Supplementary Information

Molecular modification of spiro[fluorene-9,9'-xanthene]-based dopant-free hole transporting materials for perovskite solar cells

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1. Materials, methods and synthesis of SP-Naph

2,7-Dibromo-9-fluorenone and 2-bromo-6-methoxynaphthalenewere purchased from TCI chemicals;4-methoxyanilne, tri-*tert*-butylphosphonium tetrafluoroborate ($P(^tBu)_3HBF_4$), sodium *tert*-butoxide, and tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), was purchased from Sigma-Aldrich chemicals. All reactions were carried out in a nitrogen atmosphere. The toluene solvent used in this work was distilled prior to use in the related reaction.

^1H and ^{13}C NMR spectra were obtained using a Bruker 400- or 500-MHz spectrometer using TMS as standard. Matrix-assisted laser desorption and ionization was used to describe the final molecules (MALDI-TOF). The absorption spectrum in solution was recorded on a Scimadzu UV-1800 model spectrophotometer.

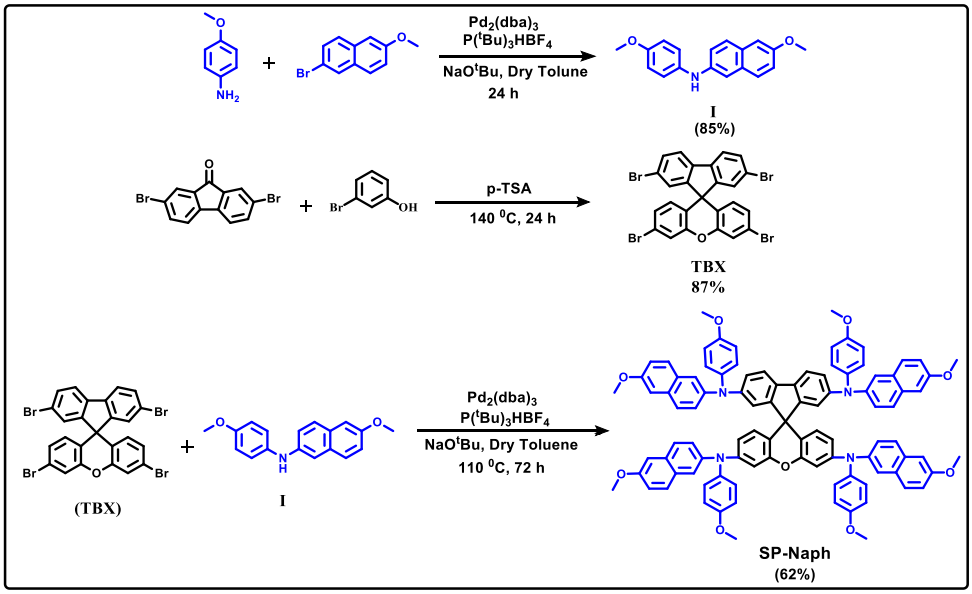
The synthetic procedure of the target compound requires 3 steps using commercially available starting materials, as shown in Scheme S1. 2,3',6',7-tetrabromospiro[fluorene-9,9'-xanthene] (TBX) was synthesized by a one-pot reaction between 2,7-Dibromo-9-fluorenone and 3-bromophenol.[1] The 6-methoxy-N-(4-methoxyphenyl)naphthalen-2-amine (I) was reacted with TBX via the Buchwald-Hartwing C-N cross-coupling reaction to afford the target compound **SP-Naph. SP-Naph** possesses good solubility in the common organic solvents Toluene, Ethyl acetate (EtOAc), Tetrahydrofuran (THF), Dichloromethane (DCM), Acetonitrile (ACN), and Dimethylformamide (DMF).

6-methoxy-N-(4-methoxyphenyl)naphthalen-2-amine (I): To a 100 mL two-neck round-bottomed flask charged with 4-Methoxyaniline (2 g, 16.23 mmol), 2-bromo-6-methoxynaphthalene (4.19 g, 17.70 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (94.17 mg, 0.32mmol), and sodium *tert*-butoxide (3.11 g, 32.46 mmol) were dissolved in dry toluene (30 mL). The reaction mixture was purged with nitrogen gas upto 30 minutes, After purged with nitrogen gas, 147.70 mg of tris(dibenzylideneacetone)dipalladium(0) (0.16 mmol) was added to reaction mixture, then purged again with nitrogen gas for 20 min. Then the reaction mixture was heated to reflux overnight. The crude mixture was poured into water and extracted with ethyl acetate. The combined organic layer was dried with anhydrous Na_2SO_4. The solvents were removed by rotary evaporator and purified by column chromatography on silica gel (100 – 200 mesh) with hexane and ethyl acetate (9:1, v/v) as an eluent to obtain **I** as a brown solid (3.85 g, 84.9% yield). **^1H NMR (400 MHz, DMSO-d_6),δ (ppm):** δ 7.93 (s, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H), 7.17 (dd, J = 6.8, 4.2 Hz, 2H), 7.12 (d, J = 8.9 Hz, 2H), 7.03 (dd, J = 8.9, 2.6 Hz, 1H), 6.90 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H), 3.73 (s, 3H).**^{13}C NMR (400 MHz, DMSO-d_6), δ (ppm):** δ 155.41, 154.22 , 141.59, 136.92,

130.26, 128.99, 128.13, 127.94, 120.61, 120.23, 118.97, 115.07, 108.23, 106.63, 55.70, 55.50. **LCMS-MS** calcd for $C_{18}H_{17}NO_2$ $[M+H]^+$ m/z 279.12; found 280.

2,3',6',7-tetrabromospiro[fluorene-9,9'-xanthene] (TBX): Compounds 2,7-dibromo-9-fluorenone (50mg, 0.148 mmol), 3-bromophenol (0.15 mL,1.48 mmol), and p-toluene sulfonic acid (58mg, 0.0591mmol) were added in a round bottom flask. The reaction mixture was heated to 140°C then stirred for 24 h under nitrogen atmosphere. The extent of a reaction was monitored by TLC. After completion of a reaction the reaction mixture cooled to room temperature then 20 mL methanol was added to a reaction mixture and stirred for 30 minutes. Then reaction mixture was filtered to obtain a white solid (87% yielded, 83.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.1 Hz, 1H), 7.52 (dd, J = 8.1, 1.8 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.21 (d, J = 1.7 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.23 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.75, 151.25, 137.50, 131.84, 129.24, 128.92, 127.28, 122.66, 121.95, 121.75, 121.64,120.34, 53.36. **MALDI-TOF:** (m/z) (calcd for $[C_{25}H_{12}Br_4O]^+$ 647.758 found 647.839

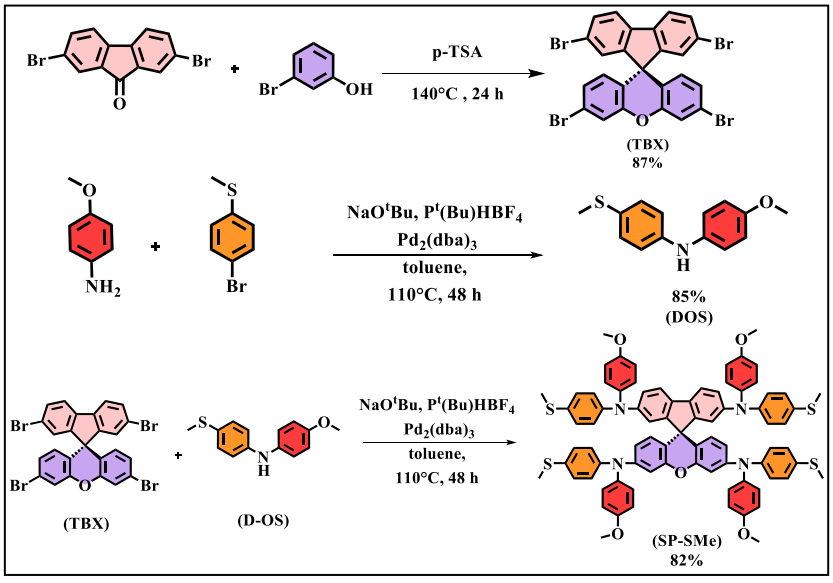
N2,N3',N6',N7-tetrakis(6-methoxynaphthalen-2-yl)-N2,N3',N6',N7-tetrakis(4-methoxyphenyl)spiro[fluorene-9,9'-xanthene]-2,3',6',7-tetraamine (SP-Naph): In a 50 mL Schlenk-tube was charged with2,3',6',7-tetrabromospiro[fluorene-9,9'-xanthene] (TBX) (200 mg, 0.308 mmol), 6-methoxy-N-(4-methoxyphenyl)naphthalen-2-amine (**I**) (517.29 mg, 1.851 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (27 mg, 0.092 mmol) and sodium *tert*-butoxide (178 mg, 1.851 mmol) dissolved in dry toluene (20 mL). The reaction mixture was purged with nitrogen gas upto 30 minutes, then tris (dibenzylideneacetone) dipalladium(0) (56 mg, 0.062 mmol) were added and the reaction mixture was heated at 100 °C for 3 days. After removal of solvent, the reaction mixture was extracted with DCM. The organic layer was washed with brine solution, and then dried over Na_2SO_4. The solvents were removed by rotary evaporator and purified by column chromatography on silica gel (100 – 200 mesh) with hexane and ethyl acetate as eluent to afford compound **SP-Naph** as color solid (275 mg, 62%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 13.9, 8.9 Hz, 4H), 7.46 (dd, *J* = 9.1, 2.1 Hz, 4H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.29 (dd, *J* = 12.4, 2.1 Hz, 4H), 7.18 (ddd, *J* = 8.9, 6.7, 2.3 Hz, 4H), 7.04 (dt, *J* = 9.1, 6.5 Hz, 18H), 6.92 (dd, *J* = 8.2, 2.1 Hz, 2H), 6.81 (dd, *J* = 9.0, 1.4 Hz, 8H), 6.57 (dd, *J* = 8.6, 2.4 Hz, 2H), 6.49 (d, *J* = 2.3 Hz, 2H), 6.43 (d, *J* = 8.6 Hz, 2H), 3.88 (d, *J* = 7.8 Hz, 12H), 3.79 (d, *J* = 10.9 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.92, 155.68, 137.43, 131.27, 129.48, 127.94, 127.88, 126.55, 125.69, 124.06, 121.79, 119.86, 119.04, 117.34, 116.65, 115.09, 114.78, 112.33, 110.67, 108.53, 106.08, 55.65, 55.35. **MALDI TOF-MS [M]+**calcd for $C_{97}H_{76}N_4O_9$ $[M+H]^+$ m/z 1441.56; found 1442.86.



Scheme S1. Synthetic routes for **SP-Naph**.

2. Materials, methods and synthesis of SP-SMe

The synthetic procedure of the target compound requires 3 steps using commercially available starting materials, as shown in Scheme S2. Compound TBX was synthesized according to the process of DOS and SP-SMe synthesized according to the process given Rakstys et al.[2]



Scheme S2. Synthetic pathway for **SP-SMe**.

2,3',6',7-tetrabromospiro[fluorene-9,9'-xanthene] (TBX): Compounds 2,7-dibromo-9-fluorenone (50mg, 0.148 mmol), 3-bromophenol (0.15 mL,1.48 mmol), and p-toluene sulfonic acid (58mg, 0.0591mmol) were added in a round bottom flask. The reaction mixture was heated

to 140°C then stirred for 24 h under nitrogen atmosphere. The extent of a reaction was monitored by TLC. After completion of a reaction the reaction mixture cooled to room temperature then 20 mL methanol was added to a reaction mixture and stirred for 30 minutes. Then reaction mixture was filtered to obtain a white solid (87% yielded, 83.4 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, J = 8.1 Hz, 1H), 7.52 (dd, J = 8.1, 1.8 Hz, 1H), 7.41 (d, J = 2.0 Hz, 1H), 7.21 (d, J = 1.7 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.23 (d, J = 8.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.75, 151.25, 137.50, 131.84, 129.24, 128.92, 127.28, 122.66, 121.95, 121.75, 121.64,120.34, 53.36. **MALDI-TOF:** (m/z) (calcd for $[C_{25}H_{12}Br_4O]^+$ 647.758 found 647.839

4-methoxy-N-(4-(methylthio)phenyl)aniline (DOS): To a 100 mL two-neck round-bottomed flask charged with 4-methoxyaniline (2g, 16.23 mmol), (4-bromophenyl)(methyl)sulfane(4.19 g,17.70 mmol), tri-tert-butylphosphoniumtetrafluoroborate (94.17 mg, 0.32 mmol), and sodium tert-butoxide (3.11 g, 32.46 mmol) were dissolved in dry toluene (30 mL). The reaction mixture was purged with nitrogen gas up to 30 minutes, after purged with nitrogen gas, 201.45 mg of tris (dibenzylideneacetone) dipalladium (0) (0.22 mmol) was added to reaction mixture, then purged again with nitrogen gas for 20 min. Then the reaction mixture was heated to reflux overnight. The crude mixture was poured into water and extracted with ethyl acetate rotary evaporator and purified by column chromatography on silica gel (230-400 mesh) with hexane and ethyl acetate (9:1, v/v) as an eluent to obtain DOS as a black solid (3.85 g, 85 % yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 7.3 Hz, 2H), 6.93 – 6.90 (m, 4H), 3.84 (s, 3H), 2.48 (s, J = 6.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.38, 143.77, 135.60, 130.59, 127.09, 122.21, 116.42, 114.79, 55.65, 18.45. **HR-MS:** (m/z) Calcd for $[C_{14}H_{15}NOS]^+$ 246.090 found 246.095

N2,N3',N6',N7-tetrakis-(4-methoxyphenyl)-N2,N3',N6',N7-tetrakis(4(methylthio)phenyl) spiro[fluorene-9,9'-xanthene]-2,3',6',7-tetraamine (SP-SMe): To a 100 mL two-neck round-bottomed flask charged with 2,3',6',7-tetrabromospiro [fluorene-9,9'-xanthene(0.2 g, 0.3086 mmol), 6-methoxy-N-(4-methoxyphenyl)naphthalen-2-amine (0.309 g, 1.2623 mmol),tri-*tert*-butylphosphonium tetrafluoroborate (0.004 g, 0.0061 mmol), and sodium*tert*-butoxide (0.178 g,1.8518 mmol) were dissolved in dry toluene (15 ml). The reaction mixture was purged with nitrogen gas up to 30 minutes, after purged with nitrogen gas, 0.006 g tris (dibenzylideneacetone) dipalladium (0) (0.006 g, 0.0061 mmol) was added to reaction mixture, then purged again with nitrogen gas for 20 min. Then the reaction mixture was heated to reflux overnight. The crude mixture was poured into water and extracted with

ethyl acetate. The combined organic layer was dried with anhydrous Na_2SO_4. The solvents were removed by rotary evaporator and purified by column chromatography on silica gel (100-200 mesh) with hexane and ethyl acetate (19:1, v/v) as an eluent to obtain SP-SMe as green solid (0.330g, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J*= 8.7 Hz, 2H), 7.04 – 6.93 (m, 7H), 6.90 – 6.82 (m, 5H), 6.81 – 6.76 (m, 2H), 6.57 (d, *J* = 2.3 Hz, 1H), 6.50 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.36 – 6.34 (m, 1H), 3.79 (s, 6H), 2.45 (d, *J* = 4.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.45, 151.66, 147.69, 147.12, 145.58, 140.12, 133.83, 131.02, 128.87, 128.44, 127.56, 127.08,124.01, 122.99, 120.61, 119.99, 118.00, 117.11, 114.91, 109.45, 55.51, 53.42, 17.11. **MALDI-TOF:** (m/z) Calcd for $[C_{81}H_{69}N_4O_5S_4]^+$ 1306.698 $[M+H]^+$ found 1306.703.

