Supporting Information

Pyridyl Functionalized Spiro [Fluorene-Xanthene] as Dopant Free Hole Transport Material for Stable Perovskite Solar Cells

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1. Experimental Section

1.1 Materials

Resorcinol and dibromo-9-fluorenone was purchased from Sigma-Aldrich chemicals. All other reagents and catalysts were purchased from commercial suppliers and used without further purification. All reactions were carried out under nitrogen atmosphere. All the solvents used in this work were distilled prior to use.

1.2 Measurement

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 400-MHz or 500-MHz spectrometer using TMS as standard and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet. Purifications were carried out through silica gel using 100- 200 mesh and 230-400 mesh. Absorption spectra in solution and solid film were recorded on Scimadzu UV-1800 model spectrophotometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a CH Instruments 620C electrochemical analyzer with a scan rate of 100 mV/s in dichloromethane using 0.1 M $TBAPF_6$ as the supporting electrolyte, a Ag/AgCl electrode as the reference electrode, a carbon-glass electrode as the working electrode, a Pt wire as the counter electrode and ferrocene/ferrocenium (Fc/Fc+) as an external reference.

1.3 Fabrication of PSC Devices.

First, the cleaned FTO-substrate (14Ω sq^{-1}) and coated the FTO with titanium diisopropoxidebis(acetylacetonate) (Sigma-Aldrich) in ethanol solution by spray pyrolysis at 500°C for 30 min to make a thickness of 40 nm compact TiO_2 layer (cl-TiO_2). Prior to deposition of compact layer the cl-TiO_2 substrates were annealed at 470°C for 30 min and cooled down to room temperature. Then a mesoporous TiO_2 film was deposited on the cl-TiO_2 coated substrate by spin coating (3000 rpm, 30s) from an ethanol solution of diluted TiO_2 paste (30 nm particle Dyesol-30NRD, Dyesol) with a mass ratio of 1:4 followed by drying at 70 °C for 10 min and sintered for 500 °C for 30 min in air. After annealing, the mesoporous TiO_2 (mp-TiO_2) substrates were cooled down to room temperature and transferred to a N_2 glove box. Subsequently, a 1.2M $CH_3NH_3PbI_3$ (CH_3NH_3I and PbI_2 equimolar ratio) perovskite precursor was prepared in dimethylformamide and dimethyl sulfoxide solution with a ratio of 4:1. The $CH_3NH_3PbI_3$ precursor solution was spin coated by two consecutive spin coating steps at 1000 rpm for 12 s followed by 4000rpm for 30 s. After 20sec of starting the second spin-coating stage, 100 μL of anhydrous chlorobenzene (99.8%) was dropped onto the spinning substrate. These perovskite deposited substrates were then heat-treated at 100°C for 30 min on a hotplate. The SPS-SPX-2TPA solutions were deposited on the individual perovskite films by spin-coating and solutions were prepared by the following details. SPS-SPX-2TPA was dissolved in 1 mL anhydrous chlorobenzene (7mM). The spiro-OMeTAD (60 mM) solution was prepared with 4-*tert*-butylpyridine (10μL) and a 0.043 mM Li-TFSI acetonitrile solution (72μL) was used. The spin-coating process was carried out at 3000 rpm for 20 s for SPS-SPX-2TPA. The Spiro-OMeTAD solutions were spin coated with 4000 rpm for 30 s. Either SPS-SPX-2TPA or Spiro-OMeTAD was spin-coated on $CH_3NH_3PbI_3$/mp-TiO_2/cl-TiO_2/FTO substrates. Finally, 80 nm of elemental gold was deposited by thermal evaporation under vacuum ($4.1x10^{-4}$ Pa) to complete the fabrication of the solar cells. The active areas of all the PSCs were 0.10 cm^2.

1.4 Fabrication of hole only devices

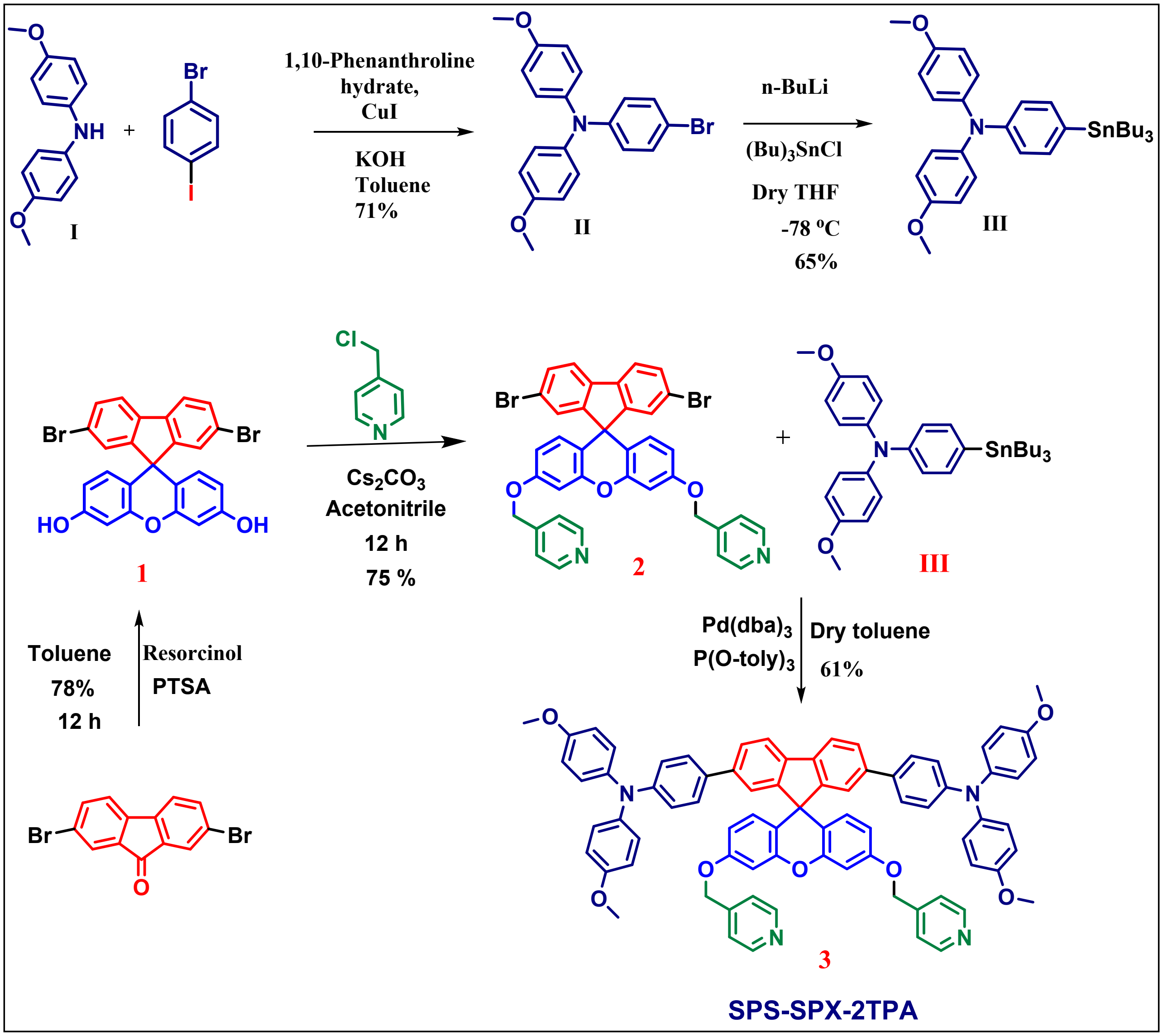
PEDOT:PSS was spin-coated on top of patterned ITO glass at 5000 rpm for 30s. Flowingly, either dopant free SPS-SPX-2TPA or doped Spiro-OMeTAD with the same concentration as the full device fabrication as mentioned above was spin-coated. 70 nm Au was evaporated with a shadow mask of 0.10 cm^2 .

