Synthesis of SOT-OH and its application as a building block for the synthesis of new dimeric and trimeric Spiro-OMeTAD Materials

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Supplementary Information

1. Experimental details

General experimental

All reagents and starting materials were obtained from commercial sources and used as received. Dry solvents were purified using a Pure Solv 500 MD™ solvent purification system or purchased from Sigma Aldrich®. All reactions were undertaken under an inert atmosphere unless otherwise stated. Flash column chromatography was carried out using 60Ä silica gel (Fluorochem®). Merck silica gel (60Ä) covered aluminium plates F254 were used for thin layer chromatography. ^{1}H and ^{13}C NMR spectra were obtained with either a Bruker AVIII 400 MHz or a Bruker AVIII 500 MHz spectrometer with chemical shift values in ppm relative to residual solvent peaks: 7.26 (^{1}H) and 77.16 (^{13}C) for chloroform, 7.16 (^{1}H) and 128.06 (^{13}C) for benzene, and 3.31 (^{1}H) and 49.00 (^{13}C) for methanol. Coupling constants, J, are reported in Hz and the following abbreviations are used to label the multiplicities: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet and br, broad. Mass spectrometry data were obtained using a JEOL JMS-700 spectrometer for EI, Bruker MicroTOF-Q for ESI and MS-700 MStation Mass Spectrometer for FAB at the University of Glasgow, or a 12T SolariX 2XR FT-ICR MS for ESI at the University of Edinburgh. Infrared spectra were obtained neat using a Thermo Scientific Nicolet iS5 FTIR spectrometer.

UV-vis spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Optical band gaps (Eg_{opt}) were estimated using the onset of the longest wavelength absorption (λ_{onset}) using Eg_{opt} (eV) = (1240/ λ_{onset}). Fluorescence measurements were carried out using a Shimadzu RF-5301PC spectrofluorimeter.

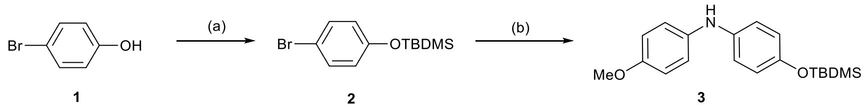
Electrochemistry was performed using a CH Instrument Electrochemical Workstation (CHI 440a), Austin, TX, USA. Ferrocene was used as an internal standard, with the ferrocenium/ferrocene (Fc^{+}/Fc) redox couple adjusted to 0.0 V. The solutions were prepared using anhydrous dichloromethane containing 5×10^{-4} M concentration of sample and electrochemical grade tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. The solutions were purged with N_2 gas for 3 minutes prior to recording the electrochemical data.

TGA and DSC were performed using a NETZSCH TG 209 F3 Tarsus® and a NETZSCH-Gerätebau gmbh DSC 214 Polyma, respectively. All the experiments were carried out under N_2 and at a rate of 10 °C/min (at -10 °C/min for cooling cycles).

Atomic force microscopy (AFM) experiments were carried out using a Bruker Innova® AFM in tapping mode. The scans area of the images is $10 \times 10\ \mu m^2$, made up of 512 lines with 512 points per line. The scans were carried out at a scan rate of 1.0 Hz. Image analysis was performed using Bruker NanoScope Analysis 1.5 program. Inherent tilt in the scan was corrected using the default bow remove process.

For the device fabrication, all the Pb based dry precursors including MABr and CsI were purchased from TCI chemicals. FAI was purchased from Greatcell Solar. Sublimed quality **Spiro-OMeTAD**, LiTFSI and tBP were purchased from Merck.

I. Synthesis of the protected side-arm **3**.



*Scheme S1. Synthesis of compound **3**. (a) TBDMSCl, imidazole, DMF, 4 h. (b) p-Anisidine, NaO^tBu, $Pd_2(dba)_3$, XPhos, toluene, 90 °C, Ar, 16 h.*

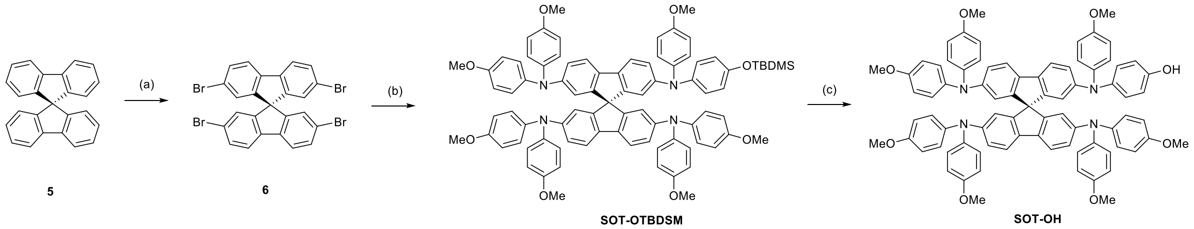
(4-Bromophenoxy)(*tert*-butyl)dimethylsilane **2**.[1]

4-Bromophenol **1** (5.08 g, 29.4 mmol) was dissolved in DMF (40 mL) and cooled to 0 °C. Imidazole (3.39 g, 49.9 mmol) was added, followed by *tert*-butyldimethylsilyl chloride (6.64 g, 44.1 mmol). The mixture was allowed to warm to room temperature and stirred for 4 h. Then, it was cooled to 0 °C and a saturated aqueous solution of NH_4Cl (40 mL) was slowly added. The mixture was extracted with Et_2O (3 × 50 mL), and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash column chromatography (SiO_2, PE), affording **2** (8.43 g, >99%) as a colourless oil. R_f = 0.32 (100% PE). δ_H (400 MHz, $CDCl_3$) 0.18 (6H, s), 0.97 (9H, s), 6.71 (2H, d, *J* 8.9), 7.32 (2H, d, *J* 8.9). δ_C (100 MHz, $CDCl_3$) −4.5, 18.2, 25.6, 113.6, 121.9, 132.3, 154.9. *m/z* (EI) 288 (M^+, 40%), 231 (100), 229 (97), 150 (22), 135 (19).

4-((*tert*-Butyldimethylsilyl)oxy)-*N*-(4-methoxyphenyl)aniline **3**.[2]

Compound **2** (3.03 g, 10.6 mmol) was dissolved in dry toluene (50 mL). *p*-Anisidine (1.43 g, 11.6 mmol), sodium *tert*-butoxide (1.42 g, 14.7 mmol), *tris*(dibenzylideneacetone) dipalladium(0) (0.386 g, 0.422 mmol) and XPhos (0.402 g, 0.845 mmol) were added sequentially. The mixture was degassed with Ar and heated to 90 °C for 16 h. The reaction was then cooled to room temperature, diluted with EtOAc (50 mL) and washed with water (3 × 100 mL). The organic extract was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash column chromatography (SiO_2, PE:Et_2O = 9:1), to produce **3** (3.03 g, 87%) as a brown solid. mp 66 – 68 °C (lit. 67 – 69 °C). R_f = 0.25 (PE:Et_2O = 9:1). δ_H (500 MHz, CD_3OD) 0.19 (6H, s), 1.01(9H, s), 3.76 (3H, s), 6.72 (2H, d, *J* 8.8), 6.82 (2H, d, *J* 9.0), 6.88 (2H, d, *J* 8.8), 6.97 (2H, d, *J* 9.0). δ_C (125 MHz, CD_3OD) −4.3, 19.0, 26.2, 56.0, 115.6, 119.5, 120.5, 121.5, 139.7, 140.8, 150.3, 155.4. *m/z* (ESI): calculated for $C_{19}H_{28}NO_2Si$ $[M + H]^+$ 330.1884; found 330.1871.

II. Synthesis of **SOT-OH** (Route B)



*Scheme S2. Synthesis of **SOT-OH** (Route B). (a) NaBr, H_2SO_4, 36% H_2O_2, DCE, 40 h. (b) **3**, 4,4′-dimethoxydiphenylamine **4**, $Pd_2(dba)_3$, XPhos, NaO^tBu, toluene, reflux, Ar, 19 h. (c) TBAF, THF, reflux, 3 h.*

2,2′,7,7′-Tetrabromo-9,9′-spirobifluorene ***6***.[3]

A solution of 10% H_2SO_4 (20 mL, 20.7 mmol) was added to a mixture of 9,9′-spirobifluorene **5** (1.00 g, 3.20 mmol) and NaBr (5.21 g, 50.6 mmol) in 1,2-dichloroethane (5 mL). To this, a solution of 36% H_2O_2 (1.78 mL, 20.7 mmol) was slowly added. The resulting mixture was stirred at room temperature for 40 h, then poured in ice-water (100 mL) and allowed to warm to room temperature while stirring. The organic fraction was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic extracts were washed with water (3 × 150 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2; PE: CH_2Cl_2 = 9:1), affording **6** (1.82 g, 90%), as a white solid. mp > 300 °C. R_f = 0.27 (PE: CH_2Cl_2 = 9:1). δ_H (400 MHz, $CDCl_3$) 6.83 (4H, d, *J* 1.8), 7.54 (4H, dd, *J* 8.2, 1.8), 7.68 (4H, d, *J* 8.2). *m/z* (EI) 636 (18), 634 (68), 632 (M^+, 100), 630 (66), 628 (17).

*N*7-4-((*tert*-Butyldimethylsilyl)oxy)phenyl-*N*2,*N*2,*N*2',*N*2',*N*7,*N*7',*N*7'-heptakis(4-methoxyphenyl)-9,9'-spirobi(fluorene)-2,2',7,7'-tetramine **SOT-OTBDMS**.

Compound **6** (0.547 g, 0.866 mmol), sodium *tert*-butoxide (0.349 g, 3.63 mmol), tris(dibenzylideneacetone)dipalladium(0) (31.7 mg, 34.6 μmol), XPhos (33.0 mg, 69.2 μmol), 4,4′-dimethoxydiphenylamine **4** (0.595 g, 2.60 mmol) and compound **3** (0.428 mg, 1.30 mmol) were dissolved in dry toluene (3 mL). The mixture was degassed with Ar for 30 minutes and then and left to stir at 110 °C for 19 h. The reaction was then cooled to room temperature and poured onto water (50 mL). The organic fraction was extracted with EtOAc (3 × 40 mL) and the combined organic extracts were washed with water (100 mL) and brine (100 mL) sequentially, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, PE:EtOAc = 7:3) to produce **SOT-OTBDMS** (0.366 g, 32%) as an off white solid. mp 143 – 145 °C. R_f = 0.32 (PE:EtOAc = 7:3). ν_{max}/cm^{-1} (neat) 2832 (O-C), 1603 (C=C), 1500 (C=C), 1462 (C-H), 1235 (O-C(Ar)), 1034 (O-C), 908 (Si-O), 822 (C=C), 779 (Si-O). δ_H (400 MHz, C_6D_6) 0.13 (6H, s), 1.00 (9H, s), 3.25 – 3.29 (21H, m), 6.69 – 6.76 (14H, m), 6.79 – 6.82 (2H, m), 6.96 – 7.08 (25H, m), 7.11 – 7.15 (2H, m), 7.18 (1H, s). δ_C (100 MHz, C_6D_6) -4.28, 18.45, 25.95, 54.95, 55.04, 66.50, 114.95, 115.12, 118.27, 118.35, 118.50, 120.60, 120.68, 120.90, 122.90, 122.96, 123.12, 125.42, 125.87, 126.07, 135.87, 135.92, 135.94, 141.80, 141.93, 142.02, 142.76, 148.13, 148.21, 148.25, 150.82, 150.88, 150.94, 151.40, 155.28, 155.97, 156.05. *m/z* (FAB): calculated for $C_{86}H_{80}N_4O_8Si$ $[M]^+$ 1324.5745; found 1324.5760.

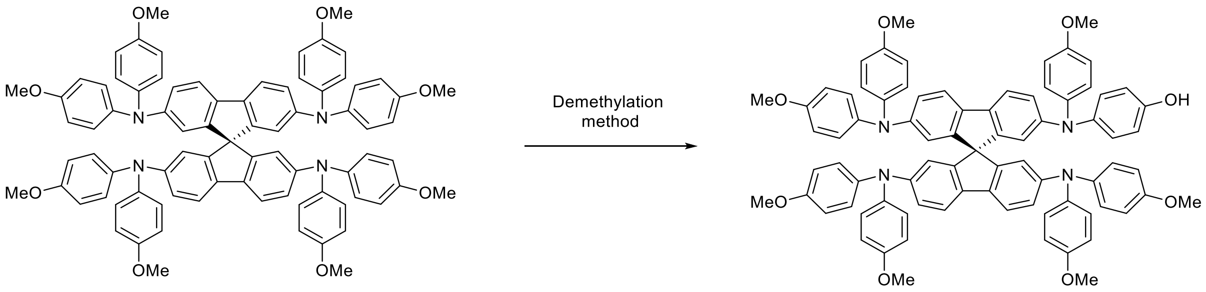
Spiro-OMeTAD (318 mg, 30%) was also isolated as a side product of the reaction. ν_{max}/cm^{-1} (neat) 2832 (O-C), 1603 (C=C), 1500 (C=C), 1462 (C-H), 1236 (O-C(Ar)), 1034 (O-C), 822 (C=C). δ_H (400 MHz, C_6D_6) 3.26 (24H, s), 6.71 – 6.77 (16H, m), 6.98 (4H, dd, *J* 8.3, 2.1), 7.01 – 7.05 (16H, m), 7.07 (4H, d, *J* 2.0), 7.14 (4H, s). δ_C (100 MHz, C_6D_6) 54.6, 66.2, 114.6, 118.0, 120.3, 122.6, 125.5, 135.6, 141.7, 147.9, 150.5, 155.6. *m/z* (EI) 1224 (M^+), 1247 ($[M + Na]^+$).

4-((4-Methoxyphenyl)((2,2',7'-tris(bis(4-methoxyphenyl)amino)-9,9'-spirobi(fluoren)-7-yl))amino)phenol **SOT-OH**.

