A Simple and Cost-Effective Thiophene-Benzene-Thiophene Based Hole Transporting Material for Stable Perovskite Solar Cells

Nousheen Syed,†[a] Ankita Sharma,†[b] Thillaiarasi Sukumar,[a] Ganesh Koyyada,[c] David Kreher, [d] Baswanth Oruganti,[e] Upendra Kumar Pandey*[b] and Kamatham Narayanaswamy *[a]

[a]Department of Chemistry, SRM University-AP, Amaravati, Andhra Pradesh, India 522240.
[b]Organic & Flexible Electronics Laboratory, Department of Electrical Engineering, School of Engineering, Shiv Nadar Institution of Eminence, G.B. Nagar, Uttar Pradesh-201314, India.
[c]School of Chemical Engineering, Yeungnam University, Daehak-ro 280, Gyeongsan, Gyeongbuk 38541, South Korea.
[d]Institut Lavoisier de Versailles, UMR CNRS 8180, UVSQ, Université Paris-Saclay, Versailles, 78035 France.
[e] School of Mathematics and Mathematical Statistics, Umeå University, SE-90187, Umeå, Sweden.

†These authors contributed equally to this work.

*E-mail: kamatham.n@srmap.edu.in, upendra.pandey@snu.edu.in

Contents

1. Materials and methods

All commercially available chemicals and reagents were used without further purification, unless otherwise noted. Tetrahydrofuran (THF) was dried over sodium/benzophenone, distilled under Argon, and stored over 4 Å molecular sieves. Chloroform dried over calcium hydride (CaH_2), distilled under Argon and stored over molecular sieves (4 Å). N, N-dimethylformamide (DMF) was dried and purified using standard techniques. Reactions were carried out under Argon atmosphere. All reactions were monitored by analytical thin layer chromatography (TLC) purchased from Merck & Co., Inc. Compounds were detected by UV irradiation, staining with I_2 and/or $KMnO_4$. Purification was carried out using a silica gel (100-200 nm) column chromatography. The Hole Transporting material (HTMs) investigated in this work were synthesized by following the procedures described below.

NMR spectra: ^1H and ^{13}C NMR spectra were recorded on a JEOL 400 MHz spectrometer in 5mm tubes with $CDCl_3$ as solvent at 25°C, unless otherwise noted. Chemical shifts were reported in δ ppm and referenced to the solvent residual peak at δ 7.26 ppm for ^1H and 77.0 ppm for ^{13}C NMR spectra in CDCl3. The abbreviations s, d, t, dd & m corresponds to multiplicities singlet, doublet, triplet, doublet of doublet and multiplet respectively.

UV-vis absorption spectra: UV-vis absorption spectra of HTMs were recorded on Shimadzu UV-2600i spectrometer at room temperature in diluted $CHCl_3$ solution (1×10^{-5} M).

MALDI-TOF: Matrix Assisted Laser Desorption Ionization (MALDI) mass spectra were recorded on Bruker Daltonics Autoflex Time of flight (TOF) equipment.

Electrochemical properties: Cyclic voltammetry (CV) was carried out on a Potentstiostat-(Biologic SP-150). The oxidation potential was measured in anhydrous CH_2Cl_2 solution at room temperature with 0.1M tetra-butylammonium hexafluorophosphate (Bu_4NPF_6) as electrolyte with a conventional three-electrode system (Working electrode: Glassy carbon; Reference electrode: Ag/Ag^+; Counter electrode: Pt wire) calibrated with ferrocene/ ferrocenium (Fc/Fc^+) as an external reference. HOMO energy levels were calculated with calibrated onset oxidation (E_{onset}^{ox}) of CV by the formula, $E_{HOMO} = -[E_{oxi} - E_{(Fc/Fc+)} + 4.8]$ (eV); $E_{(Fc/Fc+)} = 0.48$, LUMO energy levels are calculated by the equation of $E_{LUMO} = E_{HOMO} + E_g^{opt}$ (eV).[1]

Thermal properties: Thermogravimetric (TGA) and differential scanning calorimetry (DSC) analysis data were obtained from (SETARAM Instrumentation, Labsys Evo 1600) at a heating rate of 10°C/min under nitrogen atmosphere.

2. Synthesis of HTMs

The intermediates, 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (4), 1,4-dibromo-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene (1C), 2,2'-(2,5-dimethoxy-1,4-phenylene)dithiophene (2A), 2,2'-(2,5-bis(2-(2-methoxyethoxy)ethoxy)-1,4-phenylene)dithiophene (2C), 5,5'-(2,5-dimethoxy-1,4-phenylene)bis(2-bromothiophene) (3A), 5,5'-(2,5-bis(2-(2-methoxyethoxy)ethoxy)-1,4-phenylene)bis(2-bromothiophene) (3C), were prepared by methods similar to those reported in the literature.[2–4]

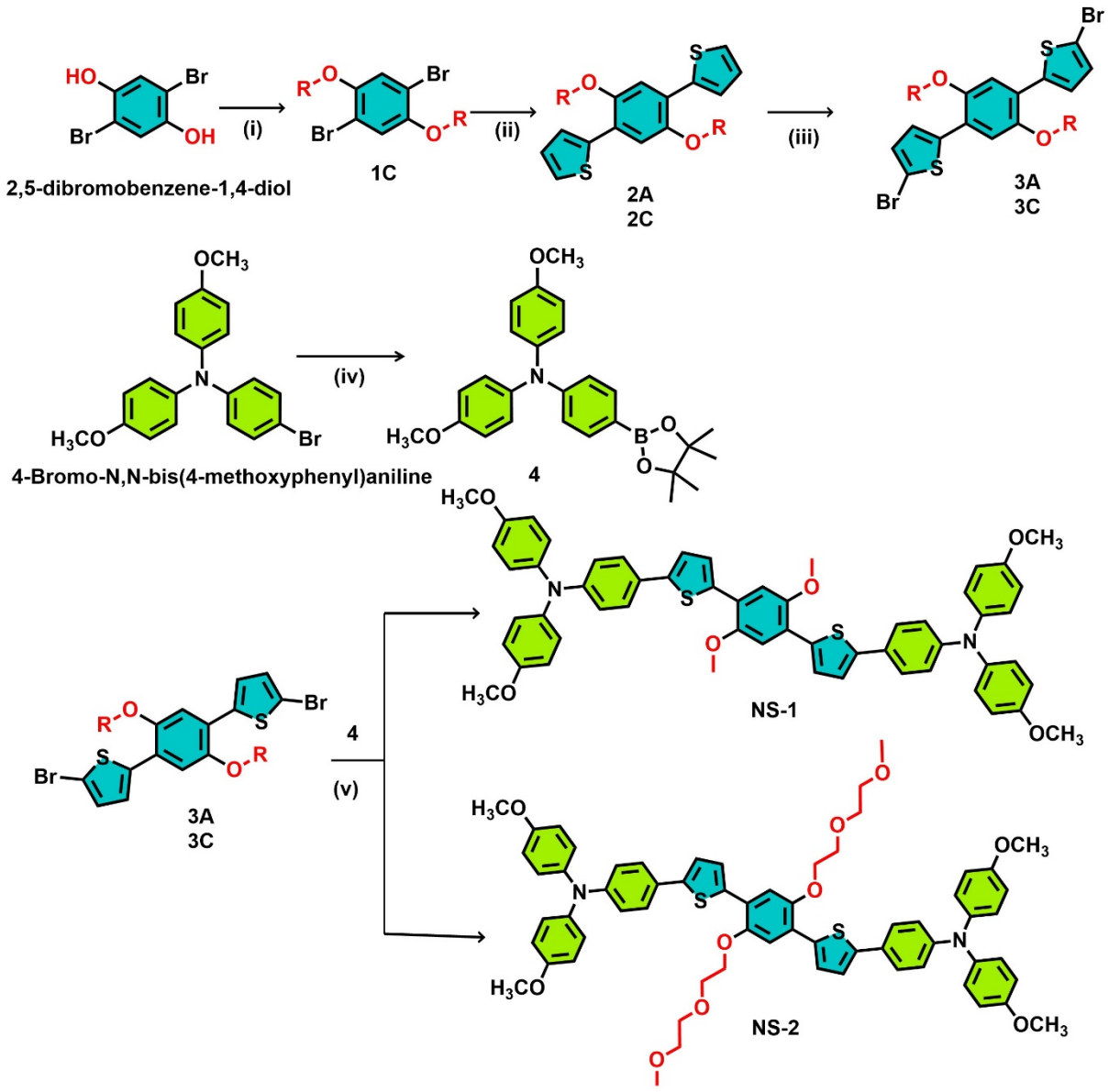
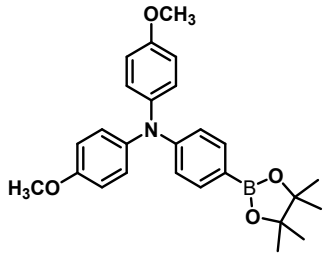


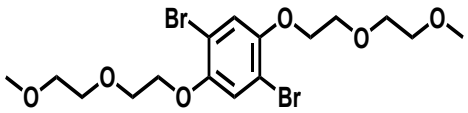
Fig S1. Synthetic scheme to prepare NS-1 and NS-2. **Reagents**: (i) 1-Bromohexane, 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate, K_2CO_3, DMF, 18-Crown-6 (ii) Thiophen-2-ylboronic acid, K_2CO_3, $Pd(Pph_3)_4$, Toulene (iii) NBS, $CHCl_3$, THF (iv) $Bis(pin)_2$, KOAc, $Pd(dppf)Cl_2$, 1,4-Dioxane (v) K_2CO_3, $Pd(Pph_3)_4$, Toulene.

4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (4)



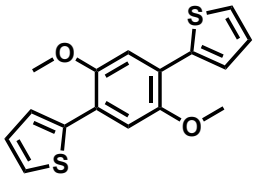
A 250 mL two-neck flask was charged with 4-bromo-N,N-bis(4-methoxyphenyl)aniline (2.4 g, 6.24mmol), Bispinacolatodiboron (1.98 g, 7.8 mmol), KOAc (3.0 g, 31.2 mmol) and Pd(dppf)Cl_2 (91.0 mg, 0.012 mmol) in 75 mL of 1,4-Dioxane were stirred under argon at 100°C for 12 hrs. The reaction was cooled to room temperature. The crude mixture was extracted with dichloromethane (DCM), then dried over $MgSO_4$, and then solvent was removed by vacuo. The residue was purified by column chromatography using silica gel as stationary phase and DCM/petroleum ether as mobile phase to give a white solid (1.9g, 71%). **^{1}H NMR** (400 MHz, CHLOROFORM-*D*) δ 7.60 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 4H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 4H), 3.80 (s, 6H), 1.32 (s, 12H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 156.65, 151.83, 140.86, 136.20, 127.57, 119.08, 115.17, 83.84, 55.91, 25.27.

1,4-dibromo-2,5-bis(2-(2-methoxyethoxy)ethoxy)benzene (1C)



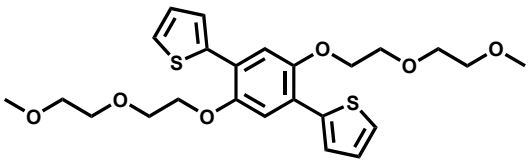
To a 100 mL single neck round bottom flask capped with a rubber septum, 2,5-dibromobenzene-1,4-diol (5g, 18.66 mmol), 2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate (17g, 65.3 mmol), K_2CO_3 (12g, 93.3 mmol), 18-Crown-6 (245 mg, 0.93mmol) and DMF (50 ml) were stirred together and refluxed at 150°C for 12 hours under an atmosphere of argon. The resultant mixture was added to water, and then it was extracted with ethyl acetate (EtOAc). The resulting extract was dried over $MgSO_4$, and the solvent was evaporated under vacuum. Column chromatography (eluent- EtOAc/petroleum ether) was employed to purify the crude product to give 1C as a white solid (5.15 g, 60%). **^{1}H NMR** (400 MHz, CHLOROFORM-*D*) δ 3.39 (s, 6H), 3.52 – 3.61 (m, 4H), 3.72 – 3.78 (m, 4H), 3.87 (t, 4H), 4.13 (t, 4H), 7.15 (s, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 59.26, 69.75, 70.39, 71.14, 72.15, 111.53, 119.33, 150.47.

2,2'-(2,5-dimethoxy-1,4-phenylene)dithiophene (2A)



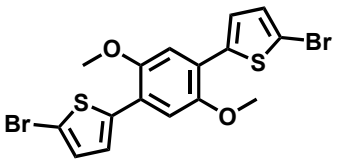
In a 100 ml of round bottom flask was charged with 1,4-dibromo-2,5-dimethoxybenzene (1.0 g, 3.38 mmol), Thiophen-2-ylboronic acid (1.08g, 8.45 mmol) and K_2CO_3 (2.33 g, 16.9 mmol) were mixed in Toluene (15 mL). Degassed with argon, then added $Pd(Pph_3)_4$ (78.11 mg, 0.0676 mmol). Then, the mixture was stirred at 110°C for 12 hrs. The mixture was extracted with EtOAc and dried over $MgSO_4$. Purification by silica gel column chromatography (eluent-hexane/DCM) gave 2A as a white solid (570 mg, 55%). **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 3.95 (s, 6H), 7.11 (t, 2H), 7.26 (s, 3H), 7.35 (d, J = 5.3 Hz, 2H), 7.54 (d, J = 2.3 Hz, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 150.10, 139.21, 127.05, 125.85, 125.61, 123.13, 112.44, 56.55.

2,2'-(2,5-bis(2-(2-methoxyethoxy)ethoxy)-1,4-phenylene)dithiophene (2C)



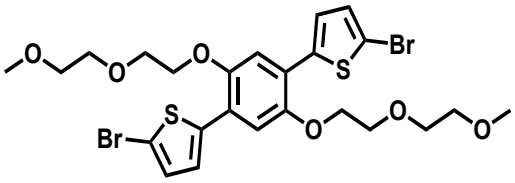
In a 100 ml of round bottom flask was charged with 1C (1.0 g, 2.12 mmol), Thiophen-2-ylboronic acid (3.25g, 25.4 mmol), and K_2CO_3 (1.46 g, 10.6 mmol), toluene (25 ml) and purged it for 20 minutes before addition of $Pd(Pph_3)_4$ (49 mg, 0.04 2mmol) and subsequent purging for 25 minutes. After that, the reaction setup was refluxed for 12 hours at 110°C in an argon environment. After cooling to room temperature, the resulting mixture was extracted with EtOAc, and the organic phase was dried over anhydrous $MgSO_4$. Then the solvent was evaporated under vacuum, and the residue was purified using EtOAc/petroleum ether as an eluent by silica gel column chromatography to give compound 2C as a colourless oil (1.0g, 98%). **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 3.40 (s, 6H), 3.56 – 3.64 (m, 4H), 3.70 – 3.78 (m, 4H), 3.94 (t, 4H), 4.25 (t, 4H), 7.03 (d, J = 3.0 Hz, 2H), 7.22 (s, 2H), 7.26 (d, J = 3.9 Hz, 3H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 59.25, 69.35, 69.92, 70.91, 72.15, 112.34, 113.37, 123.01, 125.06, 129.54, 140.23, 149.28.

5,5'-(2,5-dimethoxy-1,4-phenylene)bis(2-bromothiophene) (3A)



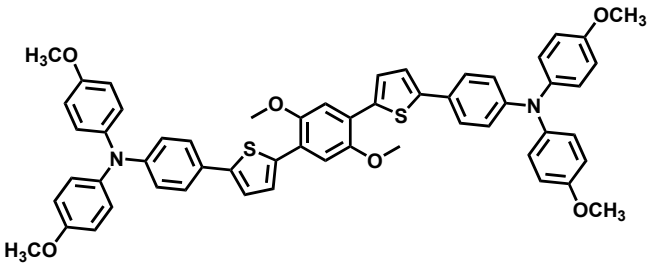
In a 50 ml two-neck round bottom flask covered with aluminium foil, compound 2A (500 mg, 1.65 mmol) was dissolved in dry 15 ml of $CHCl_3$, and the flask was cooled to 0°C under an argon atmosphere. Then, N-bromosuccinimide (NBS) (735.67 mg, 4.13 mmol) was added portion-wise, the reaction was monitored using TLC. After complete consumption of the starting material, the reaction was quenched with H_2O, and the organic phase was extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated under reduced pressure. The purification was carried out by column chromatography on flash silica as a Stationary phase with a mixture of petroleum ether/ CH_2Cl_2 as a mobile phase, which afforded the product as a White solid (600 mg, 75 %). **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 3.94 (s, 6H), 7.05 (d, J = 4.1 Hz, 2H), 7.17 (s, 2H), 7.25 (s, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-D) δ 56.55, 111.08, 113.49, 122.73, 125.00, 129.56, 140.22, 149.90.

5,5'-(2,5-bis(2-(2-methoxyethoxy)ethoxy)-1,4-phenylene)bis(2-bromothiophene) (3C)



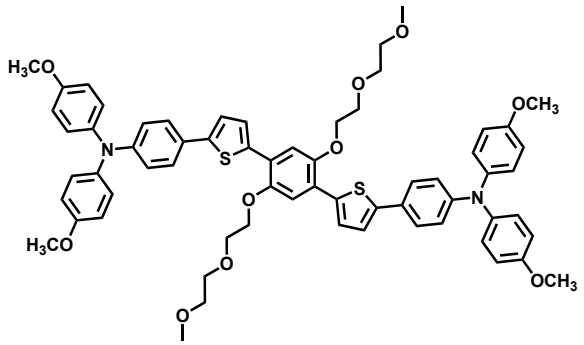
In a 100 ml two-neck round-bottom flask covered with aluminium foil, compound 2C (1.0 g, 2.1 mmol) was dissolved in dry 20 ml of THF, and the flask was cooled to 0°C under an argon atmosphere. Then, N-bromosuccinimide (NBS) (818 mg, 4.6 mmol) was added portion-wise, and the reaction was monitored using TLC. After complete consumption of the starting material, the reaction was quenched with H_2O, and the organic phase was extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated under reduced pressure. The purification was carried out by column chromatography on flash silica as a stationary phase with a mixture of petroleum ether/ CH_2Cl_2 as a mobile phase afforded the product as a white solid (1.2 g, 92 %). **^{1}H NMR** (400 MHz, CHLOROFORM-D) δ 3.39 (s, 6H), 3.59 (t, 4H), 3.73 (t, 4H), 3.93 (t, 4H), 4.24 (t, J = 5.0 Hz, 3H), 7.02 (d, J = 5.3 Hz, 2H), 7.21 (s, 2H), 7.25 (d, J = 1.1 Hz, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 59.25, 69.33, 69.92, 70.91, 72.15, 112.34, 113.37, 123.05, 125.06, 129.54, 140.23, 149.28.