Characterization

The current-voltage characteristics were measured using a solar simulator with standard air mass 1.5 sunlight (100m Wcm^{-2}, WXS-155S-10: Wacom Denso) under ambient conditions. The *J-V* curves were measured by forward (-0.2V to 1.2V forward bias) or reverse (1.2V to -0.2V) scans. The step voltage was fixed at 5-10mV and the delay time was set at100ms. *J-V* curves for all devices were measured by masking the cells with a metal mask 0.10 cm^2 area. Monochromatic incident photon-to-current conversion efficiency (IPCE) spectra were measured with a monochromatic incident light of 1×10^{16} photons cm^2 in director current mode (CEP-2000BX, Bunko-Keiki). The light intensity of the solar simulator was calibrated by a standard silicon solar cell provided by PV Measurements.

2. Synthesis

We have synthesized intermediate II and intermediate III as per previous reported literature.[1]Di-bromoSpiro-(fluorene-9-9′-xanthene) (1) was prepared from previous literature.[2]



2,7-dibromospiro[fluorene-9,9'-xanthene]-3',6'-diol (1)

To a 100 ml round bottom flask was charged with 2, 7-Dibromo-9-fluorenone (1.750 g, 5.177 mmol), resorcinol (2.280 g, 20.710 mmol), p-TsOH (100 mg, 0.051 mmol), and toluene (40 mL). The mixture was refluxed for 12h, and then cooled to room temperature. After completion of reaction, water (100 mL) was added and the mixture was continued for 0.5 h. The yellow colour precipitated from the reaction crude was isolated by filtration. Then the crude product was dissolved in alcohol (100 mL) and filtrated to remove insoluble impurity from the product. The organic solution was concentrated by vacuum evaporation and purified by column chromatography using silica gel, petroleum ether/*EtOAc* (3:1) as an eluent and afford required product-1 as a white solid (2.10 g, yield 78%).**^{1}H NMR (400 MHz, $CDCl_3$):**δ (ppm) 7.59 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 8.1, 1.8 Hz, 2H), 7.26 – 7.20 (m, 2H), 6.69 (d, J = 2.5 Hz, 2H), 6.33 (dd, J = 8.6, 2.6 Hz, 2H), 6.22 (d, J = 8.6 Hz, 2H), 5.08 (s, 2H).**13C NMR (101 MHz, $CDCl_3$)** δ 156.94, 155.80, 137.62, 131.16, 128.90, 122.42, 121.36, 115.60, 115.43, 111.63, 103.39, 29.74. **ESI-MS** calcd for $C_{25}H_{14}Br_2O_3$ $[M+H]^+$ m/z 522; found 523.

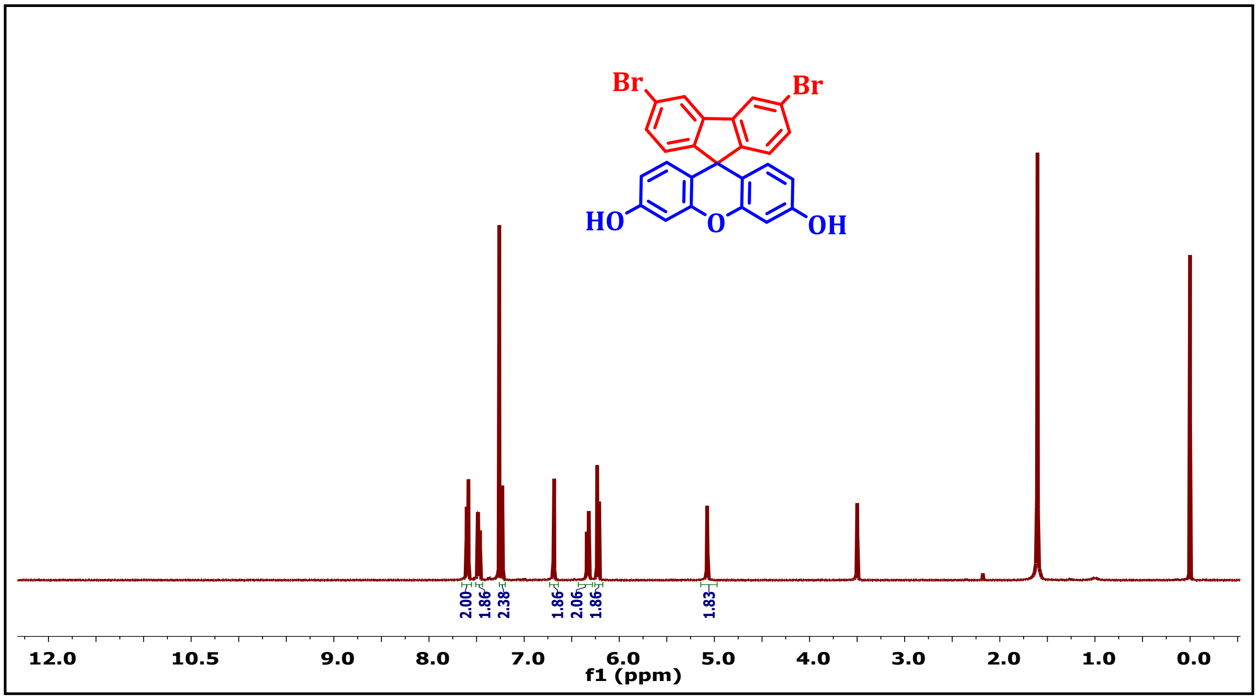
4,4'-(((2,7-dibromospiro[fluorene-9,9'-xanthene] ',6'diyl)bis(oxy))bis(methylene))dipyridine (2)

To a round bottom flask compound 1 (300mg, 0.574 mmol), cesium carbonate (561mg, 1.723 mmol) and dissolved in 30 ml of acetonitrile. After refluxing the reaction mixture upto 1.5 h at 50°C, then 4-(chloromethyl)pyridine (220mg, 1.723 mmol) was added continued the reaction for 24 h. After complete consumption of both starting materials in the reaction mixture, then the solvent was removed by vacuum pressure and then organic layer was extracted with *EtOAc* dried over sodium sulphate (Na_2SO_4). The residue was purified by column chromatography using silica gel as stationary phase and petroleum ether/ *EtOAc* as mobile phase afforded the product-**4** as colorless solid (300 mg, yield 75%).**^{1}H NMR (400 MHz, $CDCl_3$):** δ (ppm) 8.63 (d, J = 5.8 Hz, 4H), 7.61 (d, J = 8.1 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.35 (d, J = 5.9 Hz, 3H), 7.22 (d, J = 1.7 Hz, 2H), 6.77 (d, J = 2.6 Hz, 2H), 6.47 (dd, J = 8.7, 2.6 Hz, 2H), 6.29 (d, J = 8.7 Hz, 2H), 5.08 (s, 4H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.42, 156.77, 151.83, 150.00, 145.95, 137.49, 131.37, 128.96, 122.45, 121.54, 115.91, 111.56, 102.52, 68.41, 29.74. **ESI-MS** $[M]^+$ calcd for $C_{37}H_{24}Br_2N_2O_3$*m/z* 704.41; found 705.