SOT-OTBDMS (0.326 g, 0.246 mmol) was dissolved in dry THF (3 mL) and left to stir before a solution of 1.0 M tetra-*N*-butylammonium fluoride in THF (0.49 mL, 0.492 mmol) was added. The reaction mixture was left to stir at room temperature for 30 min, then it was concentrated in *vacuo*. The crude product was purified by flash column chromatography (SiO_2, PE:EtOAc = 1:1), to produce **SOT-OH** (295 mg, 99%) as an off white solid. mp 137 – 139 °C; R_f = 0.16

(PE:EtOAc = 3:2). ν_{max}/cm^{-1} (neat) 3390 (O-H), 2832 (O-C), 1603 (C=C), 1500 (C=C), 1462 (C-H), 1236 (O-C(Ar)), 1033 (O-C), 822 (C=C). δ_H (400 MHz, C_6D_6) 3.24 – 3.28 (21H, m), 6.71–6.76 (14H, m), 7.05 – 6.91 (22H, m), 7.07 (4H, d, *J* 1.8), 7.14 (4H, d, *J* 5.4). δ_C (100 MHz, C_6D_6) 54.93, 54.94, 66.50, 114.94, 118.36, 120.67, 123.01, 125.81, 125.84, 135.89, 142.01, 148.18, 150.90, 155.89, 155.91. *m/z* (FAB): calculated for $C_{80}H_{66}N_4O_8$ [M]$^+$ 1210.4881; found 1210.4915.

*III. Synthesis of **SOT-OH** via monodemethylation of **Spiro-OMeTAD** (Route A)*



Spiro-OMeTAD

SOT-OH

*Scheme S3. Synthesis of **SOT-OH** via demethylation of **Spiro-OMeTAD** (Route A). Conditions reported in Table S1.*

Table S1. Demethylation conditions attempted towards the synthesis of **SOT-OH**. For all the reactions, 50 mg of **Spiro-OMeTAD** were used as the starting material.

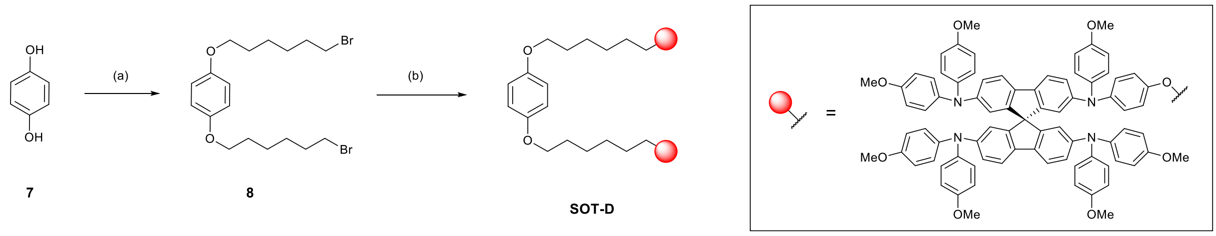
Entry	Conditions	Yield (SOT-OH)
1[4]	BBr_3 (1M, 0.5 eq.), CH_2Cl_2 (20 mL), N_2, 24 h	0%, no reaction
2	BBr_3 (1M, 1.0 eq.), CH_2Cl_2 (20 mL), N_2, 24 h	0%, no reaction
3	BBr_3 (1M, 1.5 eq.), CH_2Cl_2 (20 mL), N_2, 24 h	0%, no reaction
4	BBr_3 (1M, 2.0 eq.), CH_2Cl_2 (20 mL), N_2, 24 h	0%, no reaction
5	BBr_3 (1M, 10 eq.), CH_2Cl_2 (20 mL), N_2, 24 h	0%, over reaction
6[5]	NaI (1 eq.), 47% HBr (0.5 mL), 90 °C, air, 24 h	≈ 0%[a], no reaction
7[6]	NMP (0.4 ml), NaO^{t}Bu (2.5 eq.), $SH(CH_2)_2NEt_2\cdot HCl$ (1.2 eq.), 150 °C, N_2, 24 h	0%, no reaction
8[7]	Aliquat-336 (0.10 eq.), 47% HBr (2.0 eq.), 105 °C, N_2, 24 h	0%, decomposition
9[8]	DMI (0.5 mL), $NaN(SiMe_3)_2$ (1 M, 2 eq.), 185 °C, N_2, 12 h	21%

[a] Traces of **SOT-OH** found by TLC, but not isolated.

SOT-OH (entry 9).

Spiro-OMeTAD (50 mg, 40.8 µmol) was placed in a 5 mL microwave tube equipped with a magnetic stirrer. The system was sealed and evacuated through a septum. 1,3-Dimethyl-2-imidazolidinone (DMI, 0.5 mL) was added and the mixture was stirred for 10 min. A 2M solution of sodium *bis*(trimethylsilyl)amide ($NaN(SiMe_3)_2$) in THF (51.0 µL, 0.102 mmol) was added and the resulting mixture was stirred at 185 °C for 18 h. The reaction was then allowed to cool to room temperature, diluted with water (20 mL) and neutralised by slow addition of 10% aqueous HCl, until pH = 7. The organic fraction was extracted with EtOAc (3 × 30 mL) and the combined organic extracts were washed with water (2 × 50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, PE:EtOAc = 1:1), affording **SOT-OH** (10 mg, 21%).

*IV. Synthesis of **SOT-D***



*Scheme S4. Synthesis of **SOT-D**. (a) 1,6-Dibromohexane, 60% NaH, 18-crown-6, DMF, 20 h. (b) **SOT-OH**, 60% NaH, DMF, 60 °C, 2 h.*

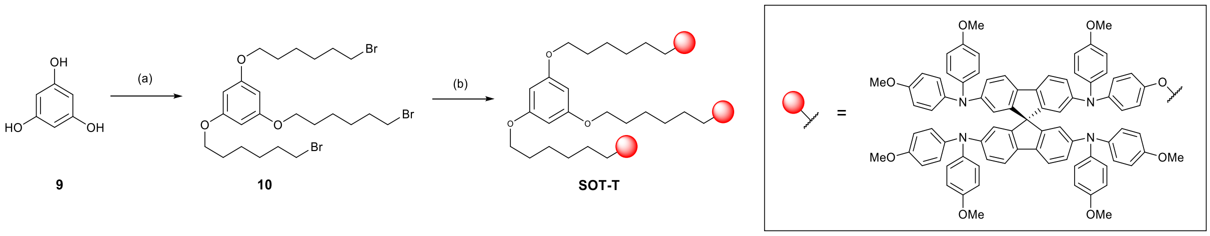
1,4-*bis*-(6-Bromohexyloxy)benzene **8**[9]

Hydroquinone **7** (0.159 g, 1.45 mmol) was dissolved in dry DMF (10 mL) before a 60% NaH dispersion in mineral oil (0.145 g, 3.62 mmol) and 18-crown-6 (0.957 g, 3.62 mmol) were added. The mixture was left to stir at room temperature for 30 min before 1,6-dibromohexane (0.668 mL, 4.34 mmol) was added dropwise. The mixture was left to stir at room temperature for a further 20 h before being quenched with a saturated aqueous solution of NH_4Cl (70 mL). The organic fraction was extracted with Et_2O (3 × 50 mL) and the combined extracts were washed with water (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, PE:EtOAc = 4:1) to produce **8** (142 mg, 22%) as a white solid. R_f = 0.41 (PE:EtOAc = 9:1). δ_H (400 MHz, $CDCl_3$) 1.46–1.54 (8H, m), 1.73–1.81 (4H, m), 1.85 – 1.93 (4H, m), 3.42 (4H, t, *J* 6.4), 3.90 (4H, t, *J* 6.4), 6.81 (4H, s). δ_C (100 MHz, $CDCl_3$) 25.5, 28.1, 29.4, 32.8, 34.0, 68.5, 115.5, 153.3. *m/z* (ESI): calculated for $C_{18}H_{28}Br_2NaO_2$ $[M+Na]^+$ 459.0336; found 459.0307.

N2,N2,N2',N7,N7,N7',N7'-Heptakis(4-methoxyphenyl)-*N2'*-(4-((6-(4-((6-(4-((4-methoxyphenyl)((2',7,7'-*tris*(*bis*(4-methoxyphenyl)amino)-9,9'-spirobi(fluoren)-2-yl))amino)phenoxy)hexyl)oxy)phenoxy)hexyl)oxy)phenyl)-9,9'-spirobi(fluorene)-2,2',7,7'-tetramine **SOT-D**

SOT-OH (0.101 g, 83.4 µmol) was dissolved in dry DMF (5 mL). A 60% dispersion of NaH in mineral oil (16 mg, 0.397 mmol) was added and the mixture was heated to 60 °C for 1.5 h. **8** (17.3 mg, 39.7 µmol) was then added and the temperature maintained at 60 °C for 2 h. The solution was allowed to cool to room temperature and quenched with a saturated aqueous solution of NH_4Cl (2 mL), diluted with EtOAc (30 mL) and washed with water (3 × 15 mL). The organic fraction was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash column chromatography (SiO_2, PE:EtOAc = 3:2) to produce **SOT-D** (54.5 g, 51%) as an off white solid. M.P. > 300 °C. $R_f = 0.12$ (PE:EtOAc = 3:2). ν_{max}/cm^{-1} (neat) 2920 (C-H), 2832 (O-C), 1603 (C=C), 1500 (C=C), 1462 (C-H), 1234 (O-C(Ar)), 1034 (O-C), 822 (C=C). δ_H (400 MHz, C_6D_6) 1.29 – 1.33 (8H, m), 1.54 – 1.65 (8H, m), 3.25 – 3.27 (42H, m), 3.58 (4H, t, *J* 6.3), 3.67 (4H, t, *J* 6.3), 6.74 (28H, d, *J* 9.0), 6.82 (4H, d, *J* 9.0), 6.88 (4H, s), 7.10 – 6.97 (48H, m), 7.14 (4H, d, *J* 2.1). δ_C (100 MHz, C_6D_6) 26.23, 29.67, 29.75, 30.22, 54.93, 60.35, 66.5, 67.96, 68.36, 114.93, 115.49, 115.73, 118.29, 118.34, 118.36, 120.69, 122.98, 123.00, 123.02, 125.83, 125.92, 135.89, 142.01, 148.18, 150.89, 153.92, 155.49, 155.92. *m/z* (ESI) calculated for $C_{178}H_{158}N_8O_{18}$ $[M]^+$ 2697.1754; found 2697.1862.

*V. Synthesis of **SOT-T***



*Scheme S5. Synthesis of **SOT-T**. (a) 1,6-Dibromohexane, 60% NaH, 18-crown-6, DMF, 91 h. (b) **SOT-OH**, 60% NaH, DMF, 60 °C, 2 h.*

1,3,5-*tris*((6-Bromohexyl)oxy)benzene **10**[10]

Phloroglucinol **9** (0.200 g, 1.59 mmol) was dissolved in dry DMF (10 mL) before a 60% NaH dispersion in mineral oil (0.159 g, 3.97 mmol) and 18-crown-6 (1.05 g, 3.97 mmol) were added. The mixture was left to stir at room temperature for 30 min before 1,6-dibromohexane (1.75 mL, 7.16 mmol) was added dropwise. The mixture was left to stir at room temperature for a further 90 h before being quenched with a saturated aqueous solution of NH_4Cl (70 mL). The organic fraction was extracted with Et_2O (3 × 50 mL) and the combined extracts were washed with water (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (SiO_2, PE:Et_2O = 19:1) to produce **10** (0.254 g, 27%) as a colourless oil. $R_f = 0.56$ (PE:Et_2O = 19:1). δ_H (400 MHz, $CDCl_3$) 1.44 –1.53 (12H, m), 1.73 – 1.83 (6H, m), 1.85 – 1.94 (6H, m), 3.42 (6H, t, *J* 6.3), 3.91 (6H, t, *J* 6.3), 6.05 (3H, s). δ_C (100 MHz, $CDCl_3$) 25.3, 27.9, 29.1, 32.7, 33.8, 67.7, 93.8, 160.9. *m/z* (ESI) calculated for $C_{24}H_{39}Br_3NaO_3$ $[M+Na]^+$ 637.0329; found 637.0357.

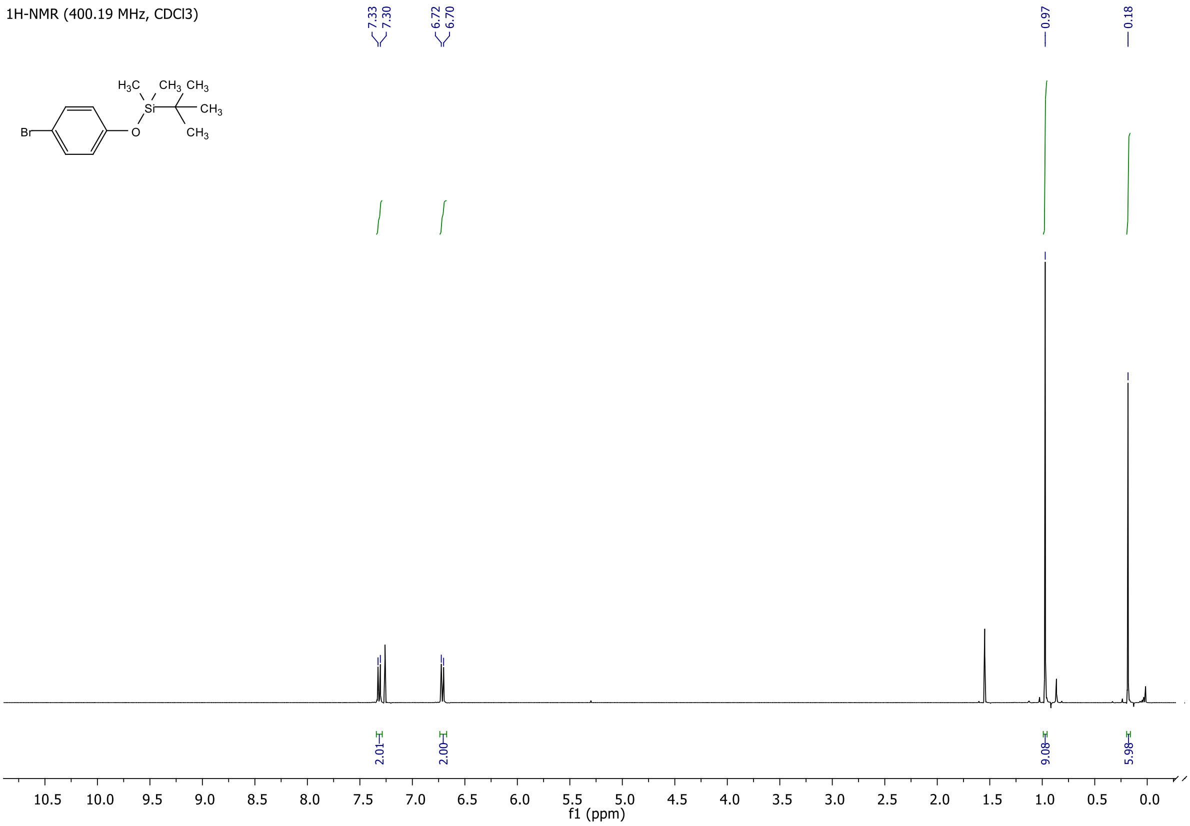
N2-(4-((6-(3,5-*bis*((6-(4-((4-Methoxyphenyl)((2',7,7'-*tris*(*bis*(4-methoxyphenyl)amino)-9,9'-spirobi(fluoren)-2-yl))amino)phenoxy)hexyl)oxy)phenoxy)hexyl)oxy)phenyl)-*N2,N2',N2',N7,N7,N7',N7'*-heptakis(4-methoxyphenyl)-9,9'-spirobi(fluorene)-2,2',7,7'-tetramine **SOT-T**