Synthesis of NS-1



3A (800mg, 1.74mmol), 4 (2.25g, 5.21 mmol), K_2CO_3(1.2 g 8.7 mmol) were mixed in Toluene (20 ml). Degassed with argon, then added $Pd(Pph_3)_4$ (40.2 mg, 0.03 mmol). Then, the mixture was stirred at 110°C for 12 hr. The mixture was extracted with EtOAc and dried over $MgSO_4$. Purification by silica gel column chromatography (eluent: hexane/ EtOAc) gave NS-1 as a yellow solid (1.0 g, 67%). **^{1}H NMR** (400 MHz, CHLOROFORM-*D*) δ 3.81 (s, 12H), 3.97 (s, 6H), 6.77 – 6.88 (m, 12H), 7.04 – 7.09 (m, 12H), 7.25 (s, 2H), 7.46 (d, *J* = 8.6 Hz, 4H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 29.82, 55.63, 56.62, 111.83, 114.85, 120.78, 121.97, 123.03, 126.76, 140.83, 144.57, 150.17, 156.09. **MALDI-TOF** calculated for $C_{56}H_{48}N_2O_6S_2$, 908.30; found 908.293.

Synthesis of NS-2:



3C (700 mg, 1.09 mmol), 4 (1.0 g, 2.3 mmol), K_2CO_3(753.24 mg, 5.45 mmol) were mixed in Toluene (25 ml). Degassed with argon, then added $Pd(Pph_3)_4$ (25 mg, 0.02 mmol). Then, the mixture was stirred at 110°C for 12 hr. The mixture was extracted with EtOAc and dried over $MgSO_4$. Purification by silica gel column chromatography (eluent: hexane/ EtOAc) gave NS-1 as a yellow solid (945 mg, 80%). **^{1}H NMR** (400 MHz, CHLOROFORM-*D*) δ 3.35 (s, 6H), 3.53 – 3.63 (m, 4H), 3.71 – 3.75 (m, 4H), 3.79 (s, 12H), 3.95 (t, *J* = 4.5 Hz, 4H), 4.27 (t, *J* = 5.1 Hz, 4H), 6.83 (d, *J* = 7.9 Hz, 8H), 6.91 (d, *J* = 8.8 Hz, 4H), 7.06 (d, *J* = 10.2 Hz, 8H), 7.15 (d, *J* = 4.9 Hz, 2H), 7.24 (s, 4H), 7.43 (d, *J* = 8.8 Hz, 4H), 7.50 (d, *J* = 3.9 Hz, 2H). **^{13}C NMR** (101 MHz, CHLOROFORM-*D*) δ 55.62, 59.21, 69.28, 70.00, 70.89,

72.11, 113.24, 114.85, 121.99, 123.41, 126.40, 126.86, 137.31, 140.83, 144.41, 148.25, 149.52, 156.08. **MALDI-TOF** calculated for $C_{64}H_{64}N_2O_{10}S_2$, 1084.40; found 1048.439.

3. Cost analysis for Intermediates and final compounds

We have estimated the synthesis costs of 1 gram of NS-1 and NS-2 based on the cost model that were reported previously.[5] The cost comparison is performed with commercially available Spiro-OMeTAD, as commonly used in laboratory-scale device fabrication.[6] The cost estimation for NS-1 and NS-2 was conducted based on the reagents and solvents utilized during their synthesis. For simplification, factors such as energy consumption and labour costs, which constitute a substantial portion of the total expenditure in large scale production, we are not included in the calculation. Notably, compared to Spiro-OMeTAD, the synthesis of NS-1 and NS-2 was efficiently completed within five synthetic steps, significantly reducing both energy and manpower requirements, thereby enhancing their overall cost-effectiveness relative to commercially available Spiro-OMeTAD.

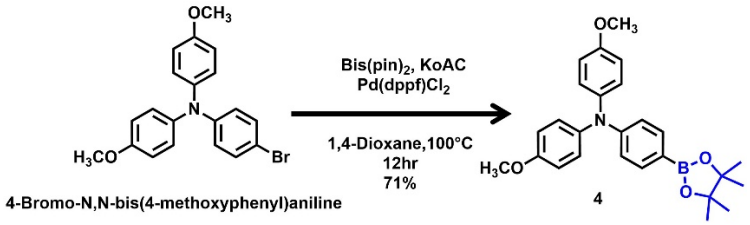


Table S1. The Material Cost (MC) for Synthesizing Intermediate 4.

Chemicals/Company	Unit Price ($)	Chemicals used for the synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (ml)	
4-bromo-N,N-bis(4-methoxyphenyl)aniline /BLD	100g/1319	2.4			31.65
Bis(pinacolato)diboron /BLD	1kg/197	1.98			0.39
KOAc /BLD	1kg/197	3.0			0.59
$Pd(dppf)Cl_2$ /BLD	100g/1575	0.09			1.43
1,4-Dioxane /SRL	25lt/ 207	75			0.62
DCM /Hyma	25lt/ 38			20	0.03
$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
DCM /Hyma	25lt/ 38		400		0.61
Silica gel / Hyma	5Kg/48	75			0.70
Petroleum ether/ Hyma	25L/44		800		1.41
Total cost					37.59

Compound (4): Yield, 71%, 1.9 g, 37.59$, The cost of **1gm is 19.78$**

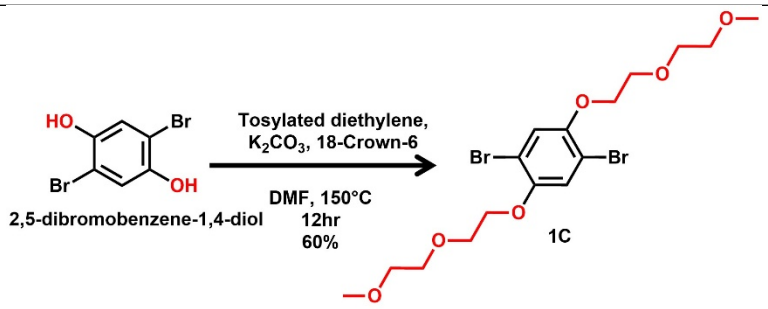


Table S2. The Material Cost (MC) for Synthesizing Intermediate 1C.

Chemicals/Company	Unit Price ($)	Chemicals used for the synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (ml)	
2,5-dibromobenzene-1,4-diol /BLD	500g/ 940	5			9.4
2-(2-methoxyethoxy)ethyl 4-methylbenzenesulfonate	-	17			-
K_2CO_3 /Hyma	1kg/ 10.8	12			0.13
18-Crown-6/ BLD	1kg/ 136	0.25			0.03
DMF / Hyma	2.5 lt/ 25.5	50			0.51
EtOAc /Hyma	25L/41.60			30	0.05
$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
EtOAc /Hyma	25L/41.60		450		0.75
Petroleum ether/ Hyma	25L/ 44		600		1.00
Silica gel/Hyma	5Kg/ 47.97	100			0.90
Total					12.93
Compound (1C): Yield, 60%, 5.15 g, 12.93$, The cost of **1gm is 2.51$**					

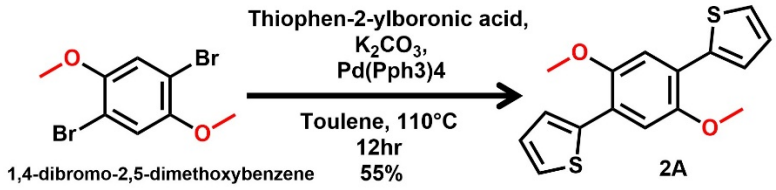


Table S3. The Material Cost (MC) for Synthesizing Intermediate 2A.

Chemicals/Company	Unit Price ($)	Chemicals used for these synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (g or ml)	

1,4-dibromo-2,5-dimethoxybenzene/ BLD	500g/ 474	1			0.95
Thiophen-2-ylboronic acid/ BLD	100g/ 115	1.08			1.24
K_2CO_3 / Hyma	1kg/ 10.8	2.33			0.25
$Pd(Pph_3)_4$ /BLD	100g/ 1003	0.078			0.78
Toluene/ Hyma	2.5lt/ 20	15			0.12
$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
EtOAc /Hyma	25L/41.6		300		0.50
Hexane/ Hyma	25L/ 44		500		0.88
DCM /Hyma	25lt/ 38			15	0.02
Silica gel/Hyma	5Kg/ 47.97	50			0.48
Total cost					5.38
Compound (2A): Yield, 55%, 0.57 g, 5.38$, The cost of **1gm is 9.4$**					

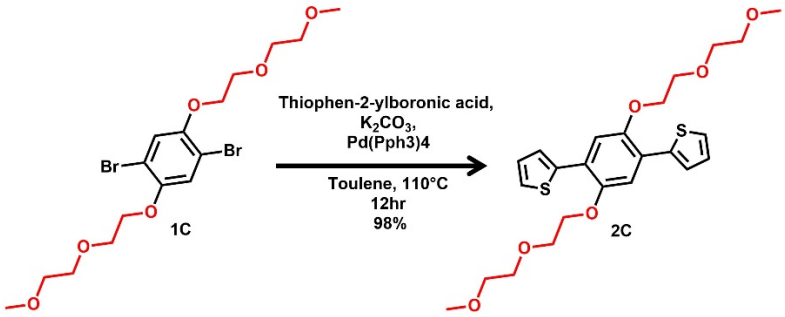


Table S4. The Material Cost (MC) for Synthesizing Intermediate 2C.

Chemicals/Company	Unit Price ($)	Chemicals used for the synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (ml)	
Intermediate 1C	-	1			-
K_2CO_3 / Hyma	1kg/ 10.8	1.46			0.01
Thiophen-2-ylboronic acid/ BLD	100g/ 115	3.25			3.73
$Pd(Pph_3)_4$ /BLD	100g/ 1003	0.049			0.5
Toluene/ Hyma	2.5lt/ 20	25			0.2
$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
DCM /Hyma	25lt/ 38			20	0.03
EtOAc /Hyma	25L/41.6		400		0.66
Hexane/ Hyma	25L/ 44		900		1.58
Silica gel/Hyma	5Kg/ 47.97	50			0.48
Total cost					7.19
Compound (2C): Yield, 98%, 1.0g, 7.19$, The cost of **1gm is 7.19$**					

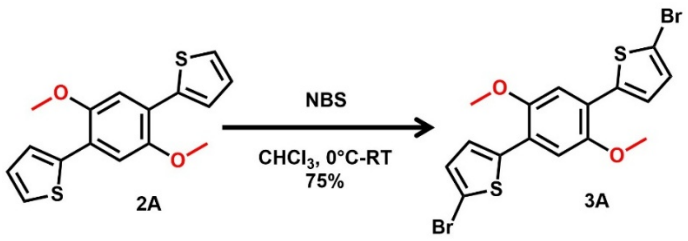


Table S5. The Material Cost (MC) for Synthesizing Intermediate 3A.

Chemicals/Company	Unit Price ($)	Chemicals used for the synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (ml)	
Intermediate 2A	-	0.5			-
$CHCl_3$ / Hyma	2.5lt/ 17	15			0.1
NBS/ BLD	500g/ 30	0.73			0.04
$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
DCM /Hyma	25lt/ 38			20	0.03
DCM /Hyma	25lt/ 38		150		0.23
Petroleum ether/ Hyma	25L/ 44		200		0.35
Silica gel/Hyma	5Kg/ 47.97	50			0.48
Total cost					1.39
Compound (3A): Yield, 75%, 0.6g, 1.39$, The cost of **1gm is 2.32$**					

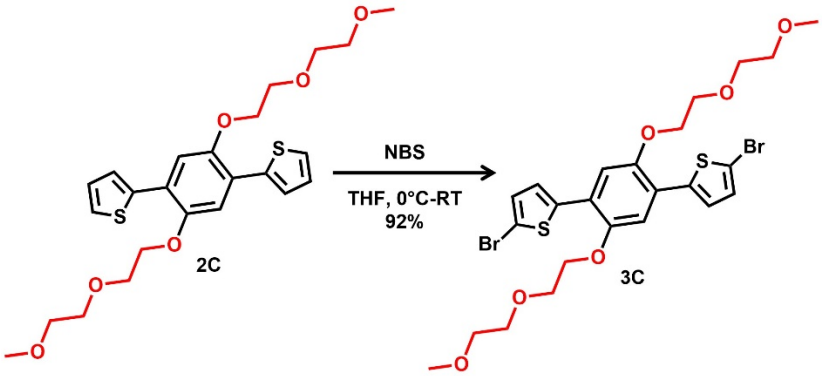


Table S6. The Material Cost (MC) for Synthesizing Intermediate 3C.

Chemicals/Company	Unit Price ($)	Chemicals used for the synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (ml)	
Intermediate 2C	-	1.0			-
THF/ Hyma	2.5lt/ 72	20			0.58
NBS/ BLD	500g/ 30	0.82			0.05

$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
DCM /Hyma	25lt/ 38			20	0.03
Petroleum ether/ Hyma	25L/ 44		450		0.80
DCM /Hyma	25lt/ 38		600		0.91
Silica gel/Hyma	5Kg/ 47.97	100			0.96
Total cost					3.50
Compound (3C): Yield, 92%, 1.2g, 3.50$, The cost of **1gm is 2.92$**					

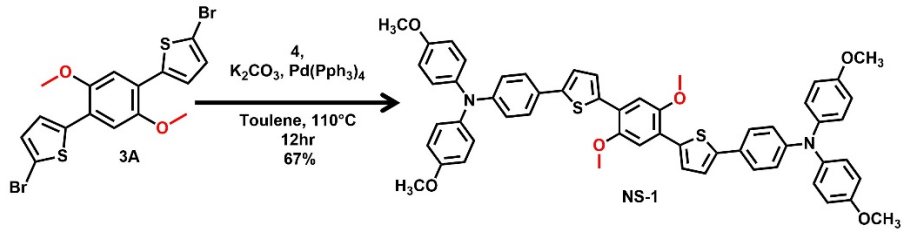


Table S7. The Material Cost (MC) for Synthesizing Intermediate NS-1.

Chemicals/Company	Unit Price ($)	Chemicals used for the synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (ml)	
Intermediate 3A	-	0.8			-
Intermediate 4	-	2.25			-
K_2CO_3 / Hyma	1kg/ 10.8	1.2			0.01
Toluene/ Hyma	2.5lt/ 20	20			0.16
$Pd(Pph_3)_4$ /BLD	100g/ 1003	0.04			0.40
EtOAc /Hyma	25L/41.6			20	0.03
Hexane/ Hyma	25L/ 44		700		1.23
$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
EtOAc /Hyma	25L/41.6		600		1.00
Silica gel/Hyma	5Kg/ 47.97	100			0.96
Total cost					3.95
Compound (NS-1): Yield, 67%, 1.0g, 3.95$, The cost of **1gm is 3.95$**					

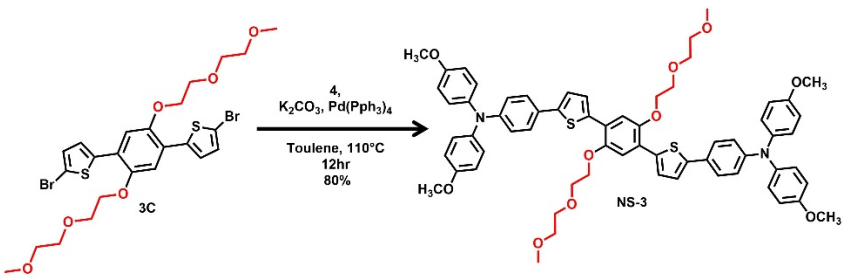


Table S8. The Material Cost (MC) for Synthesizing Intermediate NS-2.

Chemicals/Company	Unit Price ($)	Chemicals used for the synthesis			Chemical cost ($)
		Reagent (g)/ml	Solvent (ml)	Workup (ml)	
Intermediate 3C	-	1.0			-
Intermediate 4	-	1.0			-
K_2CO_3 / Hyma	1kg/ 10.8	0.75			0.001
Toluene/ Hyma	2.5lt/ 20	25			0.2
$Pd(Pph_3)_4$ /BLD	100g/ 1003	0.02			0.2
EtOAc /Hyma	25L/41.6			20	0.03
Hexane/ Hyma	25L/ 44		1000		1.76
$MgSO_4$ /Hyma	2.5 kg/ 40	10			0.16
EtOAc /Hyma	25L/41.6		700		1.16
Silica gel/Hyma	5Kg/ 47.97	100			0.96
Total cost					4.47
Compound (NS-2): Yield, 80%, 0.94g, 4.47$, The cost of **1gm is 4.75$**					

Table S9. Cost analysis of new HTMs and compared to standard Spiro-OMeTAD (CAS No.: 207739-72-8).

Compound	**Company**	**Cost per gram [₹]**	**Cost per gram [$]**
Spiro-OMeTAD	Sigma- Aldrich	49,502	580
	Ossila	45,788	525
	TCI	14,002	164
	1-Material Inc.	13,872	159
	BORUN NEW MATERIAL TECHNOLOGY LTD	20,764	238
	Average	**26,011**	**333**
NS-1	**This work**	**3,140**	**35**
NS-2		**3,320**	**37**

A detailed cost analysis of the starting materials and solvents used in the respective reactions to obtain 1 gram of NS-1 and NS-2 is provided. The yields and compound numbers correspond to those presented in the synthesis section. The cost analysis includes solvents used during purification steps, including column chromatography and crystallization. 2-(2-Methoxyethoxy)ethyl 4-methylbenzenesulfonate, used in the synthesis of IC, was prepared

in the laboratory.[7] The price conversion from INR to USD was based on the one-month average exchange rate of ₹1 = $0.012.