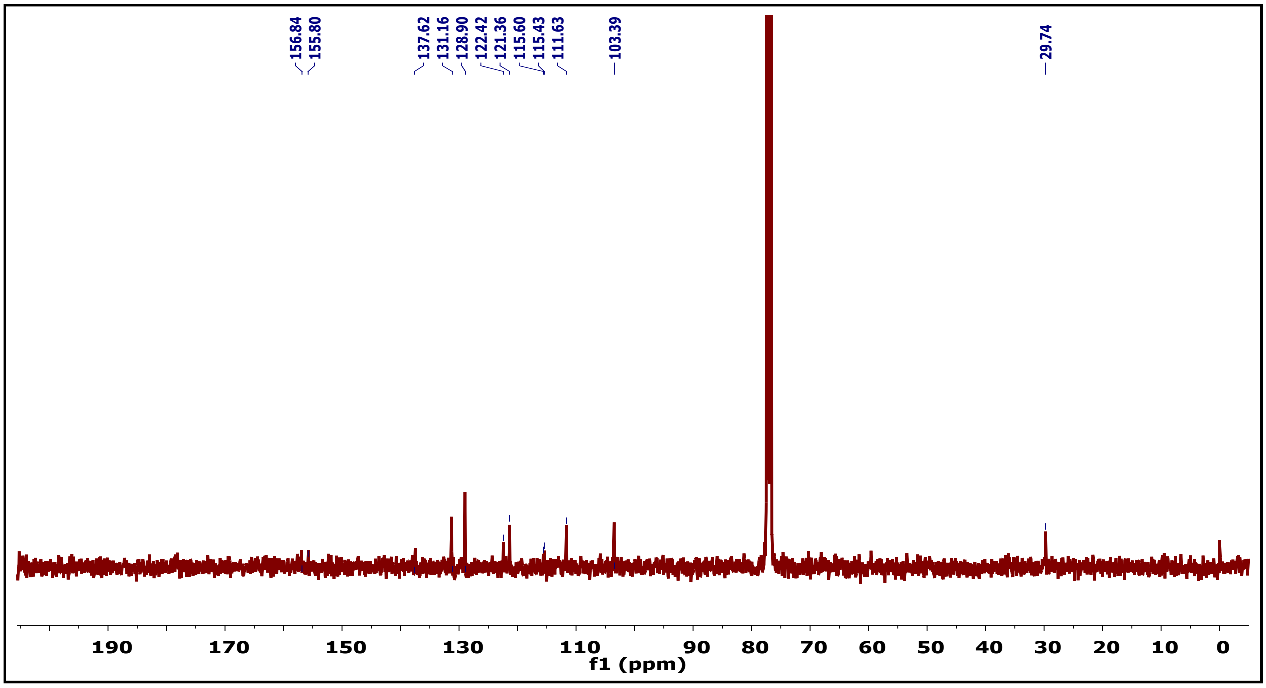
4,4'-(3',6'-bis(pyridin-4-ylmethoxy)spiro[fluorene-9,9'-xanthene]-2,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (SPS-SPX-2TPA)

In a 15 mL pressure tube was charged with compound 2 (300 mg, 0.425 mmol), 4-methoxy-N-(4-methoxyphenyl)-N-(4-(tributylstannyl)phenyl)aniline (III) (1.012g, 1.703 mmol) and dissolved in dry toluene (10 mL).The reaction mixture was purged with nitrogen gas upto 30 minutes, then tri(o-tolyl)phosphine (5%) and tris(dibenzylideneacetone)dipalladium(0)-chloroform (10%) were added and the reaction mixture was heated at 100^{o}C for 3 days. After removal of solvent, the reaction mixture was extracted with DCM, and then poured into ice-water. 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 (230 – 400 mesh) with hexane and DCM as eluent to afford compound **SPS-Si-SPSX-TPA** as green color solid (300 mg, 61%).**^{1}H NMR (300 MHz, $CDCl_3$)** δ 8.61 (s, 2H), 7.77 (t, J = 7.1 Hz, 1H), 7.66 – 7.42 (m, 2H), 7.27 (dd, J = 19.5, 8.7 Hz, 6H), 7.03 (d, J = 8.7 Hz, 4H), 6.89 (d, J = 8.3 Hz, 2H), 6.83 – 6.70 (m, 4H), 6.48 – 6.16 (m, 2H), 4.97 (d, J = 38.2 Hz, 2H), 3.77 (s, 6H).**13C NMR (101 MHz, $CDCl_3$)** δ 158.07, 157.95, 157.76, 155.99, 151.98, 149.70, 148.28, 146.37, 140.75, 137.86, 132.69, 132.33, 131.12, 129.21, 128.80 (s), 127.41, 126.57, 126.19, 123.48, 121.46, 120.62, 120.14, 118.05, 117.01, 114.72, 111.28, 102.38, 68.34, 55.43, 29.74. MALDI TOF-MS [M]+ calcd for $C_{77}H_{60}N_4O_7$ m/z 1153.34; found 1152.22.