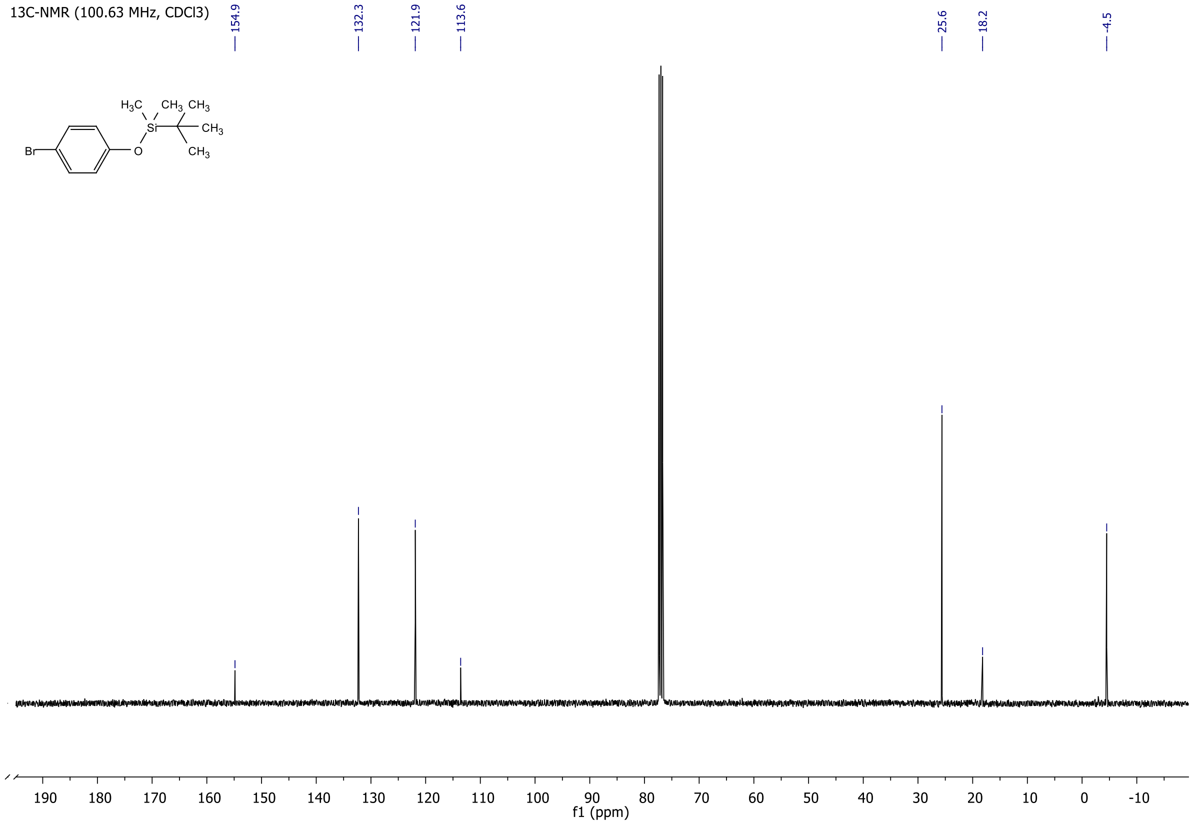
SOT-OH (0.103 g, 85.3 μmol) was dissolved in dry DMF (5 mL). A 60% dispersion of NaH in mineral oil (17 mg, 0.413 mmol) was added and the mixture was heated to 60 °C for 1.5 h. **10** (16.9 mg, 27.5 μmol) was then added and the temperature maintained at 60 °C for 2 h. The solution was cooled to room temperature and quenched with a saturated aqueous solution of NH_4Cl (2 mL), diluted with EtOAc (30 mL) and washed with water (3 × 15 mL). The organic fraction was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified via flash column chromatography (SiO_2, PE:toluene:EtOAc = 5:1:4) to produce **SOT-T**

(62.9 mg, 57%) as an off white solid. M.p. > 300 °C. R_f = 0.17 (PE:toluene:EtOAc = 5:1:4). ν_{max}/cm^{-1} (neat) 2926 (C-H), 2832 (O-C), 1603 (C=C), 1500 (C=C), 1462 (C-H), 1234 (O-C(Ar)), 1034 (O-C), 822 (C=C). δ_H (400 MHz, C_6D_6) 1.26 – 1.32 (12H, m), 1.53 – 1.63 (12H, m), 3.25 – 3.28 (63H, m), 3.58 (6H, t, *J* 6.3), 3.73 (6H, t, *J* 6.3), 6.41 (3H, s), 6.73 (42H, d, *J* 9.0), 6.81 (6H, d, *J* 9.0), 6.94 – 7.08 (78H, m), 7.13 (6H, d, *J* 1.8). δ_C (100 MHz, C_6D_6) 26.20, 26.24, 29.60, 29.67, 54.96, 54.97, 66.52, 67.94, 68.03, 94.56, 114.97, 115.54, 118.32, 120.68, 122.91, 122.96, 125.84, 125.92, 135.84, 135.89, 135.92, 141.94, 142.02, 148.20, 148.23, 150.89, 155.53, 155.96, 155.98, 161.86. *m/z* (ESI): calculated for $C_{264}H_{234}N_{12}O_{27}$ $[M]^+$ 4005.7366; found 4005.7197.

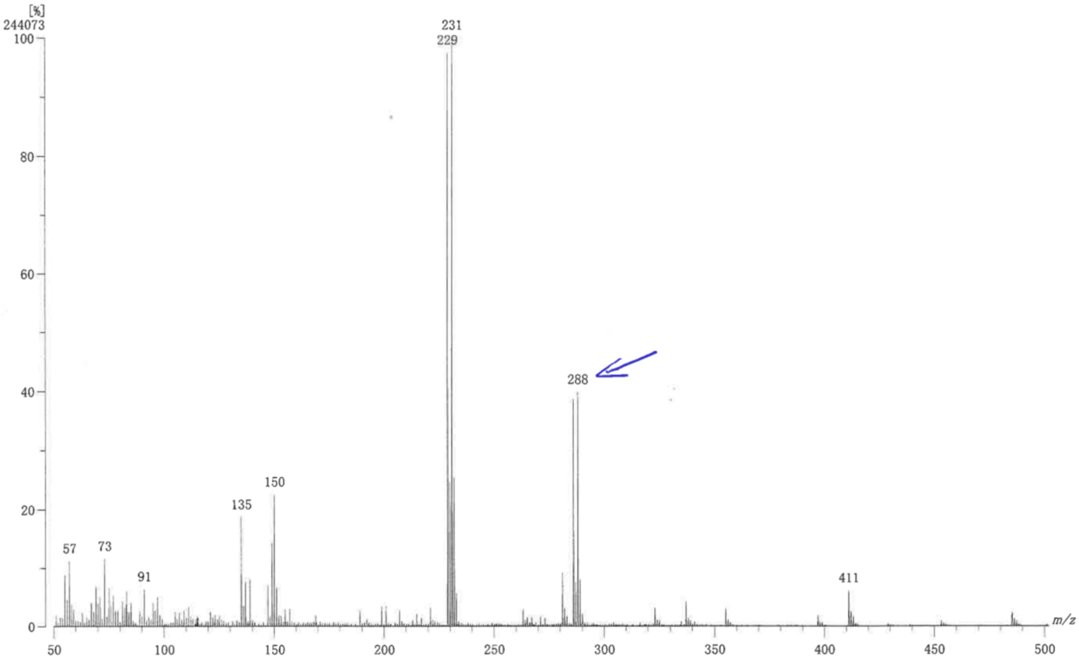
2. Spectroscopy data

Compound **2**


1H-NMR (400.19 MHz, CDCl3)

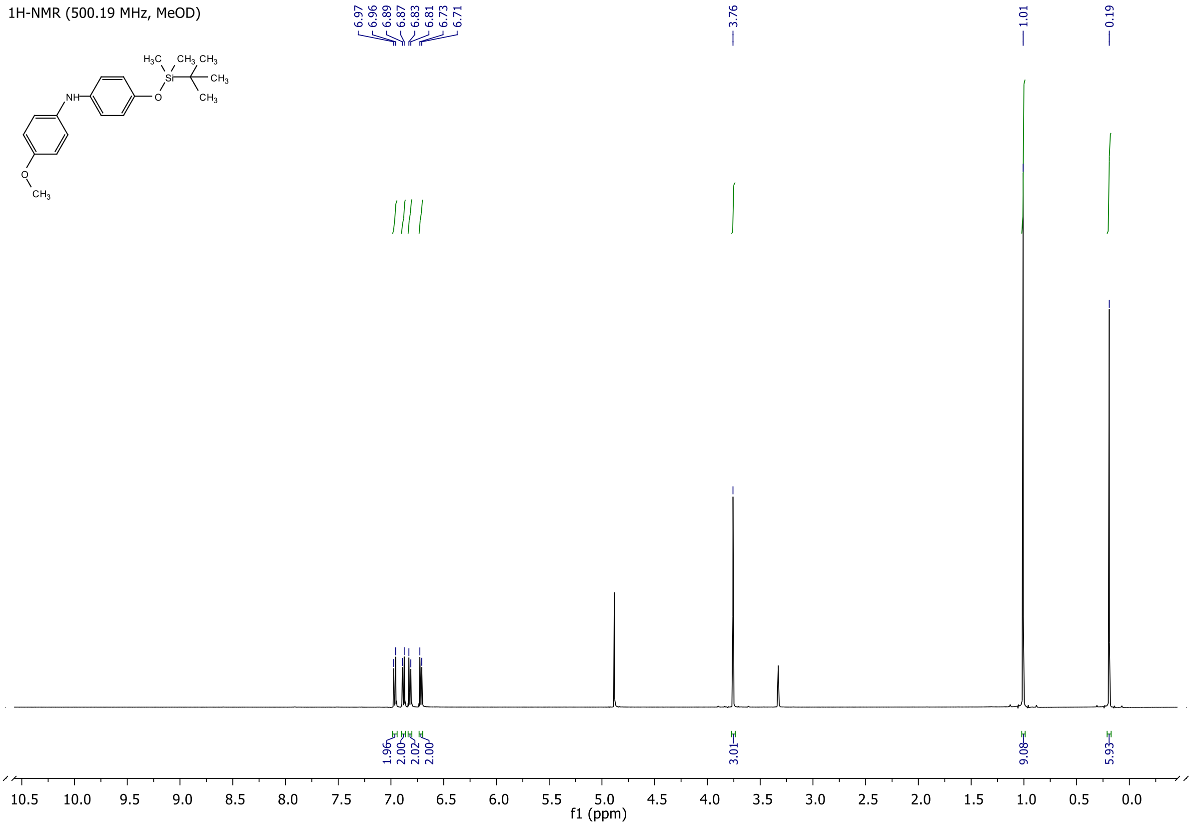

13C-NMR (100.63 MHz, CDCl3)

```
[ Mass Spectrum ]
Data : 70601 - Harkiss - AHH.121 - 001      Date : 25-Oct-2018 12:25
Instrument : EOL MStation JMS-700(2)
Sample : -
Note : -
Inlet : Direct      Ion Mode : EI+
Spectrum Type : Normal Ion  [MF-Linear]
RT : 0.15 min      Scan# : (2,5)      Temp : 3276.7 deg.C
BP : m/z 230.9896      Int. : 23.28 (244073)
Output m/z range : 50 to 502      Cut Level : 0.00 %
```

