Supporting Information

Fluorene-terminated Hole Transporting Material with Spiro[fluorene-9,9'-xanthene] Core for Perovskite Solar Cells

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Synthetic details

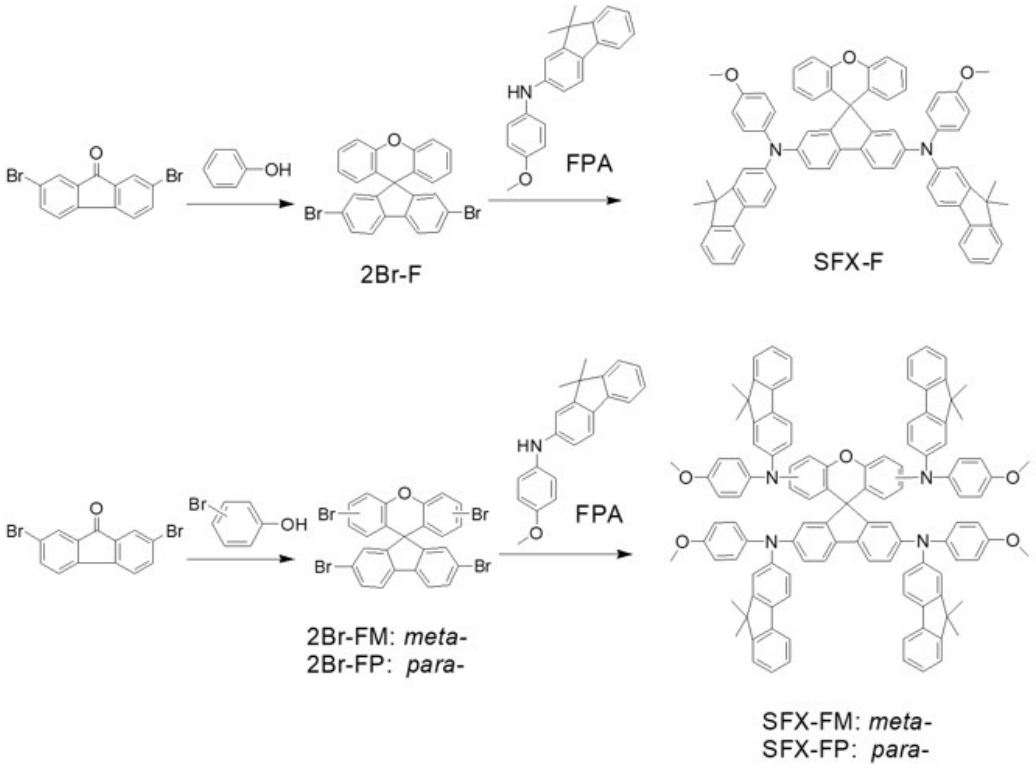
All the chemical reagents were used as received and employed directly without any further purification. The synthesis and characterization of compounds 2Br-F, 4Br-FM, 4Br-FP and FPA were followed those methods detailed in previous reports (Chiykowski et al., 2018; Jeon et al., 2018).

Measurements

The NMR spectroscopy test uses $CDCl_3$ or DMSO-d_6 as a solvent to obtain the ^1H and ^{13}C NMR spectra on a Bruker DPX. High-resolution mass spectrometry (HR-MS) was recorded with MS Bruker Daltonik Reflex III. UV-vis spectra of **SFX-F**, **SFX-FM** and **SFX-FP** in dichloromethane (CH_2Cl_2) were carried out by a CARY 5000 UV-vis near infrared spectrophotometer (Agilent, USA). Cyclic voltammetry (CV) curves were measured at a CHI 660D electrochemical workstation (Shanghai Chenhua Device Company, China). Differential scanning calorimetry (DSC) was used to collect T_g under nitrogen, the material was heated from 30 °C to 200 °C at a rate of 10 °C min^{-1}. The thermal decomposition (T_d) was tested by TGA8000 and scan to 700°C at 10°C min^{-1}. Atom force microscope (AFM) and the top view of scanning electron microscope (SEM) were used to obtained the surface morphology of hole transport layer and perovskite layer. The current density-voltage (*J-V*) curve in this study was measured by a 3A grade solar simulator (Newport, USA, 94043A) under AM1.5G illumination. The incident photon-to-electron conversion efficiency (IPCE) spectra was tested by the IPCE Measurement Tool kit (Newport, USA).

References

1. V. A. Chiykowski, Y. Cao, H. Tan, D. P. Tabor, E. H. Sargent, A. Aspuru-Guzik and C. P. Berlinguette, *Angew. Chemie - Int. Ed.*, 2018, **57,** 15529-15533.
2. N. J. Jeon, H. Na, E. H. Jung, T. Y. Yang, Y. G. Lee, G. Kim, H. W. Shin, S. Il Seok, J. Lee and J. Seo, *Nat. Energy*, 2018, **3**, 682-689.



Scheme S1. The synthetic routes of **SFX-F, SFX-FM** and **SFX-FP**

Synthesis of 2,7-dibromospiro[fluorene-9,9'-xanthene] (2Br-F): a mixture of 0.94 g phenol (10 mmol), 0.34 g 2,7-dibromo-9-fluorone (1 mmol) was heated to melt in a nitrogen atmosphere, followed by a drop of 0.26 mL methylsulfonic acid ($MeSO_3H$, d =1.48 g mL^{-1}, 385 mg, 4 mmol) and continued to react at 150 ℃ for 8 h. Cool the reaction solution to room temperature, then slowly add 80 mL methanol, with white solid precipitates. The filtered white solid was washed with a large amount of methanol to obtain 327 mg of white powder, yield 67%. ^{1}H NMR (600 MHz, DMSO-d_6) δppm= 8.00 (d, J = 8.2 Hz, 2H), 7.63 (dd, J = 8.2, 1.7 Hz, 20H), 7.31 – 7.28 (m, 4H), 7.21 (d, J = 1.7 Hz, 2H), 6.88 (ddd, J = 8.1, 6.0, 2.4 Hz, 2H), 6.29 (d, J = 7.3 Hz, 2H).

Synthesis of 2,2',7,7'-tetrabromospiro[fluorene-9,9'-xanthene] (4Br-FM)： Compound was prepared following a modified literature procedure for 4Br-F. ^{1}H NMR (600 MHz, $CDCl_3$) δppm= 7.62 (d, J = 8.2 Hz, 2H), 7.52 (dd, J = 8.2, 1.7 Hz, 2H), 7.41 (d, J = 2.0 Hz, 2H), 7.21 (d, J = 1.7 Hz, 2H), 6.96 (dd, J = 8.4, 2.0 Hz, 2H), 6.23 (d, J = 8.4 Hz, 2H).