The price of Spiro-OMeTAD, reagents, solvents and chemicals were searched from,

https://www.1-material.com/dm-spiro-dm/

https://www.chemborun.com/htm-material/spiro-ometad.html

https://www.ossila.com/products/spiro-ometad?_pos=1&_sid=44a0736ed&_ss=r

https://www.sigmaaldrich.com/IN/en/product/aldrich/792071

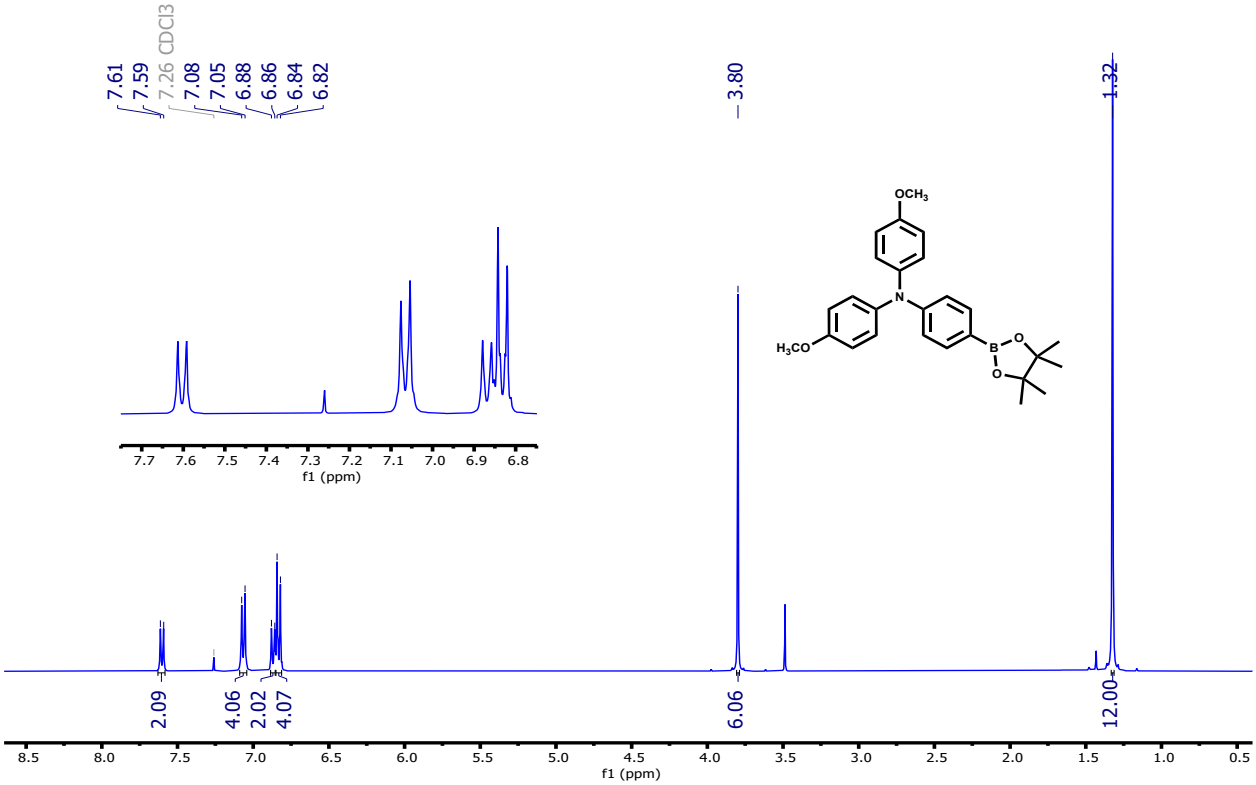
https://www.bldpharm.com/

https://www.srlchem.com/

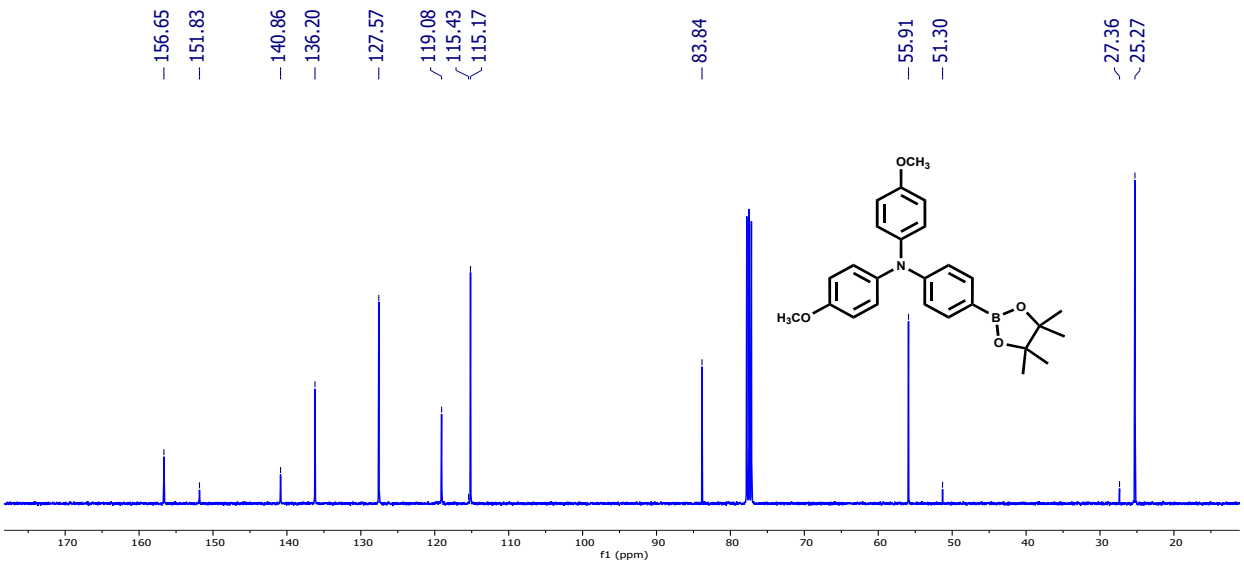
https://hymasynthesis.com/

4. Copies of NMR spectra:

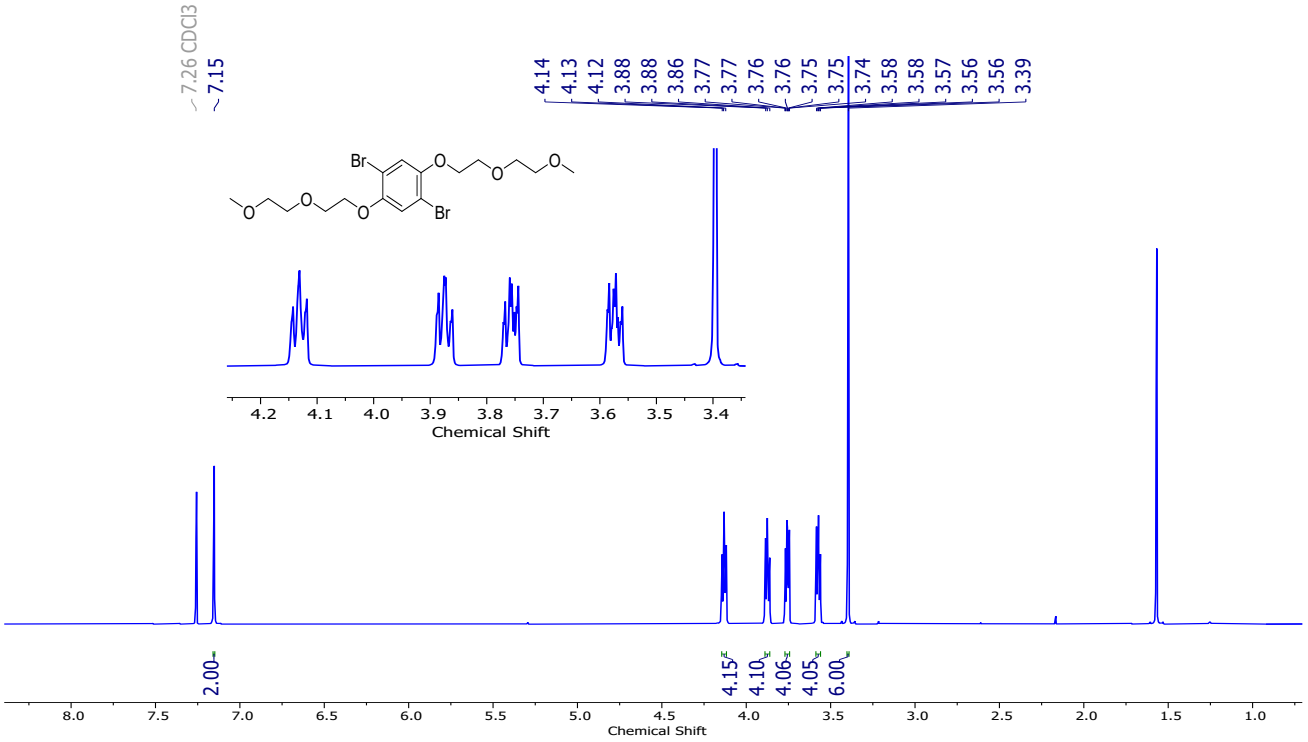
^{1}H NMR of 4:



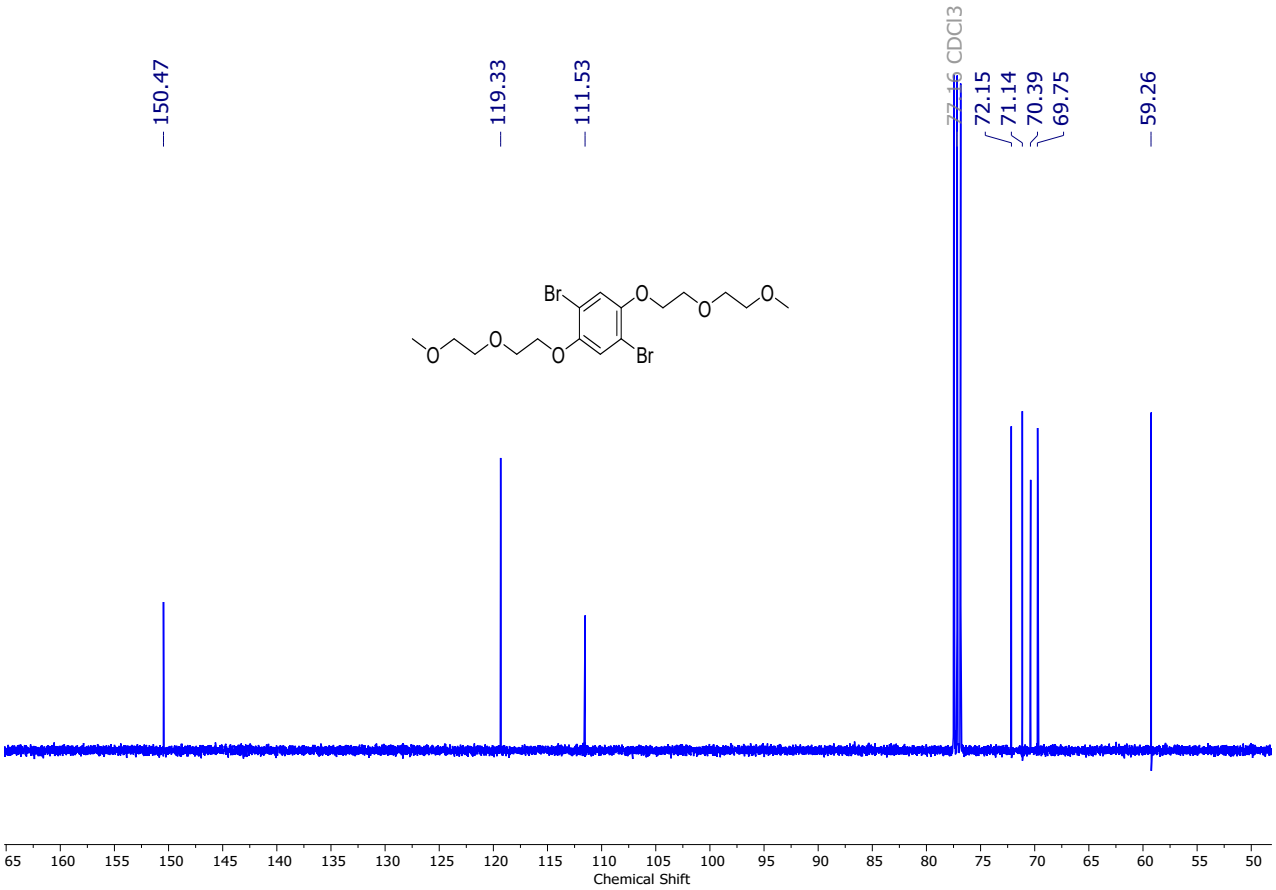
^{13}C NMR of 4:



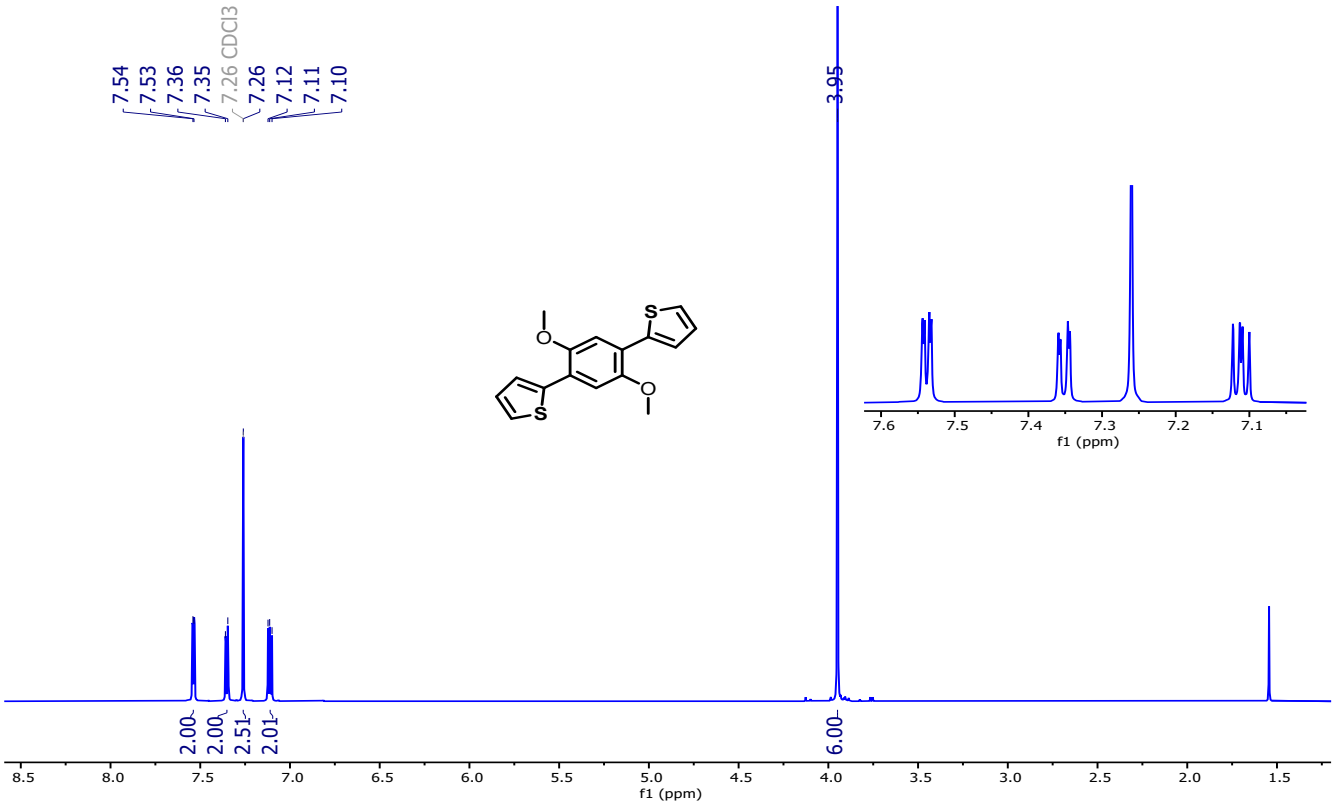
^{1}H NMR of 1C:



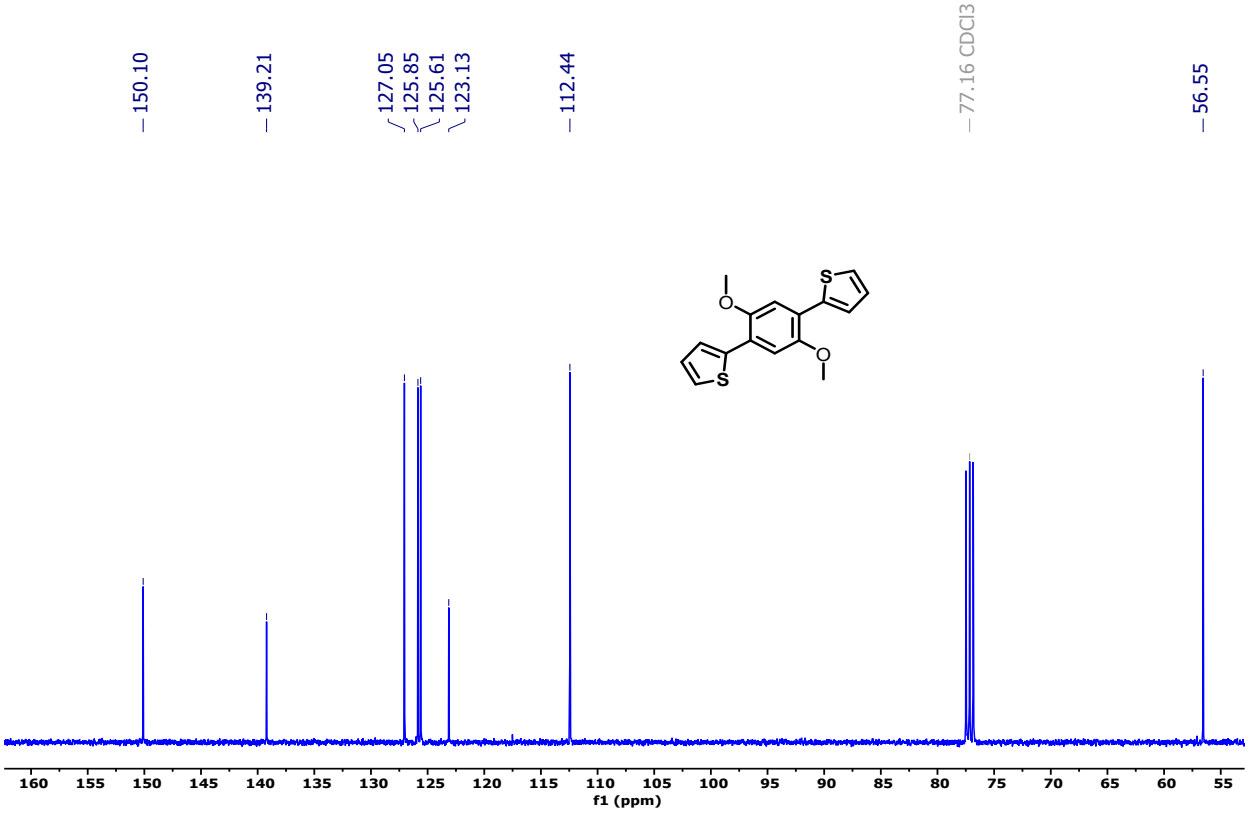
^{13}C NMR of 1C:



