

## Supporting Information

### Unsymmetrical Bifluorenylidene-Fluorene Based Hole-Transporting Material for Perovskite Solar Cells

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## 1. Experimental Section

### 1.1 Materials

2,7-Dibromo-9-fluorenone and 4-methoxamine were purchased from Sigma-Aldrich chemicals, Lawesson's reagent, and 2-bromo-9,9-dimethyl-9H-fluorene from TCI chemicals. All other reagents and catalysts were purchased from commercial suppliers and used without further purification. All reactions were carried out under a nitrogen atmosphere. The toluene solvent used in this work was distilled before use.

### 1.2 Measurement

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  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. An ESI probe was used to measure mass spectra on a Shimadzu LCMS-2010 EV model, and matrix-assisted laser desorption/ionization was used to describe the final molecules (MALDI-TOF). Purifications were carried out through silica gel using 100- 200 mesh and 230-400 mesh. The absorption spectrum in the solution was recorded on a Scimadzu UV-1800 model spectrophotometer. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with a CH Instruments 620 C electrochemical analyzer with a scan rate of 100 mV/s in dichloromethane using 0.1 M  $\text{TBAPF}_6$  as the supporting electrolyte, an 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 ( $\text{Fc}/\text{Fc}^+$ ) as an external reference. Density functional theory (DFT) at the B3LYP/6-31G (d, p) level was used to optimize the geometry of the sp-35 for the ground and charged states. A contour value of 0.025 obtained by TD-DFT at the B3LYP/6-31G (d, p) level was used to compute the frontier molecular orbitals of the sp-35. The Gaussian 09 software programme was used for all the DFT computations.

### 1.3 Solar Cell Fabrication

The following steps are required to prepare a complete device. First, conductive substrate cleaning. The FTO conductive glass is washed in the ultrasonic cleaning machine with cleaning agent, ethanol, deionized water for half an hour, and then placed in the dryer. Second, the electron transport layer is prepared. Clean and dry FTO glass was treated with UV-ozone for 20 min. The TiO<sub>2</sub> compact layer precursor solution was prepared by mixing 0.6 mL isopropyl titanate with 12 mL anhydrous ethanol. The prepared compact layer solution was sprayed on the FTO glass substrate at 500 °C, held for 40 min, and then cooled to room temperature naturally. Mesoporous TiO<sub>2</sub> solution was prepared by mixing TiO<sub>2</sub> slurry and anhydrous ethanol at a mass ratio of 1:12, and then rotating at 3000 rpm for 30 s to cover the compact layer. The prepared material was annealed at 500 °C for 30 min. Third, after being treated with UV-ozone for 10 min, the Cs<sub>0.05</sub>FA<sub>0.95</sub>PbI<sub>3</sub> perovskite films were precipitated, including PbI<sub>2</sub> (1.1M), FAI (0.95M), CsI (0.05M) and MACl (0.4M) dissolved in a mixture of 1ml DMF and DMSO (volume ratio 8:2). It was rotated at 1000 rpm for 10 s, then at 5000 rpm for 30 s. Before the end, 15 s of the second rotating coating, 150 μL chlorobenzene was dropped as the antisolvent. After the coating, it was annealed on a hot table at 100 °C and 150 °C for 30 min and 10 min respectively to obtain perovskite films. Fourth, after natural cooling, the HTM dissolved in chlorobenzene is directly spin-coated, without other special treatment in the middle, and the HTM concentration is 30, 50, and 70 mg mL<sup>-1</sup>. The dopant consists of 11.8 μL of 4-tert-butylpyridine and 6.9 μL of lithium di (trifluoromethyl sulfonyl) imide (520 mg mL<sup>-1</sup> in acetonitrile). For the control device, the spiro-OMeTAD was coated with 5000 rpm (73.5 mg in 1mL chlorobenzene, containing 29 μLTBP, 17 μL Li), other equal conditions. Finally, Au electrodes 70-80 nm thick are deposited on the top of the hole transport layer by thermal evaporation. A black mask defines the effective region of all devices, and the effective test area is 0.1225 cm<sup>2</sup>.

**Table S1:** Theoretical energy level of sp-35 and spiro-OMeTAD

HTM	HOMO (eV)	LUMO (eV)	E <sub>g</sub> (eV)
sp-35	-4.47	-1.13	3.34
spiro-OMeTAD	-4.23	-0.67	3.56