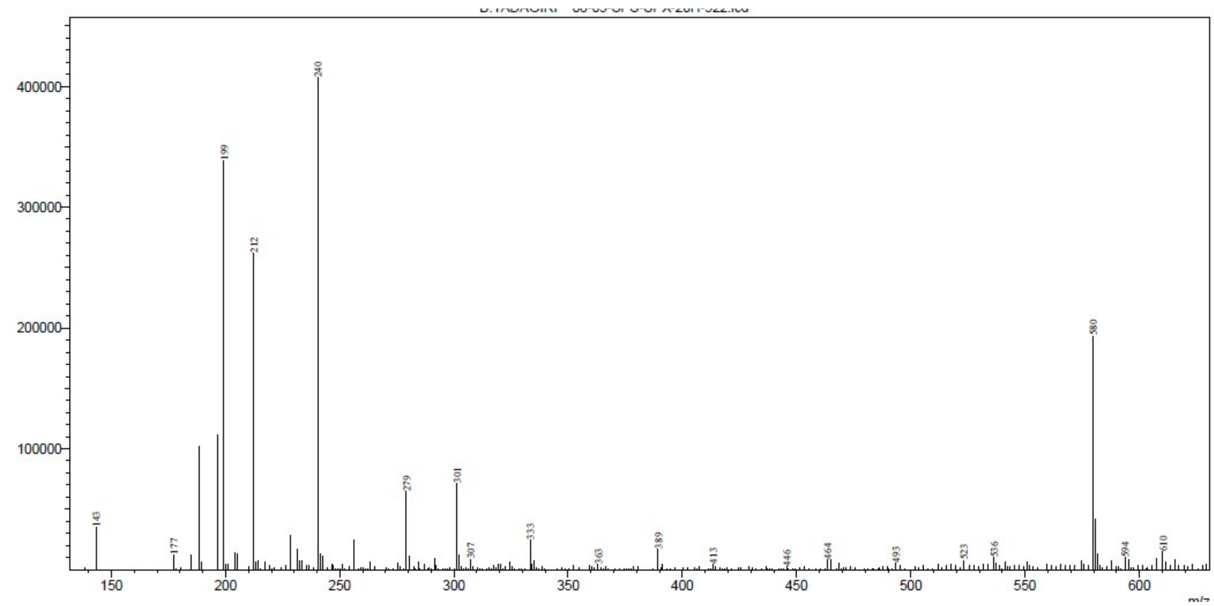
3. Copies of NMR Spectra



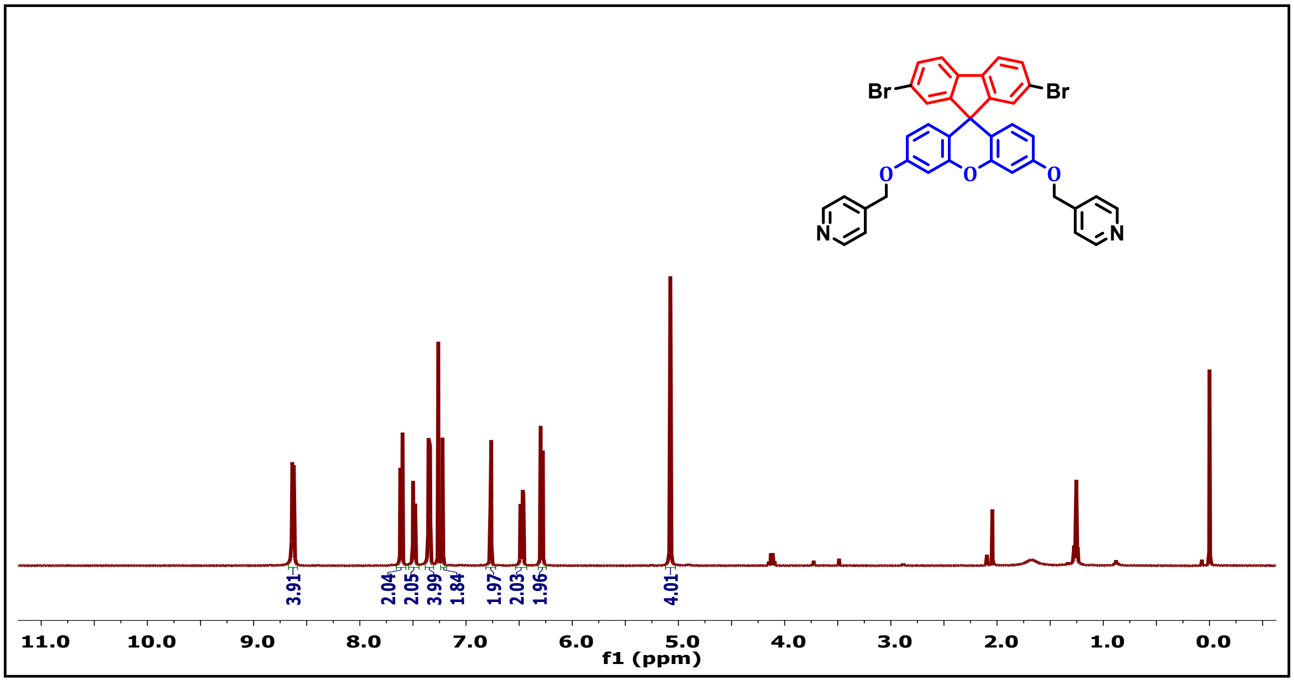
^{1}H NMR spectra of compound 1 in $CDCl_3$



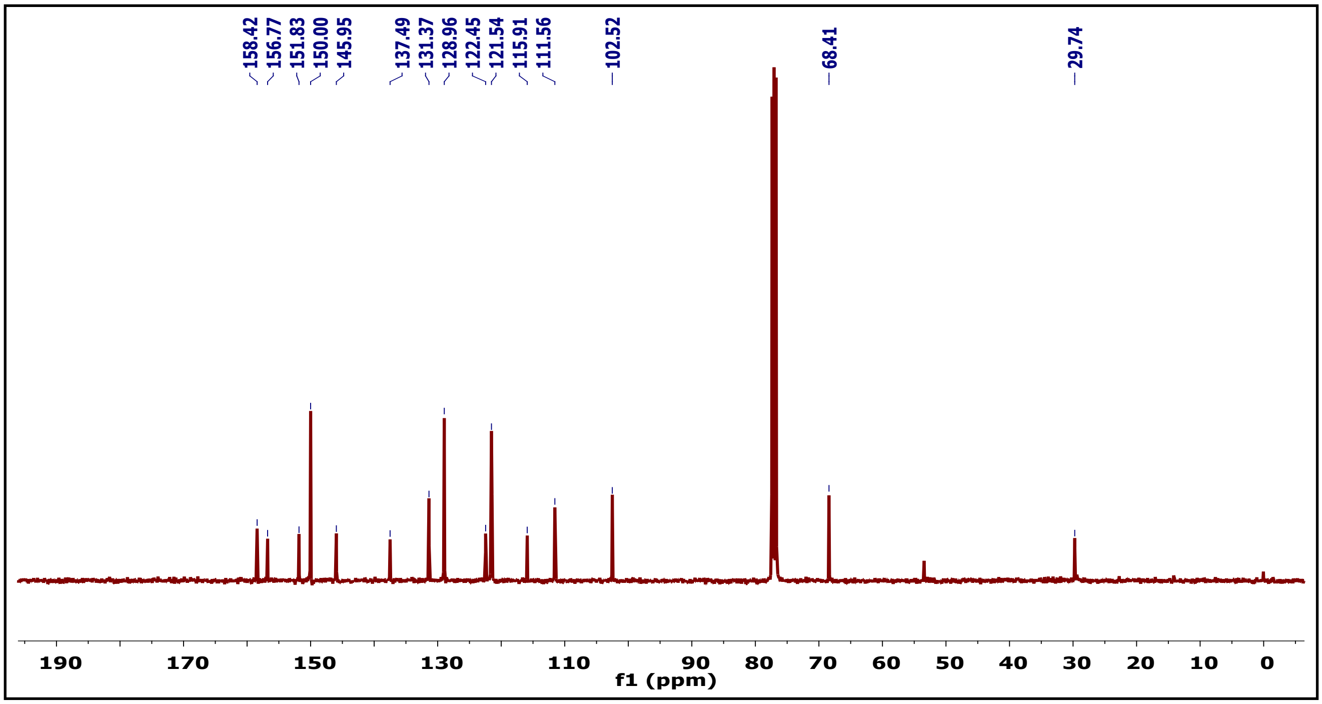
^{13}C NMR spectra of compound 1 in $CDCl_3$