3. NMR spectra and MALDI-TOF of the synthesized compounds.

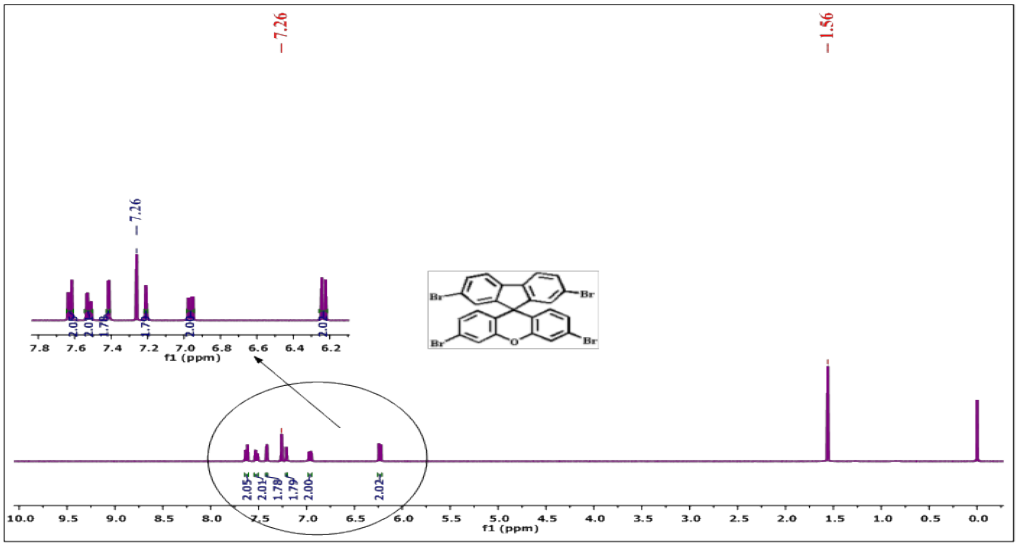


Figure S1. ^{1}H NMR spectra of **TBX** in $CDCl_3$.

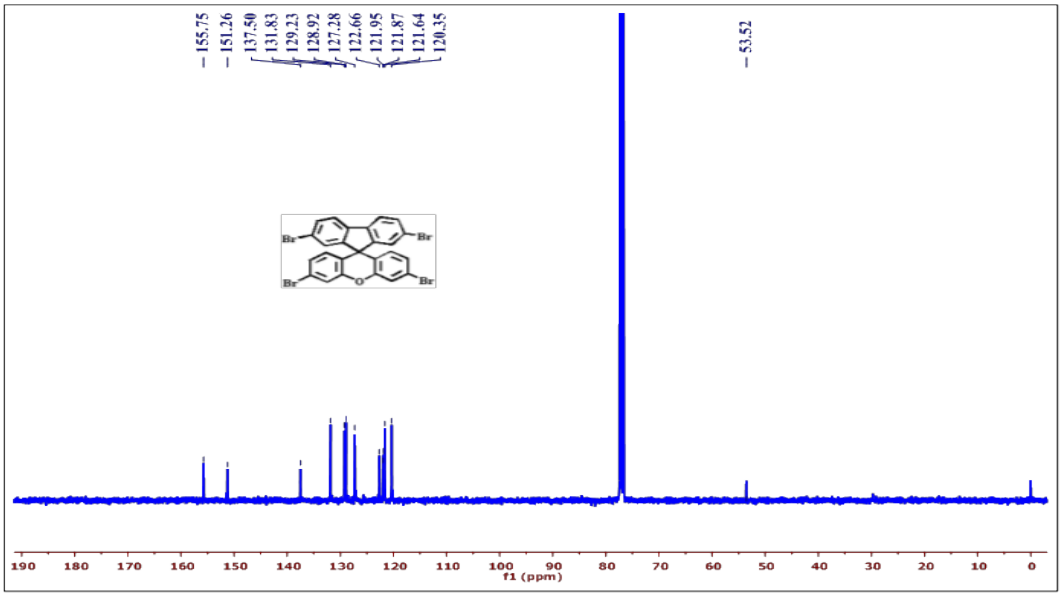


Figure S2. ^{13}C NMR spectrum of **TBX** in $CDCl_3$.

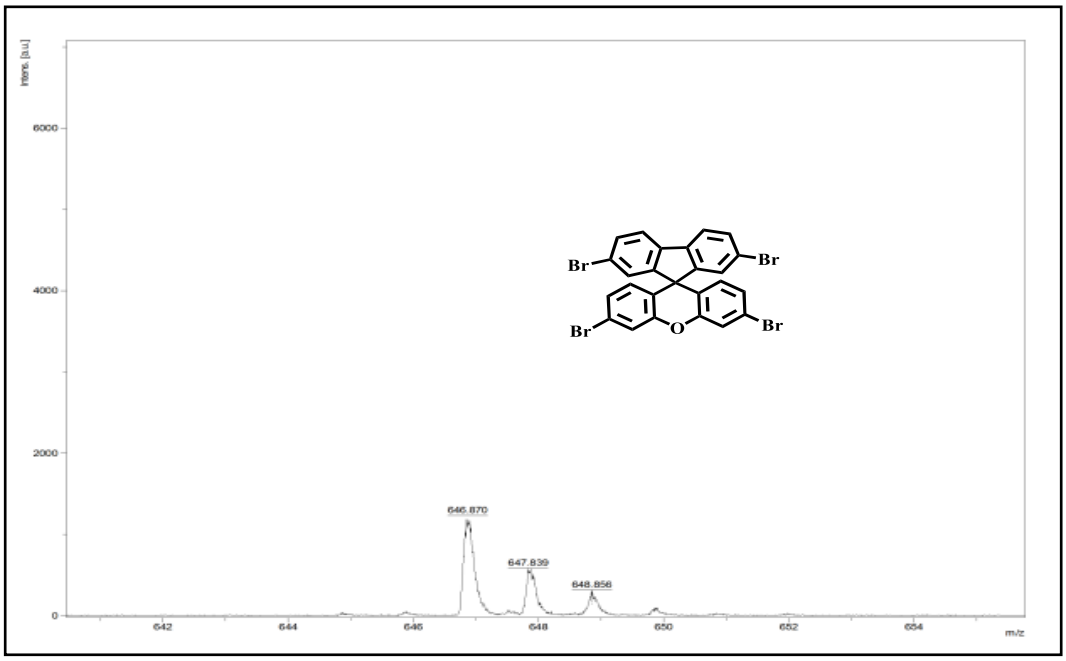


Figure S3. MALDI-TOF of **TBX**.

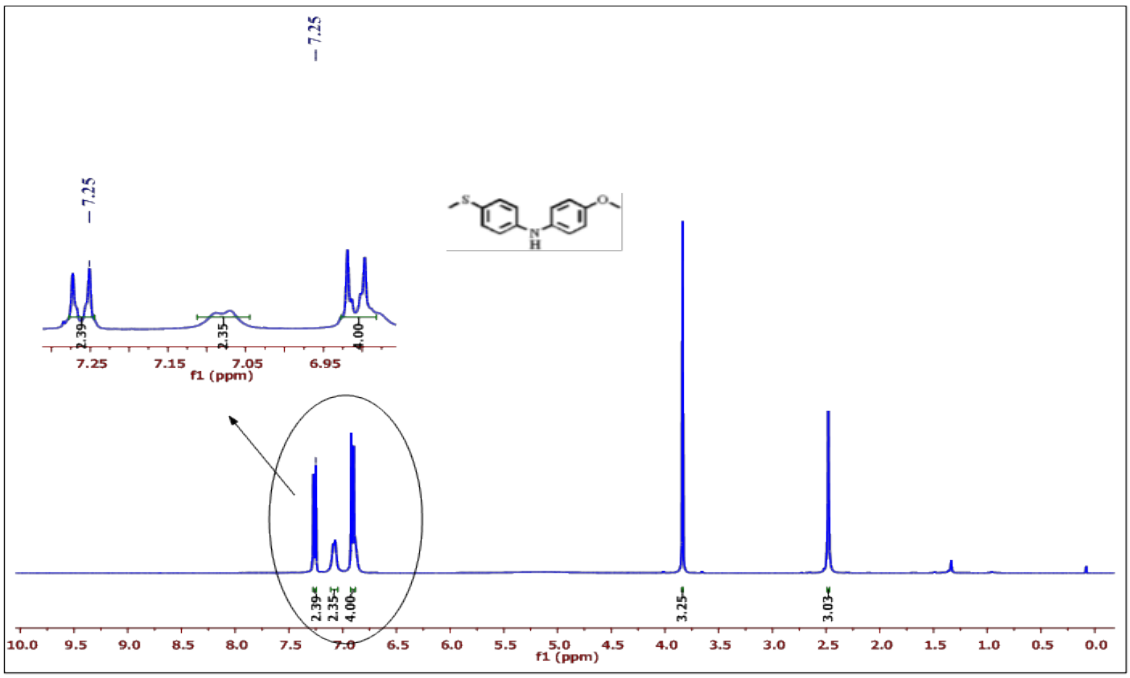


Figure S4. ^{1}H NMR spectrum of **DOS** in $CDCl_3$.

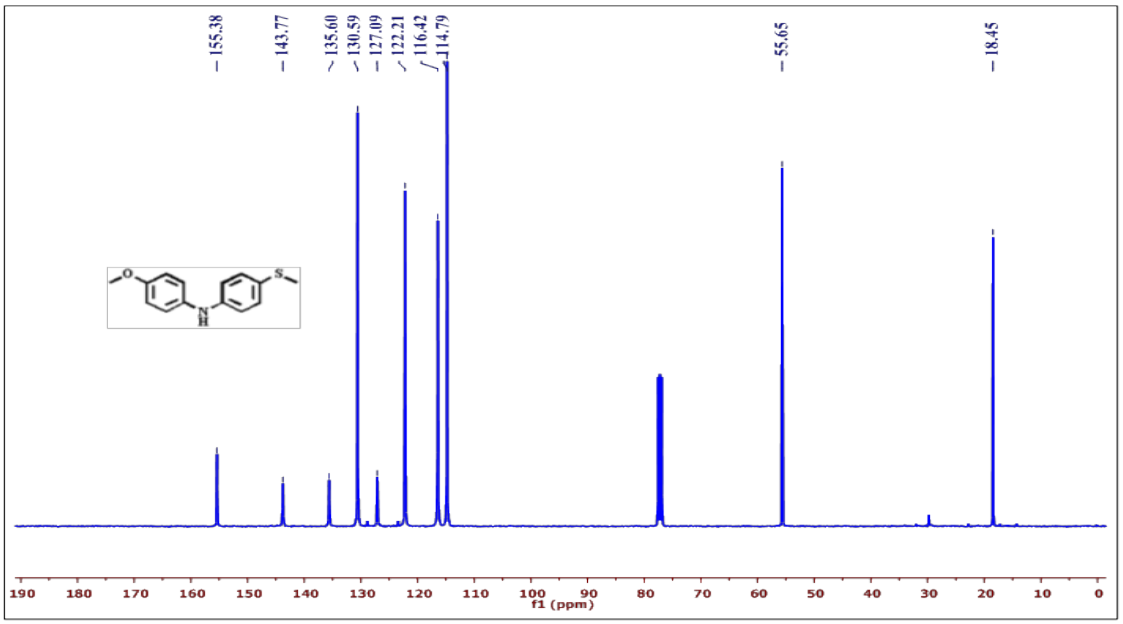


Figure S5. ^{13}C NMR spectrum of **DOS** in $CDCl_3$.

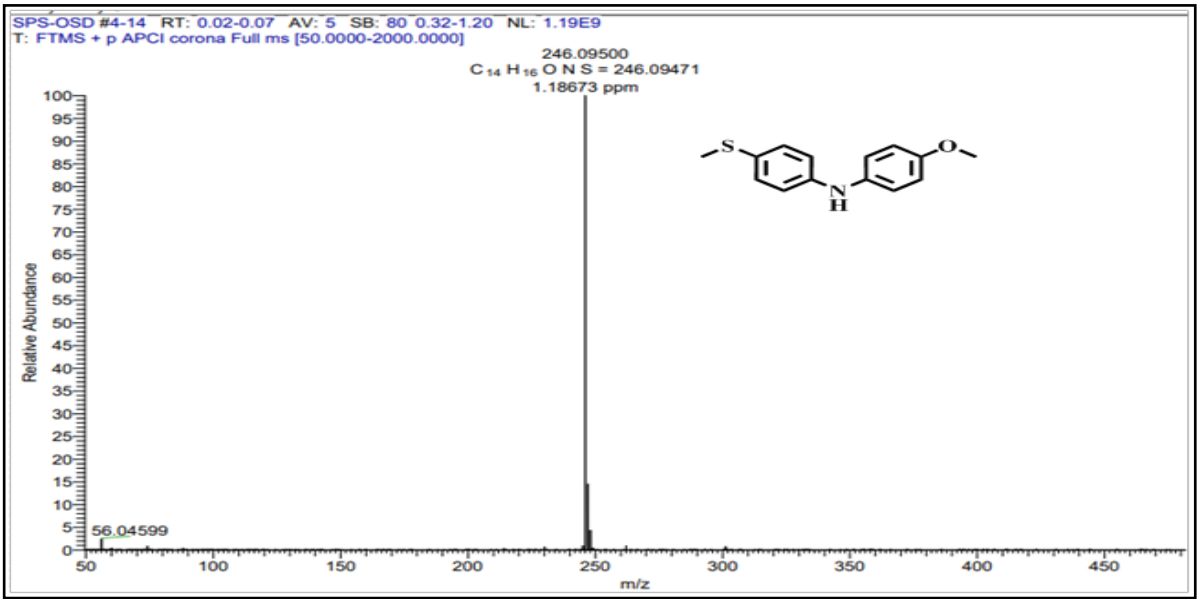


Figure S6. MALDI-TOF of **DOS**.