**Table S2.** Photophysical properties of SP-35 in different solvents

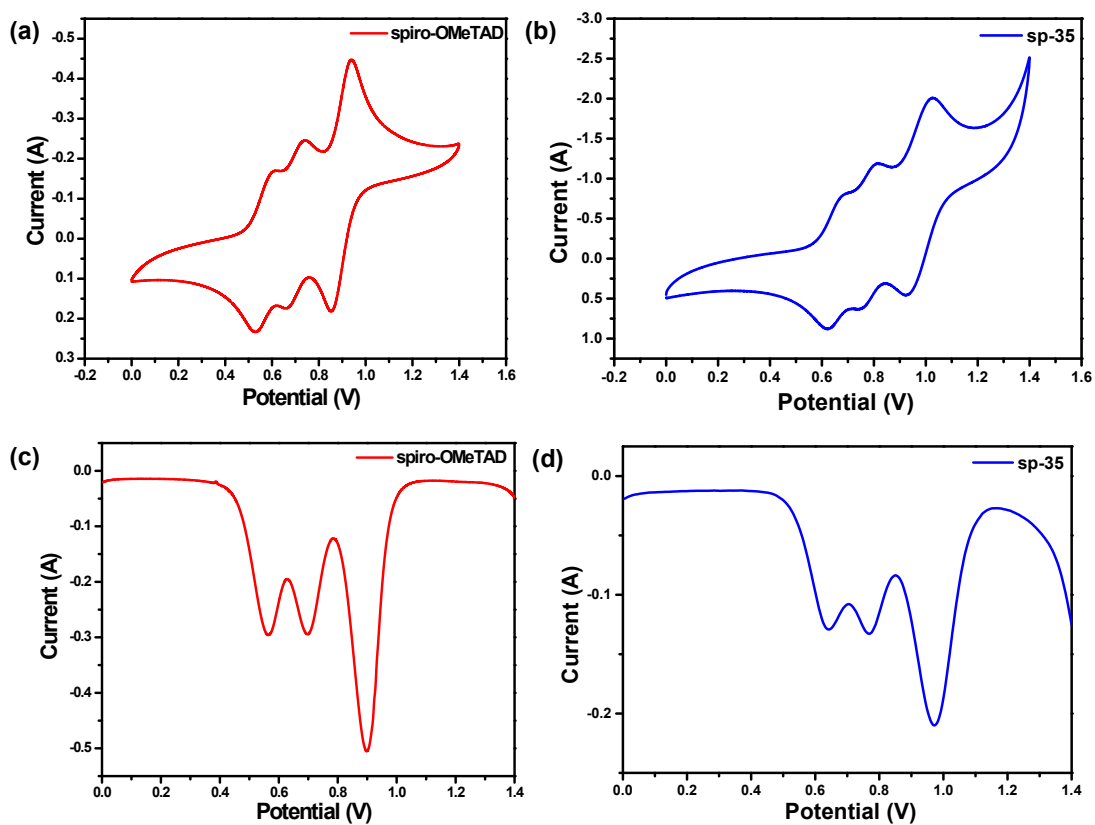
	sp-35					
	Toluene	EtOAc	THF	DCM	ACN	DMF
Absorption $\lambda_{\text{abs}}$ (nm)	399, 468	393, 463	395, 464	396, 473	392, 466	393, 469
Emission $\lambda_{\text{em}}$ (nm)	423	425	427	444	453	451

**Table S3.** Lifetime decay analysis of sp-35 in different solvent

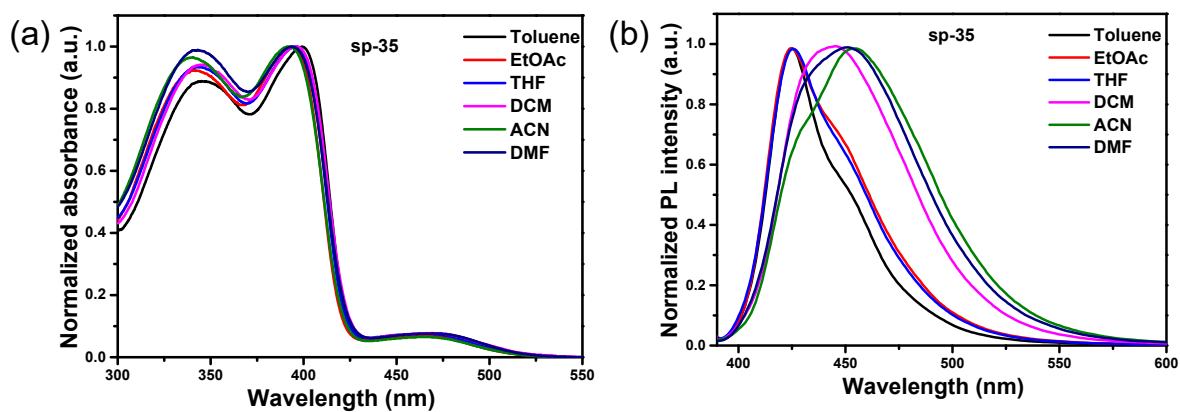
Solvents	sp-35				CHISQ	Lifetime { $\tau$ (ns)}
	$\tau_1$ (ns)	$\tau_2$ (ns)	$\alpha_1$ (%)	$\alpha_2$ (%)		
Toluene	0.846	2.503	83.06	30.47	0.64	1.46
EtOAc	0.786	3.012	69.53	30.47	0.96	2.18
THF	0.964	3.315	70.18	29.82	0.67	2.35
DCM	0.818	3.873	63.75	36.25	1.26	3.04
ACN	0.913	4.912	41.14	58.86	1.13	4.45
DMF	1.224	5.515	45.28	50.72	0.76	4.75