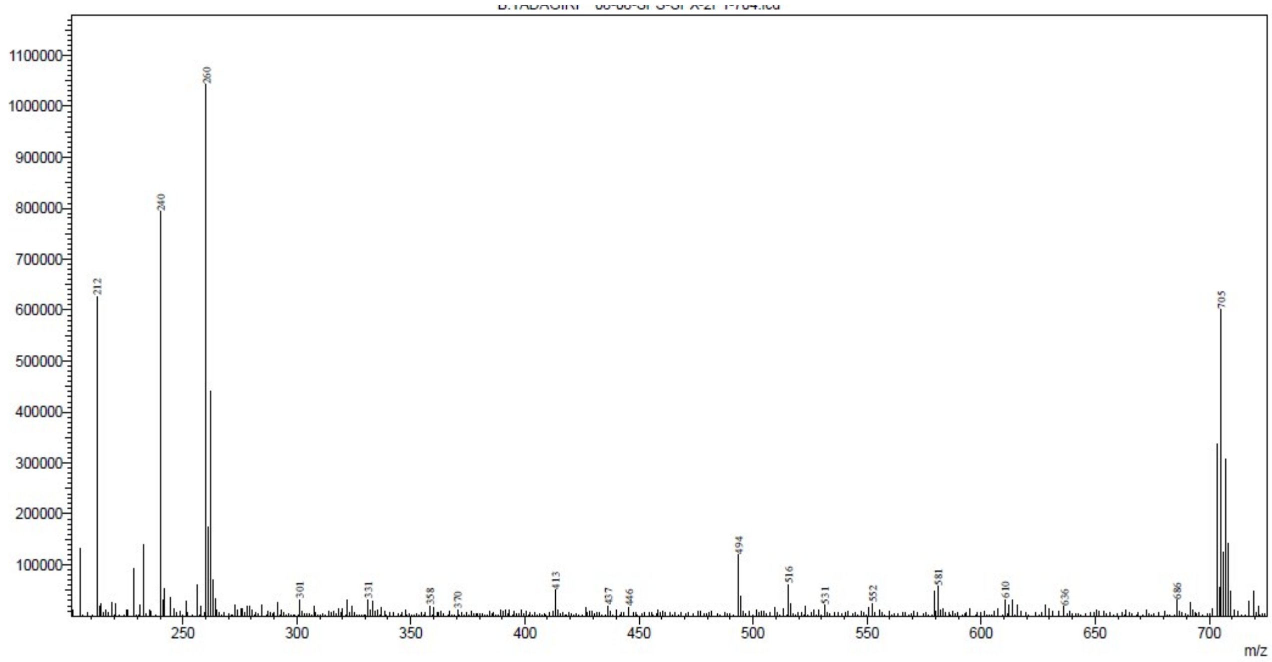
ESI mass spectra of compound 1



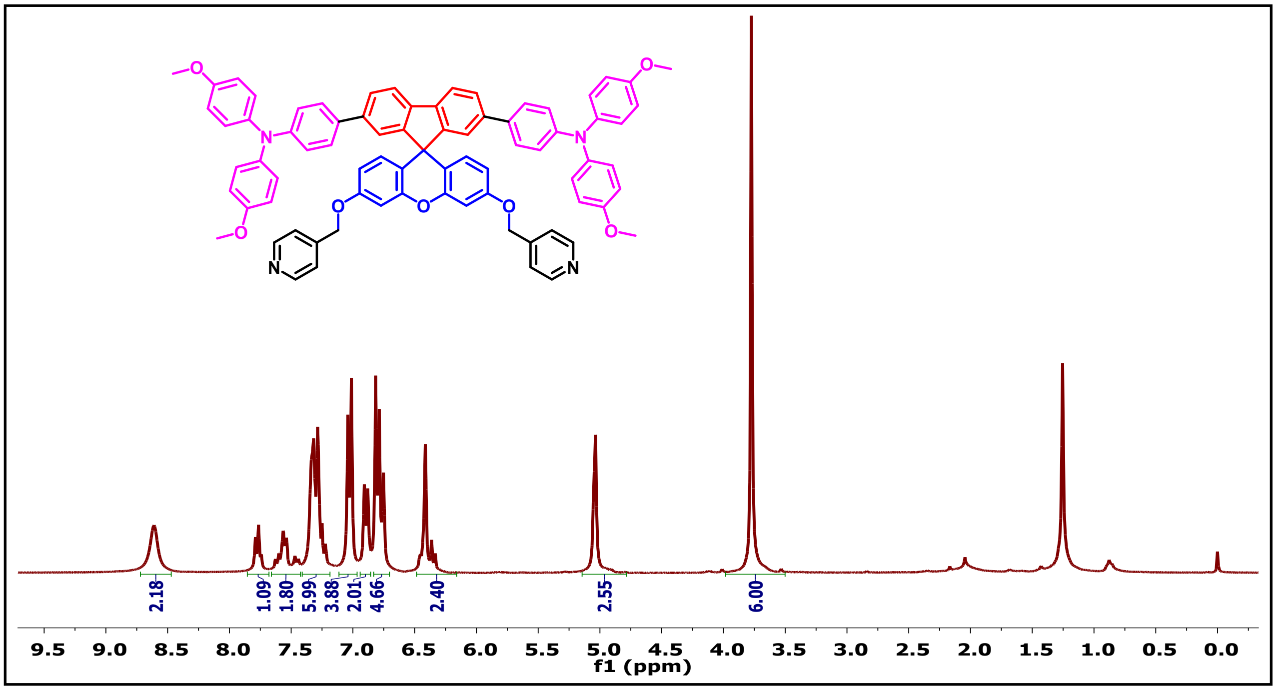
^{1}H NMR spectra of compound 2 in $CDCl_3$.



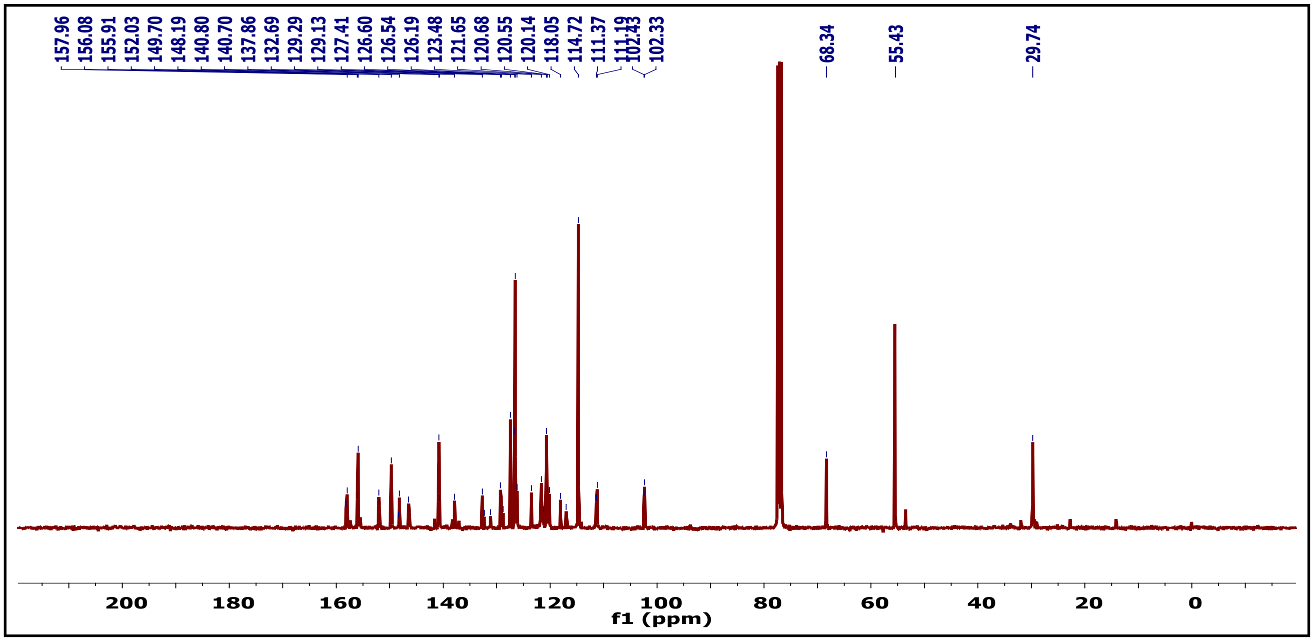
^{13}C NMR spectra of compound 2 in $CDCl_3$.