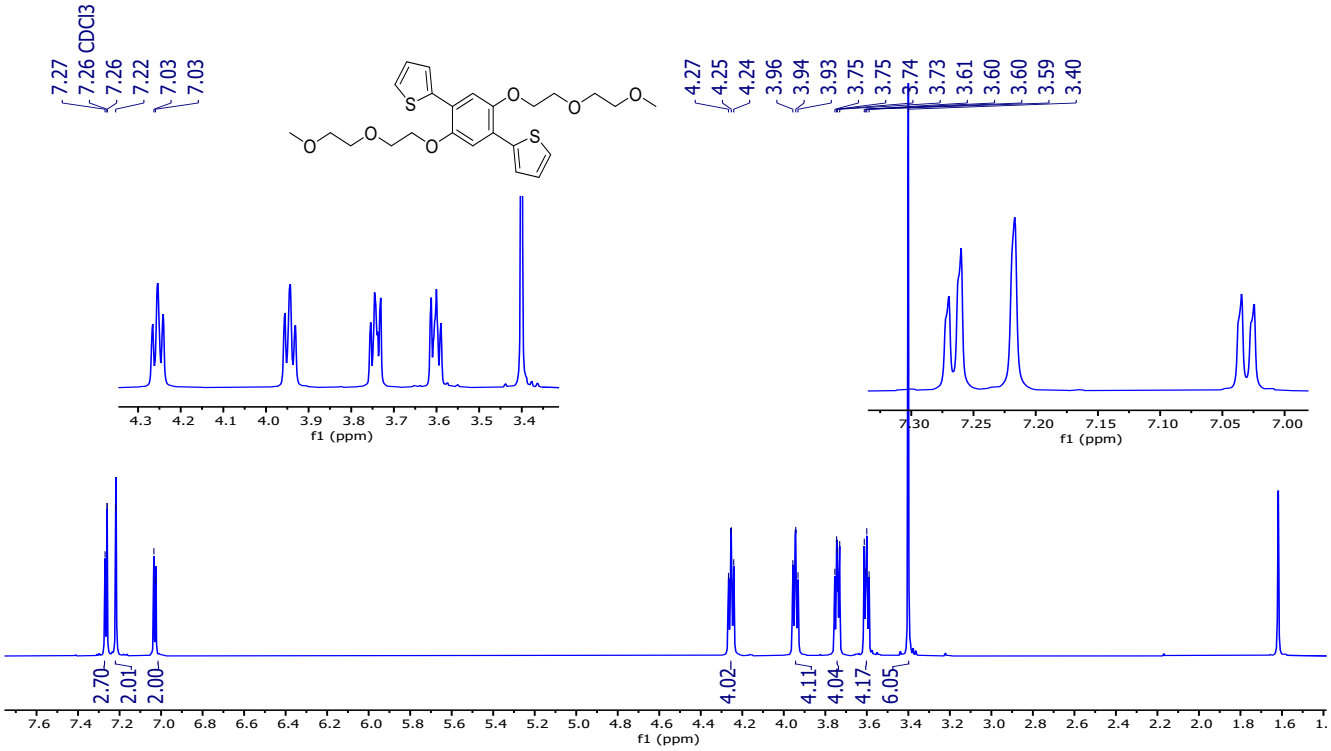
^{1}H NMR of 2A:



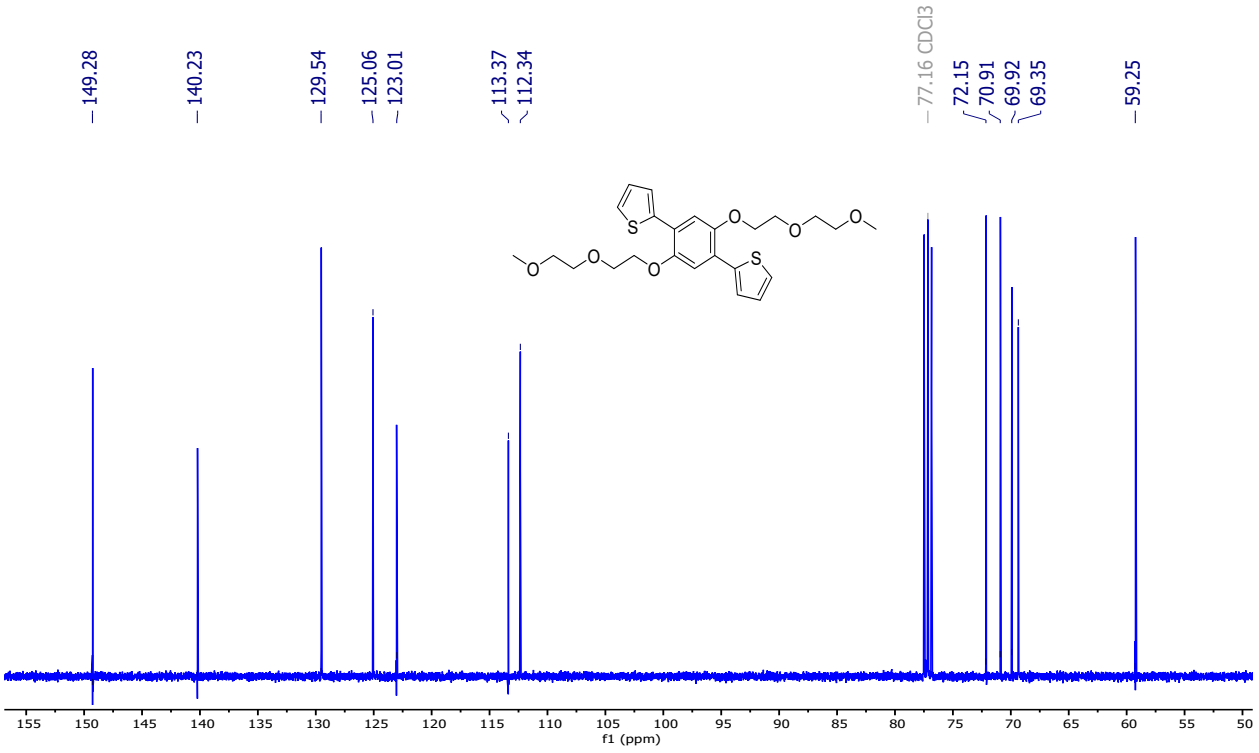
^{13}C NMR of 2A:



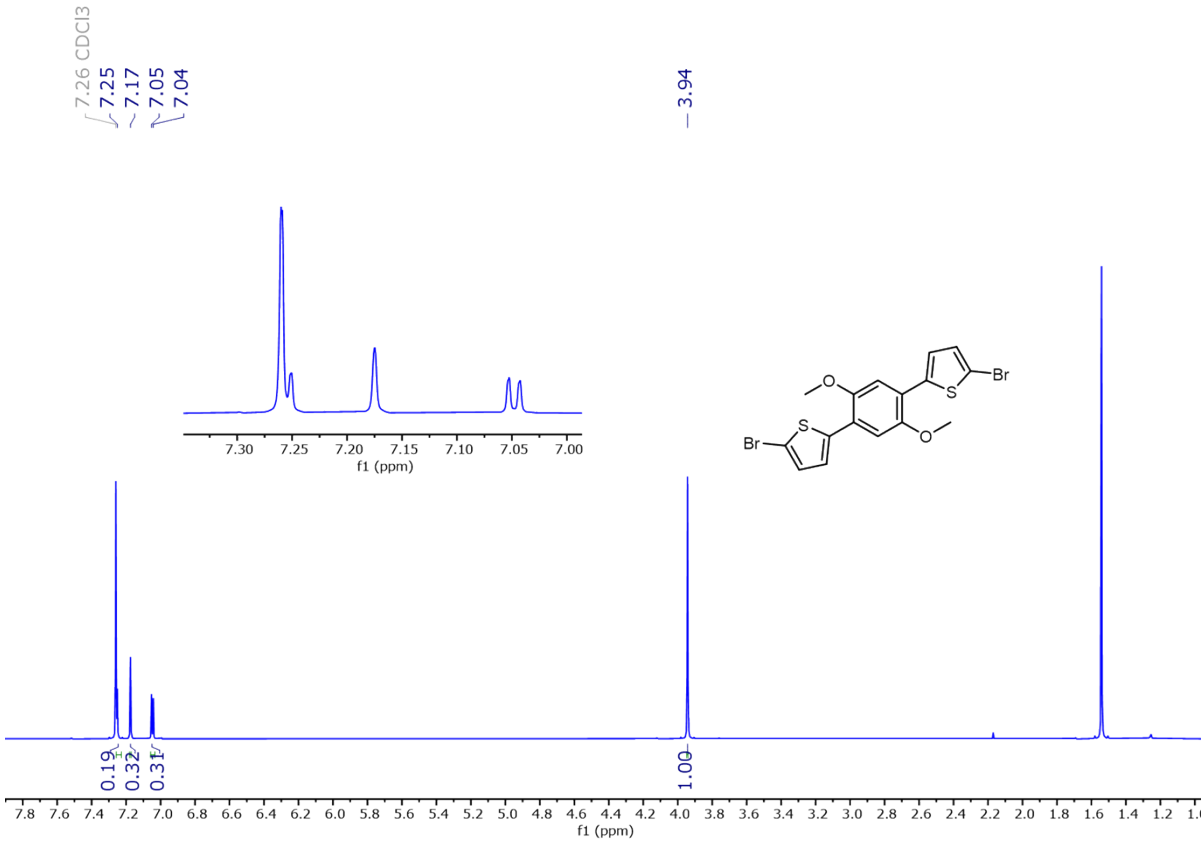
^{1}H NMR of 2C:



^{13}C NMR of 2C:



^{1}H NMR of 3A:



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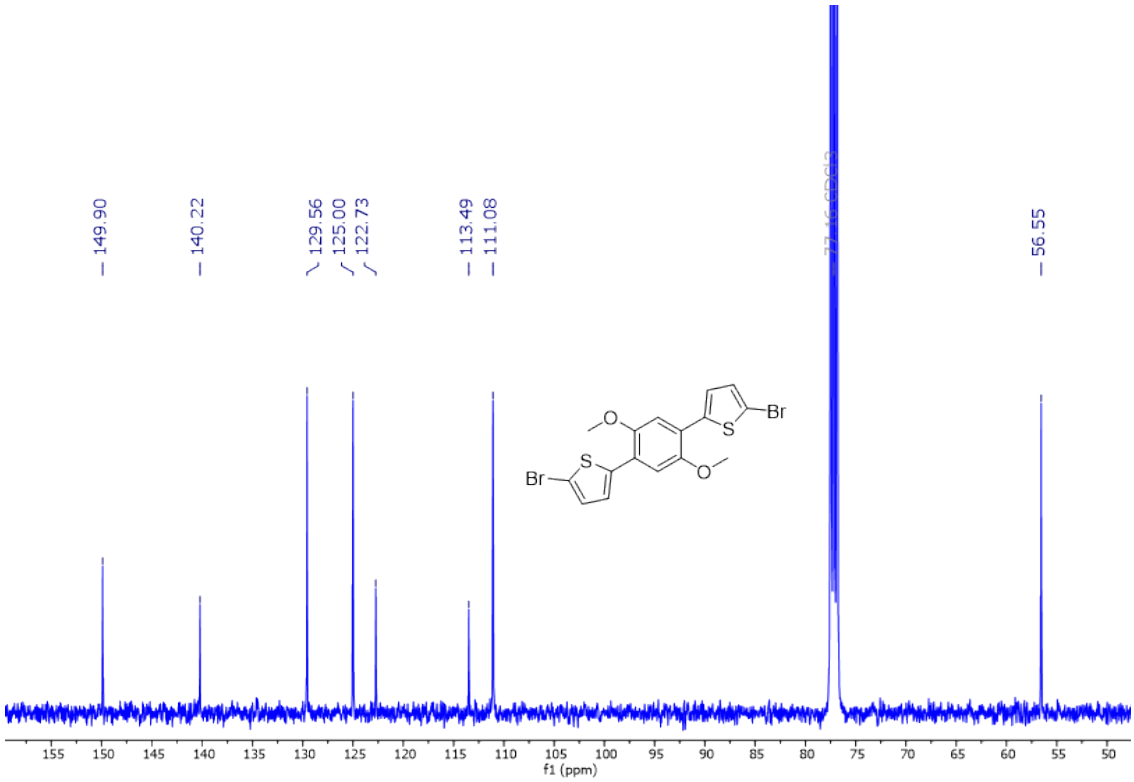
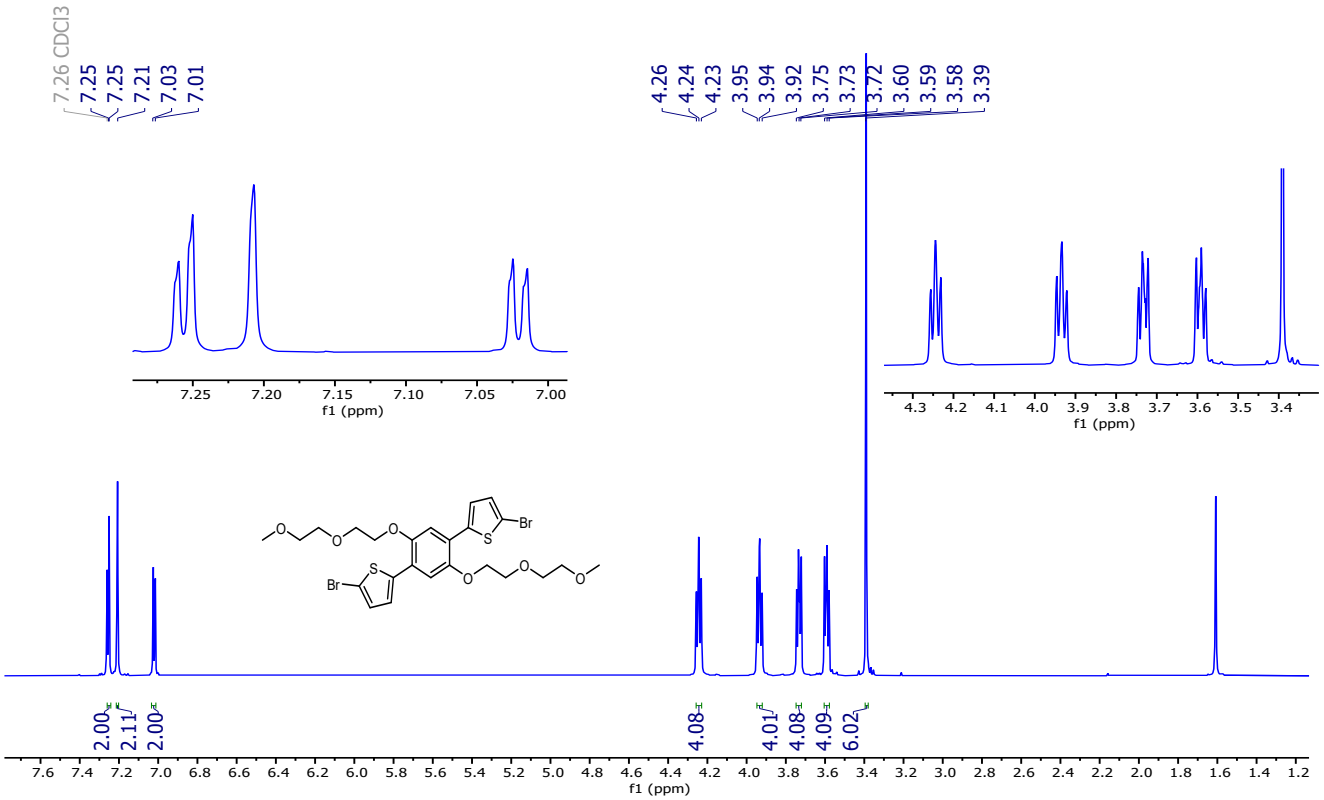
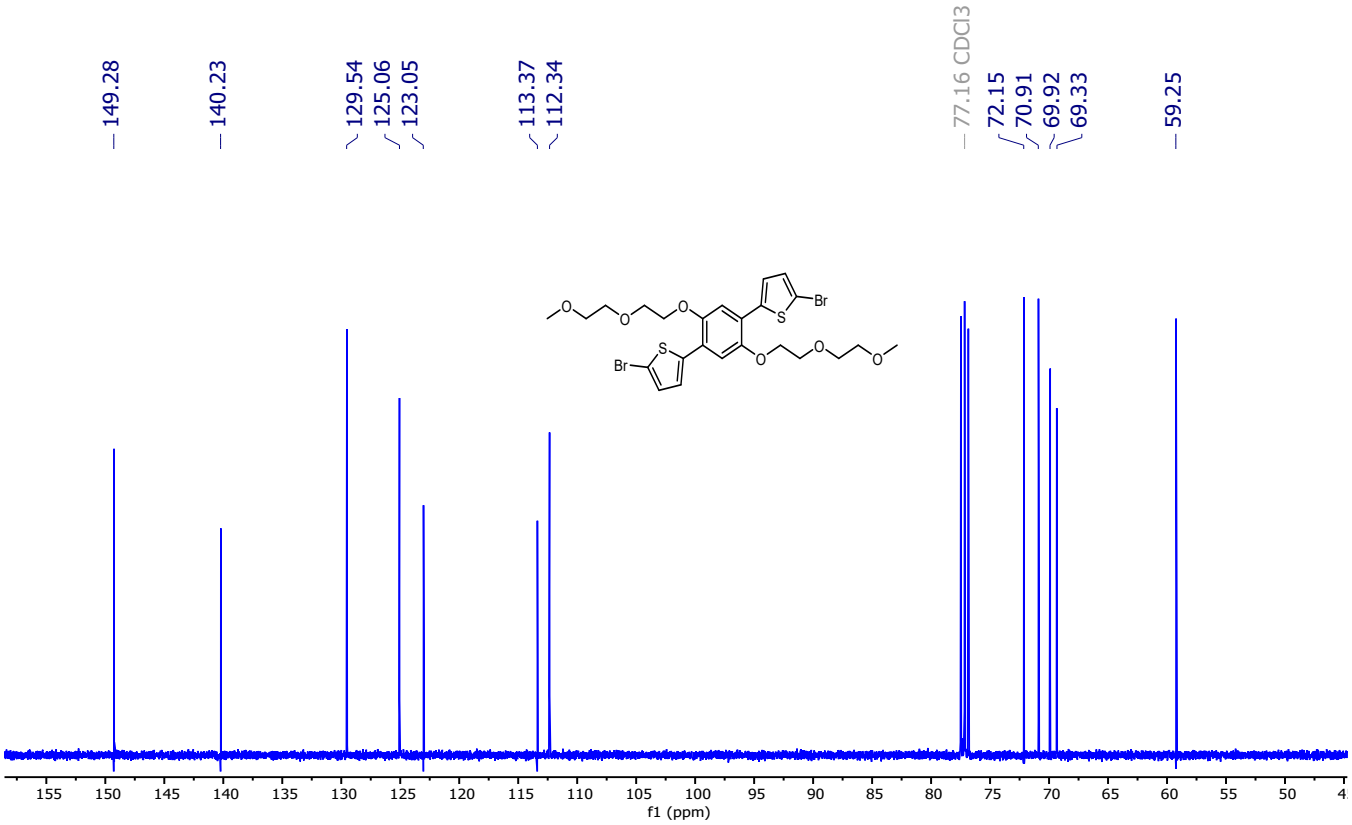