Synthesis of 2,3',6',7-tetrabromospiro[fluorene-9,9'-xanthene] (4Br-FP)： Compound was prepared following a modified literature procedure for 4Br-F. ^{1}H NMR (600 MHz, $CDCl_3$) δppm= 7.65 (d, J = 8.2 Hz, 2H), 7.55 (dd, J = 8.1, 1.7 Hz, 2H), 7.34 (dd, J = 8.8, 2.4 Hz, 2H), 7.21 (d, J =

1.6 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.42 (d, J = 2.3 Hz, 2H).

***N*2,*N*7-dis(9,9-dimethyl-9H-fluoren-2-yl)-*N*2,*N*7-dis(4-methoxyphenyl)-Spiro[fluorene-9,9-xanthene]-2,7-diamine (SFX-F):** 140 mg N-(p-methoxyphenyl)-N′-(9,9′-dimethylfluoren-2-yl)amino (0.44 mmol), 98 mg 2Br-F (0.2 mmol), 15 mg of $Pd_2(dba)_3$ (0.016 mmol), 5 mg tributylphosphine tetrafluoroborate (0.016 mmol)and 113 mg t-BuOK (1 mmol) were dissolved in 10 mL of dried toluene and heated to 110 ℃ in a nitrogen atmosphere. Then the reaction mixture was stirred at reflux for 24 h under 110 ℃. The reaction solution was cooled to room temperature and then poured into water for 10 min. The organic phase was extracted with DCM and dried with anhydrous $MgSO_4$ to obtain the crude product after removing the solvent. The crude product was isolated and purified with a column of chromatography (v:v, petroleum ether : ethyl acetate = 15 : 1) to obtain 100 mg of brown solid with a yield of 53 %. ^{1}H NMR (600 MHz, DMSO-d_6) δppm = 7.71 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 7.4 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 7.23 – 7.20 (m, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 7.3 Hz, 4H), 6.98 (s, 2H), 6.96 (d, J = 7.7 Hz, 2H), 6.88 (d, J = 8.9 Hz, 4H), 6.84 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 6.67 (s, 2H), 6.54 (d, J = 7.9 Hz, 2H), 3.73 (s, 6H), 1.11 (s, 12H). ^{13}C NMR (151 MHz, DMSO-d_6) δppm = 156.57, 156.08, 154.90, 153.39, 150.72, 147.62, 147.09, 140.05, 138.63, 133.36, 133.20, 128.87, 127.91, 127.76, 127.40, 126.88, 124.85, 124.14, 122.96, 122.21, 122.06, 121.33, 120.95, 119.80, 118.08, 117.01, 115.46, 55.65, 46.62, 27.17. HRMS (MALDI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{69}H_{54}N_2O_3$, 959.4213; found, 959.4218.

***N*2,*N*2′,*N*7,*N*7′-tetrakis(9,9-dimethyl-9H-fluoren-2-yl)-*N*2,*N*2′,*N*7,*N*7′-tetrakis(4-methoxyphenyl)-Spiro[fluorene-9,9-xanthene]-2,2′,7,7′-tetraamine (SFX-FM):** Compound was prepared following a modified literature procedure for SFX-F. ^{1}H NMR (600 MHz, DMSO-d_6) δppm= 7.66 (m, 8H), 7.59 (d, J = 8.9 Hz, 2H), 7.44 (s, 4H), 7.27 (s, 4H), 7.22 (t, J = 7.3 Hz, 4H), 7.11 (s, 4H), 7.04 (d, J = 8.7 Hz, 4H), 7.00 (d, J = 8.4 Hz, 4H), 6.94 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 8.6 Hz, 8H), 6.80 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 12.0 Hz, 4H), 6.48 (d, J = 8.9 Hz, 2H), 6.34 (d, J = 8.5 Hz, 2H), 6.23 (s, 2H), 3.73 (s, 6H), 3.70 (s, 6H), 1.27 (s, 12H), 1.22 (s, 12H). ^{13}C NMR (151 MHz, DMSO-d_6) δppm = 156.85, 156.51, 155.68, 155.16, 154.93, 153.53, 151.53, 148.31, 146.56, 140.18, 139.54, 139.14138.57, 134.43, 133.32, 133.28, 128.25, 128.06, 127.63, 127.43, 127.11, 123.77, 123.01, 122.95, 121.96, 121.36, 121.29, 120.82, 120.55, 119.93, 119.75, 118.96,

118.18, 117.22, 115.80, 115.49, 115.36, 79.61, 55.63, 55.58, 46.77, 46.69, 27.31, 27.17. HRMS (MALDI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{113}H_{92}N_4O_5$, 1585.7146; found, 1585.7144.

***N2,N3',N6',N7*-tetrakis(9,9-dimethyl-9H-fluoren-2-yl)-*N2,N3',N6',N7*-tetrakis(4-methoxyphenyl)-Spiro[fluorene-9,9-xanthene]-2,3',6',7-tetraamine (SFX-FP):** Compound was prepared following a modified literature procedure for SFX-F. ^{1}H NMR (600 MHz, DMSO-d_6) δppm= 7.69 (dd, J = 7.2, 3.5 Hz, 4H), 7.62 (t, J = 8.4 Hz, 4H), 7.51 (t, J = 7.5 Hz, 4H), 7.44 (d, J = 8.3 Hz, 2H), 7.37 – 7.23 (m, 8H), 7.11 (d, J = 1.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 3.3 Hz, 4H), 6.98 (d, J = 3.4 Hz, 4H), 6.96 (d, J = 1.8 Hz, 2H), 6.94 (s, 2H), 6.92 (s, 4H), 6.89 (d, J = 1.9 Hz, 4H), 6.83 (dd, J = 8.8, 2.6 Hz, 2H), 6.80 – 6.77 (m, 2H), 6.76 (dd, J = 8.5, 1.4 Hz, 4H), 6.39 (d, J = 2.6 Hz, 2H), 3.79 (s, 6H), 3.77 (s, 6H), 1.30 (s, 12H), 1.27 (s, 12H). ^{13}C NMR (151 MHz, DMSO-d_6) δppm = 156.48, 156.23, 154.88, 152.66, 154.65, 153.32, 153.24, 147.49, 147.40, 147.17, 146.82, 143.23, 140.17, 140.10, 138.77, 138.65, 133.25, 133.09, 132.54, 127.55, 127.37, 127.01, 126.89, 126.70, 125.91, 124.09, 122.99, 122.42, 121.74, 121.37, 121.13, 120.94, 120.36, 119.77, 119.67, 118.09, 116.76, 115.53, 115.33, 55.61, 55.59, 46.66, 46.60, 27.32. HRMS (MALDI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{113}H_{92}N_4O_5$, 1585.7146; found, 1585.7153.