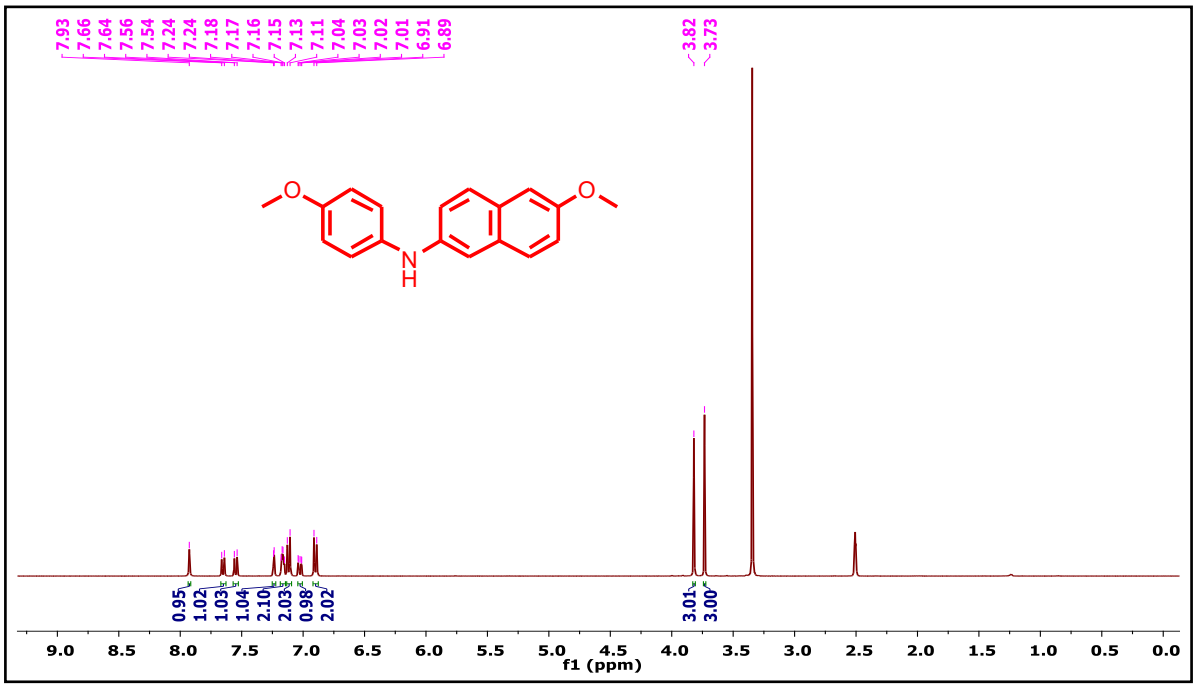


Figure S7. ^{1}H NMR spectra of **compound (I)** in DMSO-d_6

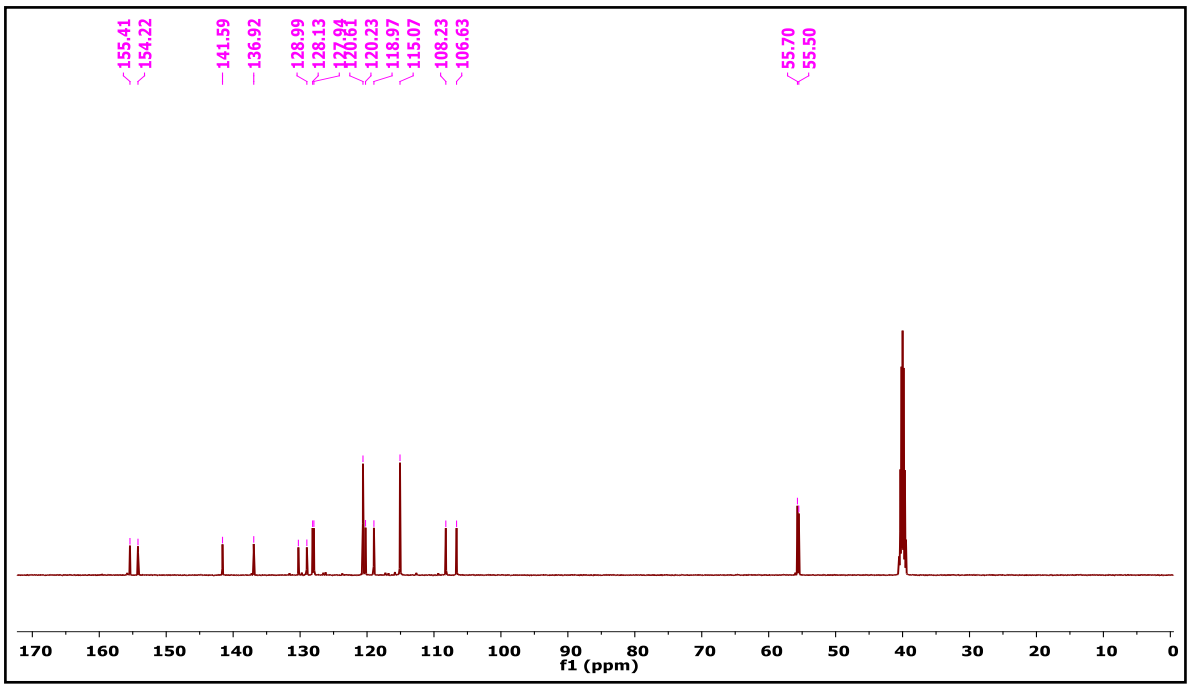


Figure S8. ^{13}C NMR spectra of **compound (I)** in DMSO-d_6

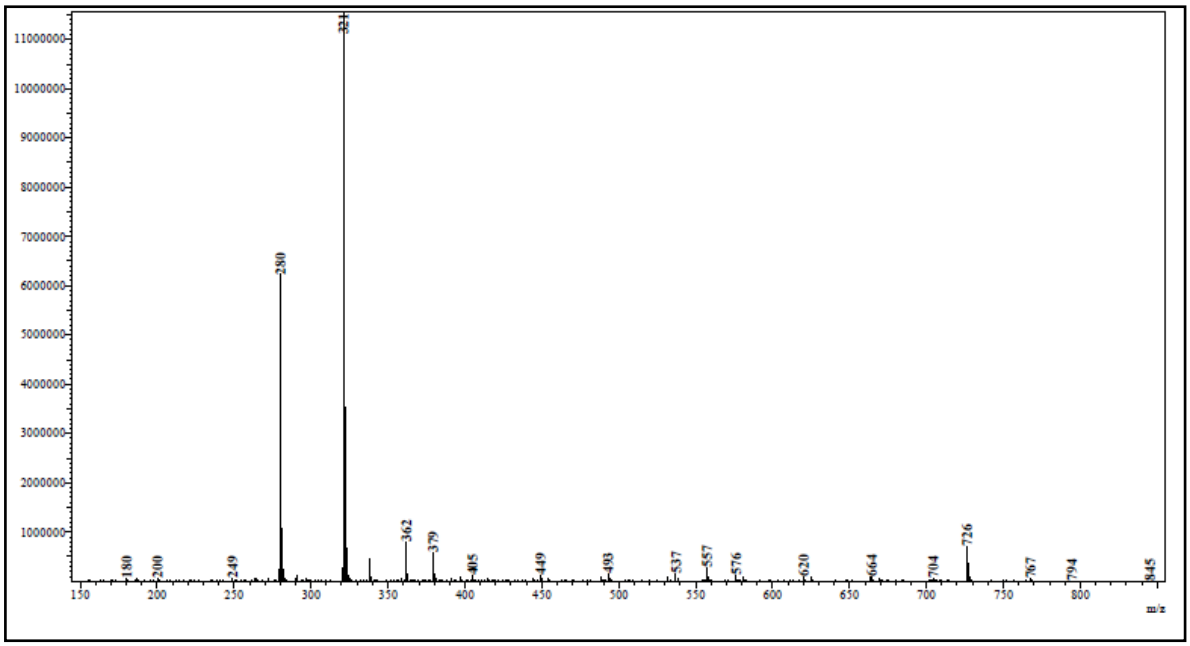


Figure S9. LCMS-MS of **compound (I)**

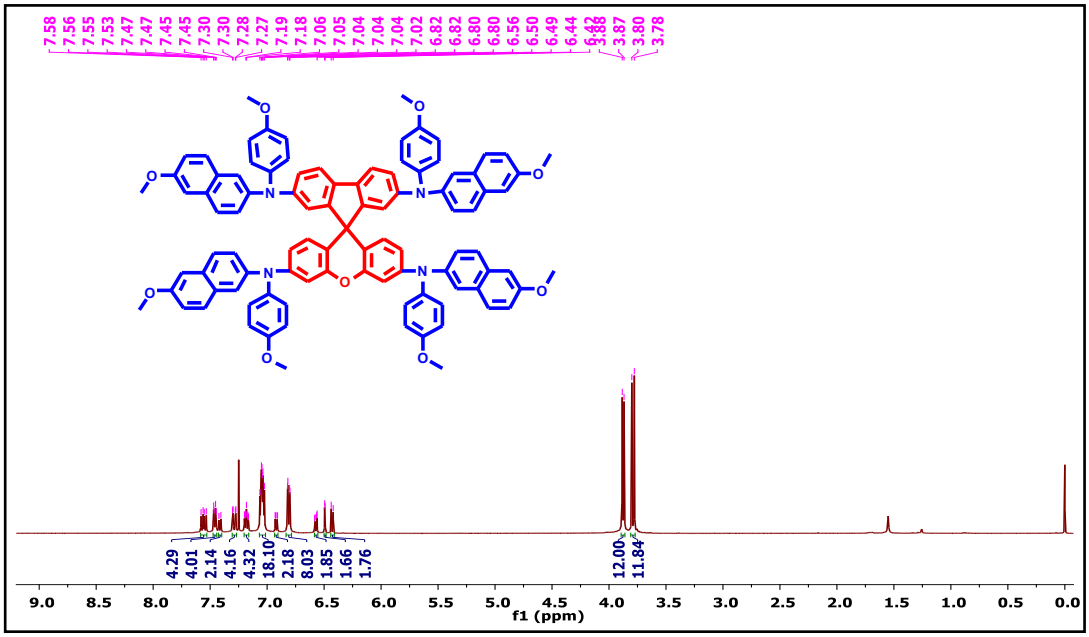


Figure S10. ^{1}H NMR spectrum of **SP-Naph** in $CDCl_3$.

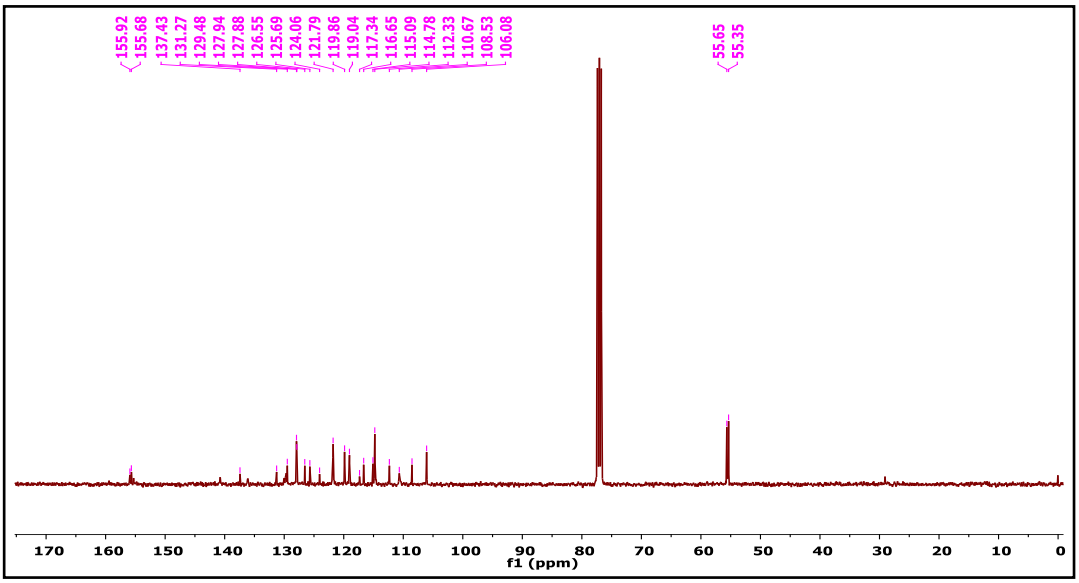


Figure S11. ^{13}C NMR spectrum of **SP-Naph** in $CDCl_3$.