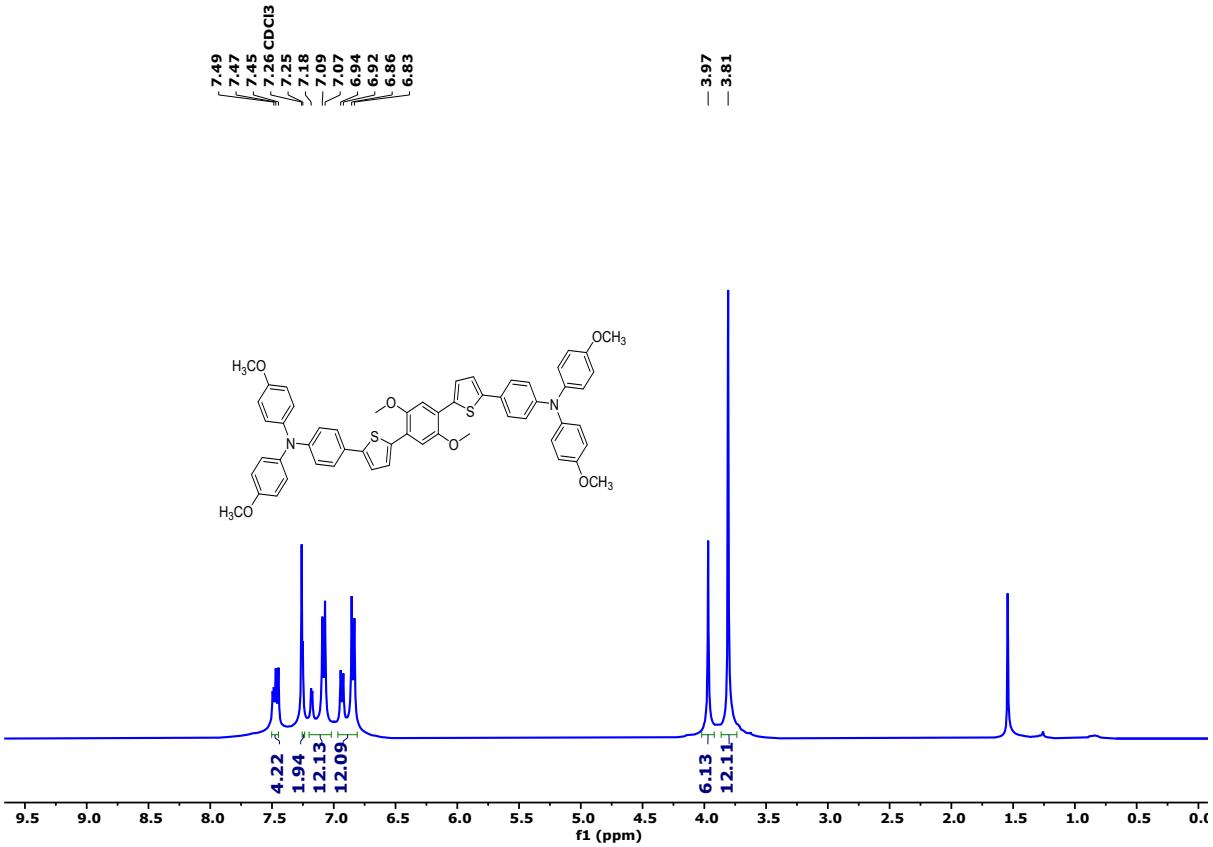
^{1}H NMR of 3C:



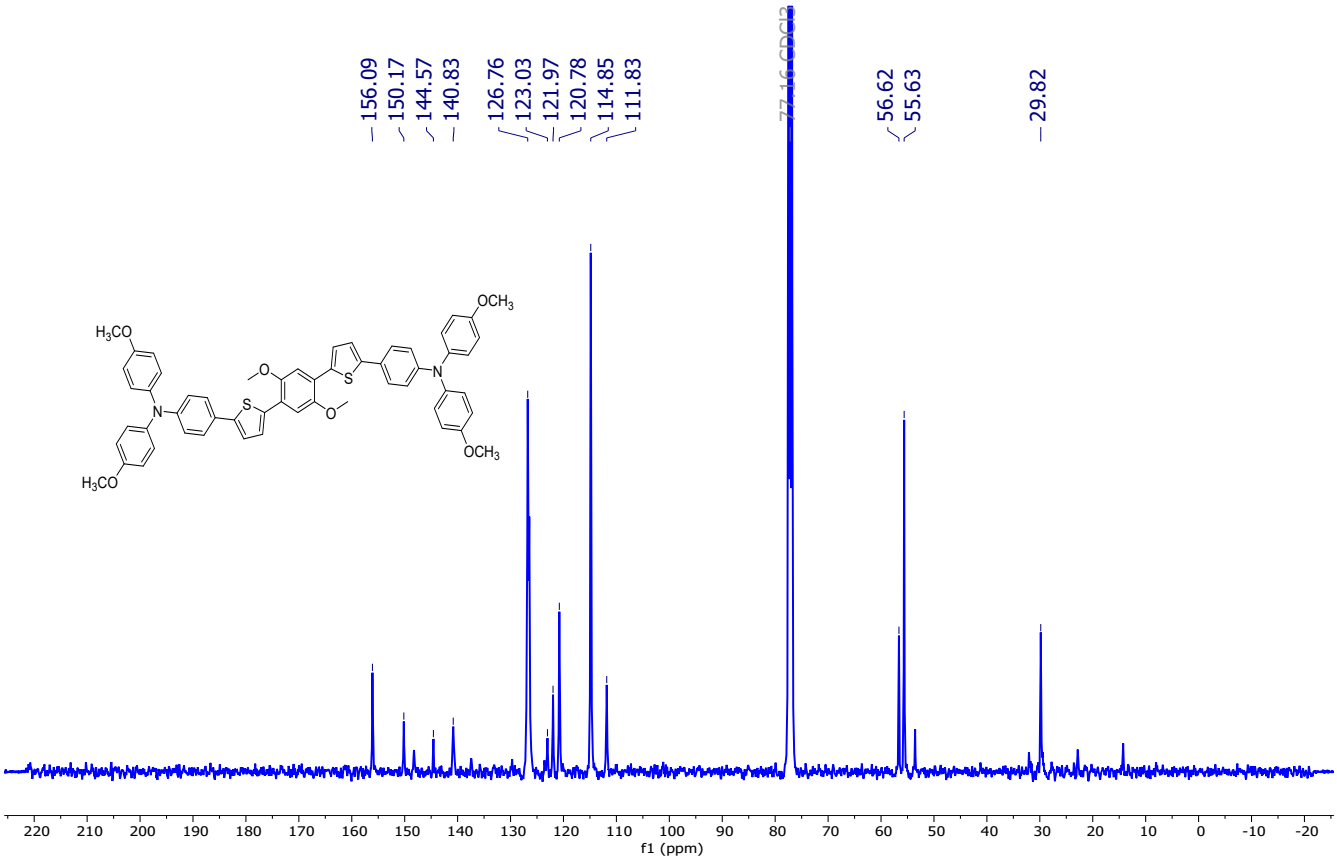
^{3}C 1NMR of 3C:



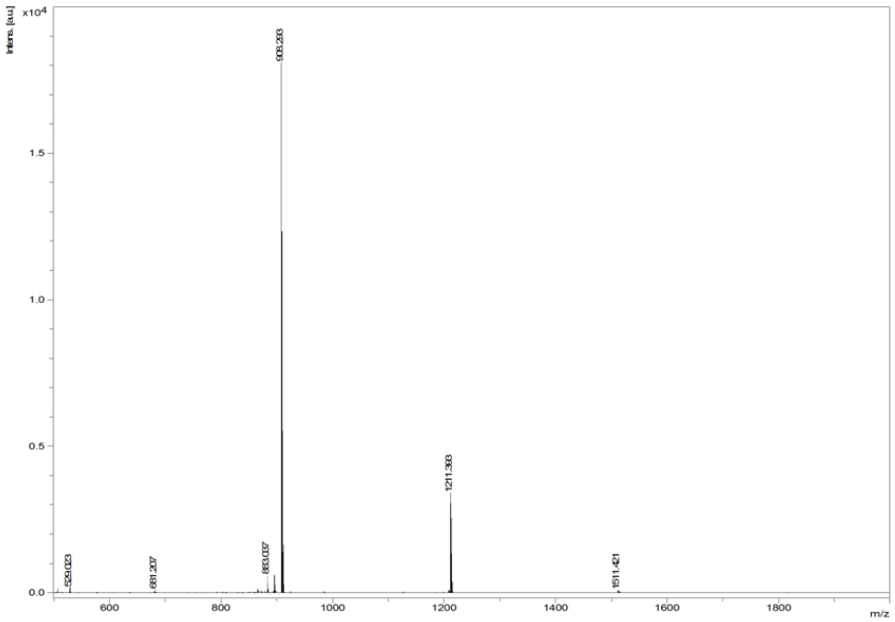
^{1}H NMR of NS-1:



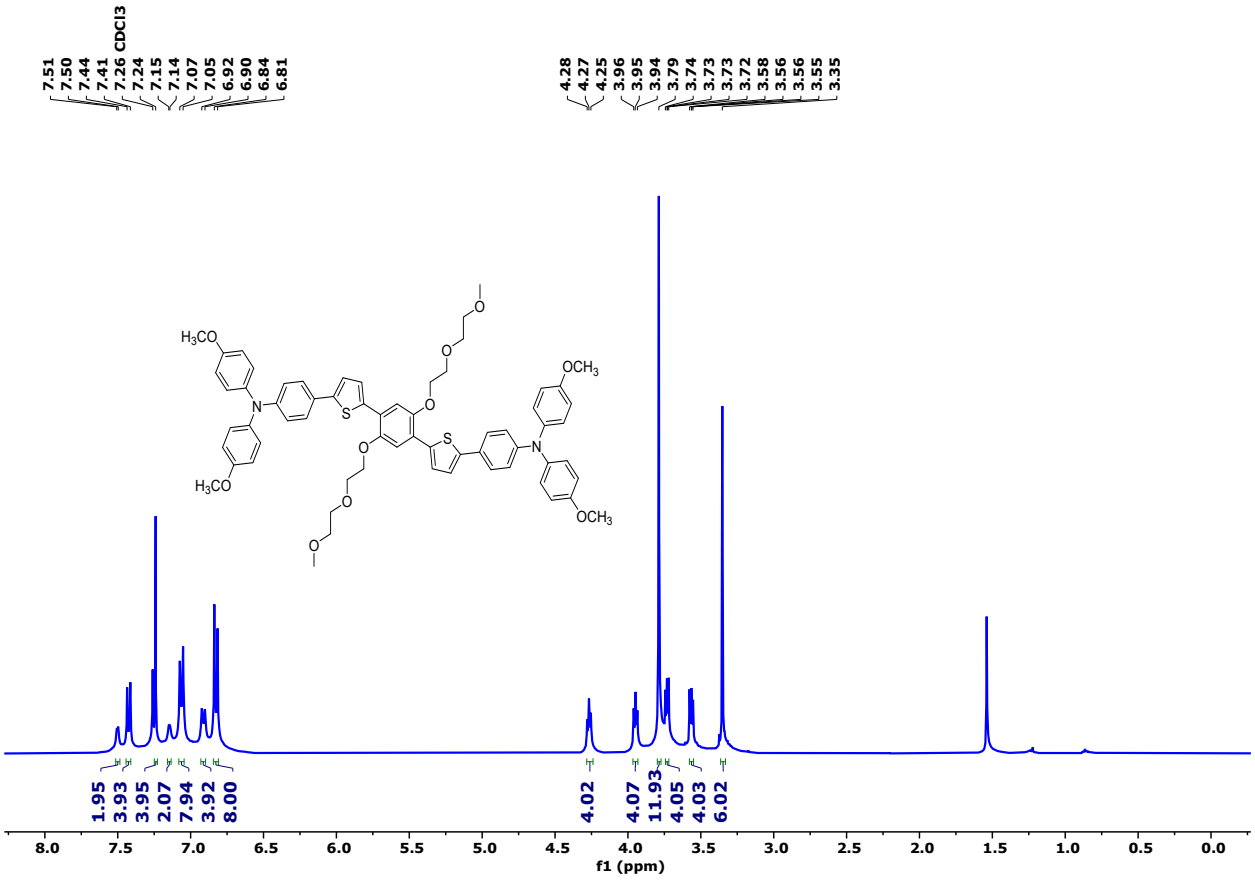
^{13}C NMR of NS-1:



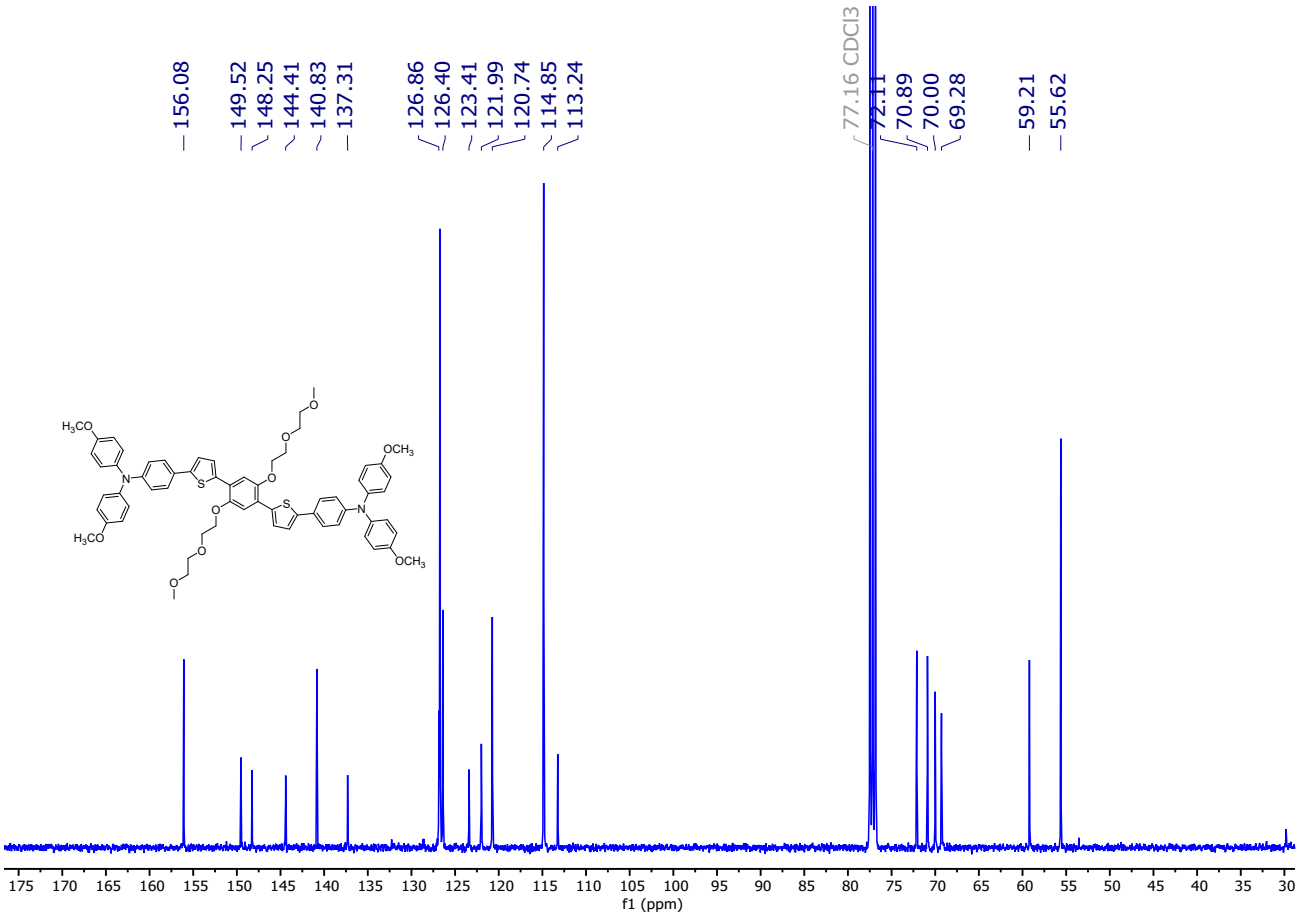
MALDI-TOF of NS-1:



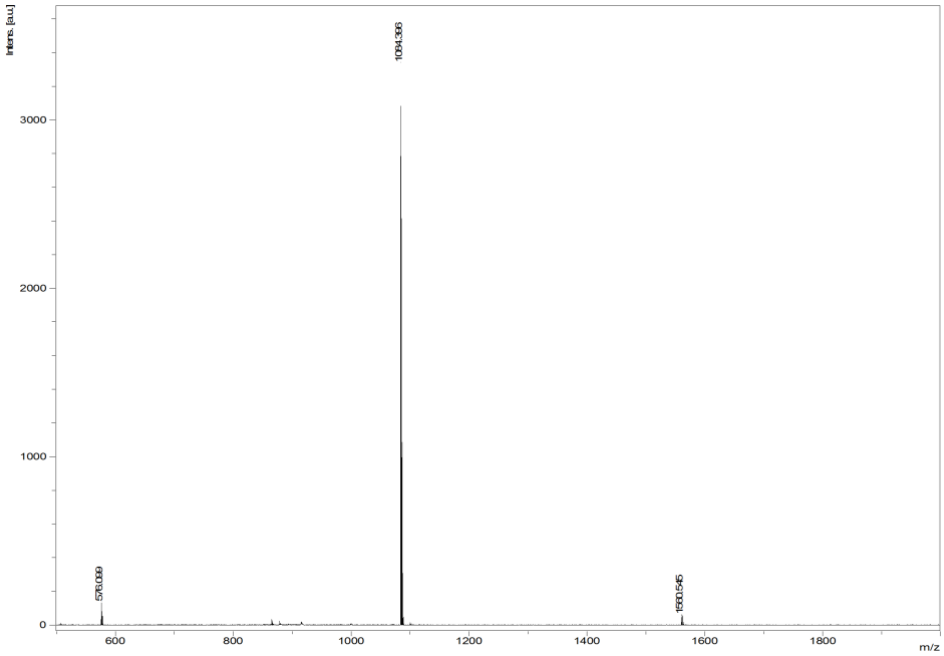
[1]H NMR of NS-2:



[13]C NMR of NS-2:



MALDI-TOF of NS-2:



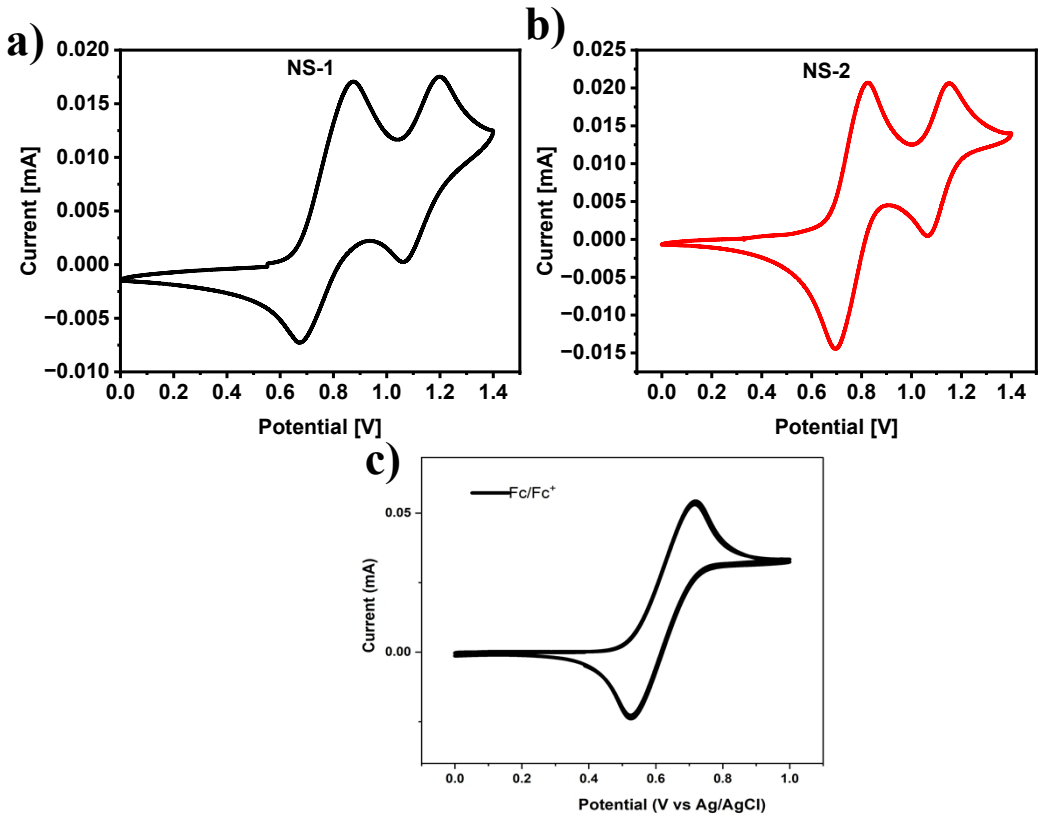


Figure S2: Cyclic voltammetry plots of a) NS-1, b) NS-2 containing 0.1 M tetra-n-butylammonium hexafluorophosphate and c) Ferrocene.