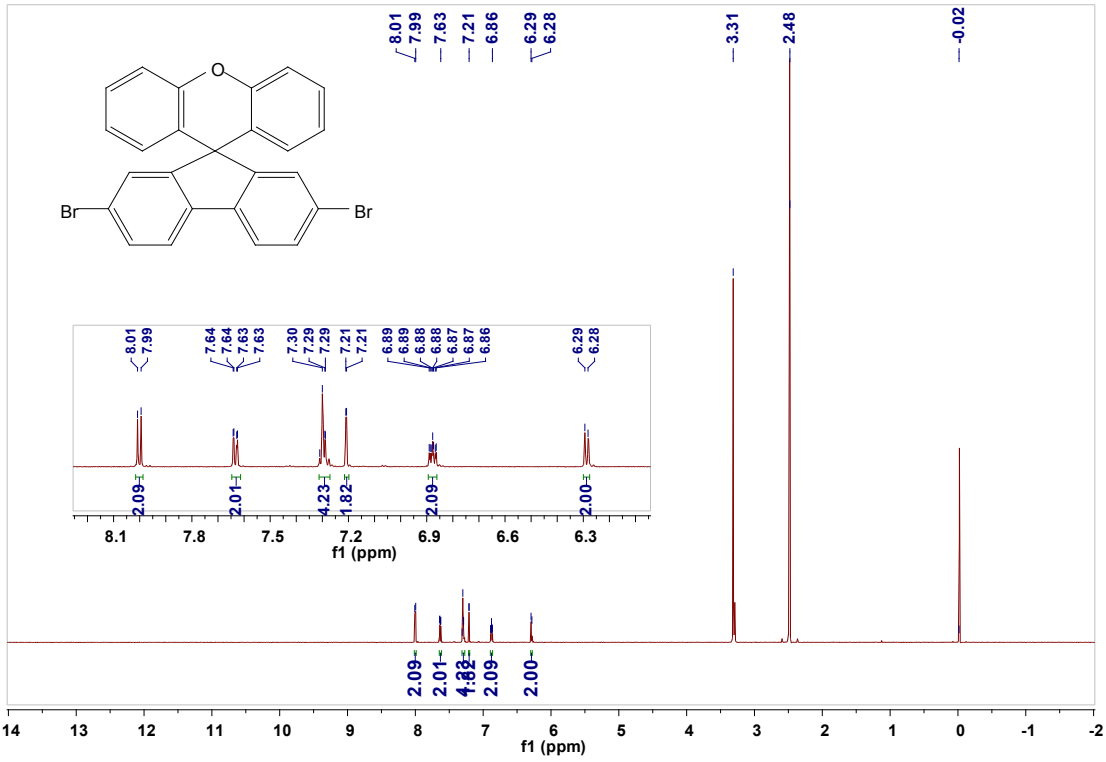


Fig. S1. ^{1}H NMR spectrum of **2Br-F**

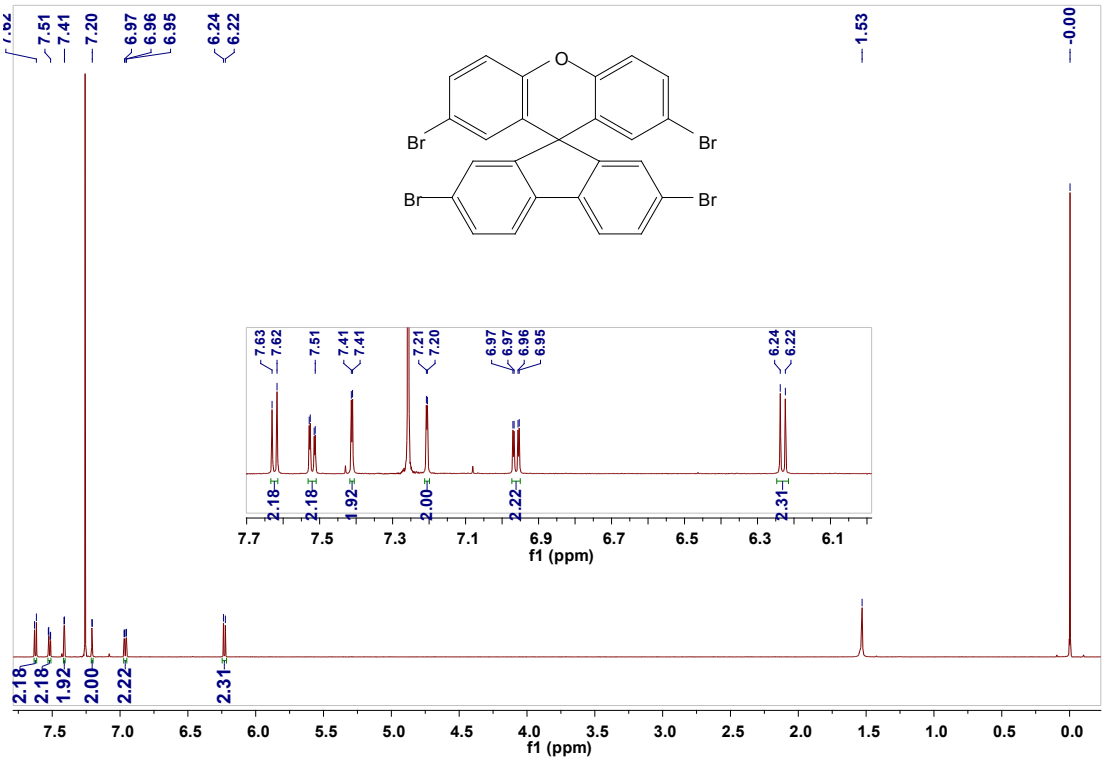


Fig. S2. ^{1}H NMR spectrum of **2Br-FM**

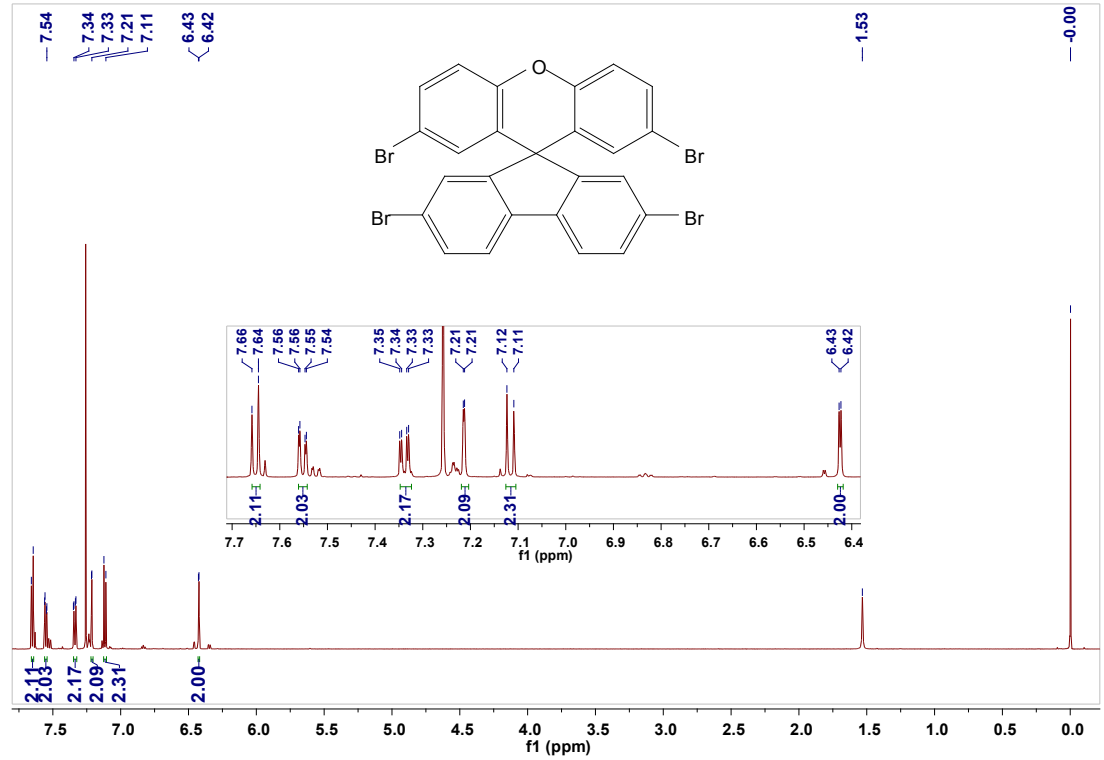


Fig. S3. ^{1}H NMR spectrum of **2Br-FP**

