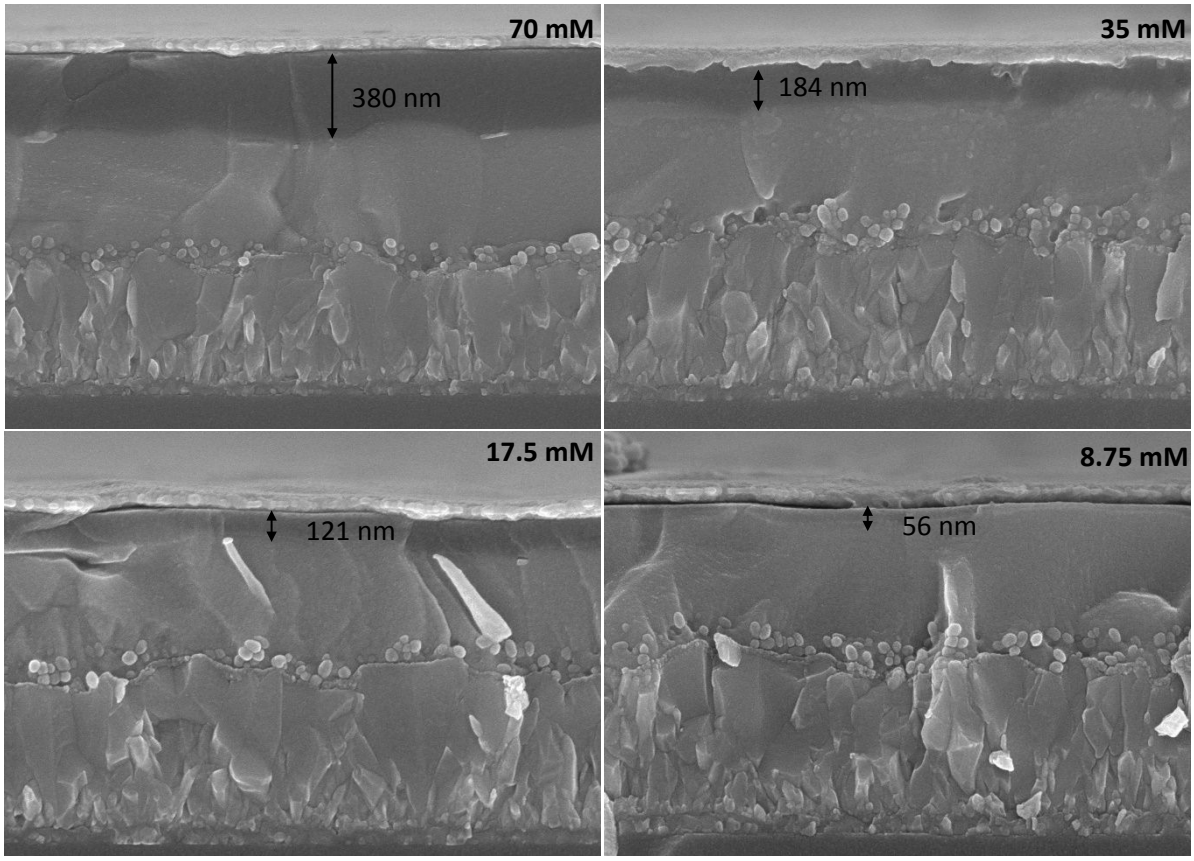

Figure S5. Cross-sectional scanning electron microscopy (SEM) images of perovskite solar cells fabricated by different concentration of SFXDAnCBZ.

Table S1. Summary of components obtained from the fitted plots of the corresponding spectra.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)
Perovskite	**3943.6**	**318.049**	**9532.6**	**71.76**	**143.8**
Spiro-OMeTAD	**25514.7**	**22.01**	**4585.76**	**58.37**	**27.5**
SFXDAnOCBZ	**4892.3**	**61.62**	**21664.8**	**24.17**	**31.0**

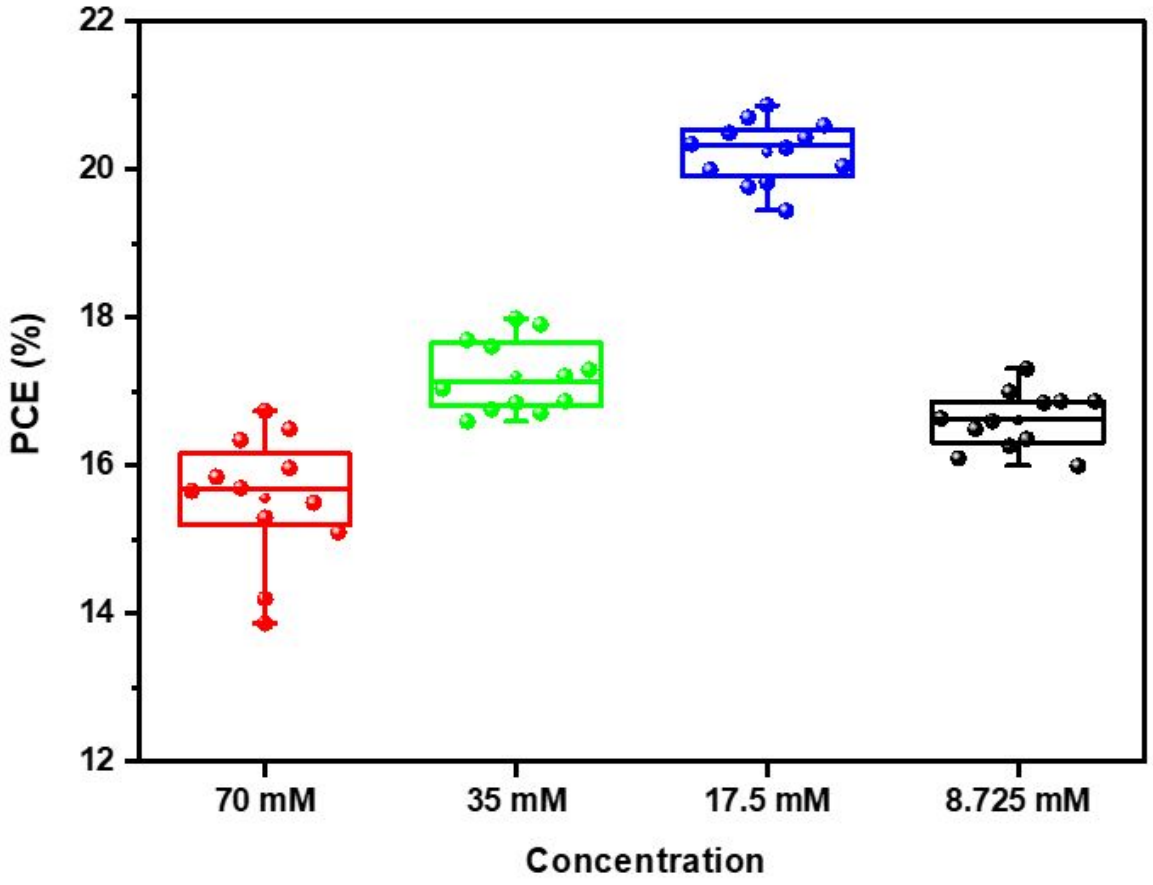

Figure S6. Power conversion efficiency (PCE) histogram of perovskite solar cells fabricated using different concentrations of SFXDAnCBZ.