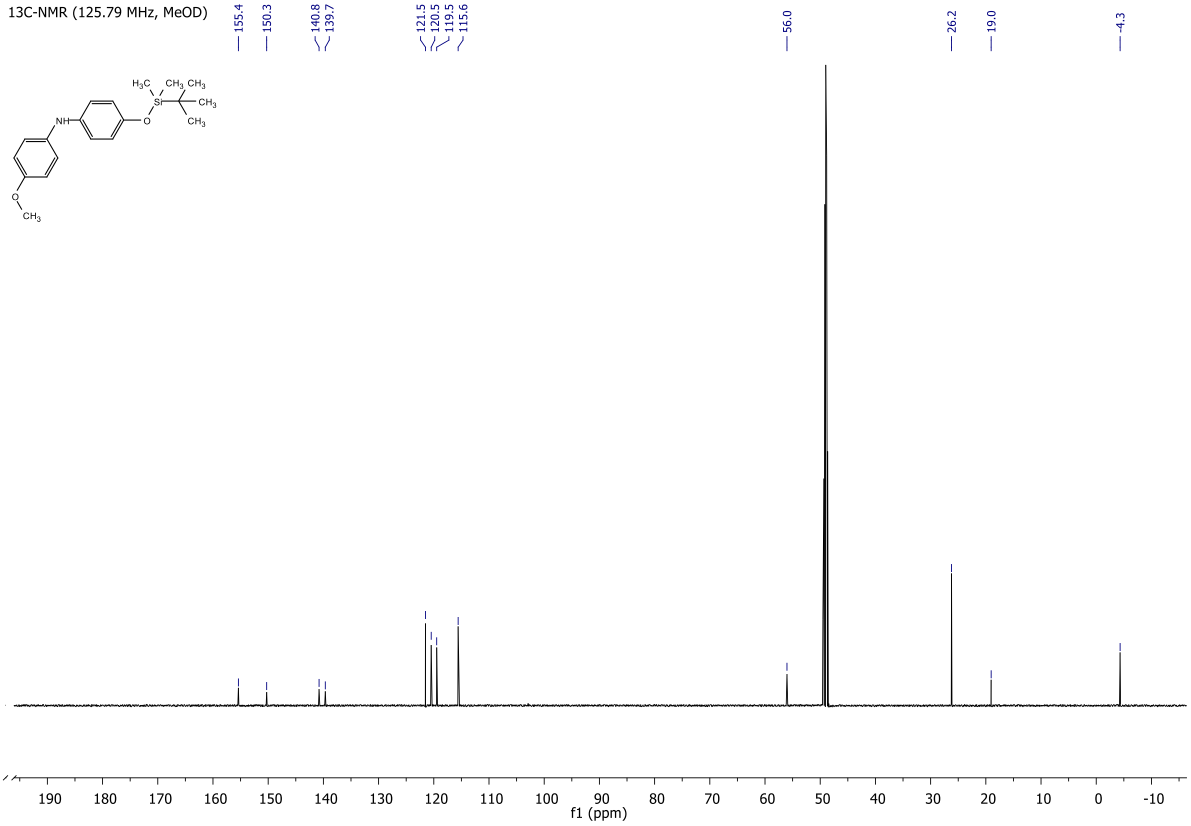


Compound **3**

1H-NMR (500.19 MHz, MeOD)

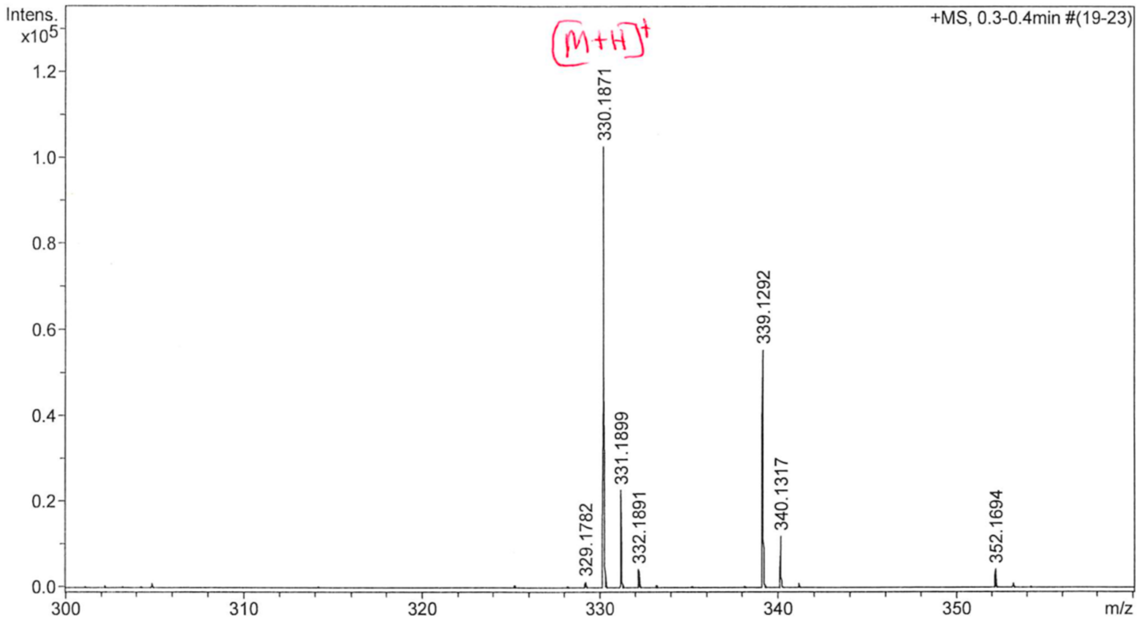


13C-NMR (125.79 MHz, MeOD)



Acquisition Parameter

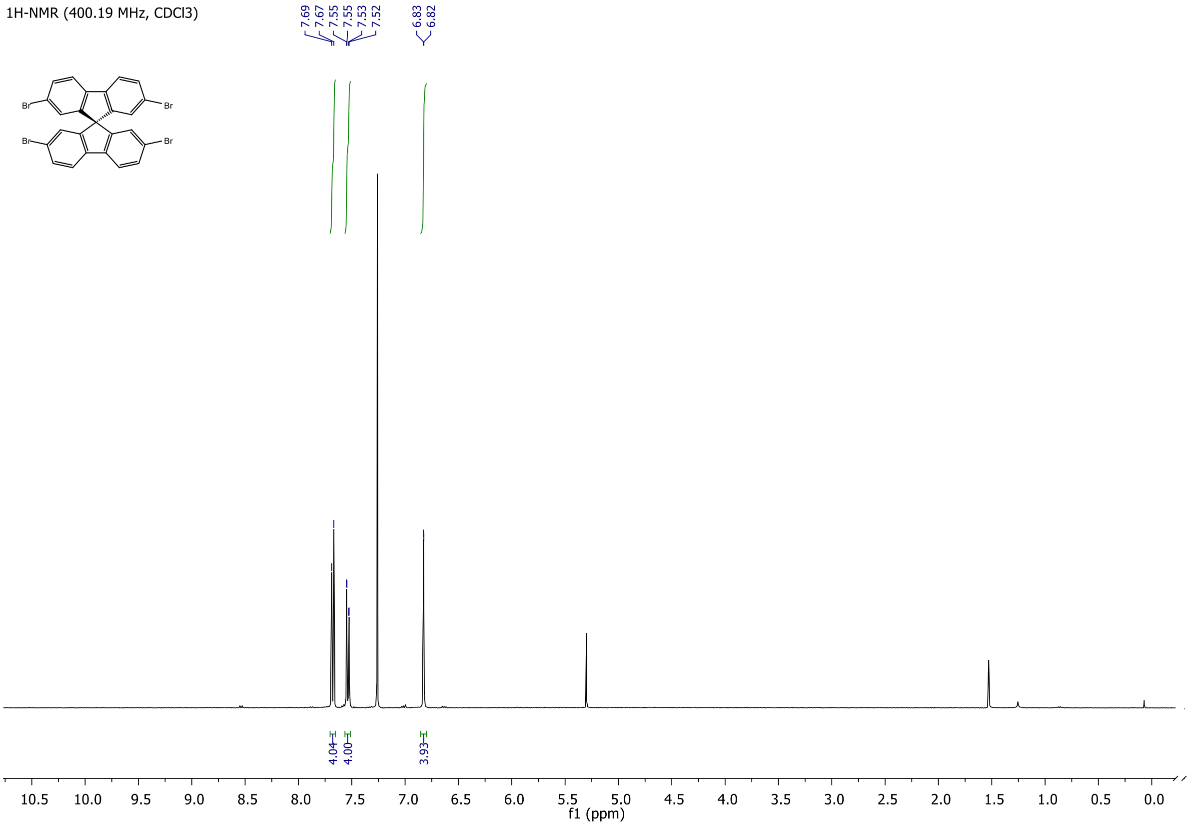
Source Type	ESI	Ion Polarity	Positive
Scan Begin	50 m/z		
Scan End	1100 m/z		



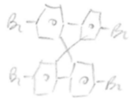
Formula	z	m/z	Meas. m/z	err [ppm]	err [mDa]
	1+		330.1871		
C 19 H 28 N O 2 Si		330.1884		3.8	1.2

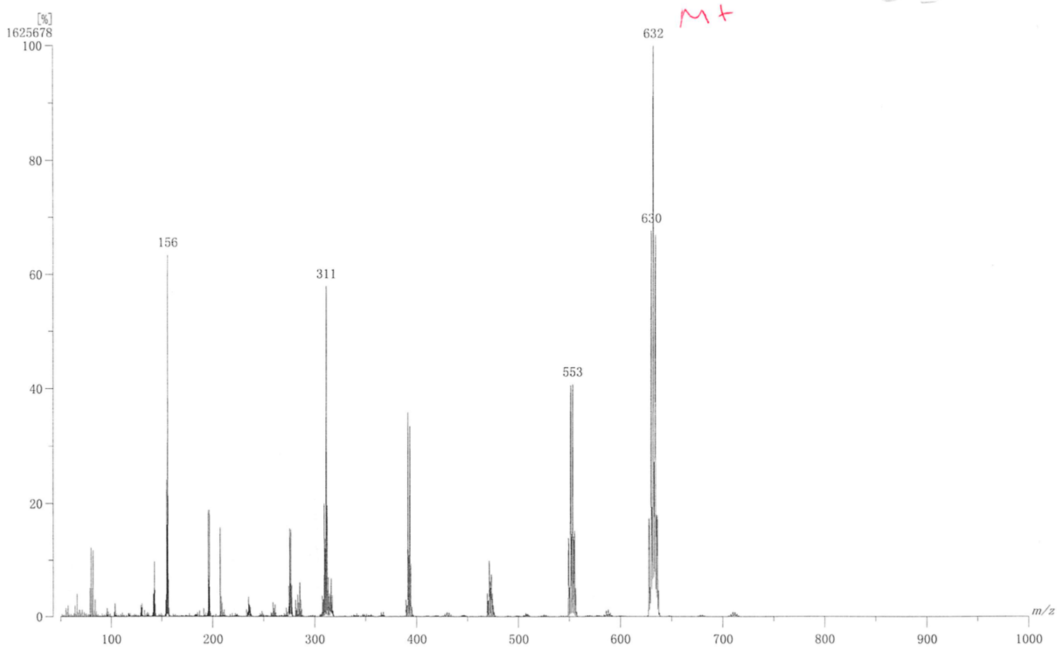
Compound **6**

1H-NMR (400.19 MHz, CDCl3)



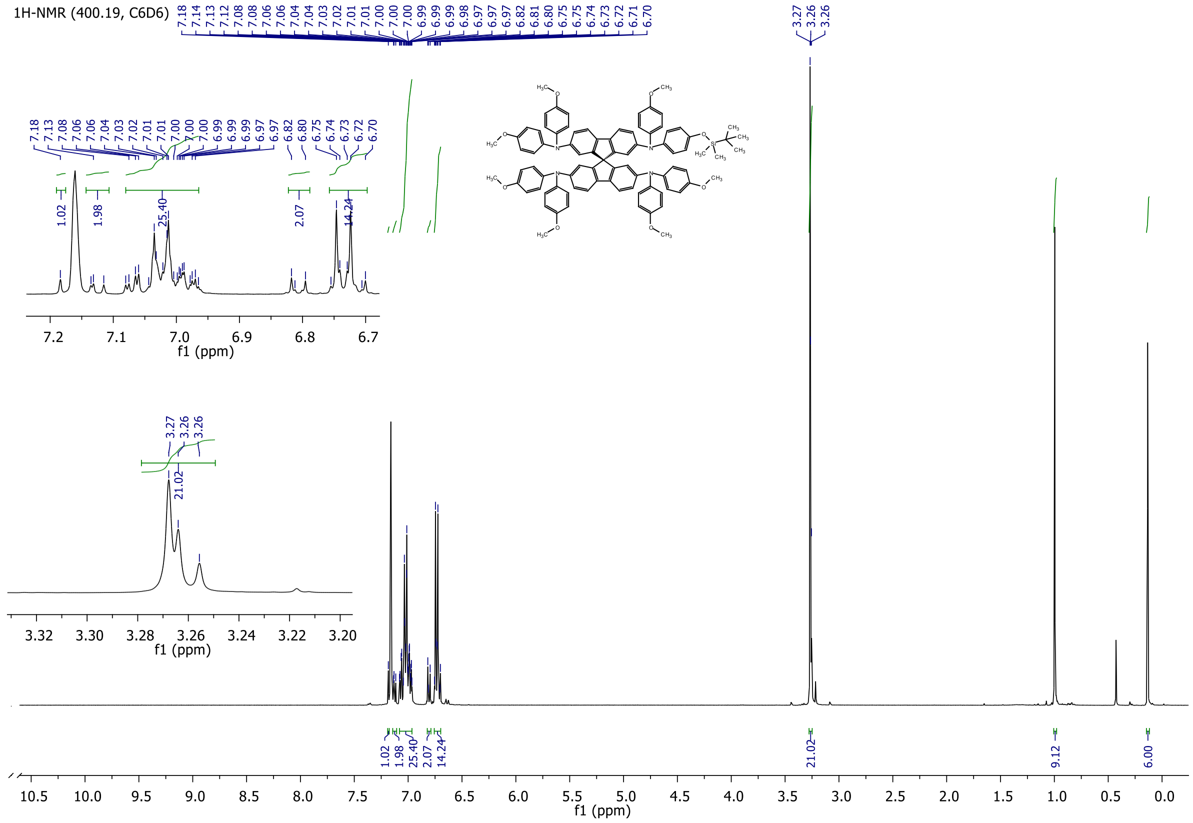
Instrument : JEOL MStation JMS-700(2)
Sample :
Note :
Inlet : Direct Ion Mode : EI+
Spectrum Type : Normal Ion [MF-Linear]
RT : 6.98 min Scan# : (53,61) Temp : 3276.7 deg.C
BP : m/z 632.1043 Int. : 155.04 (1625678)
Output m/z range : 50 to 1000 Cut Level : 0.00 %