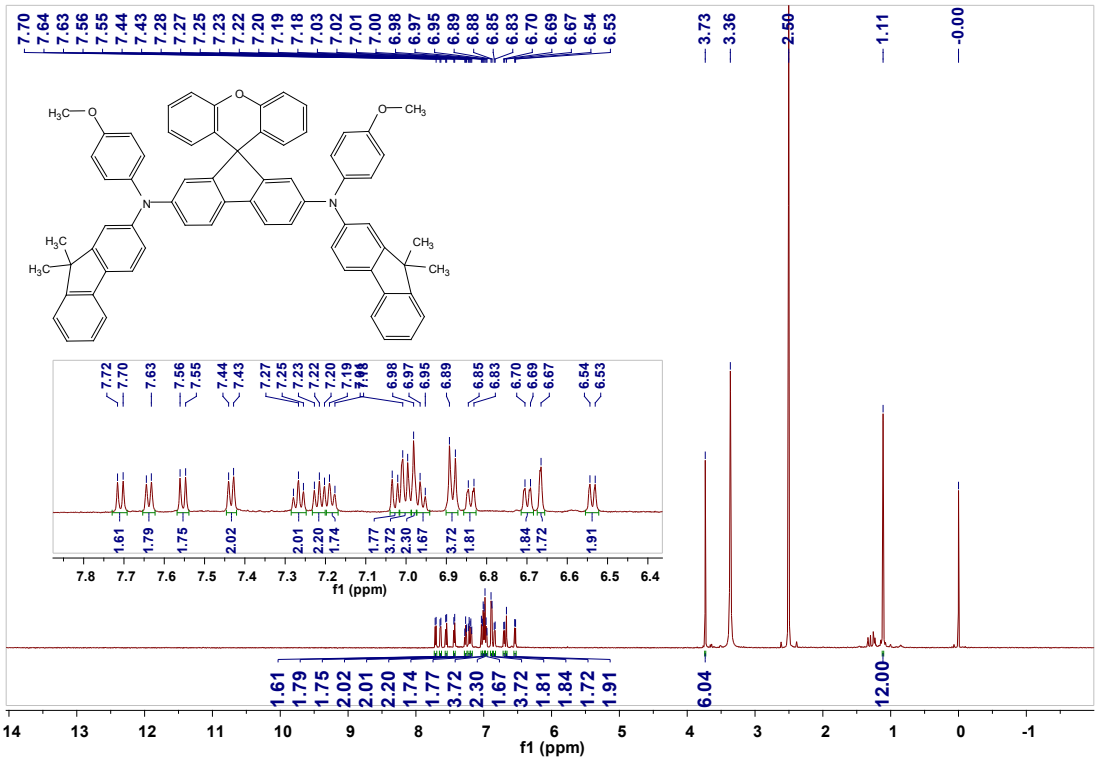


Fig. S4. ^{1}H NMR spectrum of **SFX-F**

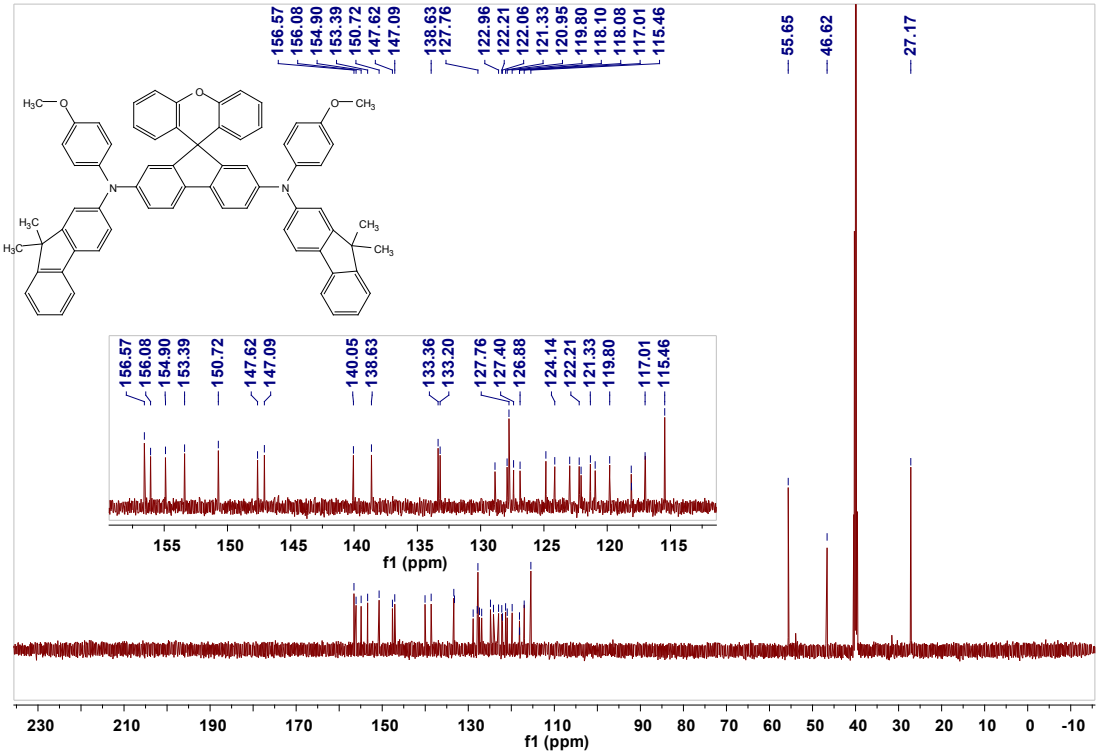


Fig. S5. ^{13}C NMR spectrum of **SFX-F**

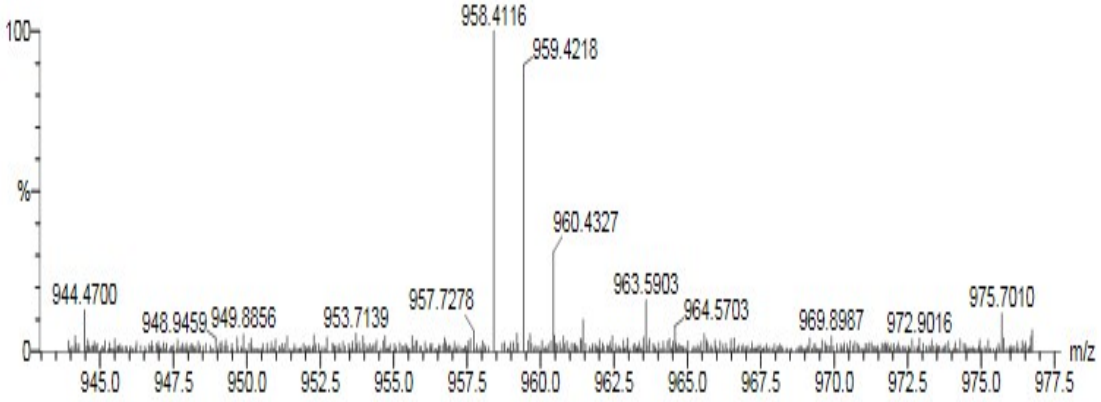


Fig. S6. MS spectrum of **SFX-F**