**Table S4.** Lifetime decay analysis of HTMS in film state

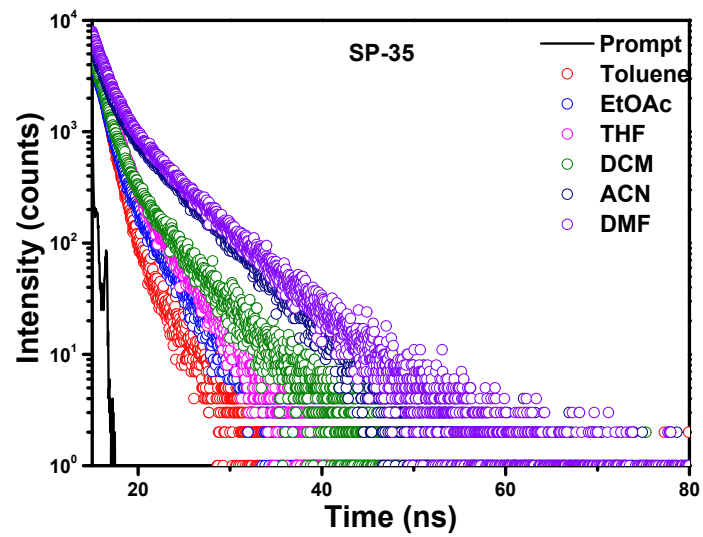
	$\tau_1$ (ns)	$\tau_2$ (ns)	$A_1$ (%)	$A_1$ (%)	Average{ $\tau$ (ns)}
Perovskite (P)	1.72	21.25	8.53	91.47	21.11
P/spiro-OMeTAD	0.94	14.78	59.12	40.88	13.62
P/ sp-35	0.74	10.25	74.66	25.34	8.58



**Figure S1.** a-b) Cyclic voltammogram and c-d) Differential pulse voltammetry spectra of sp-35 and spiro-OMeTAD HTM molecules



**Figure S2.** Normalized a) UV-Vis and b) PL emission spectra of the sp-35 in different solvents

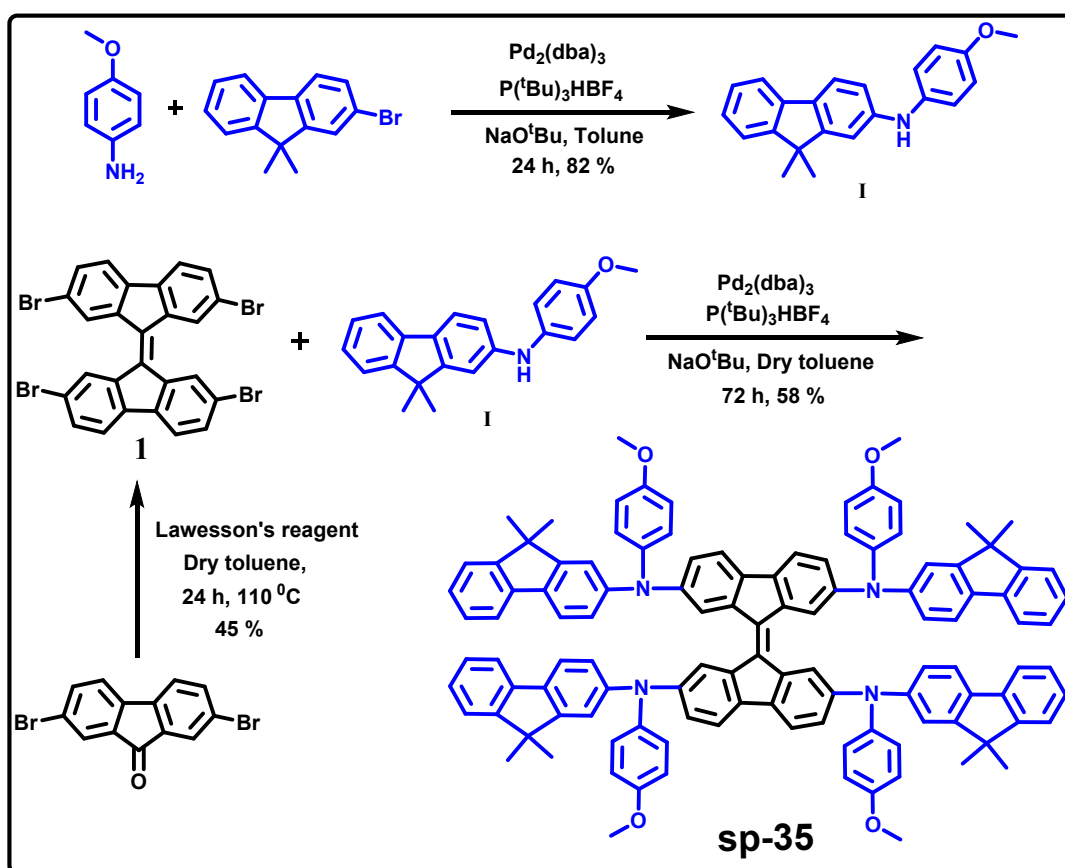


**Figure S3.** Fluorescence lifetime decay profile of sp-35



## 2. Synthesis

According to previously published literature, we have created an intermediate N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (I). 2,2',7,7'-tetrabromo-9,9'-bifluorenylidene (1) was prepared by using previously reported literature.



**Scheme 1.** Synthetic routes of sp-35 hole transporting molecule.

**N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (I):** To a 100 ml two-neck round-bottomed flask charged with 4-methoxyaniline (1 g, 8.11mmol), 2-bromo-9,9-dimethyl-9H-fluorene (2.41 g, 8.84mmol), tri-*tert*-butylphosphonium tetrafluoroborate (47.11 mg, 0.16 mmol), and sodium *tert*-butoxide (1.56 g, 16.23 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, 74.34 mg of tris (dibenzylideneacetone) dipalladium (0) (0.08 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<sub>2</sub>SO<sub>4</sub>. 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 (2.10 g, 82 % yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.28 (td, *J* = 7.4, 1.1 Hz, 1H), 7.21 (td, *J* = 7.4, 0.8 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 1.4 Hz, 1H), 6.91 – 6.85 (m, 3H), 5.60 (s, 1H), 3.81 (s, 3H), 1.44 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.49, 155.24, 153.05, 144.78, 139.57, 136.05, 131.38, 126.99, 125.84, 122.45, 121.98, 120.93, 118.94, 114.86, 114.83, 110.24, 55.67, 46.79, 27.39. LCMS-MS calcd for C<sub>22</sub>H<sub>21</sub>NO [M+H]<sup>+</sup>mol. wt.: 315.41; found 316.