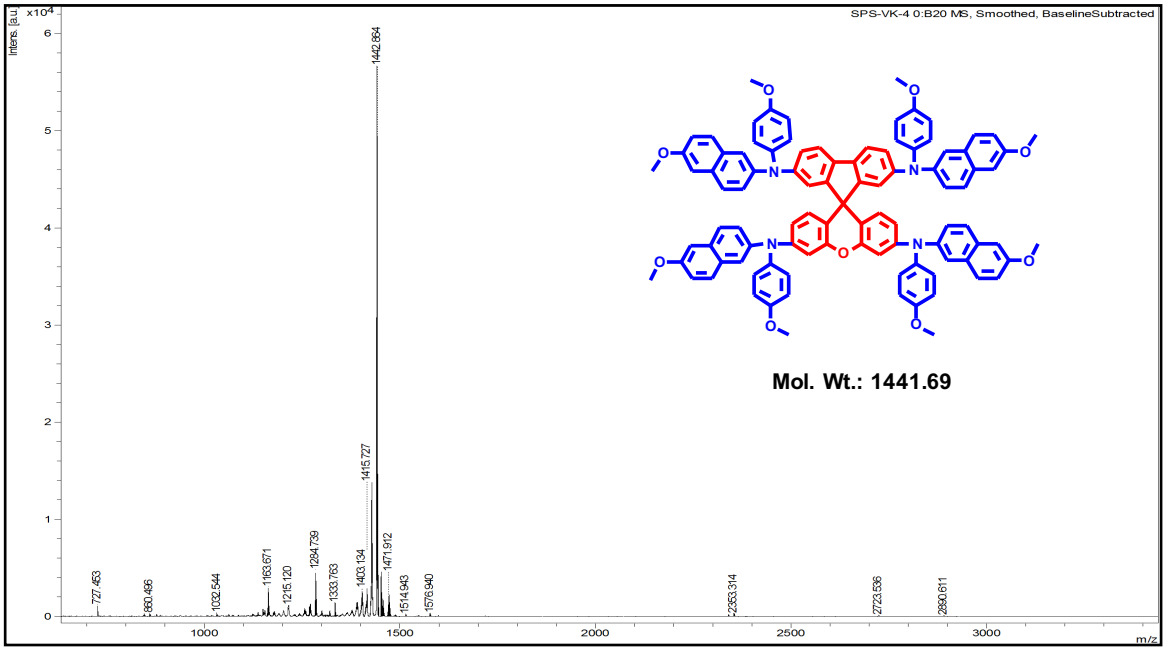


Figure S12. MALDI-TOF of **SP-Naph**.

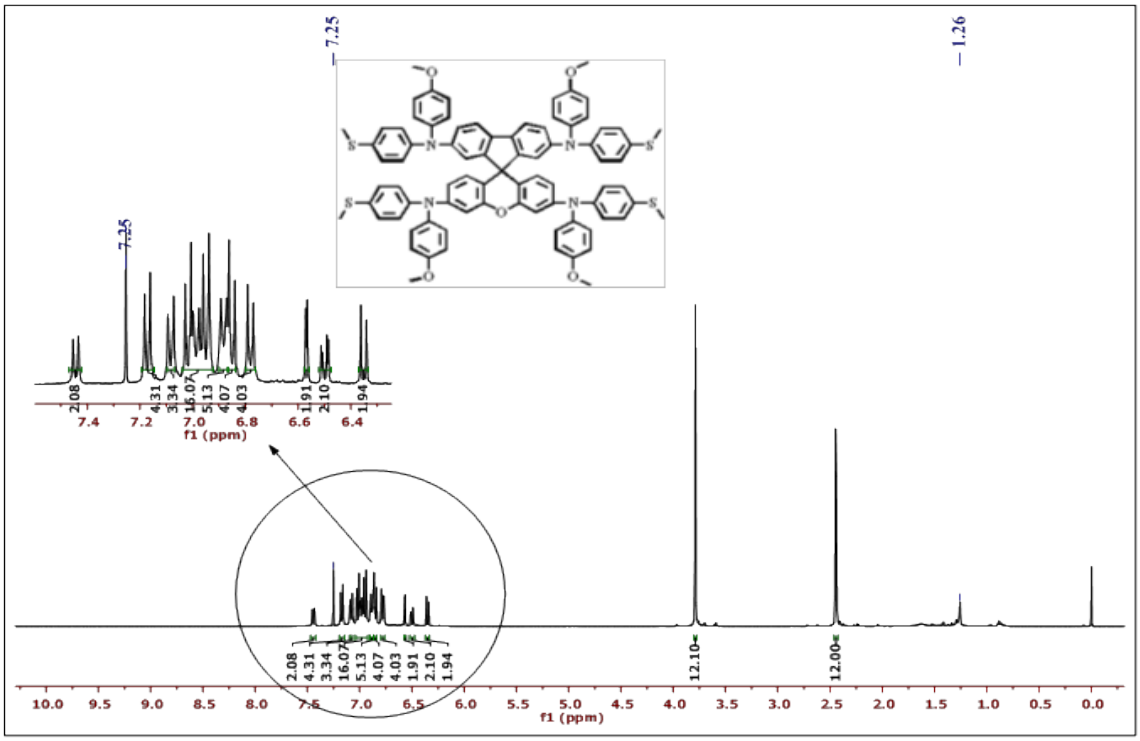


Figure S13. ^{1}H NMR spectrum of **SP-SMe** in $CDCl_3$.

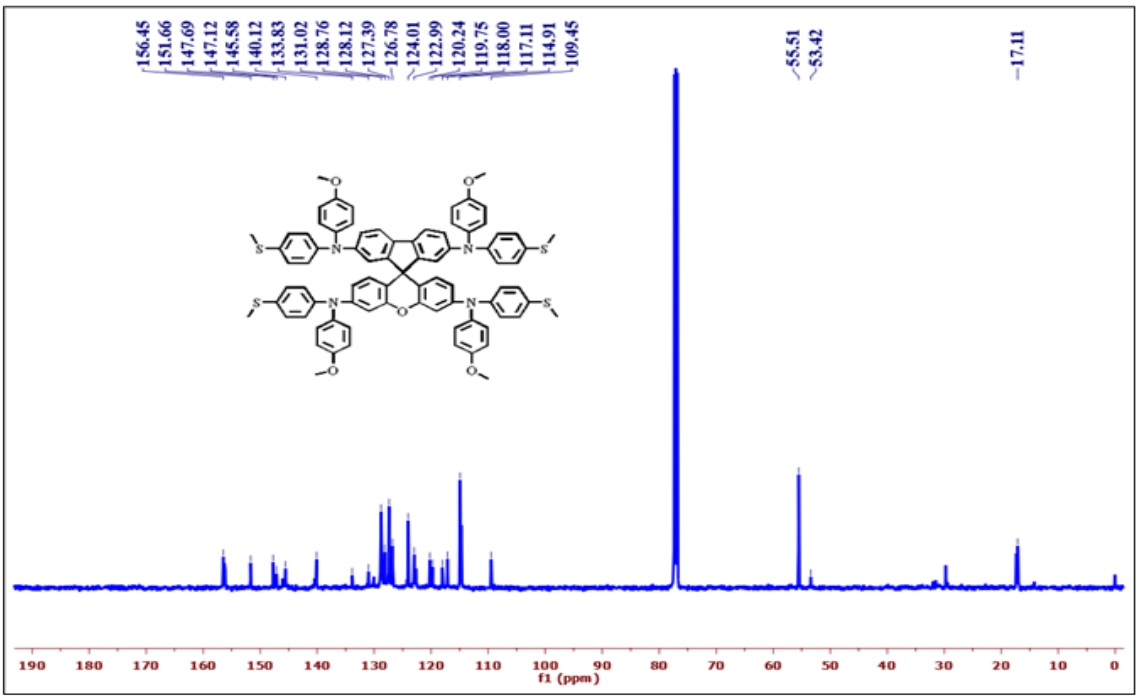


Figure S14. ^{13}C NMR spectrum of **SP-SMe** in $CDCl_3$.

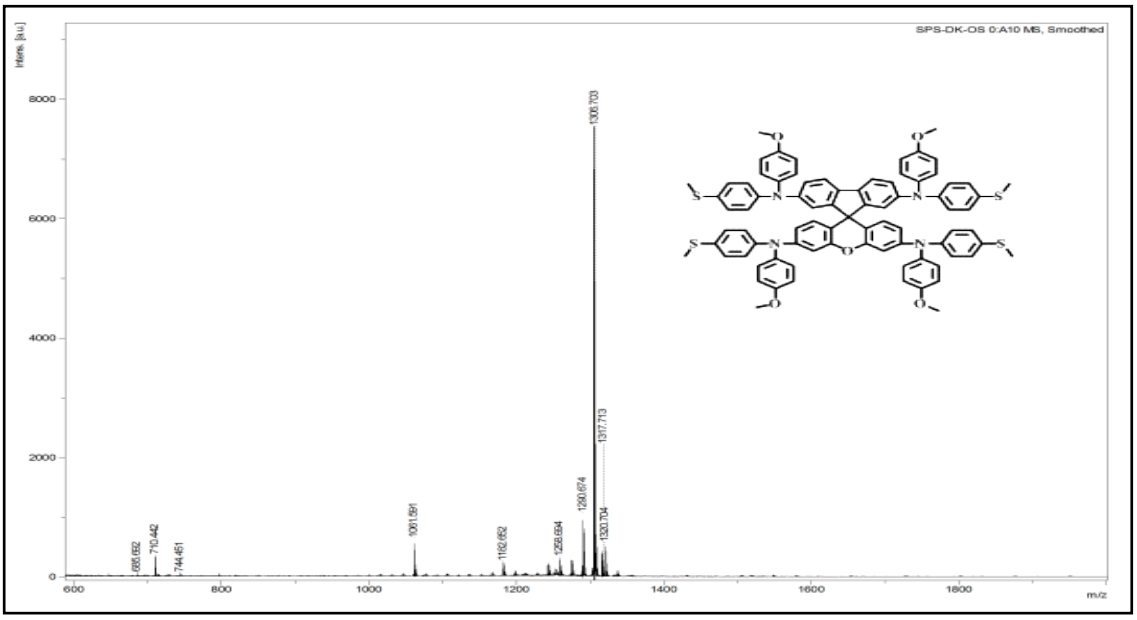
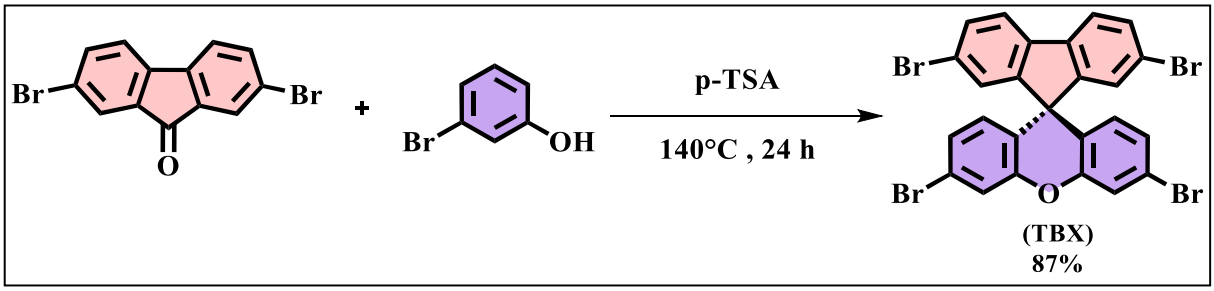


Figure S15. MALDI-TOF of **SP-SMe**.

Supporting Note 1

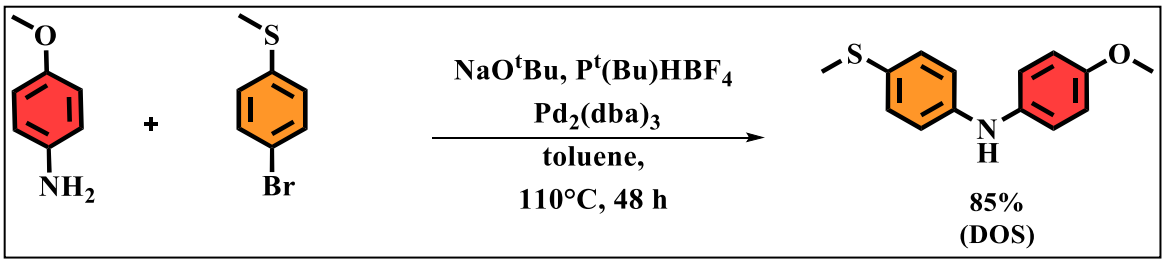
Cost calculation for SP-SMe



Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
2,7-dibromo-9-Fluorenone/TCI	437 $/kg	0.050			0.021
3-bromophenol/ Spectrochem	1,557 $/kg	0.092			0.143
p-TsOH/TCI	63 $/kg	0.058			0.003
MeOH/Finar	0.96 $/L			20 ml	0.019
Total					0.186

TBX: Yield, 87%, 0.0834 g, 0.186$

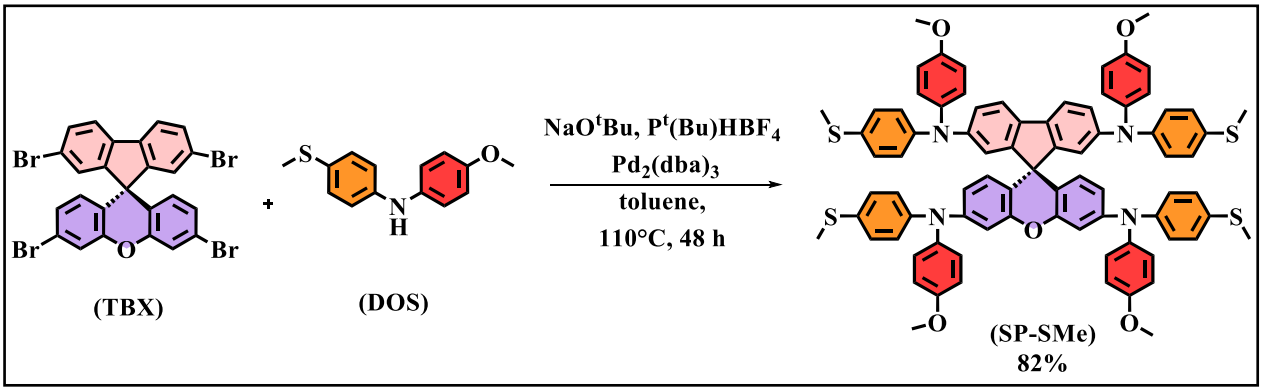
The cost of 1 g is 2.241$



Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
p-Anisidine/Alfa aesar	137 $/kg	2			0.274
(4-bromophenyl)(methyl)sulfane / TCI	2835 $/kg	4.190			11.878
Sodium tert-butoxide / TCI	259 $/kg	3.110			0.805
Tri-tert-butylphosphonium tetrafluoroborate/ TCI	37970 $/kg	0.094			3.569
Tris(dibenzylideneacetone)dipalladium /TCI	35559 $/kg	0.201			7.147
Toluene/Finar	11 $/L		30		0.330
Silica gel/Finar	17 $/kg			70 g	1.190
Petroleum ether/Finar	18$/L			200 ml	3.600
Ethyl acetate/Finar	9 $/L			50 ml	0.450
Total					29.243