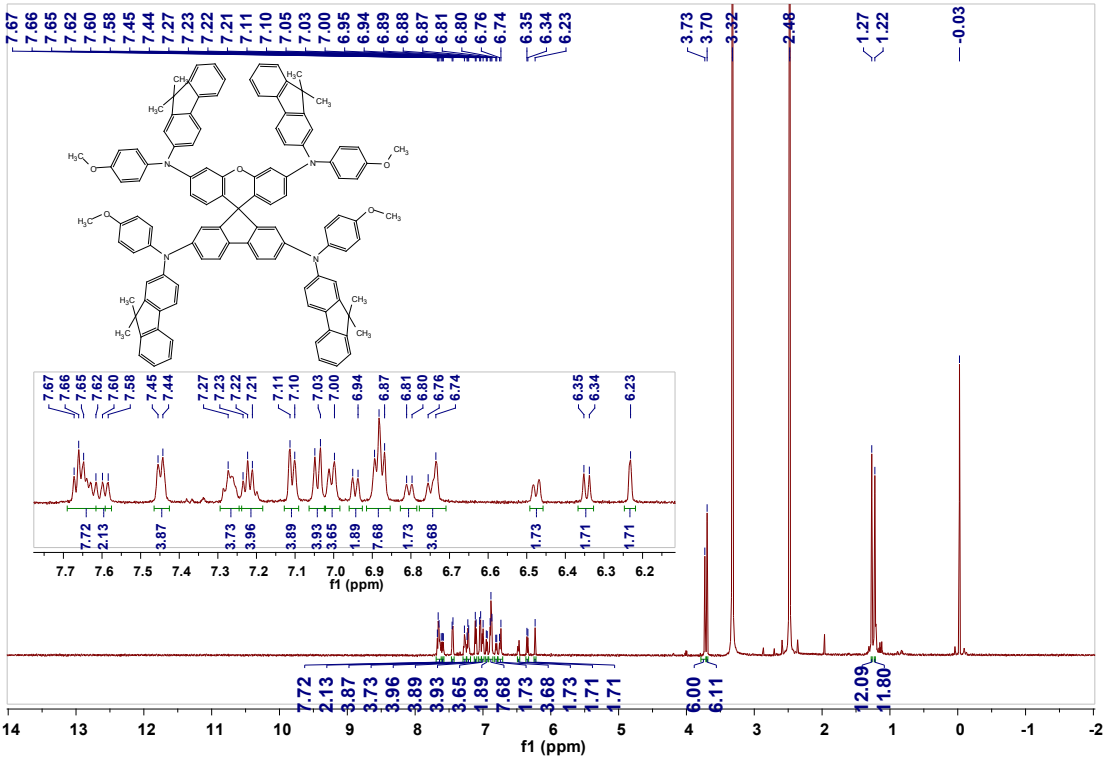


Fig. S7. ^{1}H NMR spectrum of **SFX-FM**

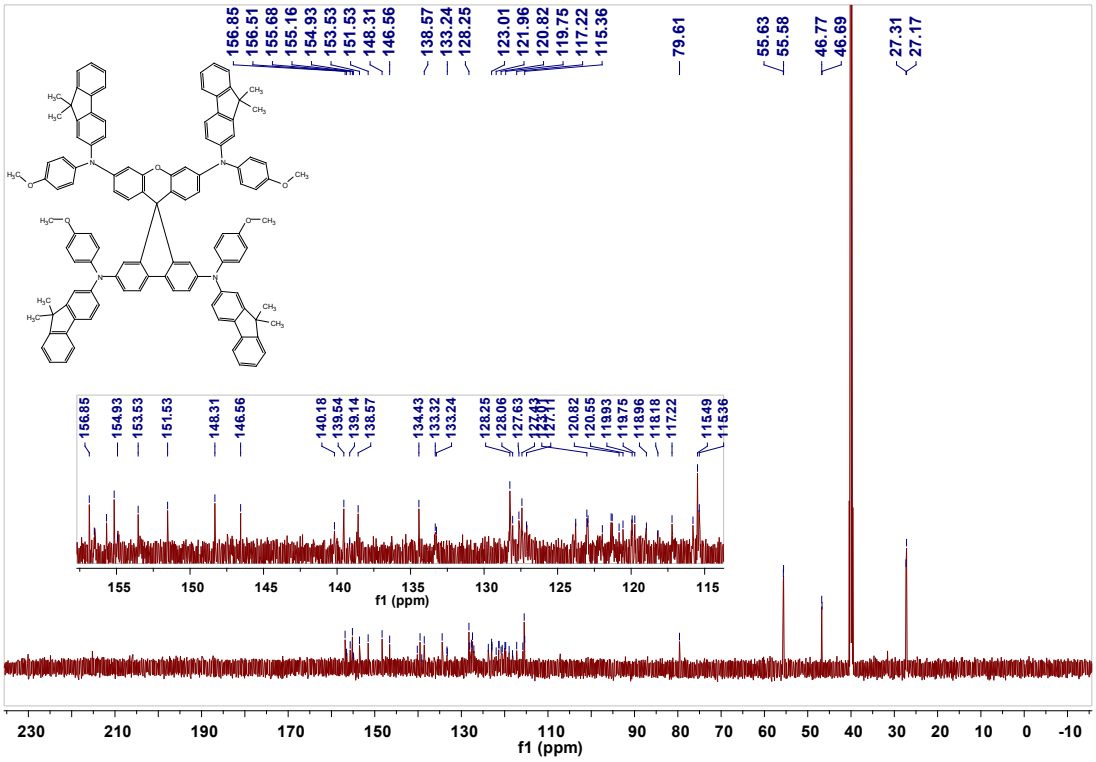


Fig. S8. ^{13}C NMR spectrum of **SFX-FM**

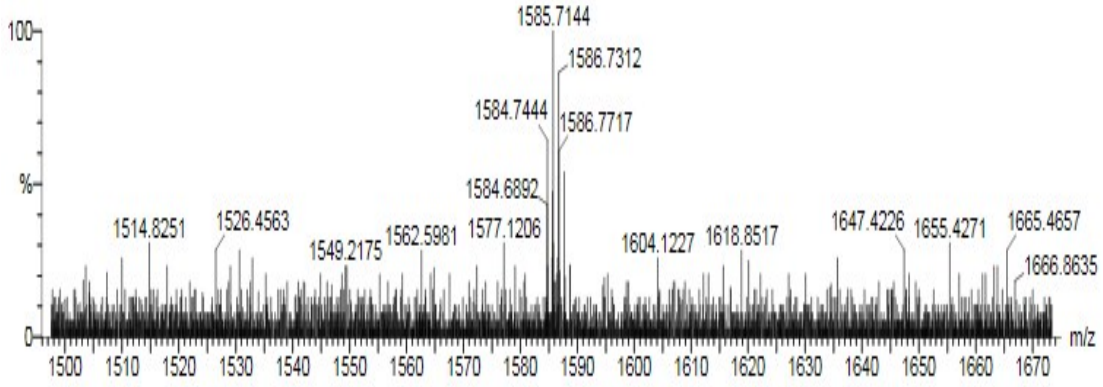


Fig. S9. MS spectrum of **SFX-FM**