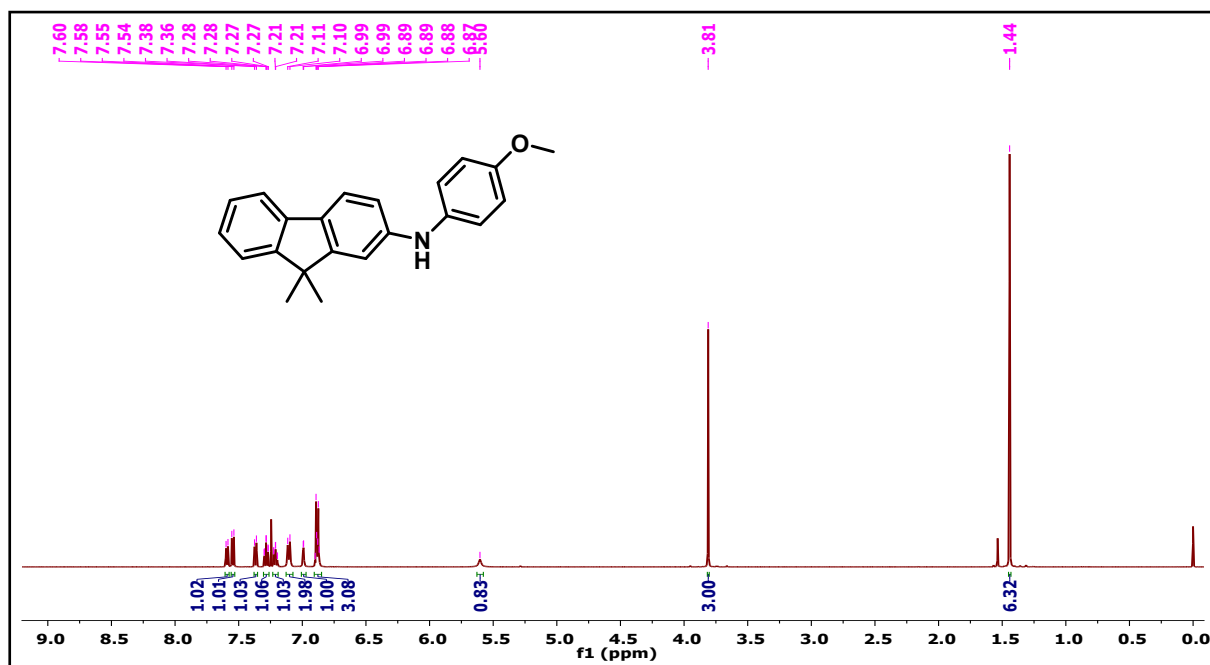
**2,2',7,7'-tetrabromo-9,9'-bifluorenylidene (1):** To a 250 ml two-neck round-bottomed flask charged with 2,7-dibromo-9*H*-fluoren-9-one (3.34 g, 9.9 mmol, 1 equiv.) and Lawesson's reagent (2 g, 4.95 mmol, 0.5 equiv.) with toluene (60 ml) was refluxed overnight. The resulting reaction mixture was cooled in ice bath, the precipitate was collected by filtration, washed with acetone and dried to give 1.44 g of orange solid in 45% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.41 (s, 4H), 7.55 (d, *J* = 8.1 Hz, 4H), 7.51 (d, *J* = 1.6 Hz, 4H). The limited solubility of compound precluded <sup>13</sup>C-NMR characterization.

**N2,N2',N7,N7'-tetrakis(9,9-dimethyl-9*H*-fluoren-2-yl)-N2,N2',N7,N7'-tetrakis(4-methoxyphenyl)-[9,9'-bifluorenylidene]-2,2',7,7'-tetraamine (sp-35):**