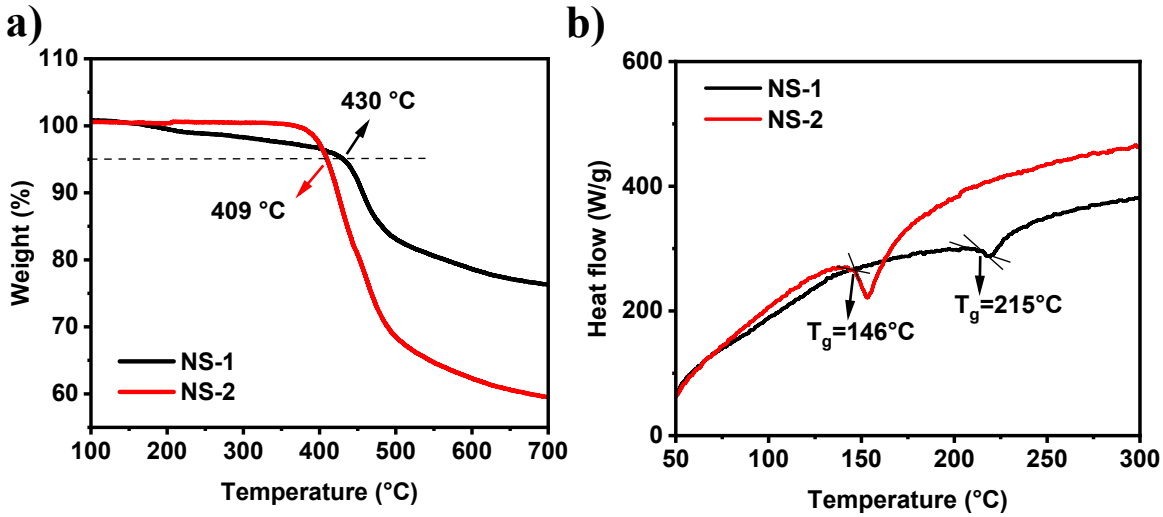


Figure S3: a) Thermogravimetric analysis (TGA) b) Differential scanning calorimetry (DSC) of HTMs with a scan rate of 10°C/min; N_2 atmosphere.

5. Computational Methodology

Geometry optimizations were performed using two different hybrid density functionals, CAM-B3LYP [8] and ωB97X-D[9] in combination with the cc-PVTZ basis set and the SMD continuum solvation model [10] considering a chloroform solvent environment. Frequency analyses were then performed at the same levels of theory to confirm that each optimized structure corresponds to a true energy minimum, as indicated by the absence of imaginary vibrational frequencies. Subsequently, the excited-state (S_1) energies were evaluated using time-dependent density functional theory (TD-DFT) at the same level of theory. All calculations were carried out with the Gaussian16 suite of programs.[11]

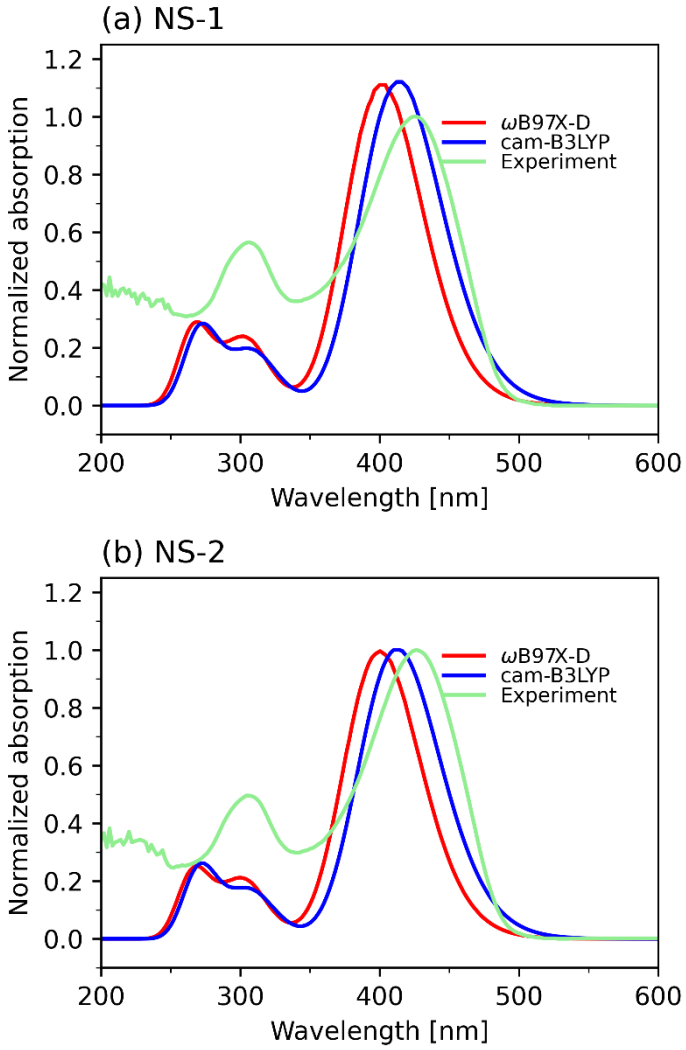


Figure S4: Comparing Theoretical and Experimental Normalized absorption spectra from UV-visible of (a) NS-1, (b) NS-2 are shown.

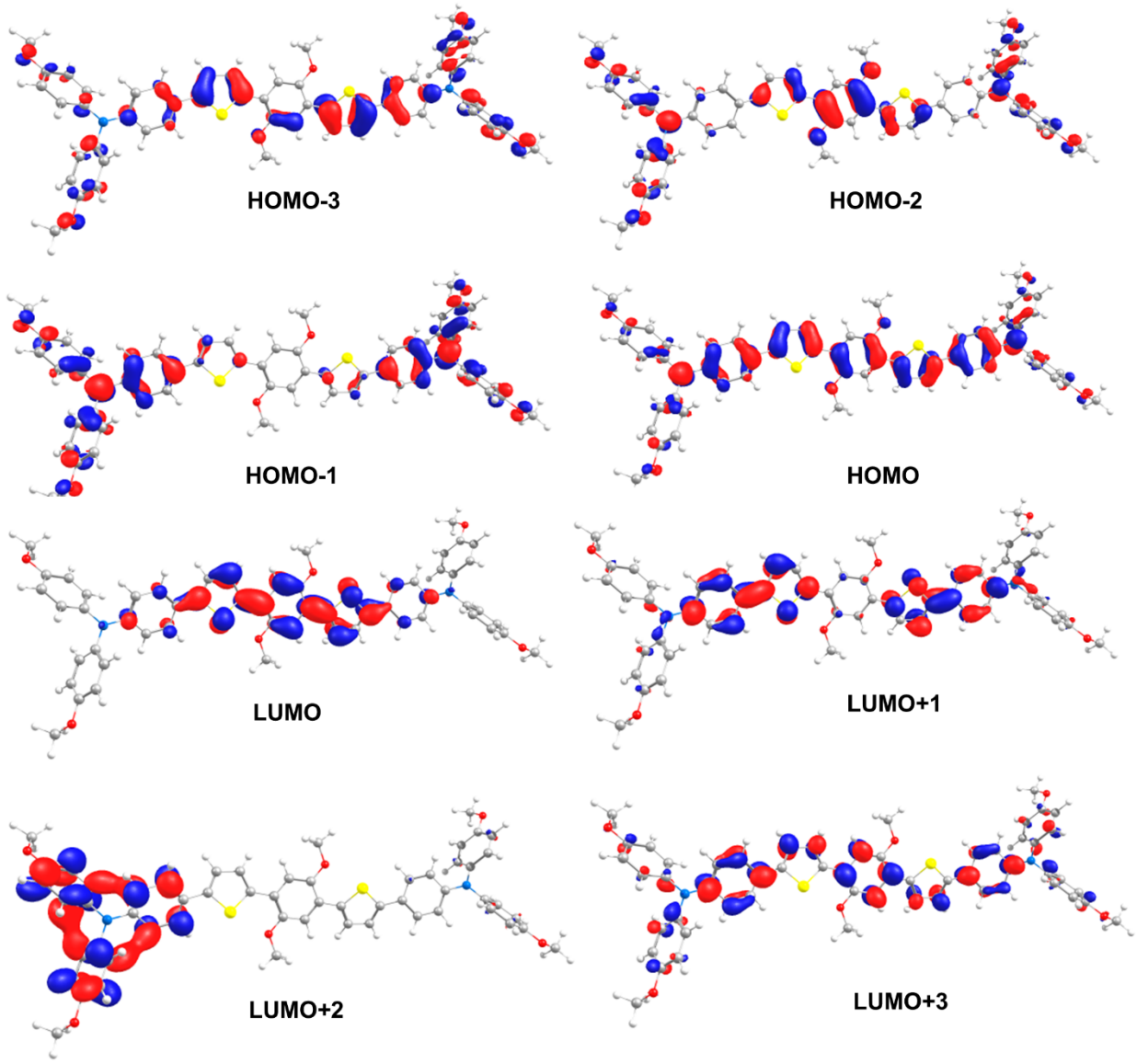


Figure S5: Frontier molecular orbital in the S_0 state of NS-1 calculated at the cam-B3LYP/cc-pVTZ /SMD level of theory

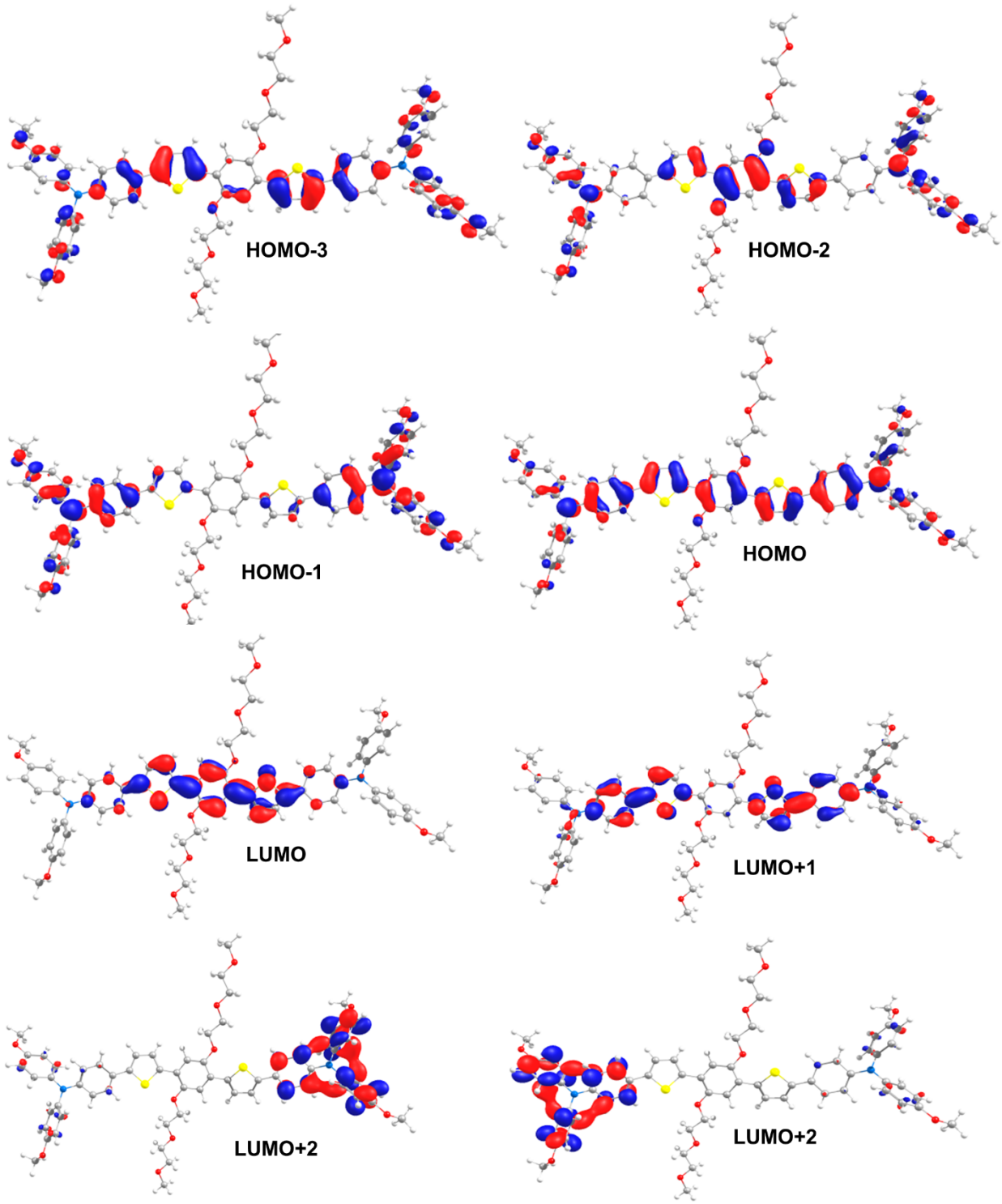


Figure S6: Frontier molecular orbital in the S_0 state of NS-2 calculated at the cam-B3LYP/cc-pVTZ /SMD level of theory

Table S10. Electrochemical properties measured from Theoretical values for the NS-1 and NS-2 molecules.

HTM theoretical	Methods[(a)]	S_1 (nm) abs	f [(b)]	E_g (eV)[(c)]	HOMO (eV)	LUMO (eV)
NS-1	cam-B3LYP	414	2.98	2.14	-7.44	-5.30
	ωB97-XD	402	2.95	2.18	-7.43	-5.25
NS-2	cam-B3LYP	413	2.97	2.15	-7.44	-5.29
	ωB97-XD	400	2.95	2.18	-7.43	-5.25
[a] All calculations were carried out using cc-pVTZ methods and the SMD solvent model. [b] Oscillator strength (f) [c] E_g = LUMO – HOMO.						

The normalized UV-vis absorption spectra of NS-1 and NS-2 compared with the theoretical and experimental data it shown in Fig. S8. Compared to ωB97-XD, cam-B3LYP shows a good agreement with the experimental values, and the excited state S_1 absorption values are shown in the table (1 and S2).

6. Space Charge Limited Current Data

Indium Tin Oxide (ITO) substrates (15 Ω/□, procured from Greatcell Solar Materials, Australia) were initially patterned using a 2 M HCl solution. Following the patterning process, the substrates underwent sequential cleaning as described in S 6.1. Initially, hole-only devices, the structure consisted of ITO/PEDOT:PSS (~90 nm)/NS-1 or NS-2 (~100 nm)/Ag (~100 nm) was fabricated. PEDOT:PSS (100 µL) was spin-coated onto UV ozone-treated ITO substrates at 4500 rpm for 65 seconds and annealed at 150 °C for 30 minutes in ambient conditions. This was followed by deposition of NS-1 or NS-2 (10 mg/mL in chloroform) via spin-coating at 1500 rpm for 45 seconds. Finally, both devices, were transferred to a thermal evaporation chamber (Hind High Vacuum, India), where a 100 nm thick silver layer was deposited under a vacuum of 3×10^{-6} mbar to complete the device structure. Both types of devices featured an active area of 6.6 mm^2. Current-voltage (*J-V*) measurements were performed using a Keithley 2450 source meter (Tektronix, USA). Layer thicknesses were characterized using a Dektak surface profiler, while the dielectric constants of NS-1 or NS-2 were measured using a high-frequency LCR meter (ZM^i2376, NF Corporation, Japan), operated at 1 V oscillation voltage across a frequency range of 20 Hz to 2 MHz.[12,13]

Table S11: Statistics of 5 best devices of Hole mobility.

S.No.	Hole Mobility ($cm^2 V^{-1} s^{-1}$) ($x 10^{-3}$)	
	NS-1	**NS-2**
1	1.02	1.22
2	1.39	2.00
3	1.12	1.47
4	1.55	1.29
5	1.47	1.59
AVG	1.31	1.51
STD	0.23	0.31

7. X-ray Diffraction (XRD) Analysis

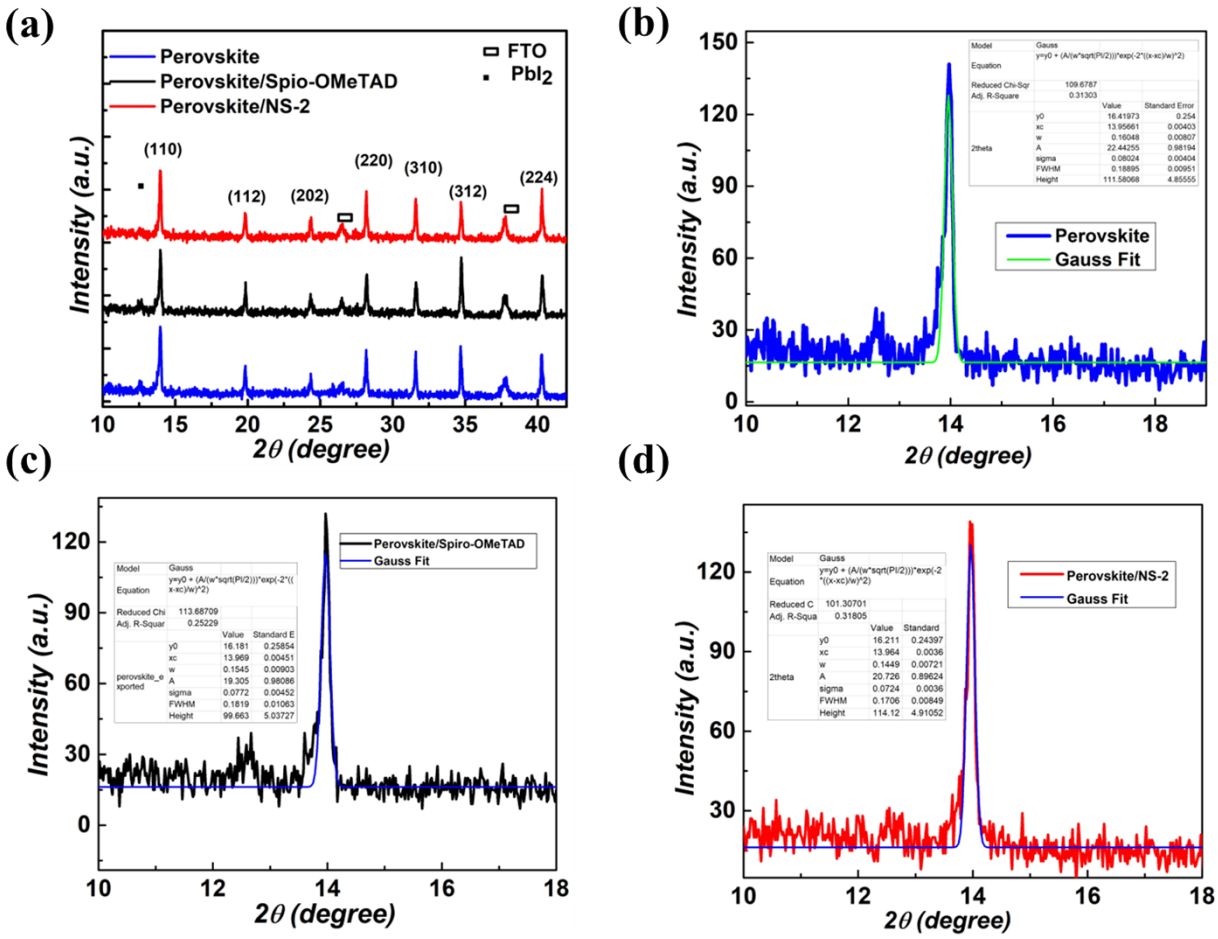


Figure S7: XRD patterns of perovskite and perovskite films with different HTMs: (a) Spiro-OMeTAD and NS-2, showing a weak Pb^{2+} peak in the Spiro-OMeTAD film that is nearly absent in NS-2, (b) raw data for perovskite, (c) raw data for Spiro-OMeTAD, and (d) raw data for NS-2.