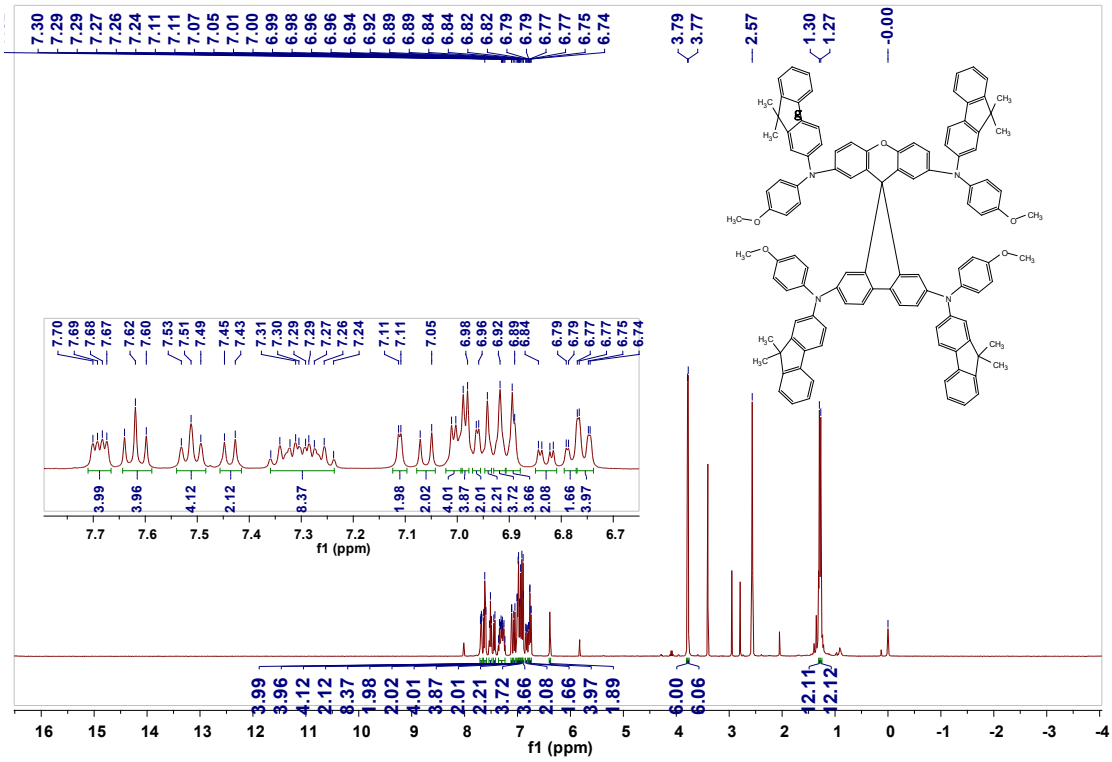


Fig. S10. ^{1}H NMR spectrum of **SFX-FP**

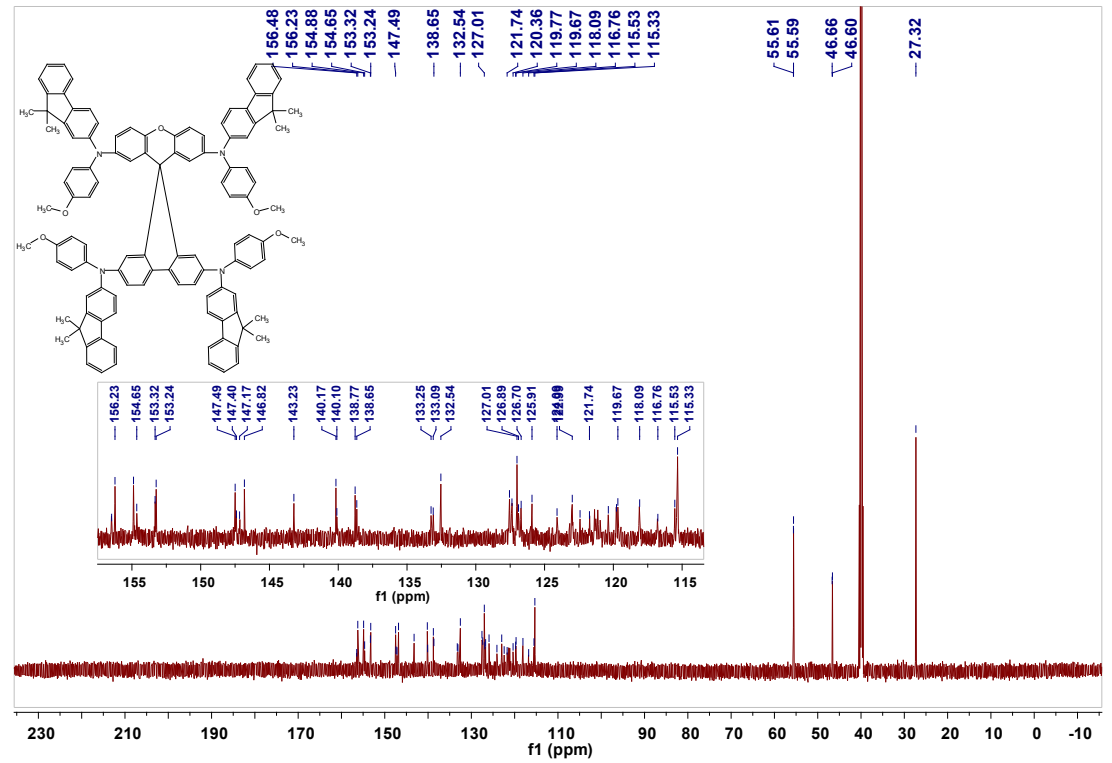


Fig. S11. ^{13}C NMR spectrum of **SFX-FP**

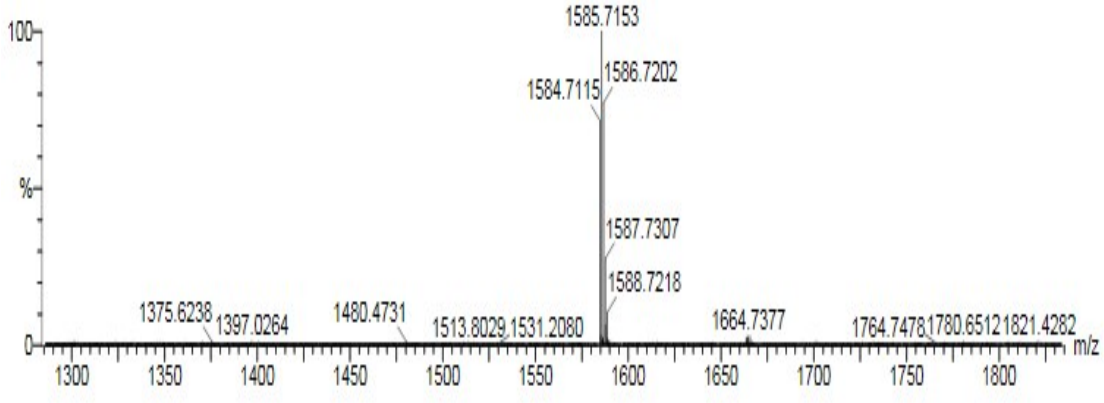


Fig. S12. MS spectrum of **SFX-FP**