DOS: Yield, 85%, 3.850 g, 29.243$

The cost of 1 g is 7.595 $



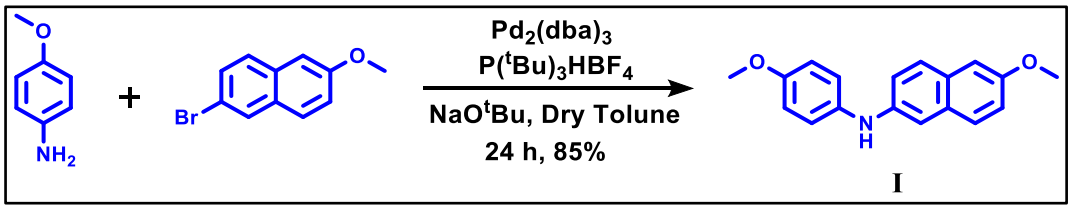
Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
TBX	2241 $/kg	0.200			0.448
DOS	7595 $/kg	0.309			2.346
Sodium tert-butoxide / TCI	259 $/kg	0.178			0.046
Tri-tert-butylphosphonium tetrafluoroborate/ TCI	37970 $/kg	0.004			0.151
Tris(dibenzylideneacetone)dipalladium /TCI	35559 $/kg	0.006			0.213
Toluene/Finar	11 $/L		20		0.220
Silica gel/Finar	17 $/kg			70 g	1.190
Petroleum ether/Finar	18$/L			200 ml	3.600
Ethyl acetate/Finar	9 $/L			50 ml	0.450
Total					8.664

SP-SMe: Yield, 82%, 0.330 g, 8.664 $

The cost of 1g is 26.254 $

This is about (1/21)th of the costs of purified Spiro-OMeTAD (565 $/g, high purity, SIGMA/Merck)

Cost calculation for SP-Naph



Chemicals/company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
p-Anisidine/Alfa aesar	137 $/kg	2			0.274
2-bromo-6-methoxynaphthalene/ TCI	942 $/kg	4.190			3.946
Sodium tert-butoxide / TCI	259 $/kg	3.110			0.805
Tri-tert-butylphosphonium tetrafluoroborate/ TCI	37970 $/kg	0.094			3.569
Tris(dibenzylideneacetone)dipalladium /TCI	35559 $/kg	0.148			5.262
Toluene/Finar	11 $/L		30		0.330
Silica gel/Finar	17 $/kg			70 g	1.190
Petroleum ether/Finar	18$/L			200 ml	3.600
Ethyl acetate/Finar	9 $/L			50 ml	0.450
Total					19.426

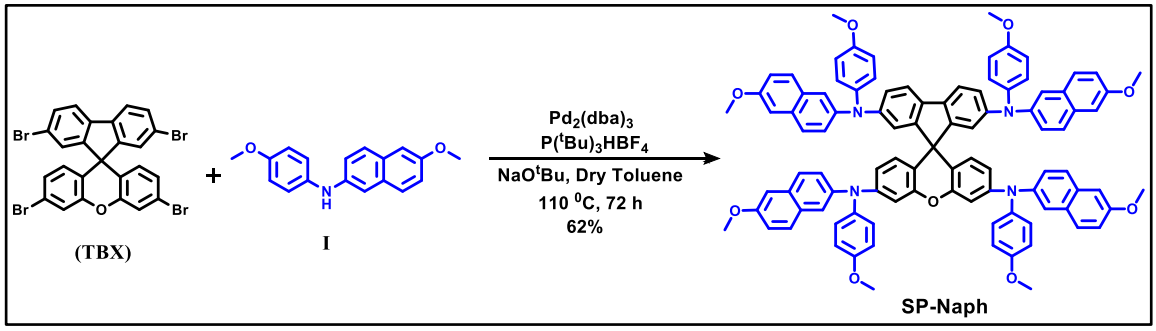
Moiety I: Yield, 85%, 3.850 g, 19.426 $

The cost of 1g is 5.046 $

Cost calculation of **TBX** same as mentioned in page number 14 (ESI).

TBX: Yield, 87%, 0.0834 g, 0.186$

The cost of 1 g is 2.241$



SP-Naph: Yield, 62%, 0.275 g, 12.896 $

The cost of 1 g is 46.894 $

Chemicals/company	**Price ($) (Kg or L)**	**Chemicals used for batch preparation**			**Chemical cost ($)**
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
TBX	2241 $/kg	0.200			0.448
I	7595 $/kg	0.517			3.926
Sodium tert-butoxide / TCI	259 $/kg	0.178			0.046
Tri-tert-butylphosphonium tetrafluoroborate/ TCI	37970 $/kg	0.027			1.025
Tris(dibenzylideneacetone)dipalladium /TCI	35559 $/kg	0.056			1.991
Toluene/Finar	11 $/L		20		0.220
Silica gel/Finar	17 $/kg			70 g	1.190
Petroleum ether/Finar	18$/L			200 ml	3.600
Ethyl acetate/Finar	9 $/L			50 ml	0.450
Total					12.896

This is about (1/12)th of the costs of purified Spiro-OMeTAD (565 $/g, high purity, SIGMA/Merck)

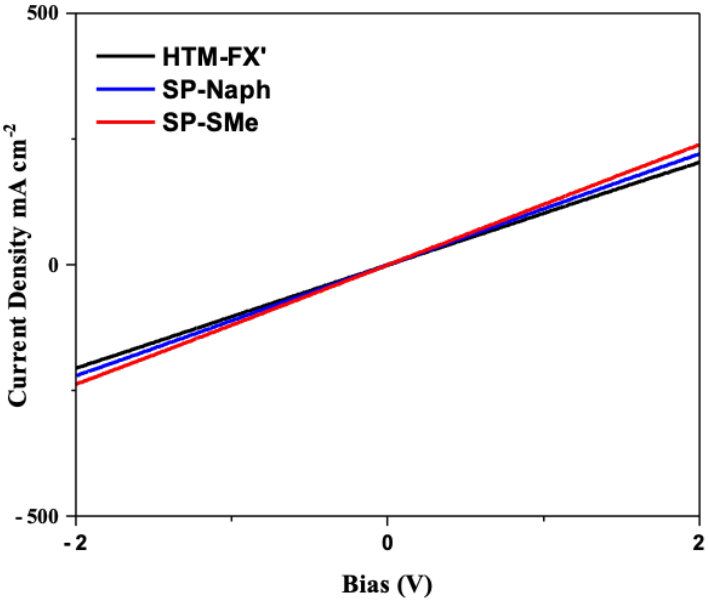


Figure S16. Current-voltage characteristics of HTM-FX', SP-Naph, and SP-SMe.

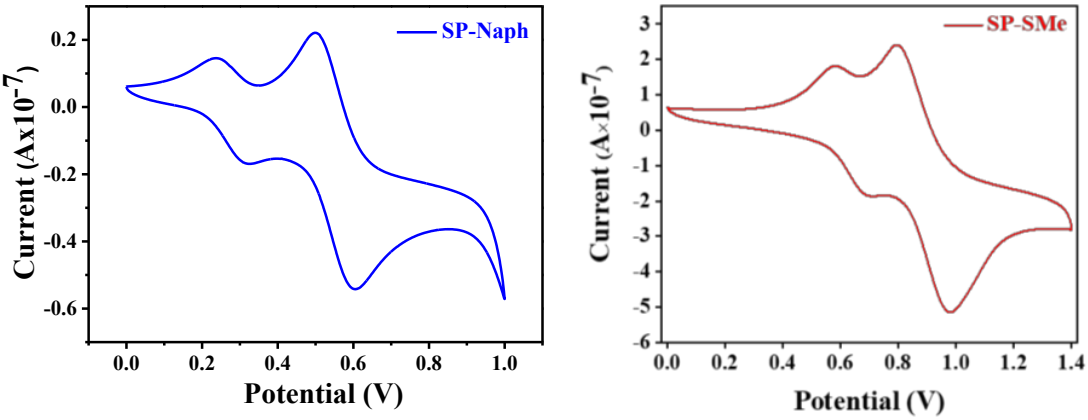


Figure S17. CV of SP-Naph and SP-SMe measured in 0.1 M tetra-nbutylammoniumhexafluorophosphate (n-Bu4NPF6) solution in 1,2-dichlorobenzene at a scan rate of 100 mV s^{-1}.

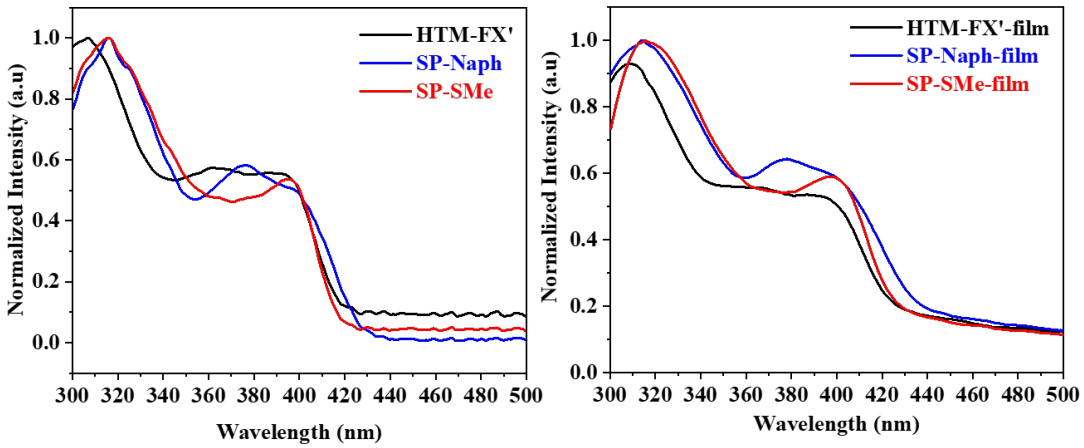


Figure S18. UV-Vis spectra of HTM-FX', SP-Naph, and SP-SMe (a) in solution and (b) as thin films.

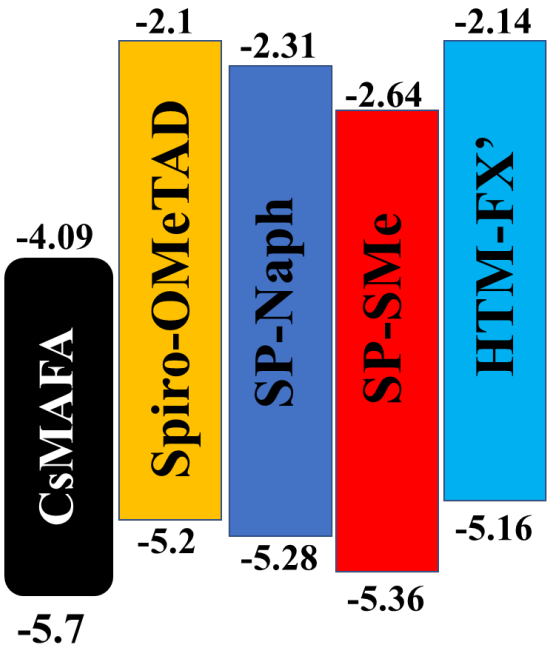


Figure S19. Energy band diagram of the used perovskite layer and HTMs. The corresponding values for perovskite and HTM-FX' were taken from the references [3] and [1], respectively.

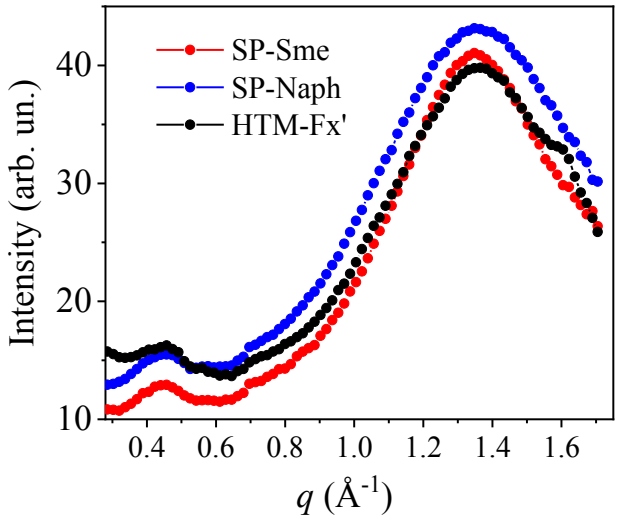


Figure S20. Intensity profiles obtained from the reciprocal GIWAXS maps (see Figure 1b in the main text).

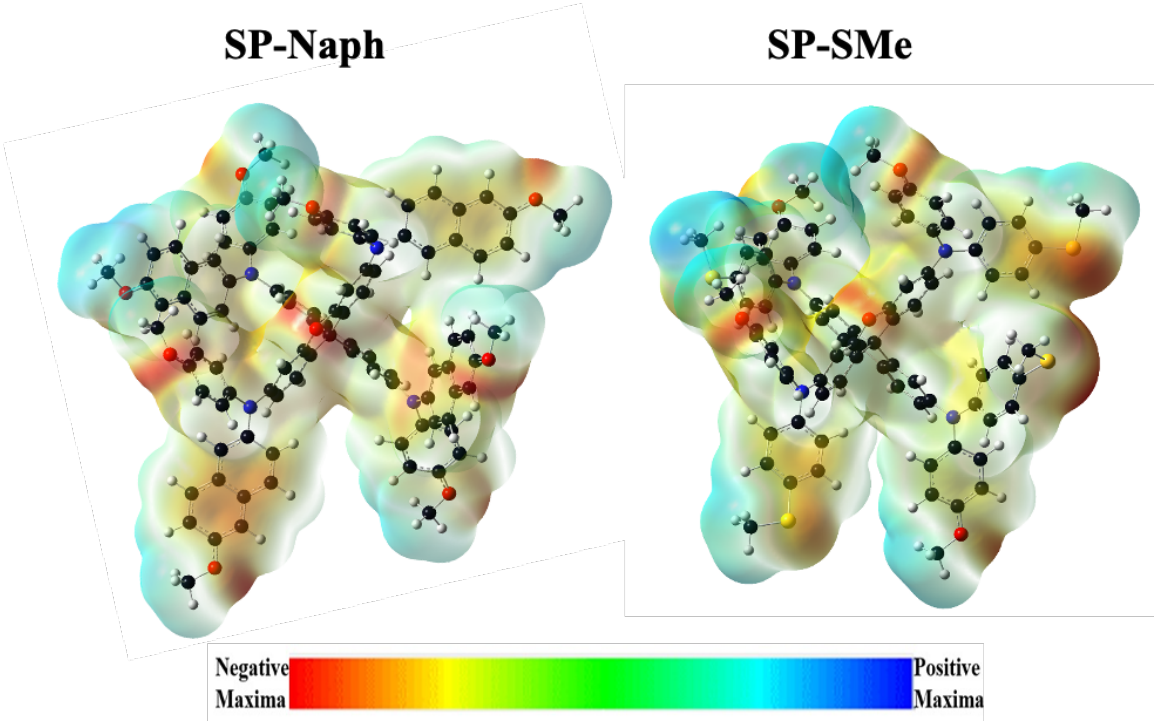


Figure S21. Electrostatic Potential (ESP) Surface Calculations for SP-Naph and SP-SMe.