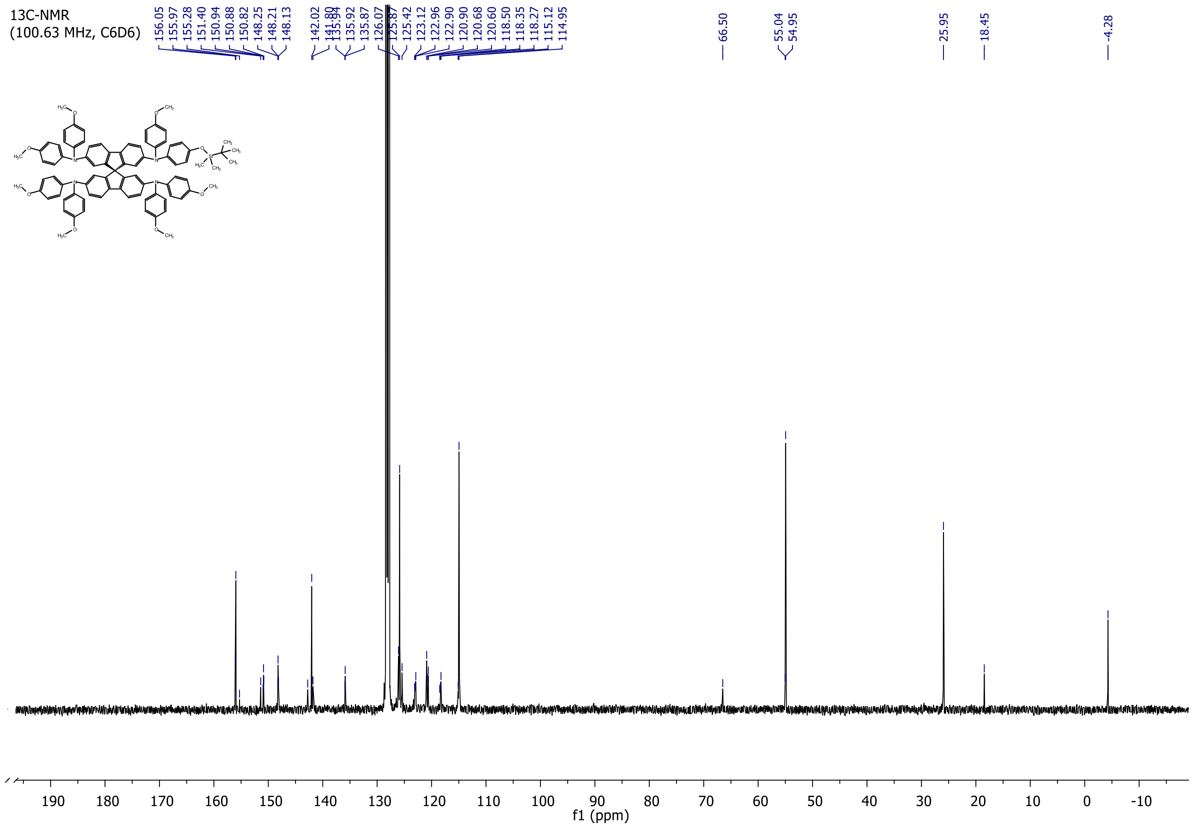


SOT-OTBDMS

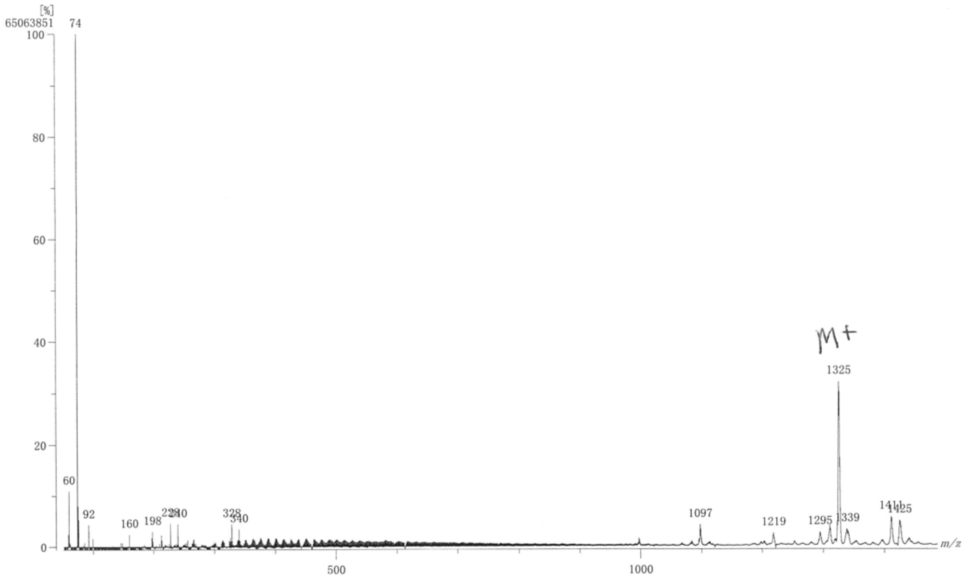
1H-NMR (400.19, C6D6)



13C-NMR
(100.63 MHz, C6D6)

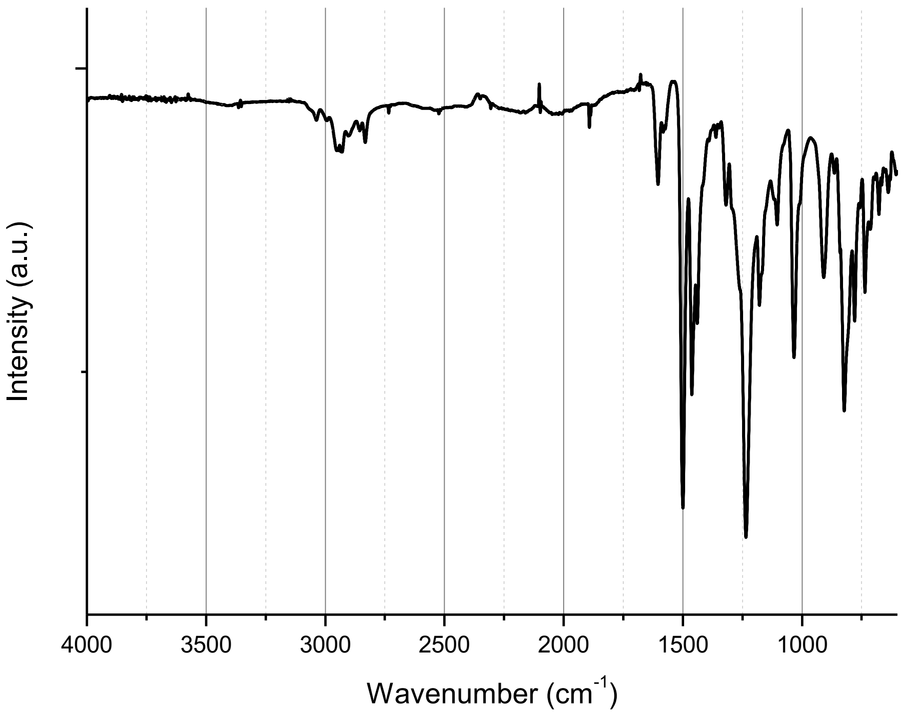


```
Note : -
Inlet : Direct       Ion Mode : FAB+
Spectrum Type : Normal Ion  [MF-Linear]
RT : 3.24 min       Scan# : (42,55)-(4,29)-(5,29)       Temp : 3276.7 deg.C
BP : m/z 73.6566       Int. : 2046.40 (21458054)
Output m/z range : 50 to 1488       Cut Level : 0.00 %
```

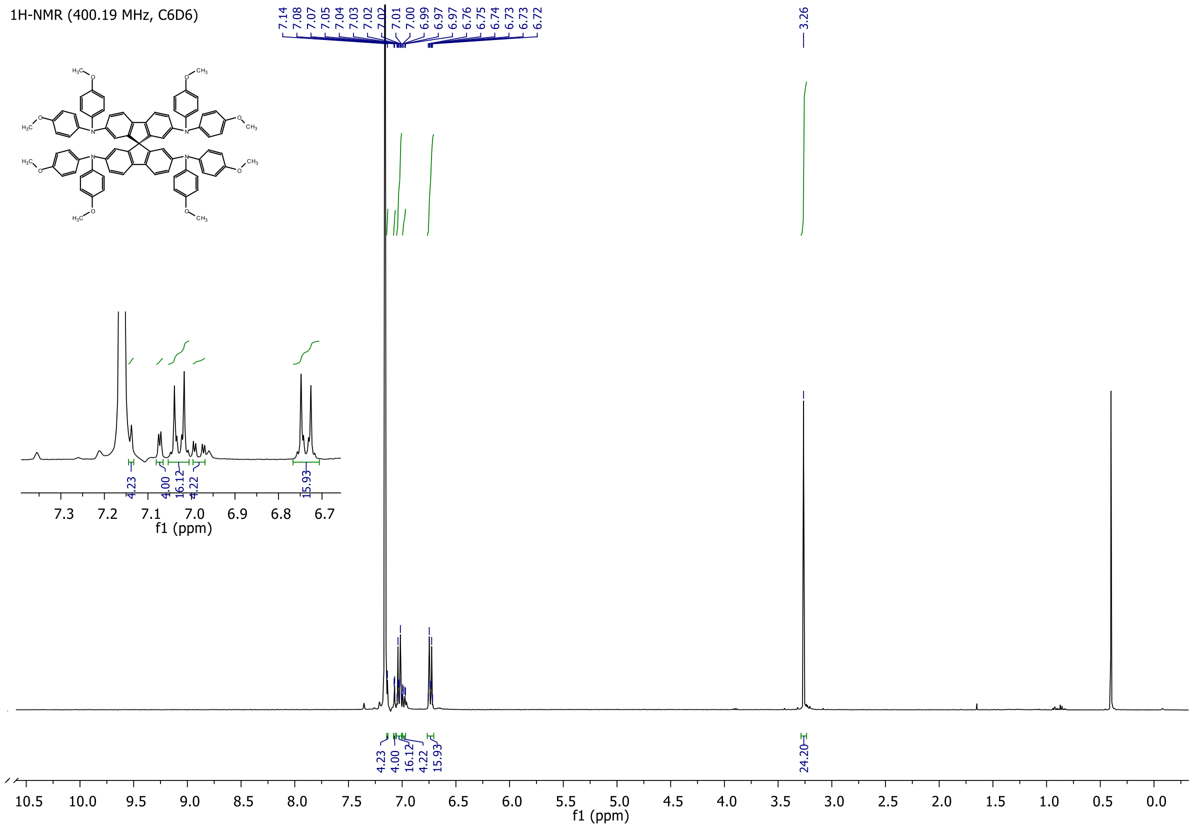


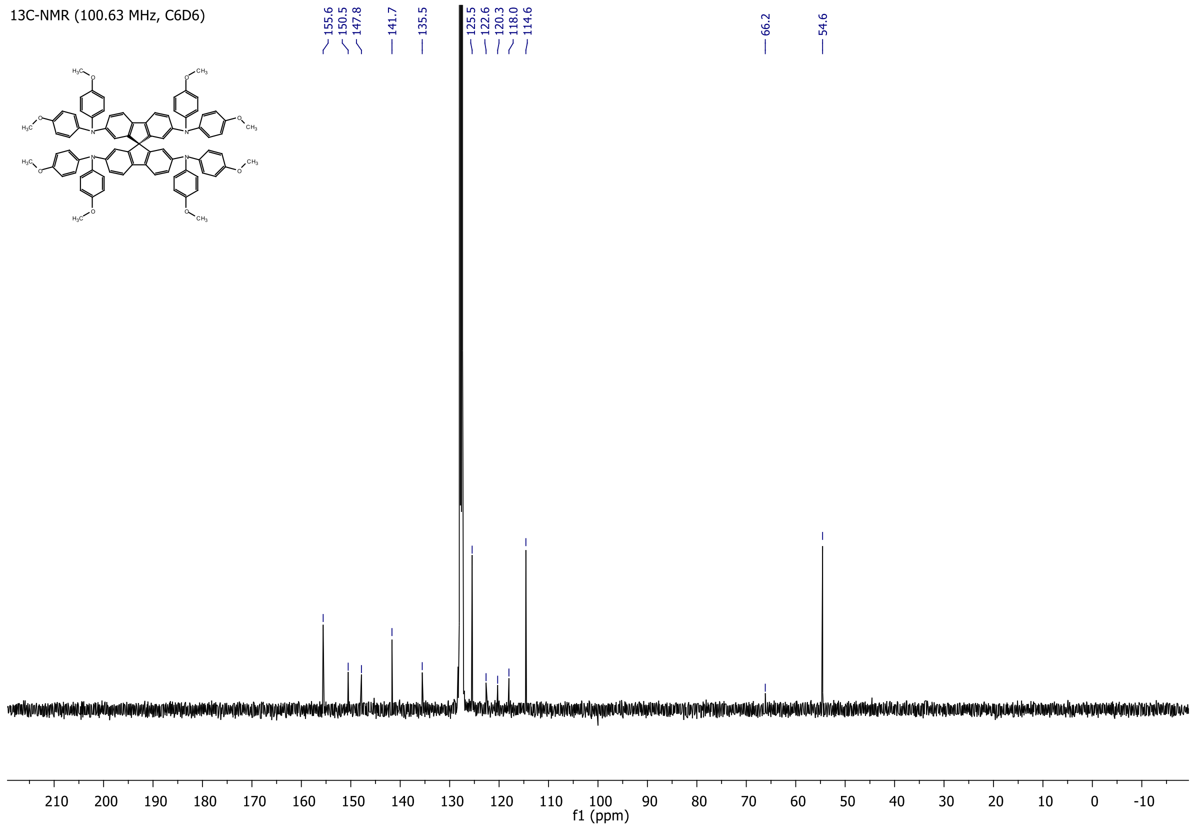
```
[ Theoretical Ion Distribution ]
Molecular Formula : C86 H80 N4 O8 Si
                    (m/z  1324.5745, MW  1325.6887, U.S. 50.0)
Base Peak :  1325.5776, Averaged MW :  1325.6820(a),  1325.6829(w)

    m/z       INT.
 1324.5745  97.5708*********************************************************
 1325.5776 100.0000**********************************************************
 1326.5801  55.4424********************************
 1327.5823  21.6504*************
 1328.5845   6.5696****
 1329.5867   1.6306*
 1330.5890   0.3420
 1331.5913   0.0621
 1332.5938   0.0099
 1333.5963   0.0014
 1334.5988   0.0002
```