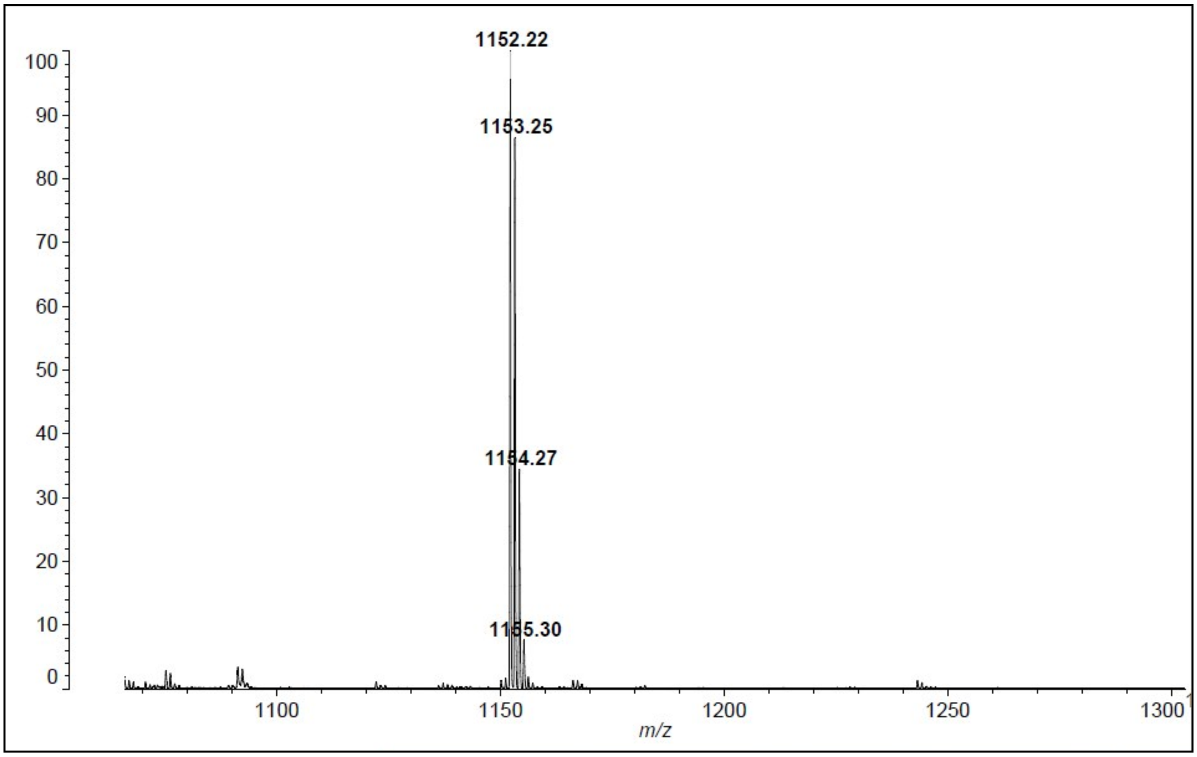
ESI mass spectra of compound 2



^{1}H NMR spectra of SPS-SPX-TPA in CDCl$_3$.



^{13}C NMR spectra of SPS-SPX-TPA in CDCl$_3$



MALDI-TOF spectra of SPS-SPX-2TPA

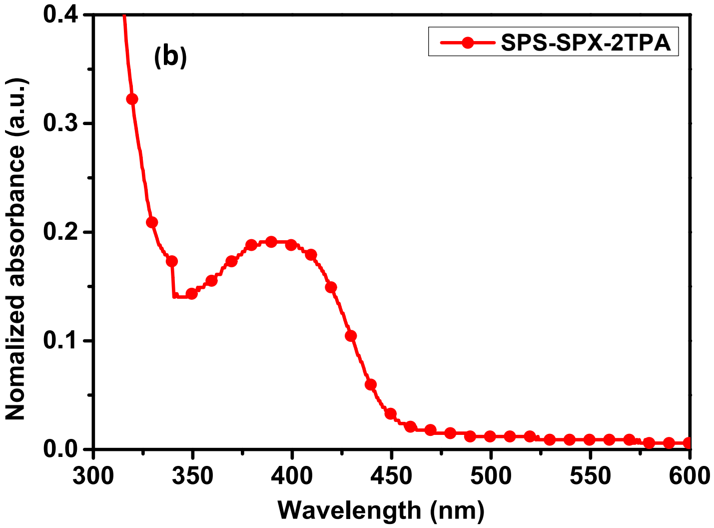


Figure S1: Thin film UV-visible absorption spectra of SPS-SPSX-2TPA

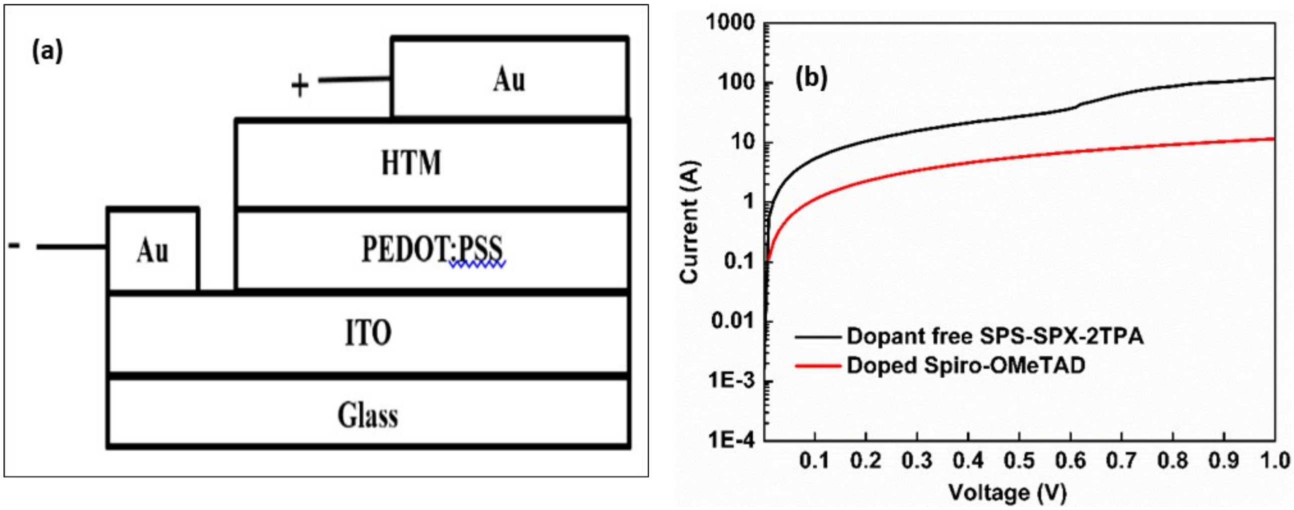


Figure S2: (a) Device structure of hole only devices, (b) hole mobility of dopant free SPS-SPSX-2TPA and doped Spiro-OMeTAD.

4. Theoretical calculations

Structural models of all molecules were first created using GaussView 5.0. These initial structures were then optimized by using density functional theory (DFT) based Becke's three parameter hybrid exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP) with 6-31G (d,p) basis set, in-vacuo. The stationary points were characterized as local minima by the frequency calculations at the same level of theory. HOMO/LUMO energy levels, frontier molecular orbitals and electrostatic potential (ESP) maps of the optimized structure were then generated using GaussView 5.0 and the formatted check files from the Gaussian 09 computation. Further, HTMs were evaluated for the first 15 singlet-singlet transitions states using TD-DFT method using CAM-B3LYP functional and 6-31G(d,p) basis set by using optimized geometry with PCM solvent model to obtain the UV-Vis spectra of HTMs. Absorption spectra (UV-Vis) and HOMO-LUMO energy transition interpretations were analyzed with Gauss Sum 2.2.5 software.[3-4]

The theoretical reorganization energy of the HTMs was calculated by using the Marcus equations. The hole and electron reorganization energies computed with the DFT analysis and calculated using the following equations:

$$\lambda_h = E^+(HTM^0) - E^+(HTM^+) + E^0(HTM^+) - E^0(HTM^0) \;\ldots\ldots\ldots\ldots (1)$$

$$\lambda_e = E^-(HTM^0) - E^-(HTM^-) + E^0(HTM^-) - E^0(HTM^0) \;\ldots\ldots\ldots\ldots\ldots (2)$$

Where, $E^+(HTM^0)/E^-(HTM^0)$ and $E^+(HTM^+)/E^-(HTM^-)$ is indicates total energy of cation/anion in neutral geometry and cation/anion optimized geometry. The $E^0(HTM^+)/E^0(HTM^-)$ and $E^0(HTM^0)$ represents total energy of the neutral molecule in cationic/anionic geometry and neutral molecule in the optimized geometry respectively.

TDDFT for SPS-SPX-2TPA and Spiro-OMeTAD

The time-dependent density functional theory (TDDFT) method was conducted to compare the UV-Visible absorption spectra of **SPS-SPX-2TPA** and Spiro-OMeTAD hole transporting materials in both experimental and theoretical method *via* exchange correlations functional and basis set in Gaussian 09. The TDDFT calculations of both **SPS-SPX-2TPA** and Spiro-OMeTAD were shows from 300 to 450 nm. In this, we mainly look into the visible region of the materials to recognize the charge transfer property. Figure S2 represents the correlation absorption spectra and oscillation strength of both **SPS-SPX-2TPA** and Spiro-OMeTAD HTMs. In the both cases experimental and theoretical absorption spectra looks similar. However, when compare to the experimental absorption spectra with theoretical absorption spectra was showed difference up to ~30 nm.