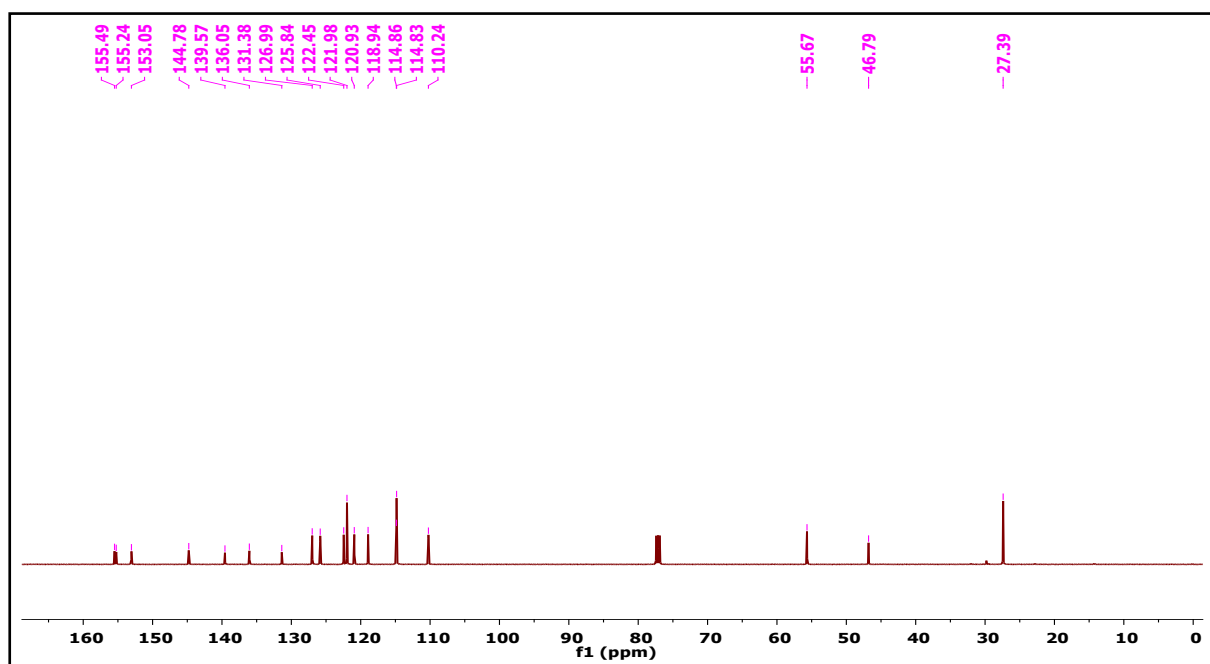
In a 50 ml Schlenk-tube was charged with 2,2',7,7'-tetrabromo-9,9'-bifluorenylidene (**1**) (200mg, 0.310 mmol), N-(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine(**I**) (587.72 mg, 1.863 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (18 mg, 0.062 mmol) and sodium *tert*-butoxide (238.32 mg, 2.48 mmol) dissolved in dry toluene (20 ml). The reaction mixture was purged with nitrogen gas up to 30 minutes, then tris (dibenzylideneacetone) dipalladium (**0**) (56.77 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<sub>2</sub>SO<sub>4</sub>. 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-35** as color solid (286 mg, 58 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 1.6 Hz, 4H), 7.57 (d, *J* = 7.4 Hz,

4H), 7.42 (d,  $J = 8.3$  Hz, 4H), 7.34 – 7.31 (m, 8H), 7.28 (d,  $J = 6.3$  Hz, 2H), 7.22 (d,  $J = 0.9$  Hz, 4H), 6.97 – 6.90 (m, 20H), 6.76 – 6.73 (m, 10H), 3.73 (s, 12H), 1.31 (s, 24H).  **$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$**  155.88, 154.77, 153.39, 147.84, 146.57, 141.72, 140.59, 139.67, 139.24, 136.04, 132.45, 126.85, 126.28, 126.04, 122.59, 122.38, 120.56, 120.47, 119.86, 119.18, 115.84, 114.84, 55.35, 46.71, 29.72, 27.06. **MALDI TOF-MS**  $[\text{M}]^+$  calcd for  $\text{C}_{114}\text{H}_{92}\text{N}_4\text{O}_4$  exact mass: 1580.71; found 1580.59.