SOT-OTBDMS



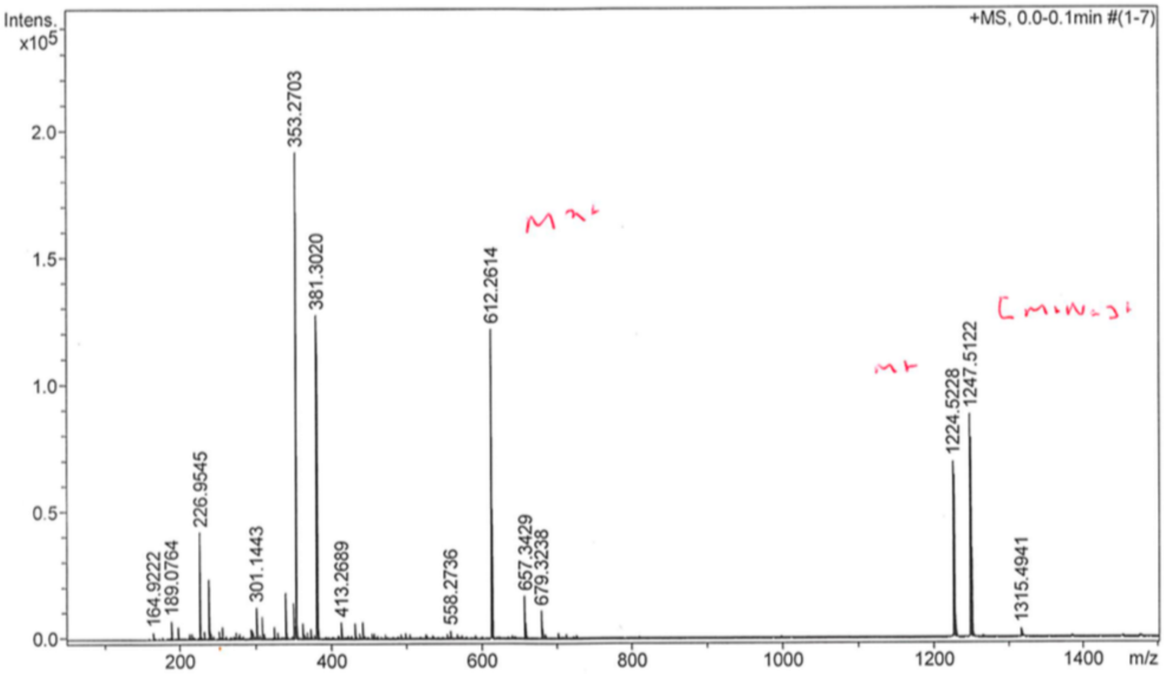
Spiro-OMeTAD

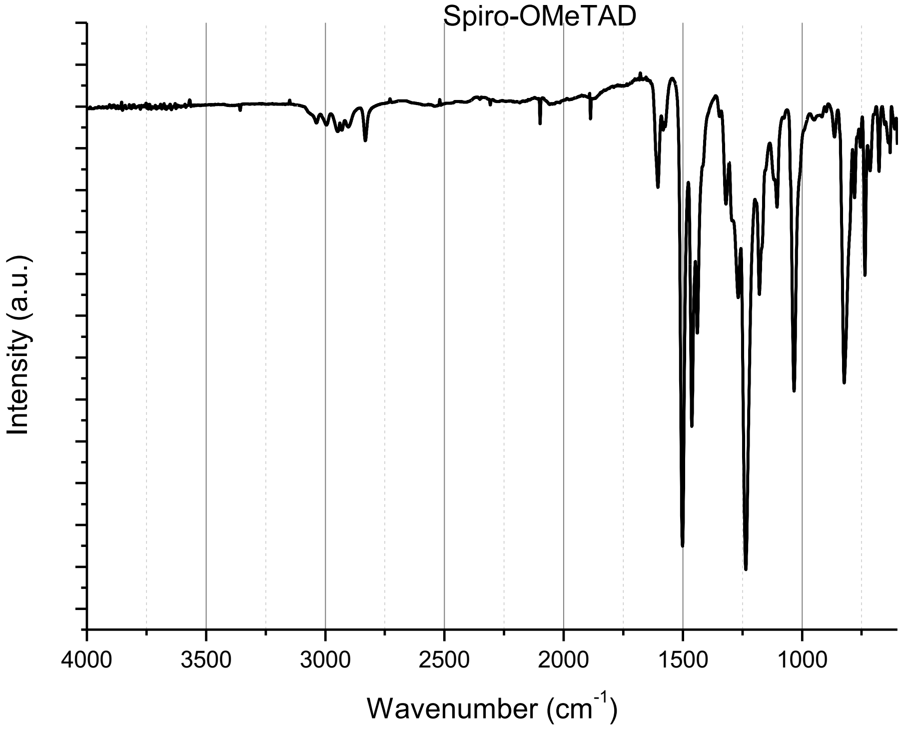

1H-NMR (400.19 MHz, C6D6)


13C-NMR (100.63 MHz, C6D6)

Acquisition Parameter

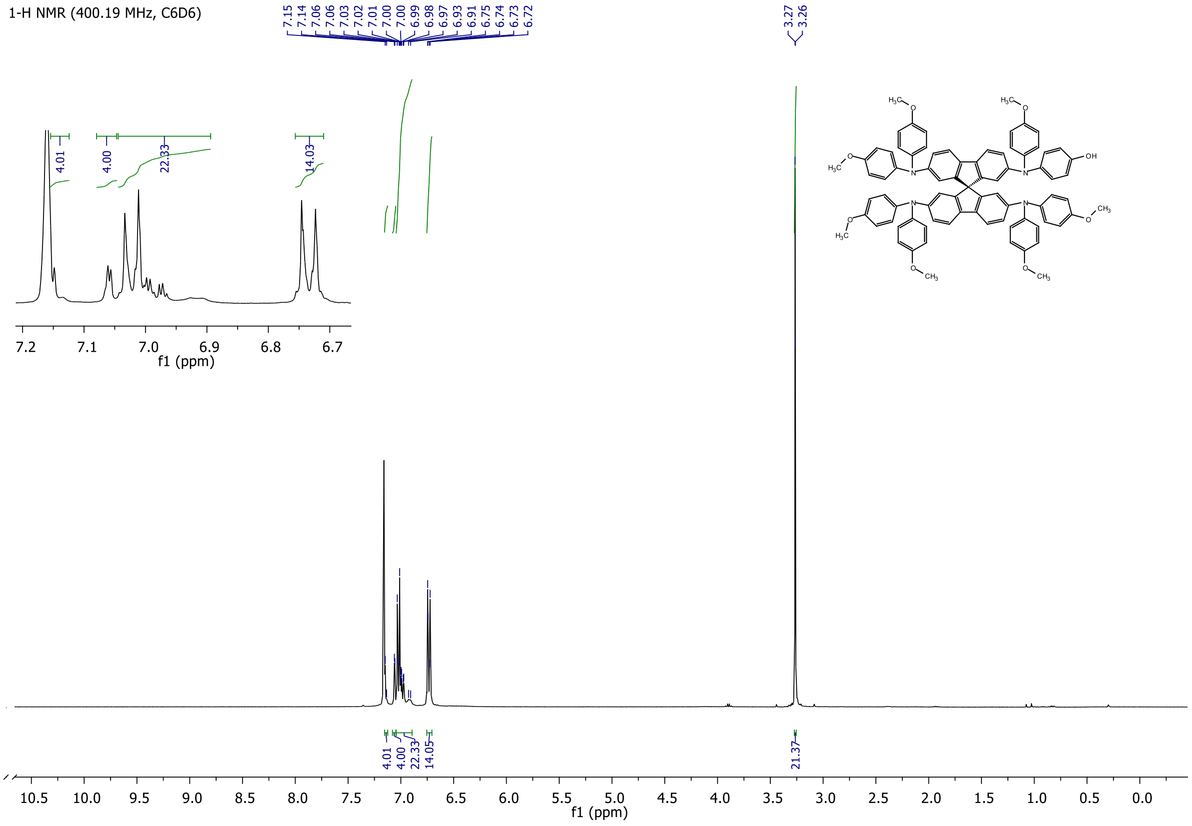
Source Type	ESI	Ion Polarity	Positive
Scan Begin	50 m/z		
Scan End	1500 m/z		



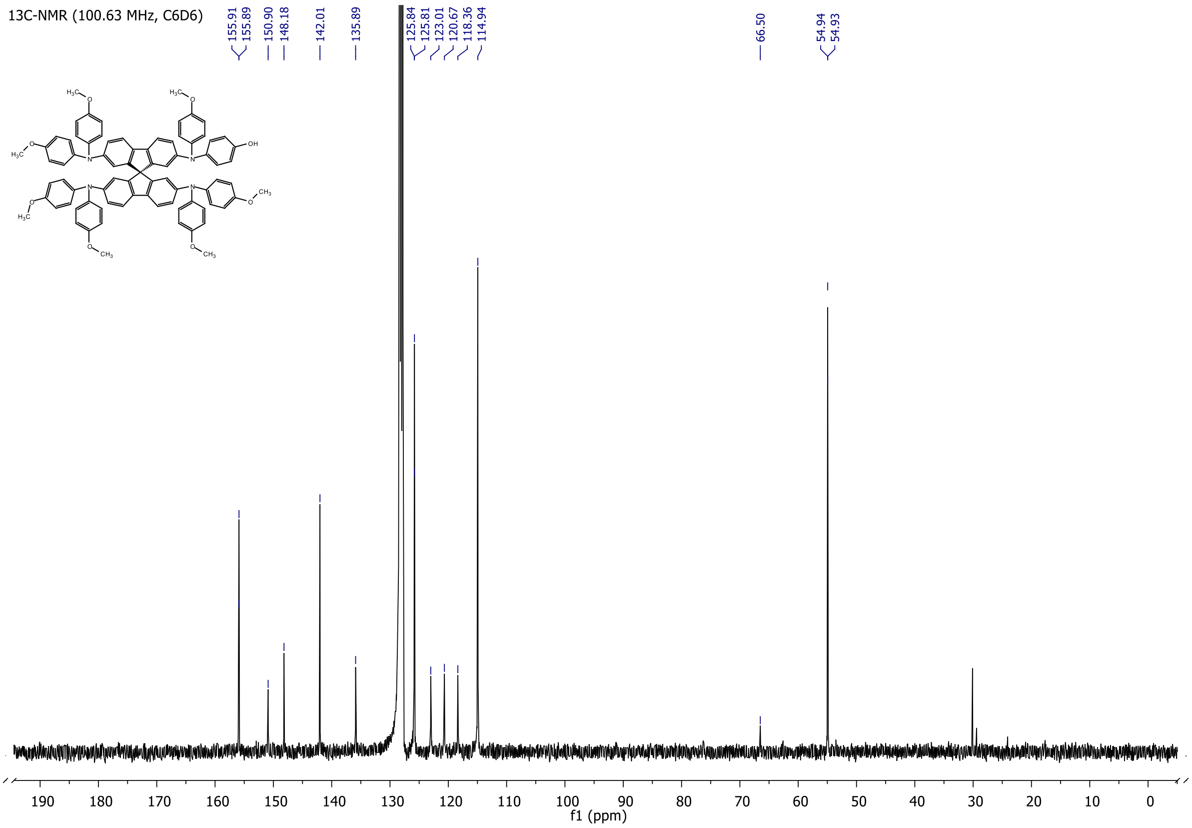


SOT-OH

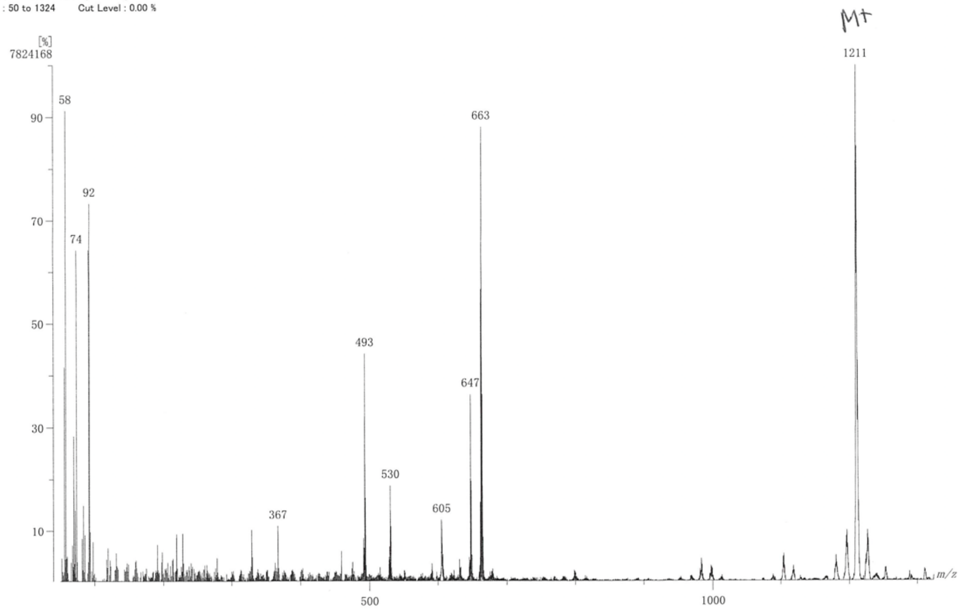
1-H NMR (400.19 MHz, C6D6)