8. Field Emission Scanning Electron Microscopy (FESEM) Cross-Sectional Analysis

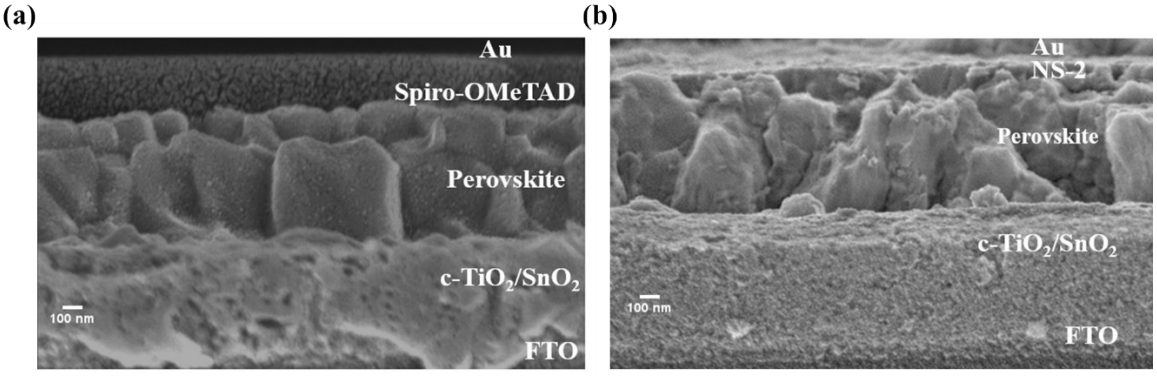


Figure S8: Cross-sectional FESEM image of the full device structure, showing the various layers: (a) Spiro-OMeTAD as the HTM and (b) NS-2 as the HTM

9. Time-Resolved Photoluminescence (TRPL) Analysis

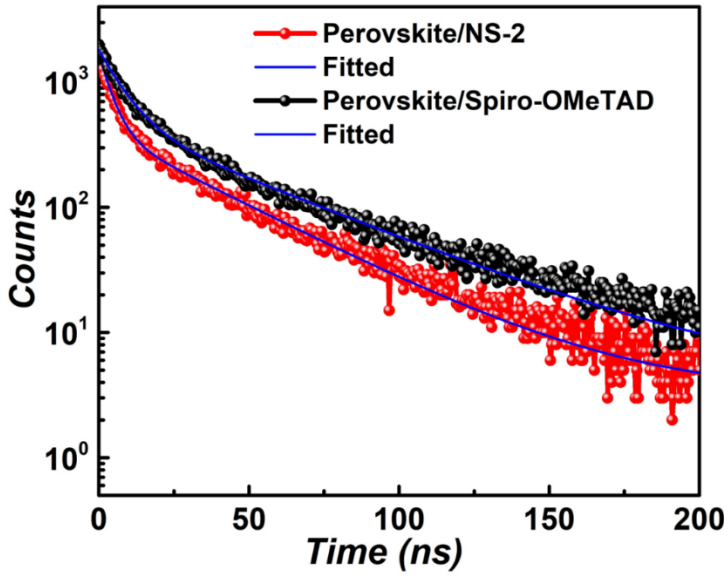


Figure S9: TRPL analysis of perovskite films with Spiro-OMeTAD and NS-2 as HTMs, showing the difference in carrier lifetimes and charge extraction efficiency.

Table S12: Summary of carrier lifetimes for perovskite films with Spiro-OMeTAD and NS-2 HTMs, derived from TRPL spectra fitting (Figure S9).

Samples	t_1 (ns)	A_1	t_2 (ns)	A_2	τ_{avg} (ns)
Perovskite/Spiro-OMeTAD	45.27	497.22	7.77	1320.74	33.53
Perovskite/NS-2	4.054	1285.02	35.52	410.50	27.25

10. Evaluate Charge Carrier Mobility and Trap Density in the HTM Layer Deposited on Perovskite

To examine the trap density and charge carrier mobility in perovskite-based devices with Spiro-OMeTAD and NS-2 as HTM, two different hole-only sample were fabricated and analysed using the SCLC technique. The first device, structure ITO/PTAA/Perovskite/Spiro-OMeTAD/Au, while the second device with the configuration ITO/PTAA/Perovskite/NS-2/Au. ITO substrates were patterned and cleaned following the standard procedure described in S6.1.To fabricate the hole-only sample, a 2 mg/ml PTAA solution in chloroform was spin-coated onto the pre-cleaned ITO substrates at 4000 rpm for 30 seconds. This was followed by annealing at 100 °C for 10 minutes. The perovskite active layer was deposited via spin-coating, as detailed in the main manuscript, over the active layer HTM Spiro-OMeTAD, and NS-2 was deposited at a rate of 3000 rpm for 30 sec. To complete the SCLC device, an 80 nm Gold (Au) layer was thermally evaporated (Hind High Vacuum, India) under a vacuum pressure of 1 $\times 10^{-6}$ mbar. The active area of the fabricated devices, determined by the overlapping region of the ITO and the top electrode, measured 0.066 cm². The thickness of each layer was confirmed using a Dektak surface profiler. Once fabrication was completed, the devices were immediately subjected to current–voltage *(J–V)* characterization using a Keithley 2400 dual-channel source meter. [14–16]

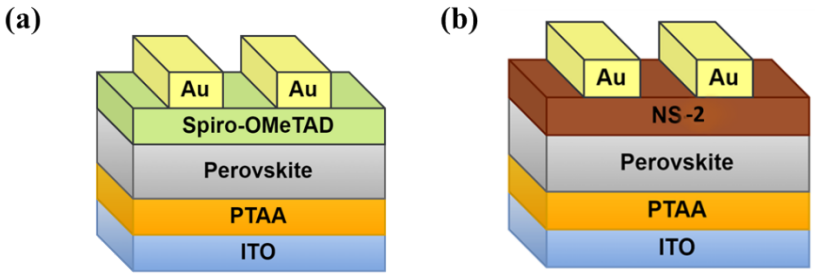


Figure S10: Schematic representation of hole-only devices: (a) perovskite with Spiro-OMeTAD and (b) perovskite with NS-2.

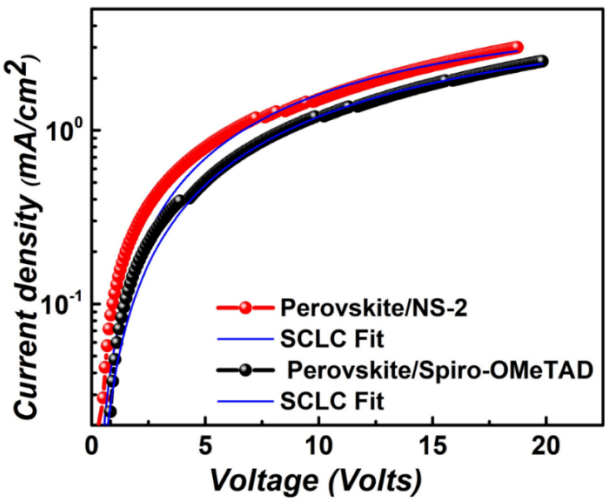


Figure S11: Charge carrier mobility for the devices illustrated in Figure S10 was determined using SCLC analysis.

11. Perovskite Solar Cell Fabrication

Material: The perovskite precursor chemicals, Methylammonium bromide (MABr) and Formamidinium iodide (FAI), were obtained from Greatcell Solar Materials. Cesium iodide (CsI), Lead(II) iodide (PbI_2), Lead (II) bromide ($PbBr_2$), and Spiro-OMeTAD were purchased from TCI. Acetonitrile (ACN), Titanium diisopropoxide bis(acetylacetonate), Dimethylformamide (DMF), Chlorobenzene, Dimethyl sulfoxide (DMSO), FK209 Co(III) TFSI salt, Bis(trifluoromethane)sulfonimide lithium salt, and 4-tert-butylpyridine were sourced from Sigma-Aldrich. Tin(IV) oxide colloidal dispersion (15% in water) was supplied by Thermo Scientific, while Titanium tetrachloride ($TiCl_4$) was obtained from Spectrochemical.

$$FTO/c\text{-}TiO_2/SnO_2/Cs_{0.05}(FA_{0.79}MA_{0.16})_{0.95}Pb(I_{0.77}Br_{0.23})_3/Spiro\text{-}OMeTADorNS\text{-}2/Ag$$

,as shown in Figure 7(a), was fabricated as follows: Fluorine-doped tin oxide (FTO) coated glass substrates (7 Ω/□, 2.5 mm^2) were first cleaned sequentially in an ultrasonic bath using a 3% Helmanex III soap solution, deionized water, acetone, and isopropanol for 20 minutes each. The substrates were then dried using nitrogen and treated with UV-ozone (Bio-BEE Tech., India) at 50°C for 20 minutes to eliminate residual contaminants. After that, a compact TiO_2 (c-TiO_2) layer was formed by dissolving 100 µL of Titanium diisopropoxide bis(acetylacetonate) and 7 µL of 2 M HCl in 1 mL of Ethanol, followed by spin coating at 6000 rpm for 40 seconds. This layer was annealed at 500°C for 1 hour to achieve a uniform, compact TiO_2 film. Post-deposition, a $TiCl_4$ (40 mM) treatment was applied at 70°C for 15 minutes, and

the film was again annealed at 500°C for 30 minutes. A SnO_2 ETL was then deposited by diluting 15% colloidal SnO_2 with deionized water in a 1:4 weight ratio, spin-coated at 3000 rpm for 30 seconds, and annealed at 150°C for 30 minutes, forming a bilayer ETL of ~40 nm. The ETL-coated substrates were immediately transferred into a nitrogen-filled glovebox (H_2O < 1 ppm, O_2 < 50 ppm) for perovskite deposition. The perovskite precursor solution was prepared by dissolving $PbBr_2$ (34.2 mg) and PbI_2 (700 mg) in a DMF:DMSO mixture (4:1 volume ratio) and stirring at 130°C for 20 minutes. This solution was then added to a second vial containing MABr (10.5 mg) and FAI (238 mg), followed by the addition of 55 µL CsI (1.5 M in DMSO), and stirred at 55°C for 1 hour. Finally, the perovskite solution was deposited using a two-step spin-coating process: 1000 rpm for 10 seconds, then 6000 rpm for 30 seconds. During the second step, 250 µL of Chlorobenzene was dripped onto the film 15 seconds before completion. The resulting film was annealed at 100°C for 1 hour, producing a layer ~500 nm thick. Finally, the HTM was prepared by dissolving 90 mg of Spiro-OMeTAD in 1 mL of Chlorobenzene and 20 mg of NS-2 in a separate 1 mL of chlorobenzene to which 22 µL of Li-TFSI solution (520 mg Li-TFSI in 1 mL ACN), 36 µL of TBP, and 20 µL of FK209 solution (300 mg FK209 in 1 mL ACN) were added and stirred for 10 minutes. This HTM solution was spin-coated at 3000 rpm for 30 seconds, forming a ~180 nm thick layer. After HTM deposition, the devices were aged inside the glovebox under controlled humidity (≤1%) conditions. At last, gold (Ag) electrodes were thermally evaporated under a vacuum of 10^{-6} bar, defining an active device area of 0.099 cm^2, followed by an additional aging period of 20 hours before measurements.

Device fabrication for *J-V* characterization:

The device fabrication procedure followed ESI Section 11 up to the perovskite layer and electrode deposition steps. Variations were limited to the preparation and deposition of the NS-1 and NS-2 HTMs, including dopant-free and doped conditions, different HTM concentrations, and varied spin-coating speeds. An initial HTM concentration of 20 mg/mL was selected based on previously reported literature,[17] and was therefore maintained constant for baseline device fabrication. For dopant-free HTMs, both NS-1 and NS-2 were dissolved in chlorobenzene (CB) at this concentration without the addition of dopants and spin-coated at 3000 rpm for 30 s. For doped HTMs, NS-1 and NS-2 solutions were prepared under identical conditions, with dopant incorporation following the standard Spiro-OMeTAD protocol as mentioned above and spin-coated at 3000 rpm for 30 s. To investigate the effect of concentration, doped NS-2 solutions with concentrations of 10, 20, 60, and 90 mg/mL were prepared in CB and deposited at 3000

rpm for 30 s. Additionally, the influence of spin-coating speed was evaluated using doped NS-2 solutions (20 mg/mL) deposited at 2000, 3000, and 4000 rpm.

Film fabrication for XRD and FE-SEM:

The film fabrication procedure followed that described in ESI Section 11 up to the deposition of the perovskite layer and Spiro-OMeTAD. NS-1 was dissolved in chlorobenzene (CB) at a concentration of 20 mg/mL, with dopant incorporation following the standard Spiro-OMeTAD protocol as described above, and the solution was spin-coated at 3000 rpm for 30 s.

Film fabrication for UV-Vis, PL, TRPL, Contact angle, Profilometer:

The film fabrication was carried out on cleaned quartz glass substrates. The preparation and deposition of the perovskite layer and Spiro-OMeTAD followed the procedure described in ESI Section 11 (above). NS-1 was dissolved in chlorobenzene (CB) at a concentration of 20 mg/mL, with dopant incorporation following the standard Spiro-OMeTAD protocol as described above, and the resulting solution was spin-coated at 3000 rpm for 30 s.

Characterization: Ultraviolet-visible (UV-Vis) absorption spectra were recorded using a Shimadzu SolidSpec-3700 spectrophotometer. The surface morphology of the films was examined by field-emission scanning electron microscopy (FE-SEM, JEM-7001F, JEOL). X-ray diffraction (XRD) measurements were performed using a Bruker D8 Discover lab-scale diffractometer with a Cu Kα radiation source ($\lambda = 0.154$ nm). Steady-state photoluminescence (PL) spectra were acquired with a Horiba Fluorolog-3 spectrofluorometer using a 450 nm excitation wavelength. Time-resolved photoluminescence (TRPL) measurements were carried out with a LifeSpec II instrument (Edinburgh Instruments). Current–voltage (*J-V*) characteristics were measured under AM 1.5G one-sun illumination using a ScienceTech solar simulator and a Keithley 2450 source meter, with an active device area of 0.099 cm^2. The water contact angle was measured using a Drop Shape Analyzer (KRÜSS, Hamburg, Germany). Layer thicknesses were determined using a Bruker Dektak XT surface profilometer. Electrochemical impedance spectroscopy (EIS) data were obtained with a Keysight E4990A Impedance Analyzer.

12. Film Thickness Measurement (Profilometer)

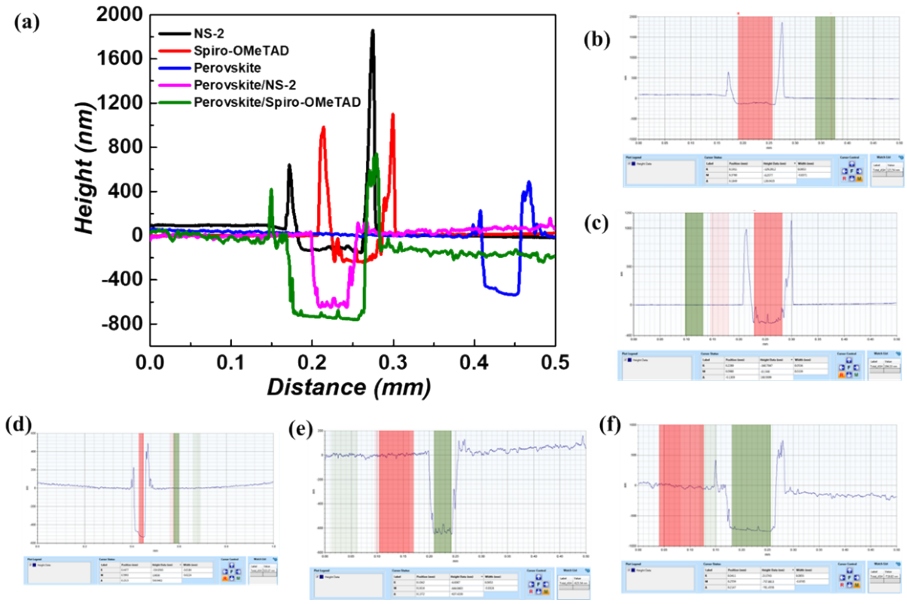


Figure S12: Dektak profilometer measurements (a) Overall scan of layer stacks, (b) NS-2 HTM, (c) Spiro-OMeTAD HTM, (d) Perovskite layer, (e) Perovskite/NS-2 stack, and (f) Perovskite/Spiro-OMeTAD stack, confirming uniform layer formation.