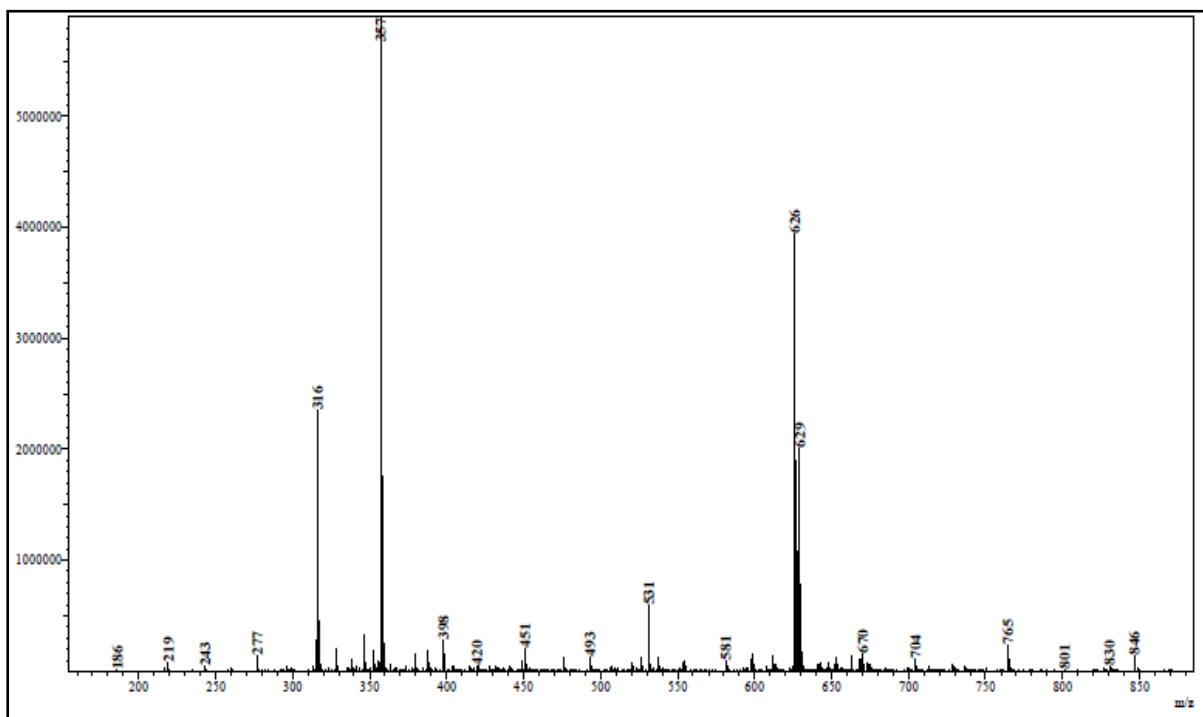
### 3. Copies of NMR Spectra



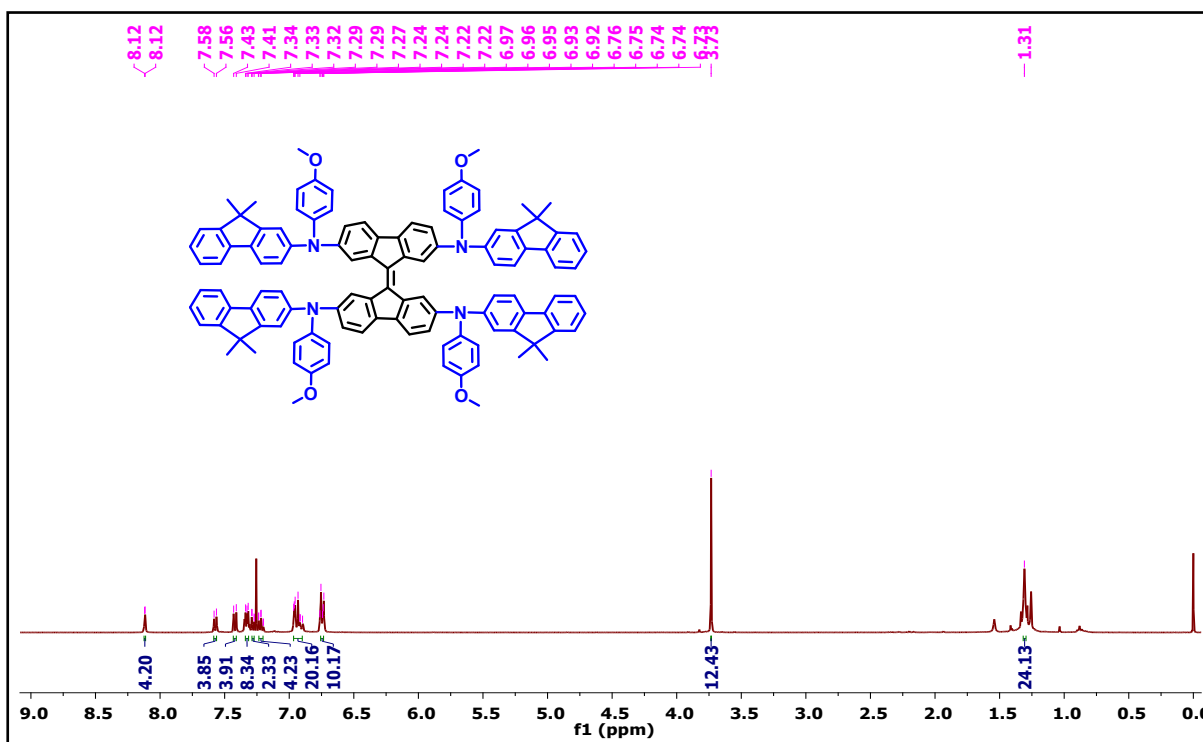
$^1\text{H}$  NMR spectra of compound (I) in  $\text{CDCl}_3$



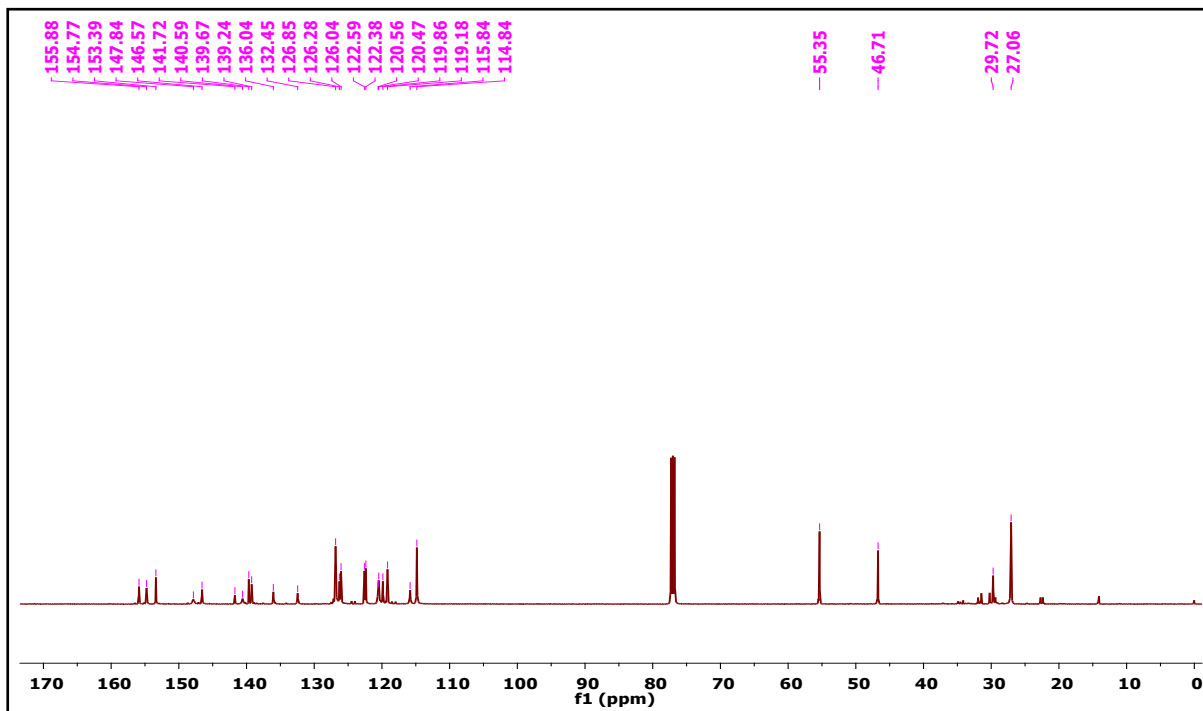
$^{13}\text{C}$  NMR spectra of compound (I) in  $\text{CDCl}_3$