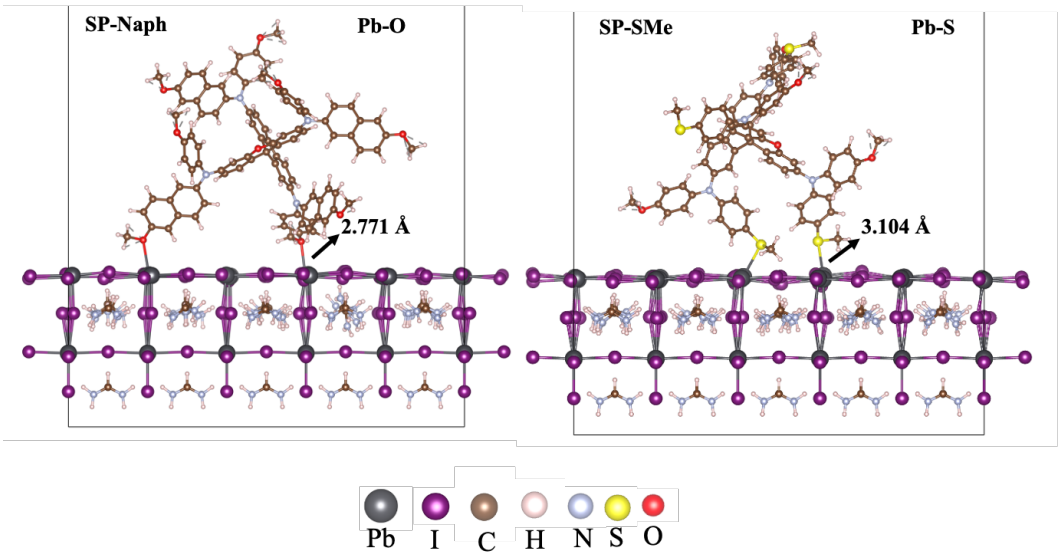


Figure S22. Side views of the absorbed (SP-Naph and SP-SMe) on the surface of perovskite.

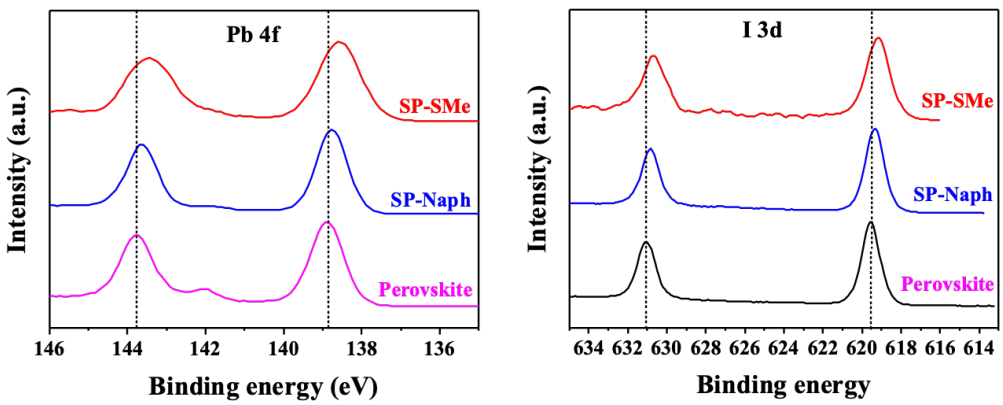


Figure S23. Pb 4f and I 3d XPS spectra of the bare perovskite, perovskite/SP-Naph and perovskite/SP-SMe films.

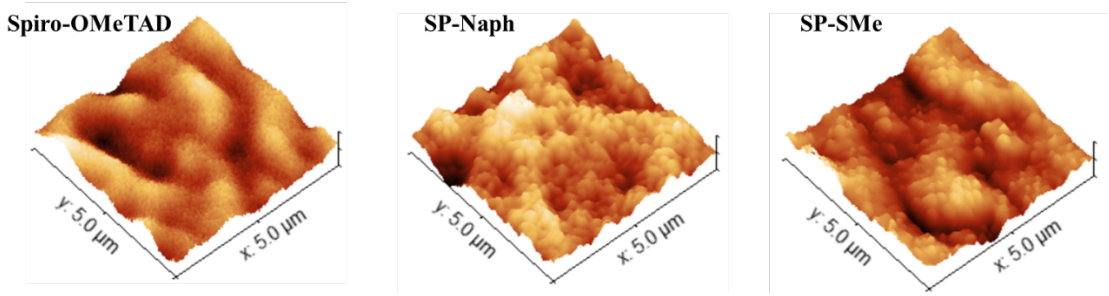


Figure S24. 3D AFM topography images of the HTMs on the top of perovskite.

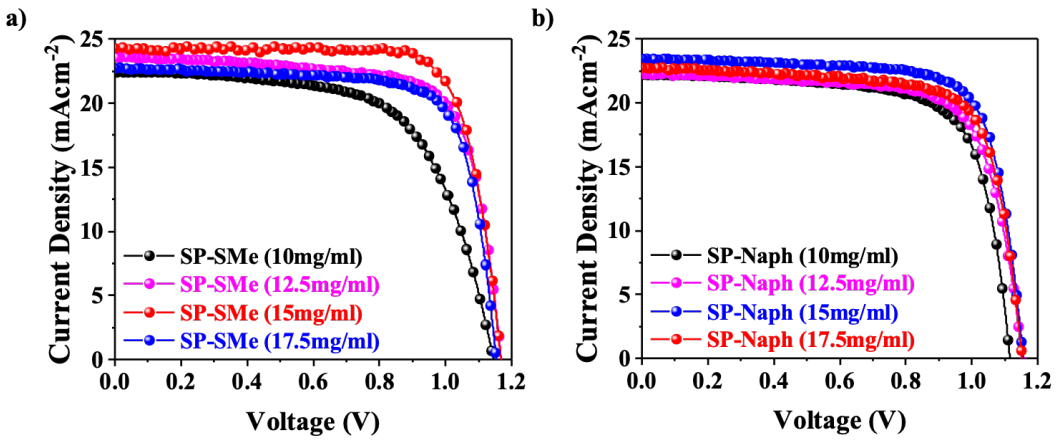


Figure S25. Current density-voltage (*J-V*) curves at different concentrations for the devices based on a) SP-Naph and b) SP-SMe HTMs.

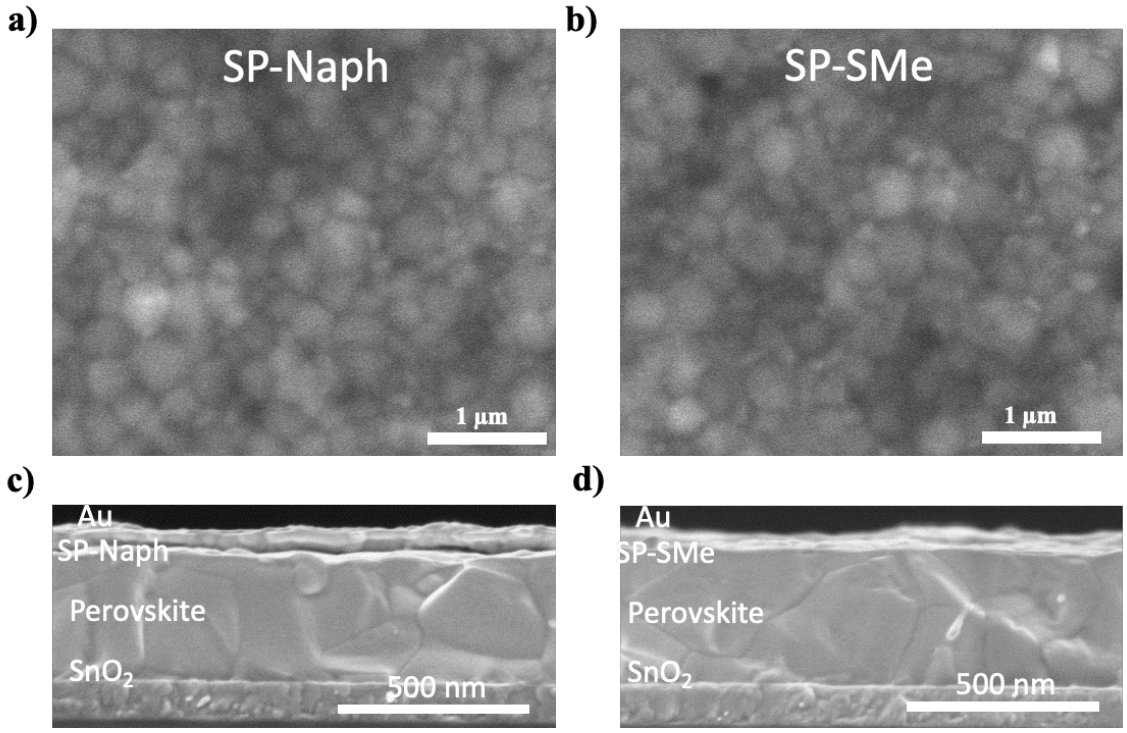


Figure S26. a-b) Top view SEM image of the SP-Naph and SP-SMe on the perovskite film. c-d) Cross–section SEM images of the SP-Naph and SP-SMe based devices.

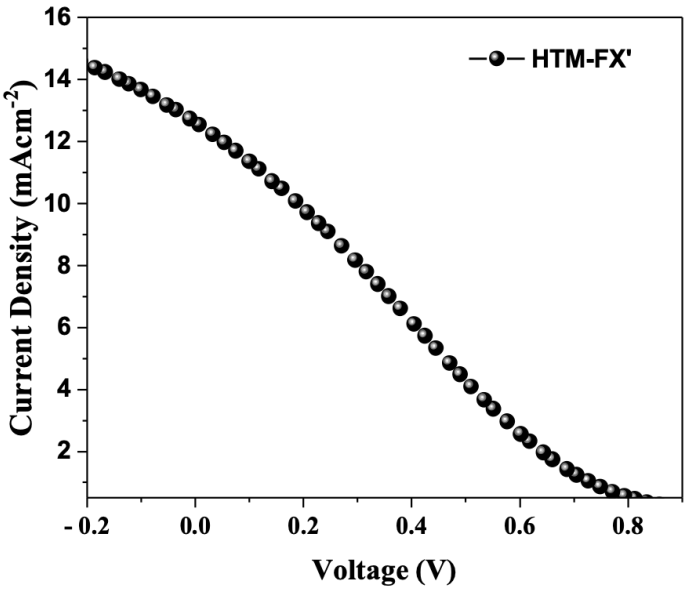


Figure S27. *J–V* curves of the HTM-FX' based device under backward scan direction.

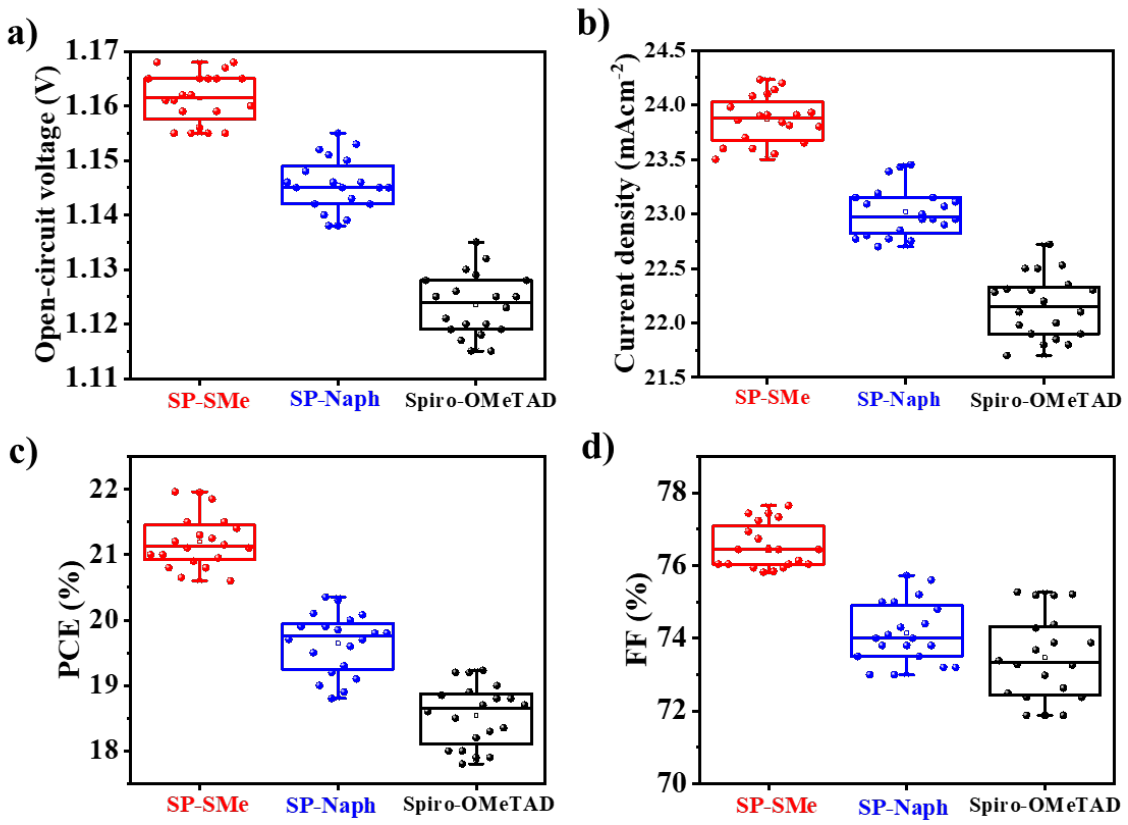


Figure S28. Statistics of the photovoltaic parameter distributions of 20 independent devices (under reverse scan direction).