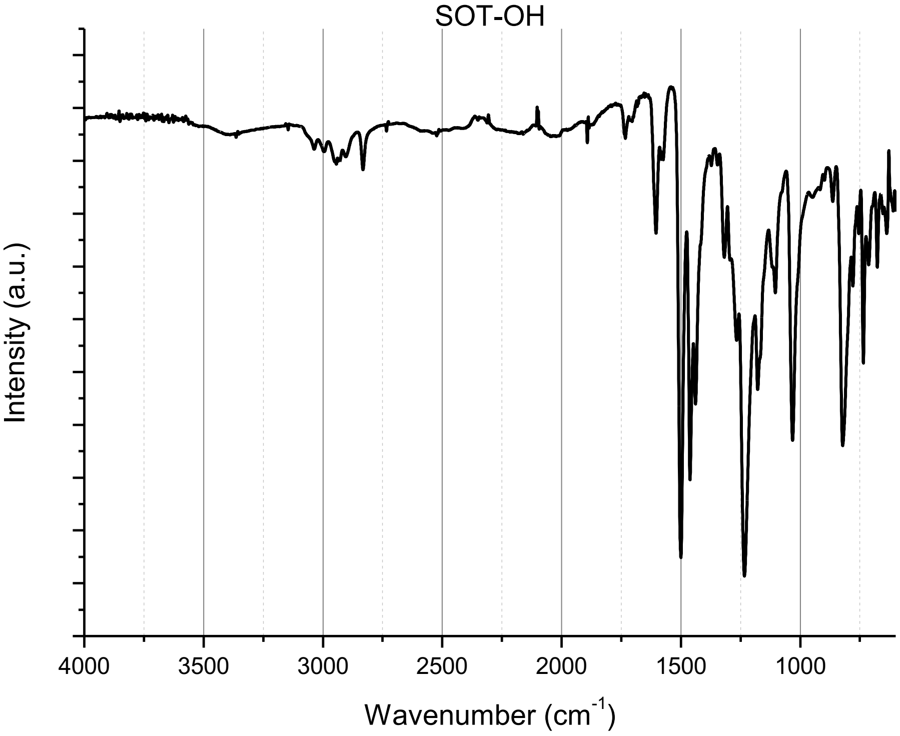
13C-NMR (100.63 MHz, C6D6)



```
Note : -
Inlet : Direct       Ion Mode : FAB+
Spectrum Type : Normal Ion  [MF-Linear]
RT : 2.61 min       Scan# : (34,44)-(4,21)-(4,21)       Temp : 3276.7 deg.C
BP : m/z 1210.5313       Int. : 162.89 (1707989)
Output m/z range : 50 to 1324       Cut Level : 0.00 %
```

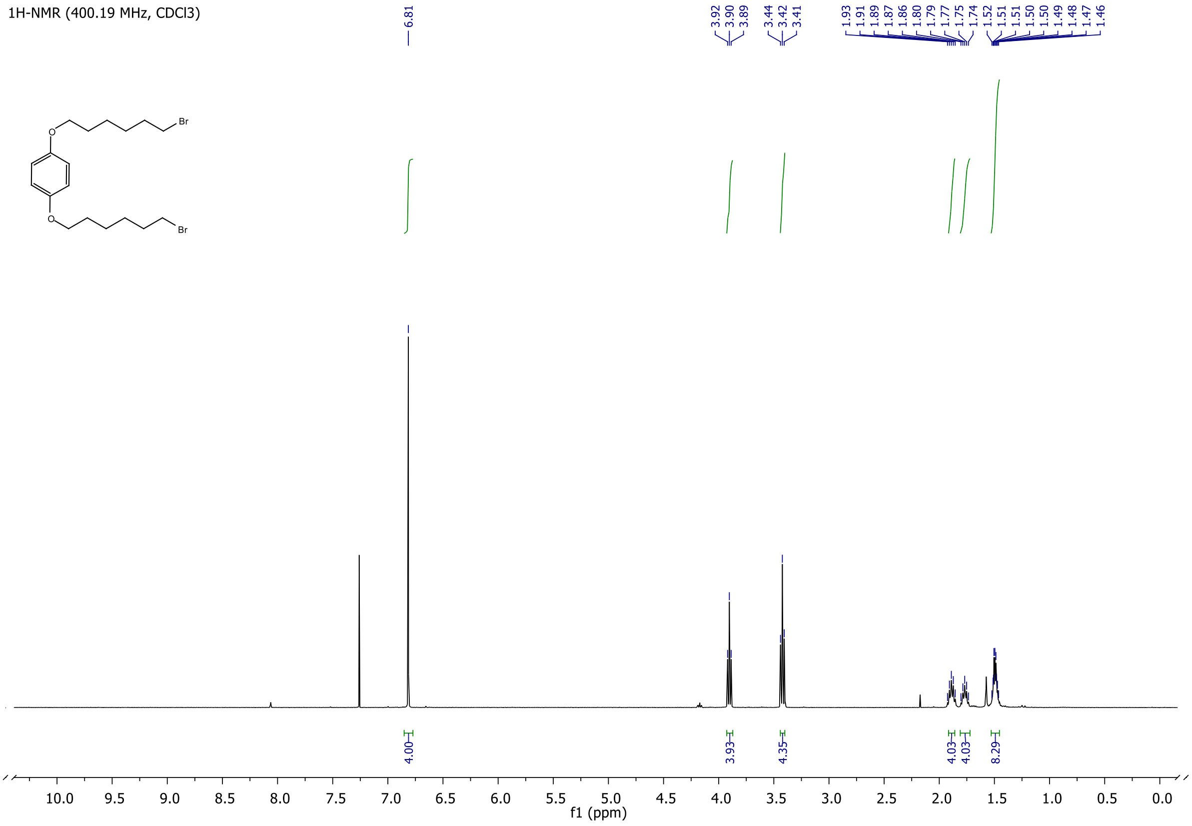


```
[ Theoretical Ion Distribution ]
Molecular Formula : C80 H66 N4 O8
                     (m/z  1210.4881, MW  1211.4260, U.S. 50.0)
Base Peak :  1210.4881, Averaged MW :  1211.4207(a),  1211.4215(w)

    m/z       INT.
 1210.4881 100.0000************************************************************
 1211.4913  90.7529*******************************************************
 1212.4945  42.2866*************************
 1213.4976  13.4645********
 1214.5006   3.2892**
 1215.5036   0.6562
 1216.5065   0.1111
 1217.5094   0.0164
 1218.5123   0.0021
 1219.5152   0.0003
```

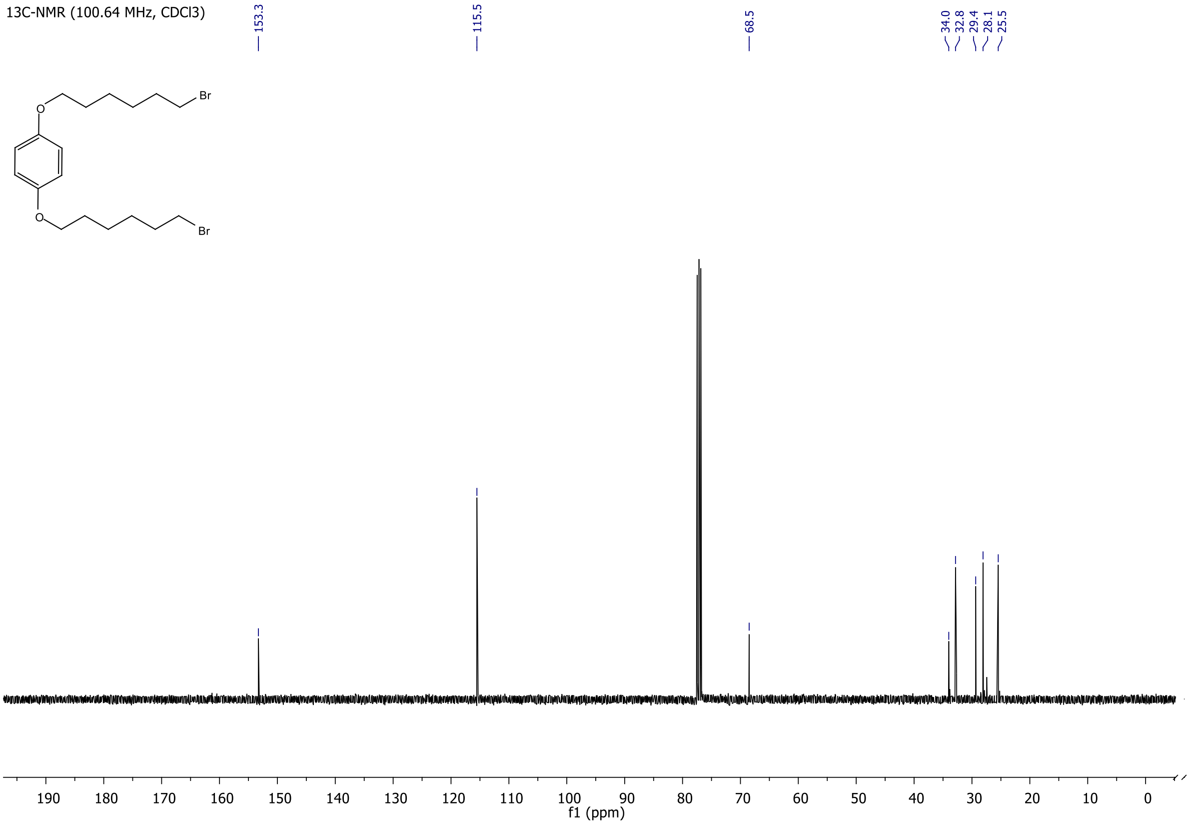


Compound 8

1H-NMR (400.19 MHz, CDCl3)

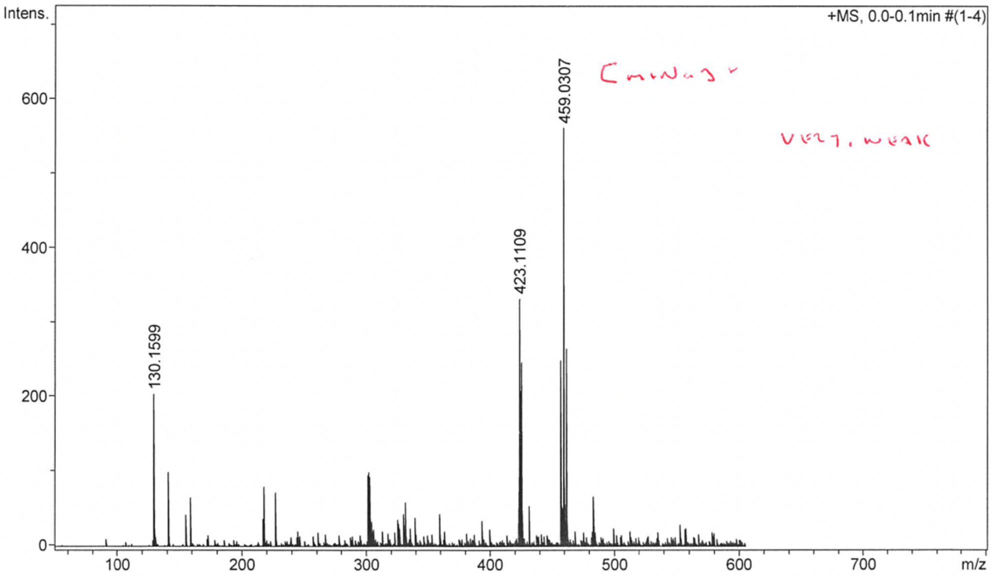


13C-NMR (100.64 MHz, CDCl3)



Acquisition Parameter

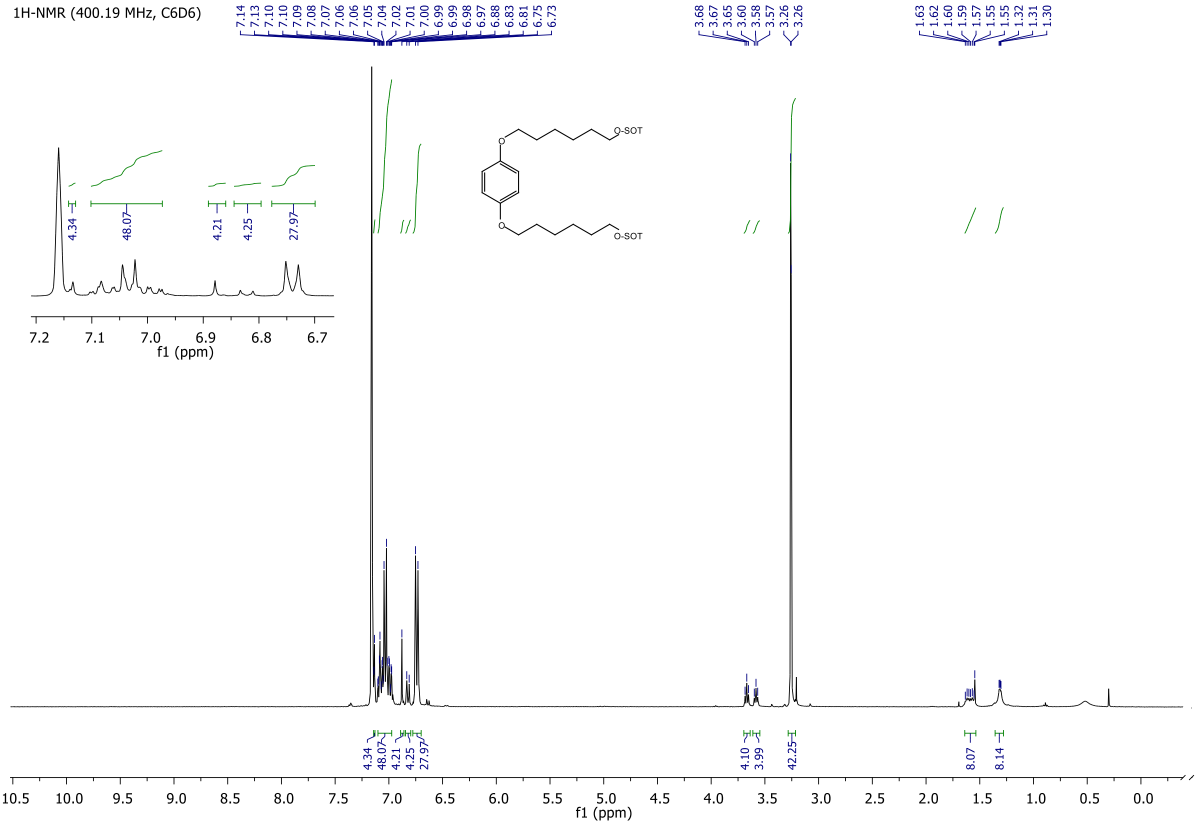
Source Type	ESI	Ion Polarity	Positive
Scan Begin	50 m/z		
Scan End	600 m/z		