13. *J-V* Characterization of Perovskite Solar Cells

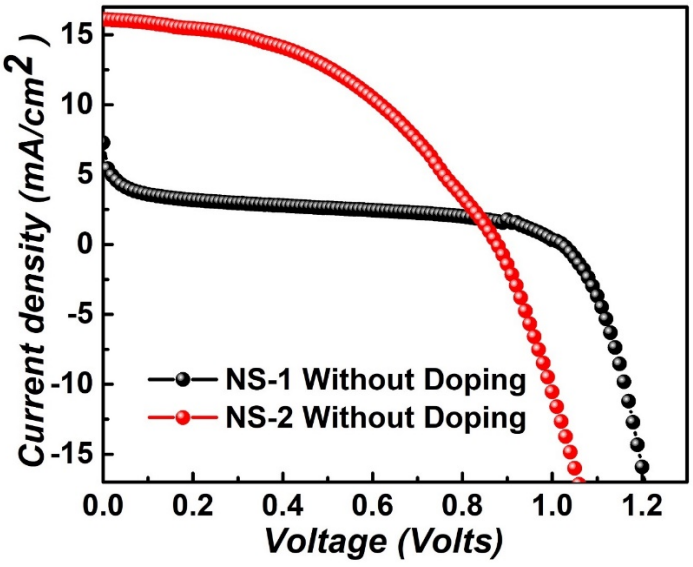


Figure S13: *J-V* characteristic for without doped NS-1 and NS-2 as HTMs in PSCs, showing the comparison of photovoltaic performance parameters.

Table S13: Summary of photovoltaic parameters for HTMs NS-1 and NS-2 (without doped), for five devices (best values in brackets).

Device Without doped	Jsc (mA cm^{-2})	Voc (V)	FF	PCE (%)
Perovskite/NS-1	6.54 ± 0.82 (7.29)	1.00 ± 0.01 (1.02)	0.22 ± 0.01 (0.24)	1.47 ± 0.10 (1.62)
Perovskite/ NS-2	17.38 ± 0.76 (16.07)	0.94 ± 0.09 (0.88)	0.44 ± 0.03 (0.46)	6.96 ± 0.64 (6.43)

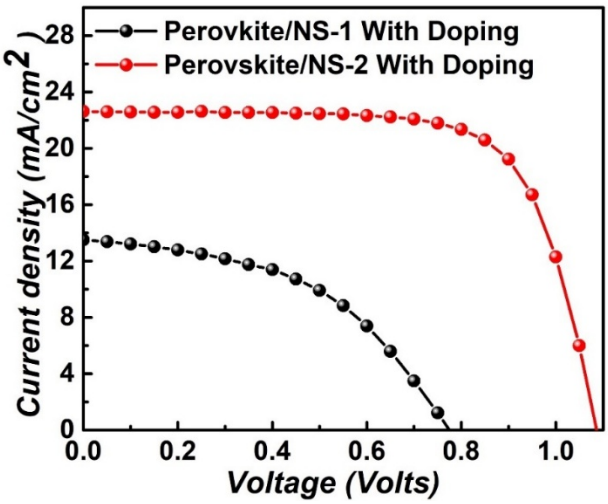


Figure S14: *J-V* characteristic for doped NS-1 and NS-2 as HTMs in PSCs, showing the comparison of photovoltaic performance parameters.

Table S14: Summary of photovoltaic parameters for HTMs NS-1 and NS-2 (doped) for five devices (best values in brackets).

Device	Jsc (mA cm^{-2})	Voc (V)	FF	PCE (%)
Perovskite/NS-1	12.75 ± 0.71 (13.51)	0.75 ± 0.05 (0.76)	0.43 ± 0.04 (0.47)	4.19 ± 0.79 (4.96)
Perovskite/ NS-2	22.57 ± 0.08 (22.63)	1.09 ± 0.01 (1.09)	0.71 ± 0.01 (0.71)	17.30 ± 0.17 (17.50)

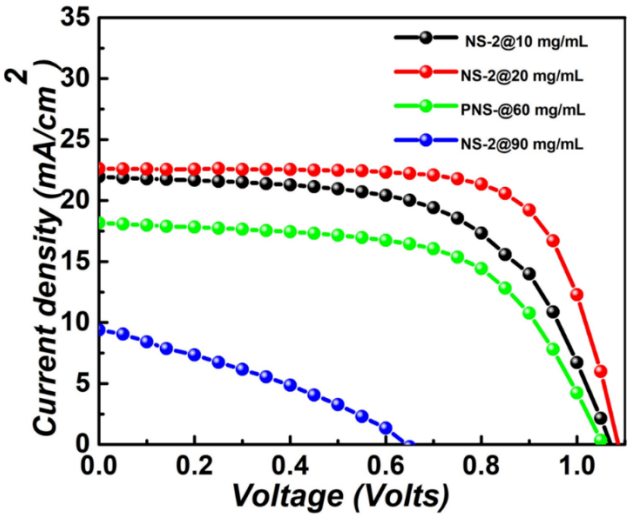


Figure S15: *J-V* curves of perovskite solar cells with different NS-2 HTM concentrations (10, 20, 60, and 90 mg/ml in CB) under standard AM 1.5G illumination, showing the impact of HTM concentration on device performance.

Table S15: Photovoltaic parameters of perovskite solar cells with varying NS-2 HTM concentrations (10, 20, 60, and 90 mg/ml in CB). Values are averaged over five devices (best values in brackets).

NS-2 concentration in the device	**Jsc (mA cm-2)**	**Voc (V)**	**FF**	**PCE (%)**
10 mg	21.68±0.18 (21.96)	1.07±0.01 (1.07)	0.57±0.02 (0.59)	13.09±0.65 (13.92)
20 mg	22.57 ± 0.08 (22.63)	1.09 ± 0.01 (1.09)	0.71 ± 0.01 (0.71)	17.30 ± 0.17 (17.50)
60 mg	18.13 ± 0.03 (18.16)	1.06 ± 0.01 (1.06)	0.55 ± 0.04 (0.60)	10.59 ± 0.89 (11.53)
90 mg	9.01 ± 0.56 (9.42)	0.40 ± 0.28 (0.64)	0.33 ± 0.01 (0.35)	1.22 ± 0.86 (1.94)

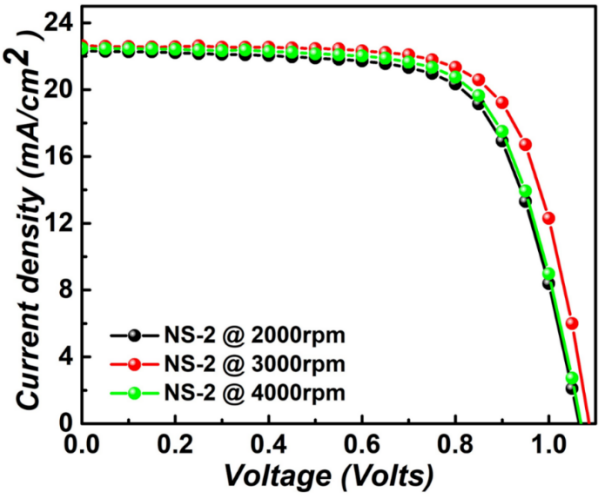


Figure S16: *J-V* characteristic of NS-2 device at different revolutions per minute (rpm), showing the effect of spin-coating speed on the photovoltaic performance parameters.

Table S16: Average photovoltaic performance of five devices using NS-2 HTM at various spin-coating rates (best values in brackets).

Device	Jsc (mA cm^{-2})	Voc (V)	FF	PCE (%)
Perovskite/NS-2 2000 rpm	22.22 ± 0.10 (22.31)	1.07 ± 0.10 (1.07)	0.67 ± 0.01 (0.68)	15.86 ± 0.33 (16.27)
Perovskite/ NS-2 3000 rpm	22.57 ± 0.08 (22.63)	1.09 ±0.01 (1.09)	0.71 ± 0.01 (0.71)	17.30 ± 0.17 (17.50)
Perovskite/ NS-2 4000 rpm	22.43 ± 0.04 (22.47)	1.07 ± 0.01 (1.07)	0.69 ± 0.01 (0.69)	16.60 ± 0.09 (16.70)

14. Statistical Distribution Analysis (Histogram)

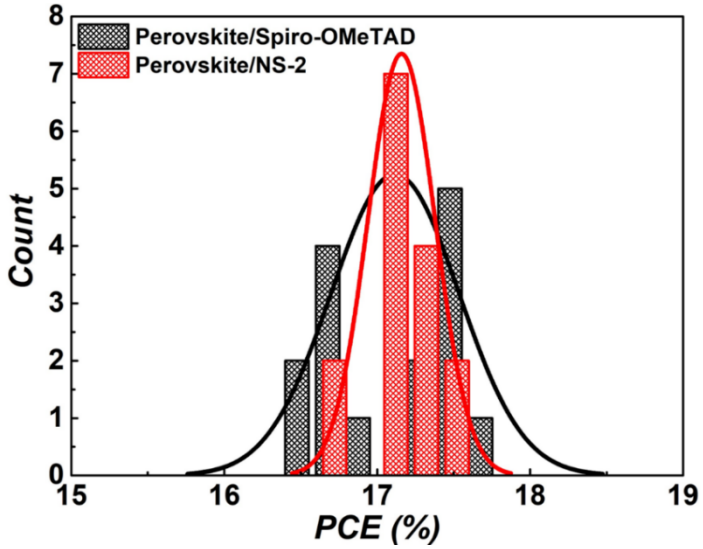


Figure S17: Histogram showing the distribution of power conversion efficiencies (PCE) for devices with Spiro-OMeTAD and NS-2 as HTMs, highlighting the performance variation and reproducibility of the devices.

15. Evaluation of Hysteresis Index

Table S17: Hysteresis index calculated from *J-V* curves of Spiro-OMeTAD and NS-2 devices, illustrating the difference in hysteresis behaviour and charge extraction efficiency between the two HTMs.

Device	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	PCE (%)	HI (%)
Perovskite/Spiro-OMeTAD Forward	23.00	1.08	0.70	17.57	
Perovskite/Spiro-OMeTAD Reverse	23.69	1.08	0.69	17.69	0.68
Perovskite/NS-2 Forward	22.63	1.08	0.71	17.47	
Perovskite/NS-2 Reverse	22.63	1.09	0.71	17.50	0.17

16. Determination of Series and Shunt Resistances

Table S18: summarizes the average series and shunt resistance for 15 best devices fabricated with both NS-2 and Spiro-OMeTAD; the performance parameters for the champion device are shown in parentheses.

Perovskite with HTM	R_s (Ω)	R_{sh} (Ω)
Spiro-OMeTAD	66.17 ± 8.69 (93.93)	10708.55 ± 2521.60 (18469.35)
NS-2	62.07 ± 4.50 (77.79)	11850.54 ± 2804.13 (18537.33)

17. Electrochemical Impedance Spectroscopy (EIS) Analysis

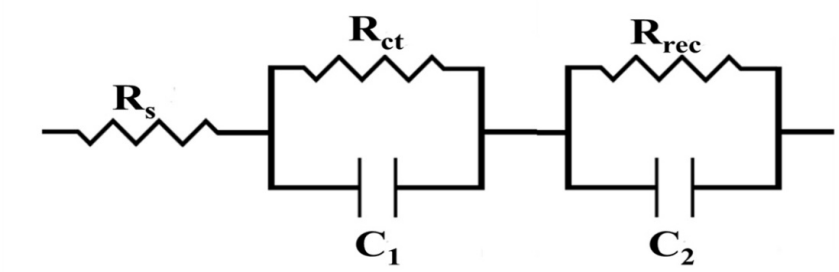


Figure S18: Equivalent circuit model for the Nyquist plot in electrochemical impedance spectroscopy (EIS) analysis, illustrating the series resistance (R_s), charge transfer resistance (R_{ct}), recombination resistance (R_{rec}), and capacitance elements corresponding to the perovskite solar cell device.

Table S19: Impedance spectral characteristics derived from EIS measurements of Spiro-OMeTAD and NS-2-based PSCs.

Devices	Rs (Ω)	R_{ct} (Ω)	R_{rec} (Ω)	C_1 (F)	C_2 (F)
Perovskite/Spiro-OMeTAD	150.7	5 429	18 775	13.43E-9	7.481E-9
Perovskite/NS-2	123.5	65.86	21 050	536 .2E-9	5.012E-9

18. Contact Angle Characterization of Films

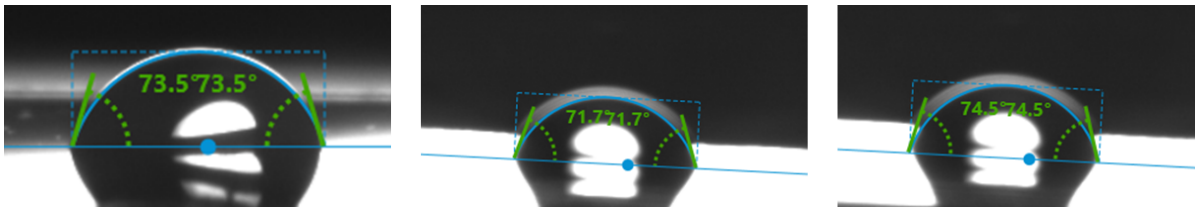


Figure S19: Contact angle values measured at three different point for perovskite/Spiro-OMeTAD.

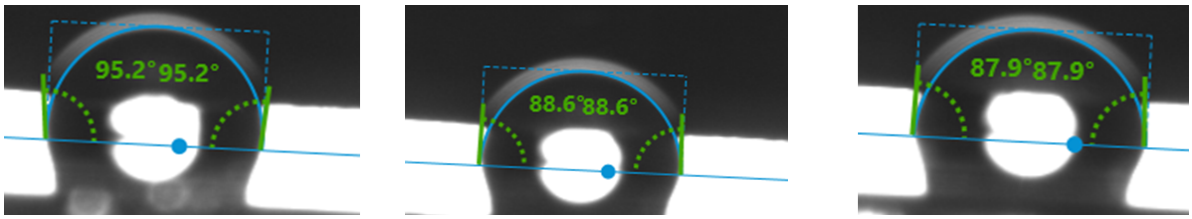


Figure S20: Contact angle values measured at three different points for perovskite/NS-2.

Table S20: Summarized contact angle values of perovskite films using Spiro-OMeTAD and NS-2 as HTMs, obtained from three different positions on each film.

Sample	**Place 1 (º)**	**Place 2 (º)**	**Place 3 (º)**	**Average ± STD (º)**
Perovskite/Spiro-OMeTAD	73.5	71.7	74.5	73.2 ± 1.4
Perovskite/NS-2	95.2	88.6	87.9	90.6 ± 4.0

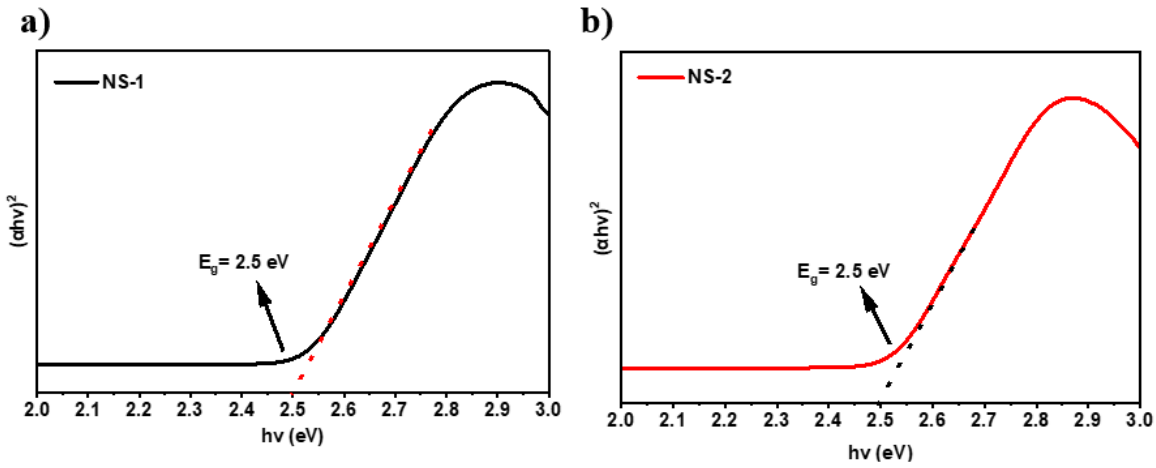


Figure S21: The band gap of HTMs measured by UV-vis absorption spectra of HTMs in thin film.

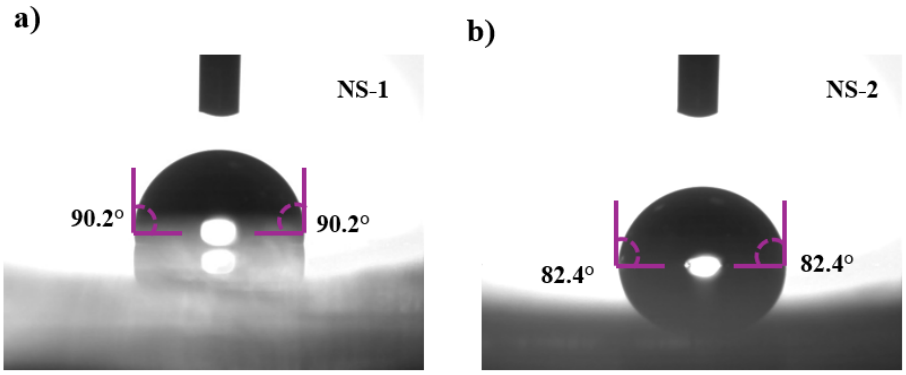


Figure S22: Water contact angle of water droplets on films coated with HTMs.

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Cartesian Coordinates (in Å) and thermal free energy (*E*, in Hartree)

Geometries optimized at the cam-B3LYP/6-31g (d,p) level of theory

NS-1

$E(S_0)$ = -3518.839941

6	-1.380672000	0.006081000	-0.758275000
6	-0.394977000	0.923420000	-1.118693000
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6	-12.707548000	-2.281305000	-0.525753000
6	-11.091965000	-2.179941000	-2.279975000
6	-13.424147000	-3.239340000	-1.229076000
1	-13.073622000	-1.949326000	0.435739000

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6	-12.960680000	-3.681044000	-2.459278000
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8	-13.778446000	3.597318000	1.573607000
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8	2.027292000	-1.762676000	0.798269000
6	-1.727792000	3.275749000	0.049547000
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1	-1.144168000	3.425879000	-0.861274000
6	-3.049227000	3.996684000	-0.060293000
1	-3.617412000	3.613745000	-0.914792000
1	-3.643275000	3.829919000	0.844744000
6	-3.917149000	6.161649000	-0.344672000
1	-4.514547000	5.849915000	-1.208491000
1	-4.543627000	6.070348000	0.549459000
6	-3.474151000	7.593477000	-0.516344000
1	-2.871584000	7.902624000	0.345933000
1	-2.848849000	7.685172000	-1.412212000
8	-2.761895000	5.363829000	-0.225338000

8	-4.627970000	8.389540000	-0.629630000
6	-4.331860000	9.754970000	-0.793605000
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6	1.733883000	-3.128815000	1.025140000
1	1.148627000	-3.249065000	1.939510000
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6	3.056059000	-3.843111000	1.165118000
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6	3.928503000	-5.984280000	1.580699000
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6	3.489673000	-7.400666000	1.858345000
1	2.882201000	-7.773200000	1.025113000
1	2.870500000	-7.427981000	2.762770000
8	4.646171000	-8.184030000	2.022027000
6	4.354577000	-9.533503000	2.291669000
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1	5.300273000	-10.059781000	2.403719000
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