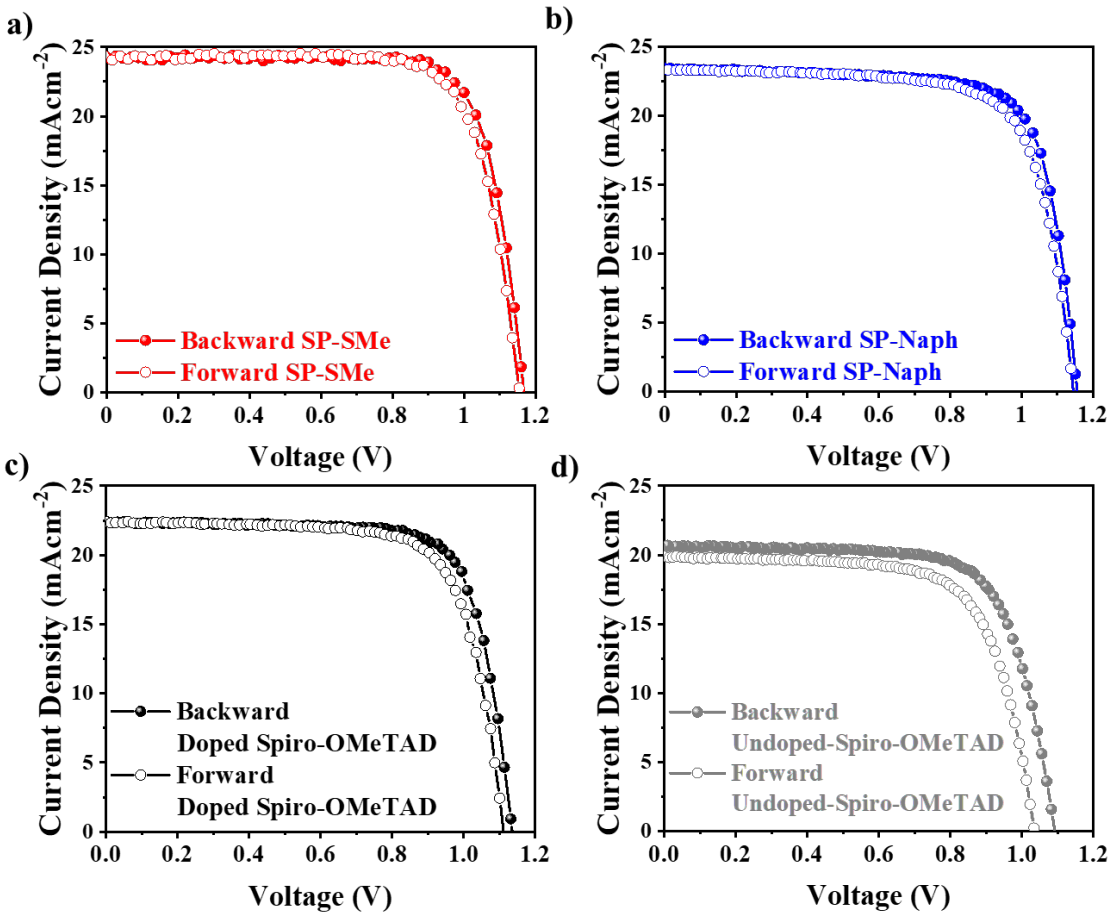


Figure S29. *J–V* curves of the Spiro-OMeTAD, SP-SMe, and SP-Naph based devices under both forward and backward scan directions.

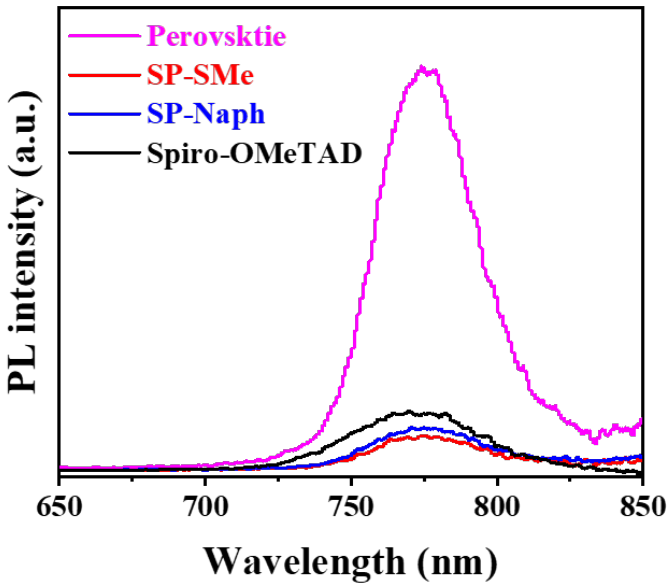


Figure S30. Steady-state PL spectra of the bare perovskite, perovskite/spiro-OMeTAD, perovskite/SP-Naph and perovskite/SP-SMe films.

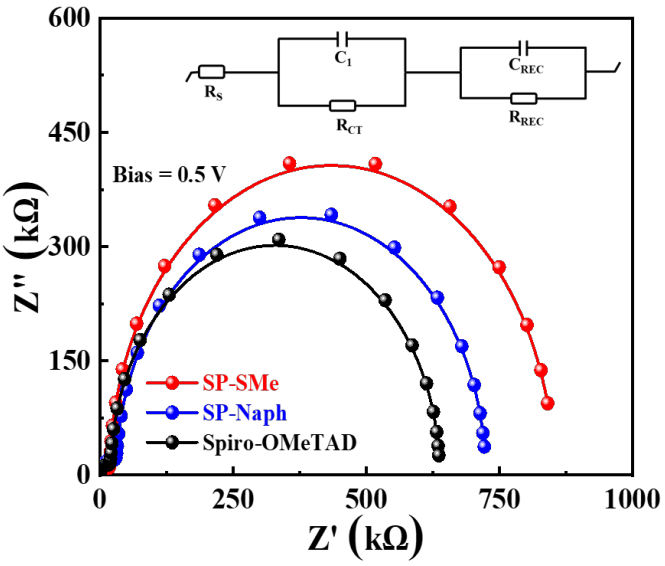


Figure S31. Nyquist plots of PSCs with the fitted circuit.

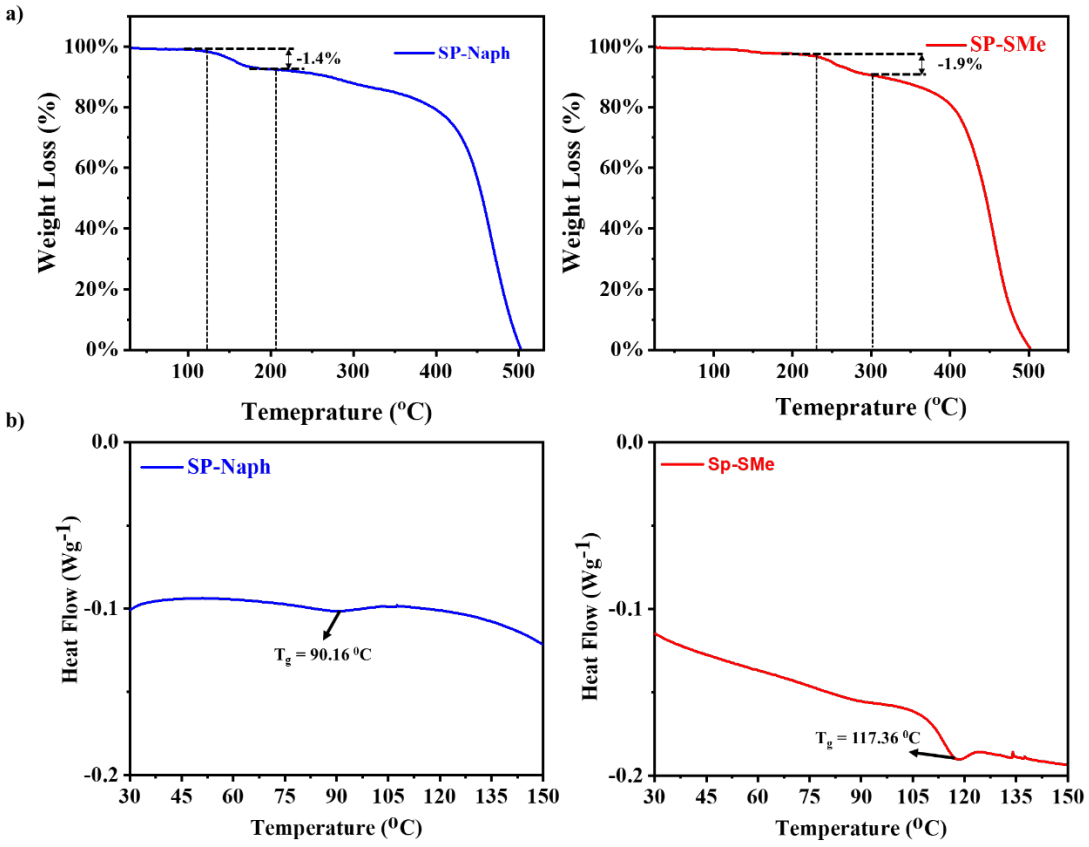


Figure S32. a) TGA curves b) DSC curves of SP-Naph and SP-SMe HTMs.

Table S1. Conductivity measurement of HTM-FX', SP-Naph and SP-SMe while the conductivity of Spiro-OMeTAD taken from literature.[4]		
Molecules (HTMs)	**Slope**	**Conductivity (S cm^{-1})**
Spiro-OMeTAD	-	2.5×10^{-7}
HTM-FX'	101.59401 ± 0.04651	5.94×10^{-6}
SP-Naph	109.91878 ± 0.02173	6.41×10^{-6}
SP-SMe	118.61813 ± 0.02406	6.94×10^{-6}

Table S2. The HOMO LUMO and band gap of SP-Naph and SP-SMe			
HTMs	**HOMO[a](eV)**	**LUMO[b](eV)**	**E_g[c](eV)**
SP-Naph	-5.28	-2.31	2.97
SP-SMe	-5.36	-2.64	2.72
SFX-FX'	-5.16	-2.14	3.02
[a] LUMO values were calculated by ELUMO = E_g- HOMO, [b]HOMO values were calculated by CV, [c]E_g = band gap obtained by UV-Visible			

Table S3. The adsorption energies of different modes of SP-Naph and SP-SMe with undercoordinated Pb^{+2}.	
Interaction Mode	**Adsorption Energies**
Undercoordinated Pb with Oxygen (Pb-O)	-2.62750137eV
Undercoordinated Pb with Sulphur (Pb-S)	-3.35122678 eV

Table S4. Photovoltaic parameters of SP-Naph and SP-SMe with different concentrations					
HTMs	**HTLs conc (mg/ml)**	**V_{OC} (V)**	**J_{SC} (mAcm^{-2})**	**FF (%)**	**PCE (%)**
SP-Naph	**10**	**1.142**	**22.36**	**66.69**	**17.04**
	12.5	**1.165**	**23.58**	**72.91**	**19.98**
	15	**1.167**	**24.23**	**77.65**	**21.95**
	17.5	**1.154**	**22.72**	**74.96**	**19.65**

SP-SMe	**10**	**1.117**	**22.18**	**69.54**	**17.22**
	12.5	**1.154**	**22.32**	**72.36**	**18.60**
	15	**1.155**	**23.45**	**75.73**	**20.51**
	17.5	**1.150**	**22.73**	**73.60**	**19.15**

Table S5. Solar cell parameters were recorded under forward and backward scan directions for SP-SMe, SP-Naph and Sprio-OMeTAD devices.

HTMs	**Scan direction**	**V_{OC} (V)**	**J_{SC} ($mAcm^{-2}$)**	**FF (%)**	**PCE (%)**	**PCE_{avg} (%)**	**HI (%)**
Undoped Spiro-OMeTAD	Backward	1.08	20.64	70.11	15.62	14.78	10.75
	Forward	1.03	19.84	67.89	13.94		
Spiro-OMeTAD	Backward	1.13	22.50	75.27	19.23	18.73	5.14
	Forward	1.11	22.37	73.34	18.24		
SP-Naph	Backward	1.15	23.45	75.73	20.51	20.21	2.87
	Forward	1.14	23.40	74.50	19.92		
SP-SMe	Backward	1.16	24.23	77.65	21.95	21.75	1.86
	Forward	1.15	24.22	76.82	21.54		

Table S6. Carrier lifetimes of HTMs deposited on perovskite films.

Molecules	**τ_1 (ns)**	**τ_2 (ns)**
Perovskite	1400	
Spiro	6	47
SP-Naph	1.8	67
SP-SMe	0.6	15

Table S7. Fitted parameters of PSCs devices from EIS.			
HTMs	**R_s (Ω)** [a]	**R_{ct} (kΩ)**[b]	**R_{rec} (kΩ)**[c]
SP-Naph	23.2	40.1	760.7
SP-SMe	19.3	18.4	833.4
Spiro-OMeTAD	27.4	51.4	710.3
[a] Series resistance, [b] Contact Resistance, [c] Recombination Resistance			

Table S8. DFT/ B3LYP/6-31g (d,p) optimized geometrical Cartesian coordinates of SP-SMe. Thestructure is at a global minimum (no imaginary frequency).