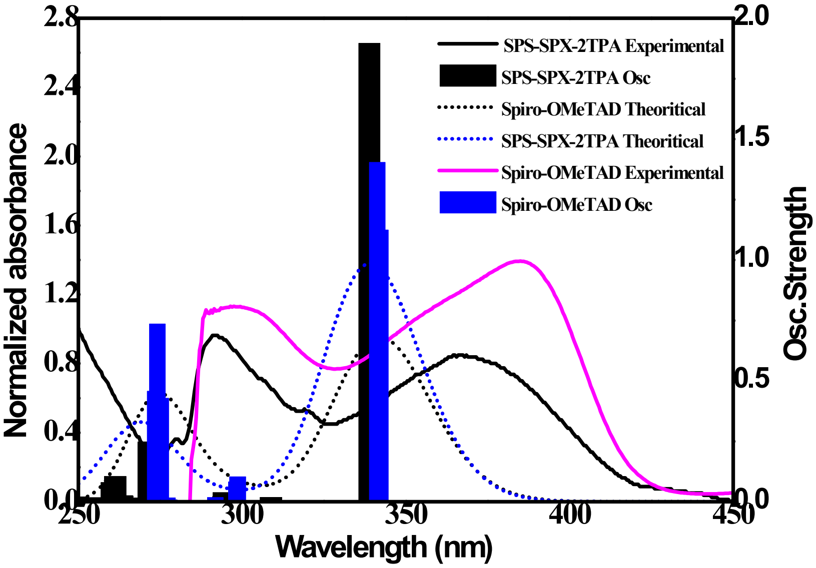


Figure S3. Correlation absorption spectra of SPS-SPX-2TPA and Spiro-OMeTAD HTMs.

Table S1. a) Ground state optimization was performed with DFT B3LYP/6-31G (d,p) level theory in gas phase. b) Singlet excited state properties of at TDDFT, CAM-B3LYP 6-31G(d,p) level theory in Chloroform solvent in CPCM model.

System	$\lambda_{abs}{}^{b}$ (nm)	Os^{b}	Percentage of major molecular orbital contribution
SPS-SFX-2TPA	339	2.6554	H-2→LUMO (13%) H-1→L+3 (10%) HOMO→LUMO (67%)
	271	0.3467	H-1→L+11 (18%) H-1→L+12 (25%) HOMO→L+11 (15%) HOMO→L+12 (30%)
	268	0.021	H-2→LUMO (19%) H-2→L+4 (16%) HOMO→L+4 (13%)
Spiro-OMeTAD	342	1.1242	H-1→L+1 (39%),

			HOMO→LUMO (48%)
	278	0.002	H-1→LUMO (28%) H-1→L+1 (15%) HOMO→L+1 (26%)
	274	0.7357	H-3→L+10 (11%) H-1→L+11 (16%) HOMO→L+11 (11%)

λ_{max} =Theoretical absorbance in nm, f =Oscillator strength

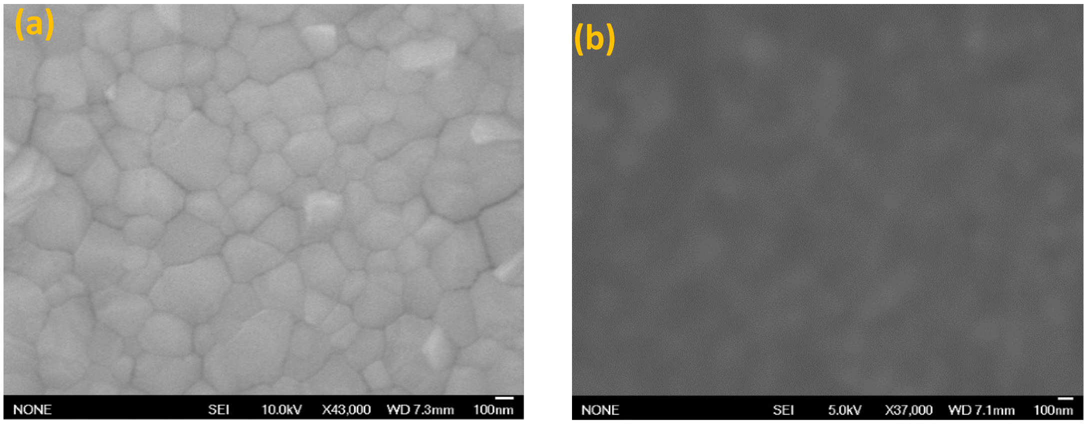


Figure S4. Surface morphology of the (a) MAPbI$_3$ perovskite layer and (b) SPS-SPX-2TPA on top of the perovskite layer.

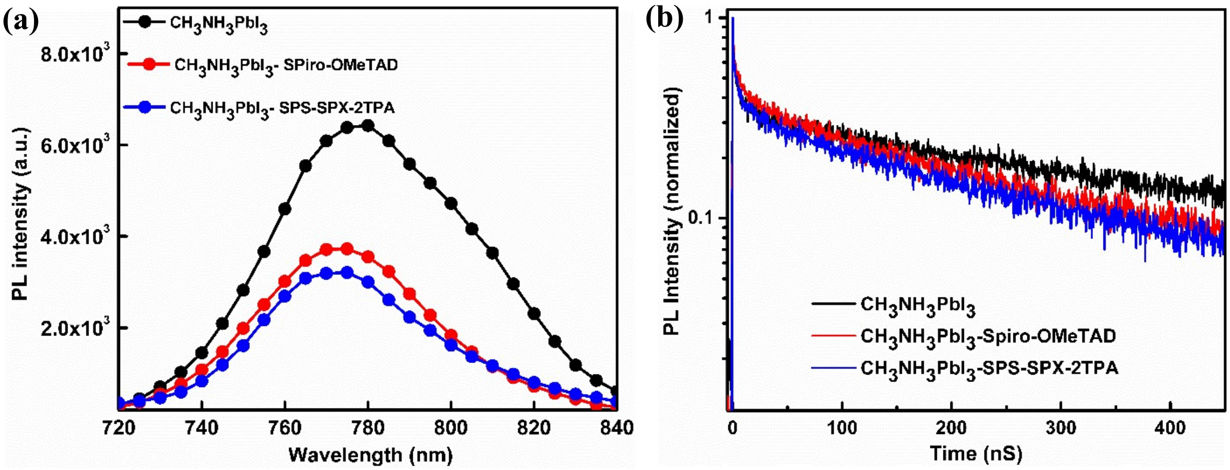


Figure S5. a) Steady state and b) time-resolved photoluminescence (PL) measured of bare perovskite film (black), and hole-transport layers SPS-SPX-2TPA and Spiro-OMeTAD deposited on perovskite. Bare glass substrate was used for the deposition of all perovskite films.