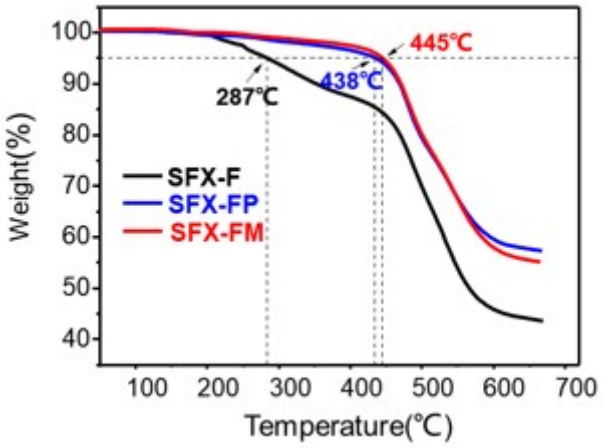


Fig. S13. TGA thermograms of **SFX-F**, **SFX-FM** and **SFX-FP** at a scan rate of 10 °C/min.

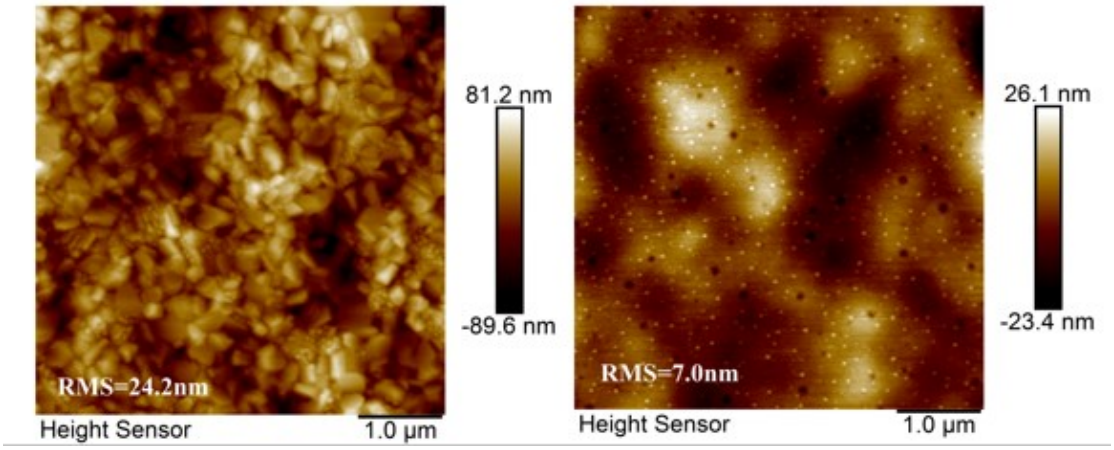


Fig. S14. AFM images of FTO/TiO_2/perovskite and FTO/TiO_2/perovskite/*spiro*-OMeTAD.