Electronic Energy= -5315.527451*Hartree*

Symbol	X	Y	Z
C	2.682458	-2.76941	-3.67425
C	2.898515	-2.82676	-2.28526
C	2.098176	-2.05157	-1.42643
C	1.132912	-1.21921	-1.96817
C	0.926648	-1.1486	-3.35946
C	1.69919	-1.94178	-4.21273
C	0.178991	-0.27481	-1.22034
C	-0.57834	0.361635	-2.40392
C	-0.13043	-0.16977	-3.62857
C	-1.57634	1.320754	-2.35678
C	-2.16392	1.762283	-3.5579
C	-1.71714	1.229032	-4.78255
C	-0.70291	0.275488	-4.8228
N	-3.19245	2.74021	-3.53987
N	3.921744	-3.65884	-1.75142
C	0.949172	0.761755	-0.40267
C	0.592517	1.075854	0.911705
O	-0.45246	0.471635	1.568443
C	-1.0754	-0.60548	0.98381
C	-0.79171	-1.03518	-0.31528
C	2.042515	1.456622	-0.94221
C	2.746677	2.408501	-0.21982
C	2.380147	2.6983	1.109367
C	1.293075	2.018966	1.666475
C	-2.00977	-1.25353	1.793202
C	-2.71579	-2.35826	1.307495
C	-2.44049	-2.81159	0.001901

C	-1.49452	-2.15897	-0.77463
N	3.098518	3.656401	1.863835
N	-3.69397	-2.99298	2.108588
C	-3.19867	3.772219	-4.52408
C	-4.21465	2.700488	-2.55884
C	-4.53062	-2.21145	2.961631
C	-3.87962	-4.39877	2.048914
C	2.413283	4.507602	2.779335
C	4.514747	3.73127	1.76948
C	4.055714	-4.99237	-2.24005
C	4.815618	-3.15557	-0.78017
C	5.363447	-3.99867	0.204241
C	6.25221	-3.49745	1.150094
C	6.604086	-2.14062	1.162944
C	6.060276	-1.30197	0.180901
C	5.187146	-1.79859	-0.78081
C	2.938837	-5.82794	-2.33622
C	3.050216	-7.12627	-2.83774
C	4.300641	-7.61545	-3.23165
C	5.427549	-6.78588	-3.12917
C	5.304672	-5.48928	-2.65121
C	1.255526	5.190357	2.392051
C	0.572572	6.017977	3.285451
C	1.060942	6.194154	4.584741
C	2.228196	5.522863	4.976854
C	2.887859	4.683434	4.090689
C	5.163796	4.971937	1.741764
C	6.554731	5.053386	1.682208
C	7.335796	3.892743	1.633629
C	6.687126	2.64613	1.653591
C	5.301777	2.566881	1.726572
C	-2.03636	4.496468	-4.8078
C	-2.02869	5.495695	-5.78324
C	-3.20495	5.801395	-6.47668
C	-4.37781	5.087066	-6.18957
C	-4.3715	4.079963	-5.23542
C	-4.72661	3.882965	-2.00591
C	-5.75315	3.850789	-1.06305
C	-6.29183	2.632053	-0.6365
C	-5.77556	1.445674	-1.18204
C	-4.75943	1.477137	-2.12835
C	-5.16524	-4.95583	2.063726
C	-5.35013	-6.33757	2.027785
C	-4.25207	-7.20273	1.960534

C	-2.96274	-6.64595	1.941256
C	-2.77805	-5.27073	1.993451
C	-5.16236	-1.05789	2.485959
C	-5.97501	-0.28383	3.316218
C	-6.18591	-0.67746	4.642509
C	-5.56442	-1.83871	5.124982
C	-4.73926	-2.58867	4.298797
O	4.528329	-8.86882	-3.72492
S	7.768815	-1.49956	2.367459
S	9.118235	3.870943	1.546472
O	0.482269	6.987496	5.536103
O	-6.96913	-0.00549	5.538888
S	-4.36195	-8.9834	1.889448
S	-7.59754	2.468027	0.573135
O	-3.31588	6.763707	-7.44055
C	3.424518	-9.752	-3.84291
C	-2.15898	7.514137	-7.77238
C	-8.16713	4.181938	0.814293
C	-6.1451	-9.30522	2.075897
C	-7.62044	1.175165	5.098473
C	-0.70349	7.684601	5.192865
C	6.663113	-1.17537	3.797758
C	9.565548	5.635426	1.610723
H	3.302991	-3.37344	-4.32768
H	2.252467	-2.1006	-0.3534
H	1.558122	-1.9037	-5.28928
H	-1.90872	1.732594	-1.40932
H	-2.17775	1.569692	-5.70345
H	-0.37866	-0.12397	-5.7798
H	2.337155	1.247133	-1.9662
H	3.579151	2.933508	-0.67413
H	0.981933	2.200182	2.688219
H	-2.17638	-0.87857	2.795731
H	-2.97889	-3.66304	-0.39779
H	-1.30506	-2.51409	-1.7832
H	5.091389	-5.0482	0.221691
H	6.672372	-4.16526	1.895991
H	6.338413	-0.253	0.157366
H	4.788899	-1.13382	-1.53867
H	1.969152	-5.45723	-2.02023
H	2.162516	-7.744	-2.90149
H	6.389028	-7.17615	-3.44598
H	6.179917	-4.85105	-2.58864
H	0.878448	5.067711	1.382041

H	-0.32426	6.525826	2.951384
H	2.591354	5.662627	5.989672
H	3.782763	4.158717	4.408293
H	4.574333	5.882381	1.772402
H	7.014991	6.034553	1.662893
H	7.272096	1.729719	1.637544
H	4.820523	1.594646	1.751586
H	-1.12427	4.271732	-4.26461
H	-1.10827	6.03238	-5.97961
H	-5.28021	5.329183	-6.74121
H	-5.28015	3.52342	-5.03056
H	-4.31861	4.838198	-2.31827
H	-6.11434	4.79018	-0.66019
H	-6.19058	0.487219	-0.88204
H	-4.38669	0.548106	-2.54551
H	-6.02933	-4.30138	2.106432
H	-6.36275	-6.7242	2.039309
H	-2.09407	-7.2976	1.904628
H	-1.77304	-4.86256	1.994782
H	-5.00848	-0.75025	1.456799
H	-6.44111	0.606244	2.909896
H	-5.73101	-2.12569	6.158016
H	-4.252	-3.47849	4.683849
H	3.824302	-10.6816	-4.25043
H	2.660809	-9.35821	-4.52604
H	2.961578	-9.95544	-2.8687
H	-2.46506	8.210758	-8.55415
H	-1.35515	6.872564	-8.15608
H	-1.78234	8.081846	-6.91162
H	-9.02692	4.117438	1.484233
H	-8.48629	4.627815	-0.13051
H	-7.40087	4.803418	1.283256
H	-6.24904	-10.3921	2.082586
H	-6.71864	-8.90179	1.238162
H	-6.52591	-8.90689	3.019244
H	-8.18174	1.547711	5.956868
H	-8.31436	0.972033	4.272697
H	-6.90143	1.939385	4.776617
H	-0.99485	8.242285	6.084183
H	-1.5137	6.996907	4.917398
H	-0.5368	8.388315	4.366789
H	7.300603	-0.8073	4.605313
H	6.166828	-2.09208	4.122752
H	5.918425	-0.41442	3.555298

H	10.65674	5.66262	1.584462
H	9.22252	6.103174	2.536676
H	9.178823	6.182254	0.747493

Table S9. DFT/ B3LYP/6-31g (d,p) optimized geometrical Cartesian coordinates of SP-Naph. The structure is at a global minimum (no imaginary frequency).

Electronic Energy= -4638.1987416 *Hartree*

Symbol	X	Y	Z
C	2.006272	-3.46295	-3.66883
C	2.038129	-3.6348	-2.27049
C	1.4689	-2.64335	-1.44517
C	0.889562	-1.52784	-2.02494
C	0.833097	-1.37158	-3.42428
C	1.399858	-2.34904	-4.24506
C	0.222782	-0.33691	-1.31408
C	-0.26865	0.479662	-2.52558
C	0.116367	-0.13136	-3.73324
C	-0.99099	1.661681	-2.51323
C	-1.36621	2.251745	-3.73436
C	-0.97365	1.646056	-4.94382
C	-0.23105	0.467817	-4.94806
N	-2.1412	3.442157	-3.75191
N	2.61712	-4.80015	-1.70851
C	1.23205	0.466782	-0.49111
C	0.990035	0.820591	0.837838
O	-0.14291	0.447657	1.520069
C	-1.08358	-0.32797	0.886909
C	-0.95001	-0.76469	-0.43459
C	2.431224	0.931264	-1.05358
C	3.331238	1.716411	-0.34901
C	3.067322	2.063555	0.992423
C	1.891205	1.587743	1.580214
C	-2.19317	-0.65809	1.666616
C	-3.22699	-1.42937	1.128368
C	-3.10319	-1.89639	-0.19442
C	-1.9817	-1.56761	-0.94237
N	3.946052	2.900502	1.720084
N	-4.38229	-1.70989	1.899465
C	-1.78923	4.493533	-4.64868
C	-3.18843	3.628408	-2.81571
C	-4.98691	-0.66178	2.657617
C	-5.04251	-2.95864	1.764672

C	3.43513	3.754542	2.744818
C	5.347873	2.900114	1.487124
C	2.527905	-6.04057	-2.40847
C	3.343187	-4.75324	-0.48943
C	3.24433	-5.84582	0.424232
C	3.927613	-5.83595	1.613716
C	4.740769	-4.72992	1.991118
C	4.830528	-3.62588	1.081834
C	4.139971	-3.67318	-0.15558
C	1.293949	-6.52102	-2.85902
C	1.199618	-7.73108	-3.54842
C	2.350729	-8.49471	-3.77598
C	3.58992	-8.02551	-3.31661
C	3.67788	-6.81028	-2.65188
C	2.368245	4.623147	2.493196
C	1.8694	5.459602	3.493002
C	2.456587	5.453325	4.763961
C	3.535345	4.594836	5.019796
C	4.00997	3.749807	4.026301
C	6.044729	4.145747	1.471069
C	7.398356	4.194702	1.257841
C	8.153764	3.009842	1.027946
C	7.456298	1.756725	1.031624
C	6.058346	1.731744	1.280494
C	-0.45923	4.90037	-4.79124
C	-0.10564	5.911469	-5.68804
C	-1.09508	6.549998	-6.4427
C	-2.43385	6.15526	-6.29648
C	-2.77386	5.135227	-5.42054
C	-3.44281	4.863052	-2.24435
C	-4.51989	5.046898	-1.3389
C	-5.34866	3.932567	-0.98447
C	-5.0633	2.673218	-1.58553
C	-4.02843	2.524552	-2.47289
C	-6.42099	-3.05198	1.70544
C	-7.06873	-4.31131	1.613884
C	-6.2852	-5.5104	1.554718
C	-4.86767	-5.38333	1.611057
C	-4.26572	-4.15616	1.721376
C	-5.11549	0.627062	2.130233
C	-5.68665	1.659929	2.876664
C	-6.17005	1.403187	4.163772
C	-6.05543	0.109776	4.695918
C	-5.46137	-0.9042	3.958198

O	2.373865	-9.69529	-4.42804
O	2.057519	6.235374	5.810781
O	-6.76118	2.332466	4.972718
O	-0.86663	7.5554	-7.34022
C	1.146768	-10.2192	-4.90912
C	0.469572	7.991415	-7.52846
C	-6.84744	3.668152	4.498065
C	0.962737	7.114344	5.610048
C	5.441568	-4.6824	3.216593
C	6.212106	-3.58291	3.552259
C	6.304565	-2.48428	2.658774
C	5.628001	-2.51627	1.457742
O	6.850387	-3.63443	4.761449
C	7.628699	-2.51999	5.166395
C	9.546759	3.033801	0.797046
C	10.25081	1.86319	0.575785
C	9.5699	0.618932	0.578955
C	8.209274	0.577292	0.80052
O	11.59582	1.994429	0.36253
C	12.36253	0.826486	0.118886
C	-4.80494	6.302936	-0.74608
C	-5.84227	6.462563	0.148968
C	-6.65593	5.353814	0.494249
C	-6.41107	4.114432	-0.07052
C	-8.47983	-4.43432	1.559093
C	-9.09465	-5.66419	1.453118
C	-8.31176	-6.84578	1.398639
C	-6.93144	-6.76167	1.449576
O	-8.83986	-8.10487	1.29569
C	-10.2493	-8.24751	1.245504
O	-7.6993	5.422863	1.383746
C	-8.07327	6.694504	1.890392
H	2.456728	-4.21842	-4.30266
H	1.482646	-2.76117	-0.36712
H	1.382366	-2.24804	-5.3268
H	-1.27632	2.129713	-1.5766
H	-1.26745	2.106137	-5.88124
H	0.050495	0.013647	-5.89413
H	2.647936	0.685395	-2.08897
H	4.231608	2.07495	-0.83328
H	1.644783	1.814768	2.609923
H	-2.24213	-0.29033	2.684563
H	-3.89493	-2.4941	-0.63122
H	-1.90826	-1.91939	-1.96726

H	2.612744	-6.68864	0.165718
H	3.836664	-6.67694	2.295942
H	4.229614	-2.83359	-0.8373
H	0.397316	-5.9389	-2.67268
H	0.227718	-8.07071	-3.88578
H	4.47389	-8.62568	-3.50515
H	4.642048	-6.44791	-2.31047
H	1.916238	4.639131	1.5069
H	1.037468	6.114916	3.264732
H	3.976144	4.596934	6.011136
H	4.836421	3.078363	4.235081
H	5.482467	5.059741	1.628672
H	7.910861	5.15294	1.247714
H	5.54227	0.777058	1.305081
H	0.311214	4.416055	-4.2003
H	0.935997	6.196259	-5.77576
H	-3.18939	6.653779	-6.89473
H	-3.80995	4.828088	-5.32334
H	-2.8156	5.713055	-2.49308
H	-5.69406	1.821597	-1.34469
H	-3.83853	1.559497	-2.92918
H	-7.02546	-2.1512	1.73839
H	-4.25936	-6.28349	1.583438
H	-3.18547	-4.08075	1.784417
H	-4.75216	0.836102	1.129504
H	-5.75906	2.646385	2.435074
H	-6.42471	-0.07306	5.699691
H	-5.36473	-1.89752	4.383946
H	1.391512	-11.1673	-5.39028
H	0.680855	-9.55144	-5.64536
H	0.43568	-10.4027	-4.09327
H	0.426233	8.783135	-8.27783
H	1.112925	7.181712	-7.89667
H	0.899459	8.395241	-6.60258
H	-7.33843	4.235481	5.290723
H	-7.43818	3.744396	3.577301
H	-5.85232	4.093732	4.313433
H	0.809303	7.626923	6.560807
H	0.048355	6.569055	5.342805
H	1.17609	7.857671	4.830887
H	5.380125	-5.5113	3.914986
H	6.899468	-1.61498	2.912633
H	5.695829	-1.67181	0.777147
H	8.02778	-2.77492	6.149396

H	7.024039	-1.60797	5.250937
H	8.463894	-2.33212	4.479269
H	10.08394	3.977193	0.790094
H	10.10854	-0.30471	0.403947
H	7.700491	-0.38246	0.793356
H	13.38911	1.166823	-0.02519
H	12.02999	0.300001	-0.78503
H	12.33224	0.132247	0.968674
H	-4.18619	7.157812	-1.00587
H	-6.02672	7.438329	0.582356
H	-7.05089	3.27896	0.196706
H	-9.08687	-3.53385	1.601801
H	-10.1761	-5.71758	1.413925
H	-6.34908	-7.67695	1.406973
H	-10.4397	-9.31913	1.16746
H	-10.6813	-7.74335	0.371139
H	-10.7325	-7.86402	2.153632
H	-8.94766	6.521653	2.519716
H	-8.34249	7.38948	1.085044
H	-7.27827	7.144384	2.499391

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