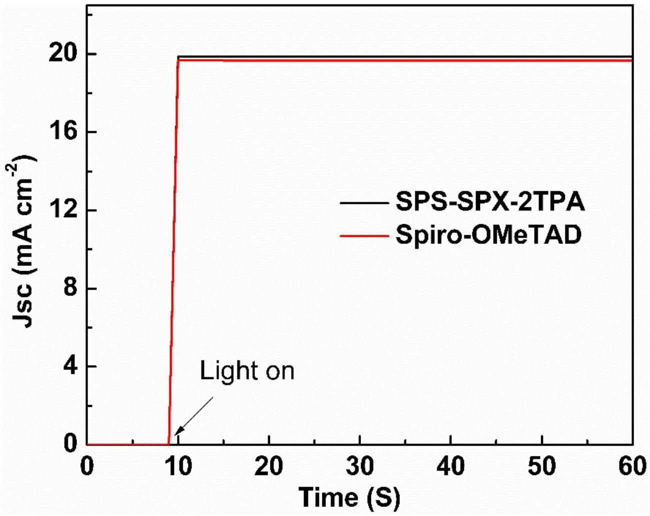


Figure S6. Stabilized Current Density (J_{SC}) of the PSCs fabricated with SPS-SPX-2TPA and Spiro-OMeTAD

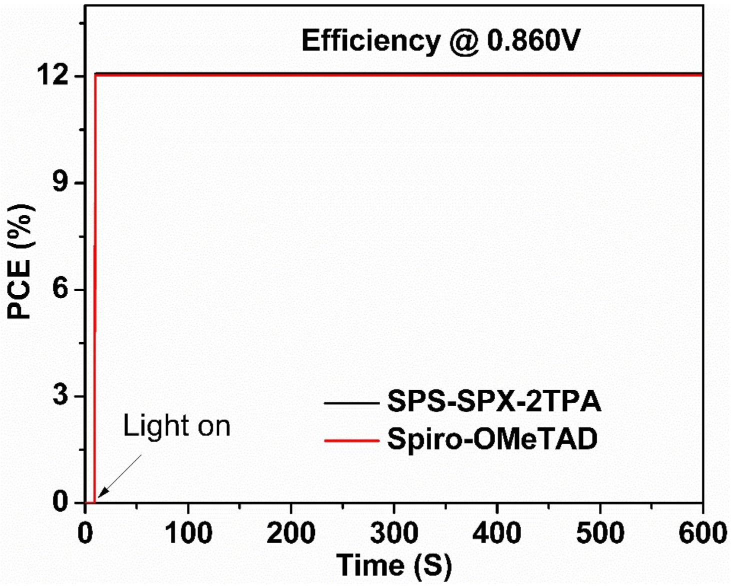


Figure S7. Steady state PCE of the PSCs fabricated with SPS-SPX-2TPA and Spiro-OMeTAD at maximum power point 0f 0.860V

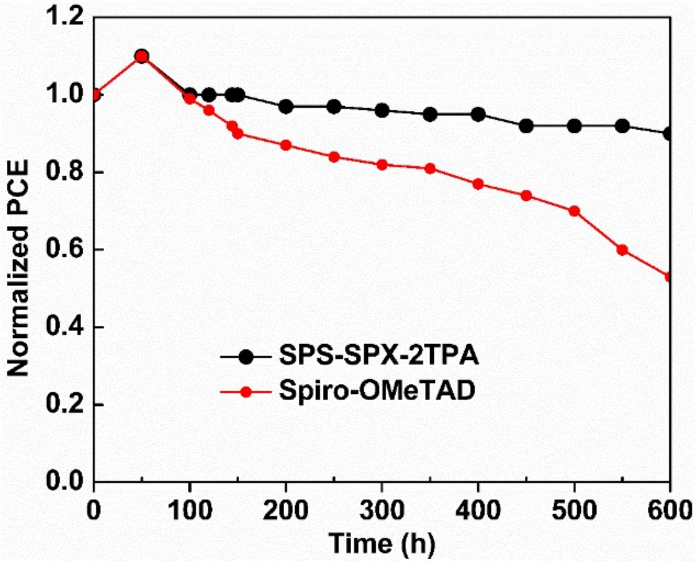
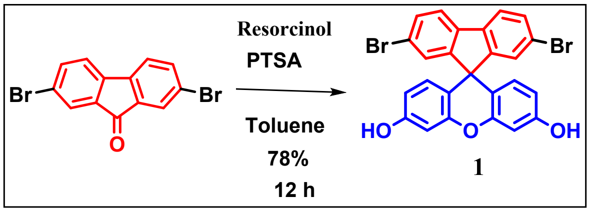


Figure S8. Maximum power point tracking (MPPT) under 1 sun at room temperature of the PSCs fabricated with SPS-SPX-2TPA and Spiro-OMeTAD HTMs.

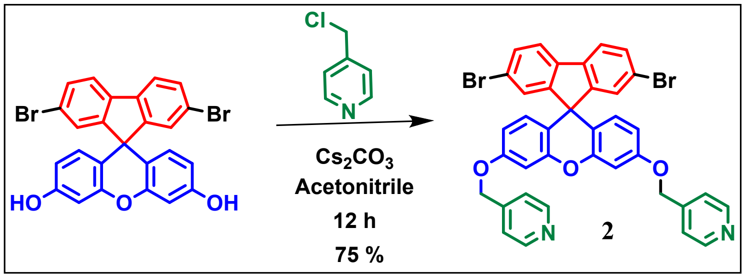
5. Cost for the Synthesis of SPS-SPX-2TPA HTM



Chemicals/Company	Price ($) (Kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (g)	Solvent (ml)	Workup (g or ml)	
Resorcinol/TCI	159$/kg	0.650			0.103
dibromo9-Fluorenone/TCI	437 $/kg	1			0.437
p-TsOH/TCI	63 $/kg	0.060			0.037
Toluene/Finar	11 $/L		30		0.330
Silica gel/Finar	17 $/kg			100 g	1.7
Petroleum ether/Finar	18$/L			250 ml	4.5
Ethyl acetate/Finar	9 $/L			100 ml	0.9
Total					8.007

Compound (1): Yield, 78%, 1.20 g, 8.007$

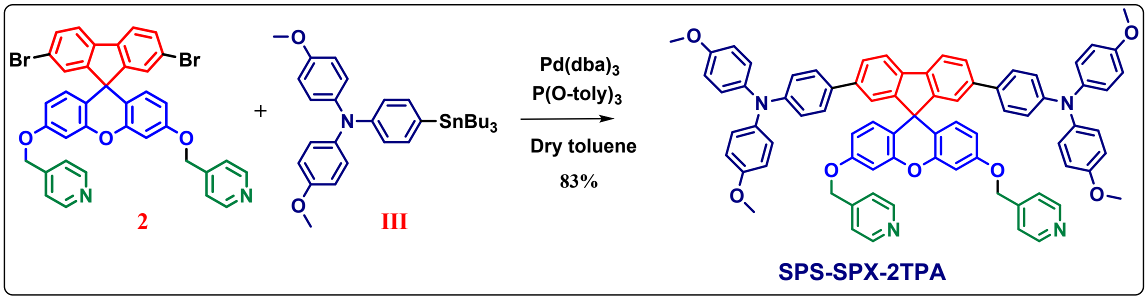
The cost of 1gm is 6.67 $



Chemicals/Company	Price ($) (kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (g)	Solvent (ml)	Workup (g or ml)	
Compound (1)	6670$/kg	0.300			20.010
4-chloromethyl pyridine/Alfa	3080 $/kg	0.200			0.308
Cesium carbonate/Finar	657 $/kg	0.300			0.065
Acetonitrile/Finar	14$/L		30		0.420
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	0.45
Total					26.043

Compound (2): Yield, 75%, 0.300g, 26.443$

The cost of 1gm is 88.143$



Chemicals/Company	Price ($) (kg or L)	Chemicals used for batch preparation			Chemical cost ($)
		Reagent (g)	Solvent (ml)	Workup (g or ml)	
Compound (2)	88143$/kg	0.300			26.442
Compound (III)/TCI	38841 $/kg	1.010			38.841
Pd(dba)$_3$/TCI	35559 $/kg	0.003			0.0001
P(*o*-toly)$_3$/TCI	4978$/L	0.002			0.00001
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	0.45
Total					70.853

Compound (SPS-SPX-2TPA): Yield, 83%, 0.410g, 70.853$

The cost of 1gm is 172.810$

This is about 1/3 of the costs of purified Spiro-OMeTAD (~500 $/g, high purity, Merck).

6. References

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