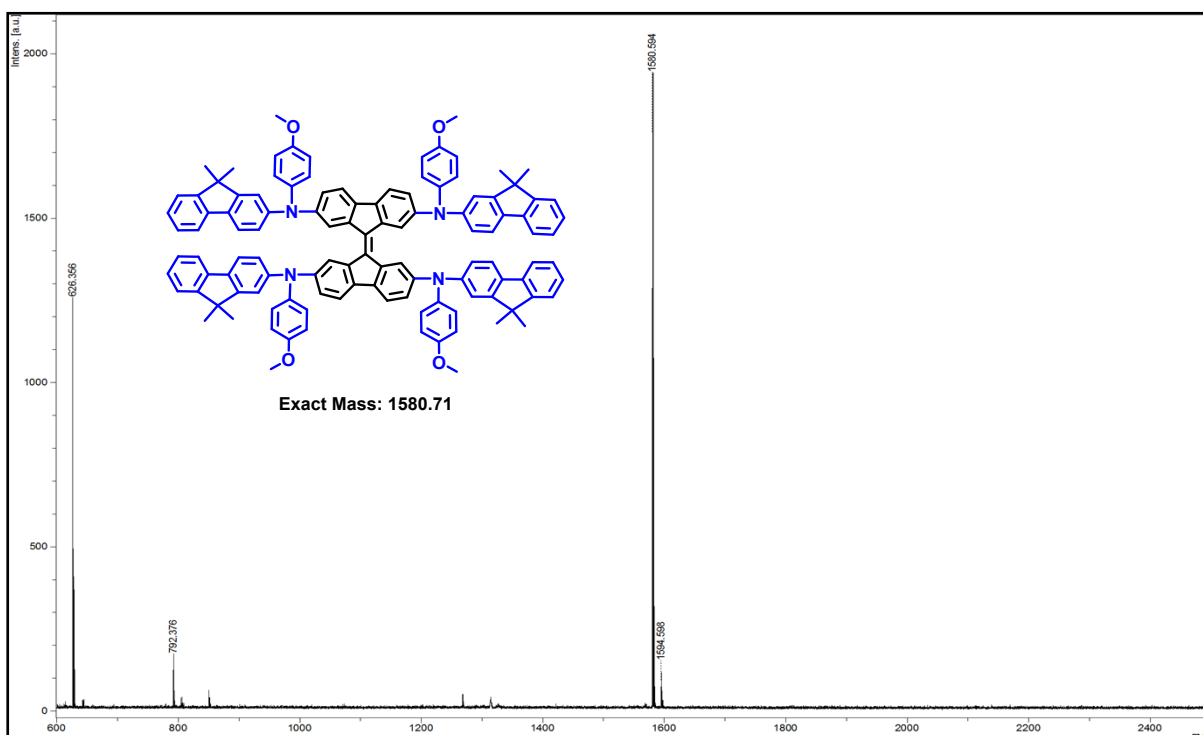
LCMS-MS of compound (1)



<sup>1</sup>H NMR spectra of sp-35 in CDCl<sub>3</sub>



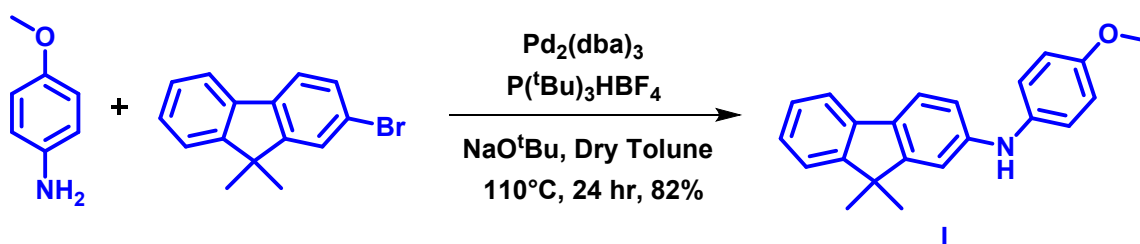
**<sup>13</sup>C NMR spectra of sp-35 in CDCl<sub>3</sub>**