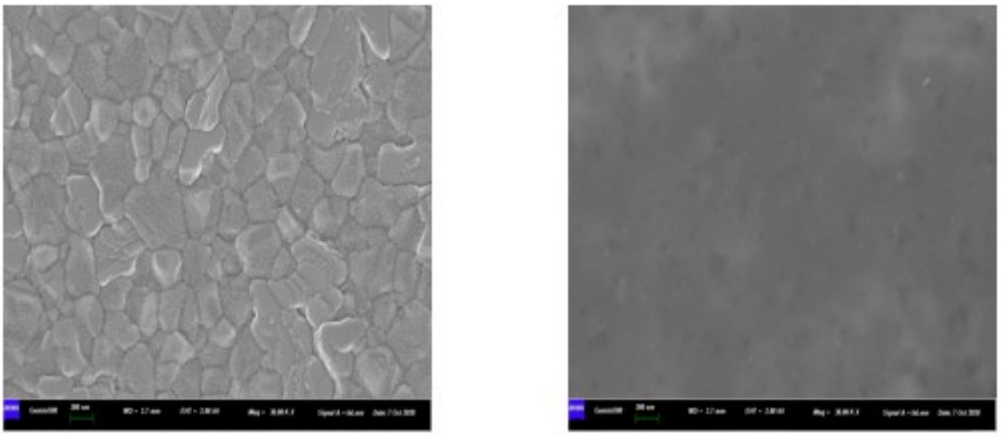


Fig. S15. SEM images of FTO/TiO_2/perovskite and FTO/TiO_2/perovskite/*spiro*-OMeTAD.

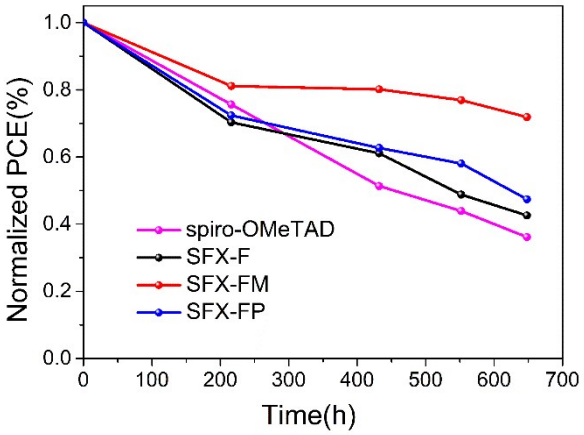


Fig. S16. E□ciency evolution of the PSC devices in a humidity (30 RH) environment at 25 °C for 648 h, under AM 1.5 illumination of 100 mW cm^{-2}.

Table S1 Materials quantities and cost evaluation for the synthesis of **SFX-F**

Chemical	Weight Reagent g/g	Weight Solvent g/g	Weight Workup g/g	Price of Chemical $/kg	Chemical Cost $	Target product $/g
2,7-Dibromo-9-fluorenone	0.34			3851	1.31	
$MeSO_3H$		0.385		120.5	0.05	
Phenol	0.94			18.23	0.02	
Methanol			100	2.21	0.22	**Product** 20.91
2-Bromo-9,9'-dimethylfluorene	0.68			2053	1.4	
4-Methoxyaniline	0.37			123.77	0.05	
Toluene		50		6.25	0.18	

Ethyl acetate			1100	3.47	2.42	
Petroleum ether			1500	3	4.41	
Silicone powder			400	4.93	2.45	
Tri-tert-butylphosphine	0.05			34118	1.7	
Tri-tert-butylphosphonium tetrafluoroborate	0.005			82671	0.4	
Sodium tert-butoxide	0.48 g			383.84	0.18	
Potassium tert-butoxide	0.113			704.64	0.08	
$Pd_2(dba)_3$	0.09			55351	4.98	
CH_2Cl_2			600	2.31	1.36	

Table S2 Materials quantities and cost evaluation for the synthesis of **SFX-FM**

Chemical	**Weight Reagent g/g**	**Weight Solvent g/g**	**Weight Workup g/g**	**Price of Chemical $/kg**	**Chemical Cost $**	**Target product $/g**
2,7-Dibromo-9-fluorenone	0.34			3851	1.31	
$MeSO_3H$		0.385		120.5	0.05	
3-Bromophenol	1.73			642.83	1.12	
2-Bromo-9,9'-dimethylfluorene	0.68			2053	1.4	
4-Methoxyaniline	0.37			123.77	0.05	
Toluene		50		6.25	0.18	
Ethyl acetate			1100	3.47	2.42	
Petroleum ether			1500	3	4.41	**Product** 23.97
Silicone powder			400	4.93	2.45	
Tri-tert-butylphosphine	0.05			34118	1.7	
Tri-tert-butylphosphonium tetrafluoroborate	0.007			82671	0.58	
Sodium tert-butoxide	0.48 g			383.84	0.18	
Potassium tert-butoxide	0.17			704.64	0.12	
$Pd_2(dba)_3$	0.12			55351	6.64	
CH_2Cl_2			600	2.31	1.36	

Table S3 Materials quantities and cost evaluation for the synthesis of **SFX-FP**

Chemical	Weight Reagent g/g	Weight Solvent g/g	Weight Workup g/g	Price of Chemical $/kg	Chemical Cost $	Target product $/g
2,7-Dibromo-9-fluorenone	0.34			3851	1.31	
$MeSO_3H$		0.385		120.5	0.05	
4-Bromophenol	1.73			385	0.67	
2-Bromo-9,9'-dimethylfluorene	0.68			2053	1.4	
4-Methoxyaniline	0.37			123.77	0.05	
Toluene		50		6.25	0.18	
Ethyl acetate			1100	3.47	2.42	
Petroleum ether			1500	3	4.41	**Product**
Silicone powder			400	4.93	2.45	23.52
Tri-tert-butylphosphine	0.05			34118	1.7	
Tri-tert-butylphosphonium tetrafluoroborate	0.007			82671	0.58	
Sodium tert-butoxide	0.48 g			383.84	0.18	
Potassium tert-butoxide	0.17			704.64	0.12	
$Pd_2(dba)_3$	0.12			55351	6.64	
CH_2Cl_2			600	2.31	1.36	