**MALDI-TOF spectra of sp-35**

#### 4. Cost Calculation

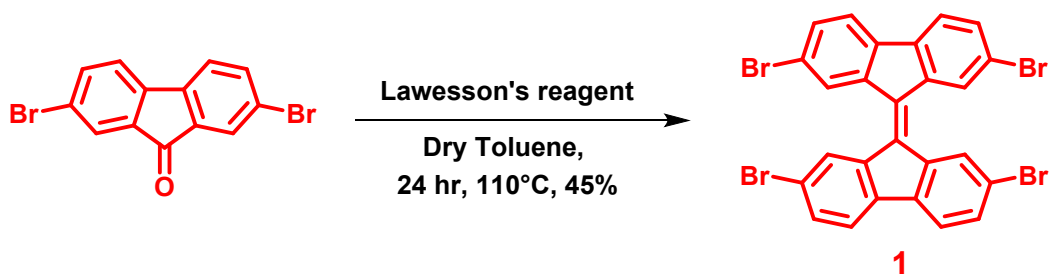
Based on the cost analysis table provided below, it is evident that the synthesized HTM, namely **sp-35**, is significantly more cost-effective than the commercially available spiro-OMeTAD. **sp-35** is 1/11<sup>th</sup> of the cost of purified spiro-OMeTAD (also priced at \$565 per gram with high purity, commercially available).



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	1.00			0.137
2-bromo-9,9-dimethyl-9H-fluorene / TCI	3658 \$/kg	2.410			8.815
Sodium tert-butoxide / TCI	259 \$/kg	1.560			0.404
Tri-tert-butylphosphonium tetrafluoroborate/ TCI	37970 \$/kg	0.047			1.784
Tris(dibenzylideneacetone)dipalladium /TCI	35559 \$/kg	0.074			0.263
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					16.973

**Moiety I:** Yield, 82%, 2.10 g, 16.973 \$

The cost of 1gm is 8.082 \$

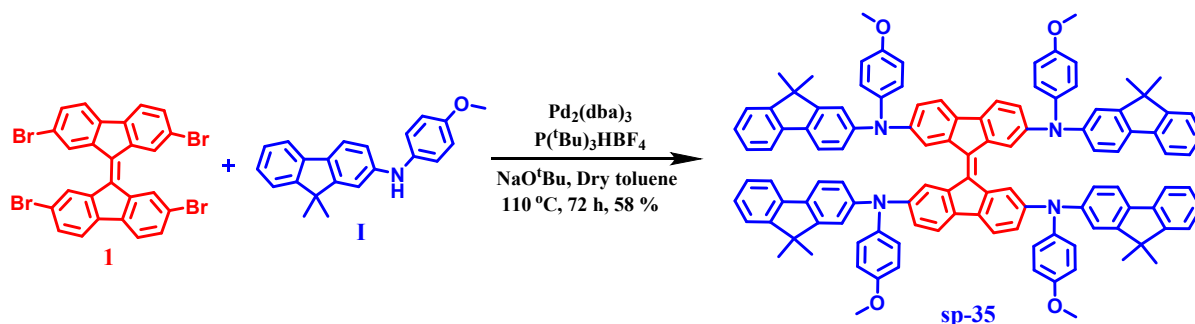


Chemicals/company	Price (\$) (Kg or L)	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
2,7-dibromo-9-Fluorenone/TCI	437 \$/kg	3.34			1.459
Lawesson's reagent/TCI	1070 \$/kg	2.00			2.140
Toluene/Finar	11 \$/L		60		0.660
<b>Total</b>					<b>4.259</b>

**Moiety 1:** Yield, 45%, 1.44 g, 4.259 \$

The cost of 1gm is 2.957 \$





Chemicals/company	Price (\$) (Kg or L)	Chemicals used for batch preparation			Chemical cost (\$)
		Reagent (in g)	Solvent (in ml)	Workup (in g or ml)	
<b>1</b>	2957 \$/kg	0.200			0.591
<b>I</b>	8082 \$/kg	0.587			4.744
Sodium tert-butoxide/ TCI	259 \$/kg	0.238			0.061
Tri-tert-butylphosphonium tetrafluoroborate/ TCI	37970 \$/kg	0.018			0.683
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					13.530

**sp-35:** Yield, 58%, 0.286 g, 13.530 \$

The cost of 1gm is 47.307 \$

This is about **1/11<sup>th</sup>** of the cost of purified spiro-OMeTAD (565 \$/g, high purity, commercially available)

## 4. References

- (1) Jeong, M.; Choi, I. W.; Yim, K.; Jeong, S.; Kim, M.; Choi, S. J.; Cho, Y.; An, J.-H.; Kim, H.-B.; Jo, Y.; Kang, S.-H.; Bae, J.-H.; Lee, C.-W.; Kim, D. S.; Yang, C. Large-Area Perovskite Solar Cells Employing Spiro-Naph Hole Transport Material. *Nat. Photonics* **2022**, *16* (2), 119–125. <https://doi.org/10.1038/s41566-021-00931-7>.
- (2) Rakstys, K.; Saliba, M.; Gao, P.; Gratia, P.; Kamarauskas, E.; Paek, S.; Jankauskas, V.; Nazeeruddin, M. K. Highly Efficient Perovskite Solar Cells Employing an Easily Attainable Bifluorenylidene-Based Hole-Transporting Material. *Angew. Chemie Int. Ed.* **2016**, *55* (26), 7464–7468. <https://doi.org/https://doi.org/10.1002/anie.201602545>.