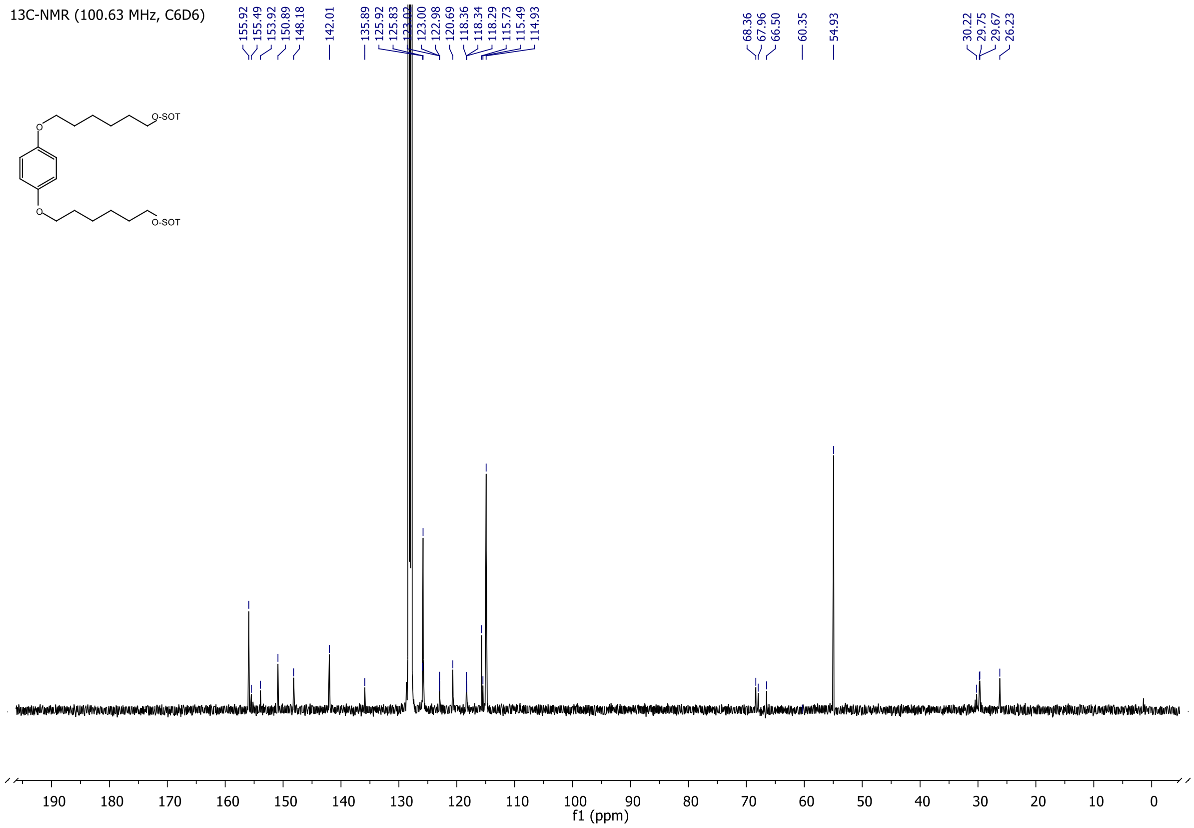


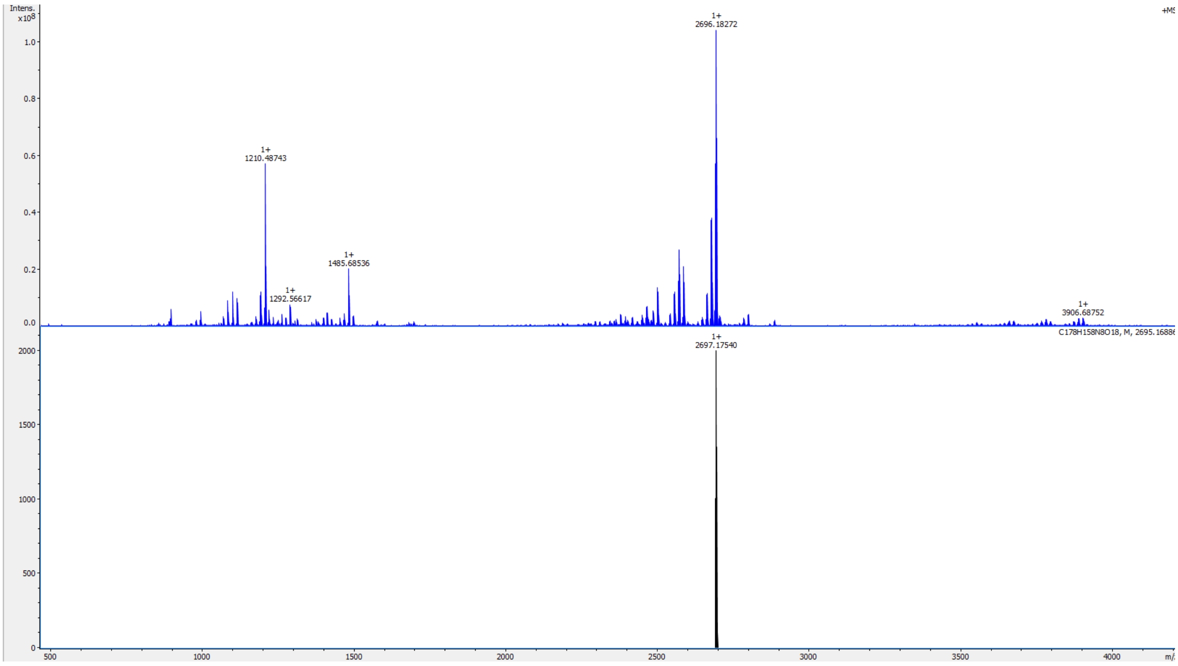
$[m+Na]^+$

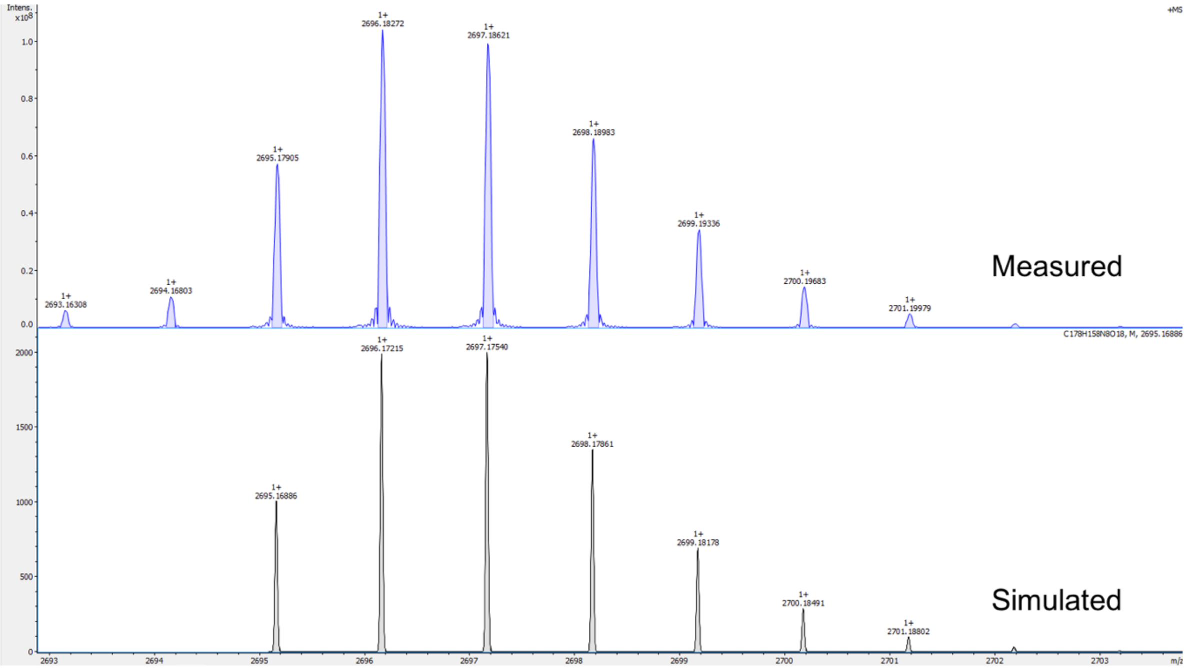
very, weak

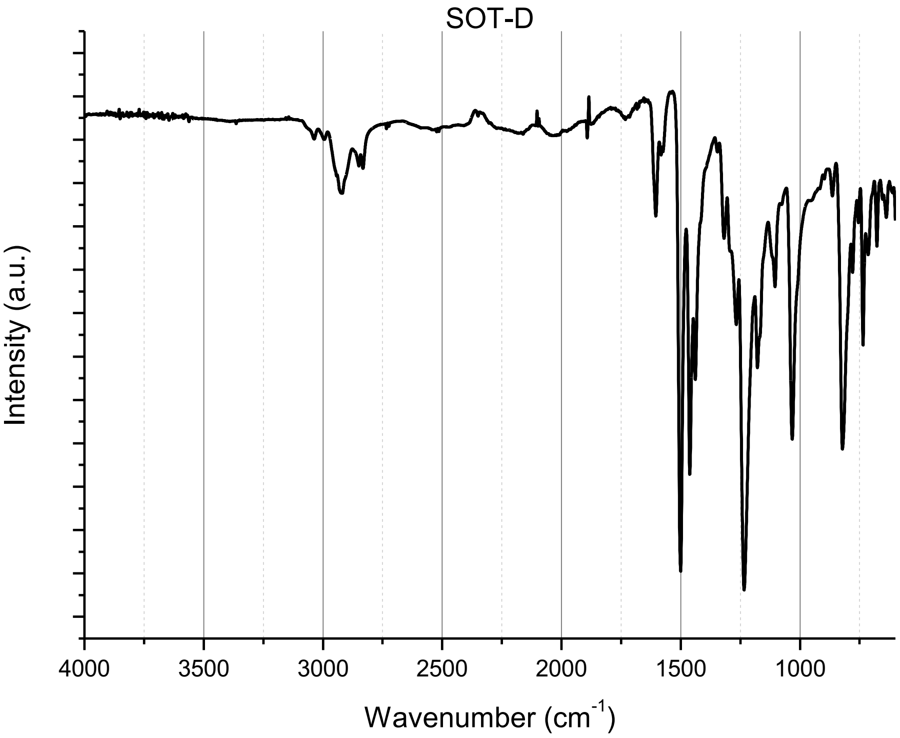
SOT-D


1H-NMR (400.19 MHz, C6D6)
7.14 7.13 7.10 7.10 7.09 7.08 7.07 7.06 7.06 7.05 7.04 7.02 7.01 7.00 6.99 6.99 6.98 6.97 6.88 6.83 6.81 6.75 6.73
3.68 3.67 3.65 3.60 3.58 3.57 3.26 3.26
1.63 1.62 1.60 1.59 1.57 1.55 1.55 1.32 1.31 1.30
O-SOT
O
O
O-SOT
4.34
48.07
4.21
4.25
27.97
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
4.34
48.07
4.21
4.25
27.97
4.10
3.99
42.25
8.07
8.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

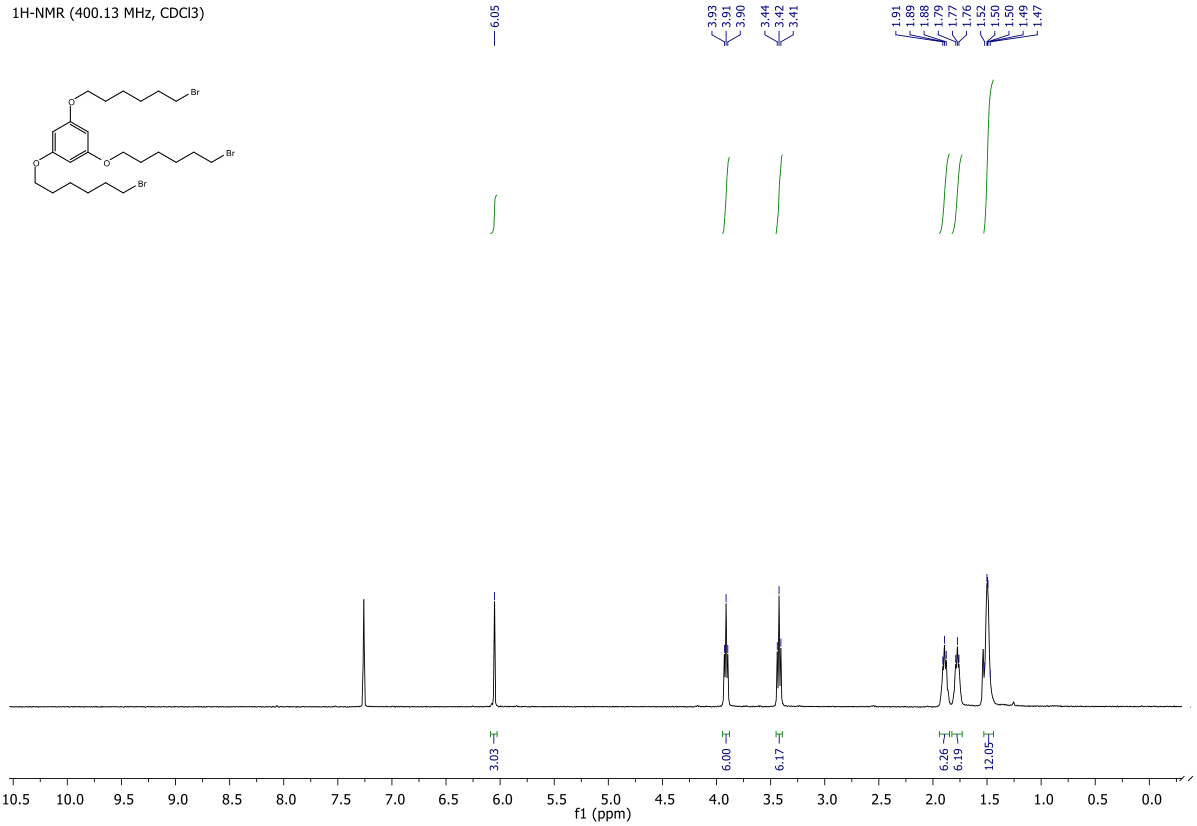

13C-NMR (100.63 MHz, C6D6)
155.92 155.49 153.92 150.89 148.18
142.01
135.89 125.92 125.83 123.00 123.00 122.98 120.69 118.36 118.34 118.29 115.73 115.49 114.93
68.36 67.96 66.50
60.35
54.93
30.22 29.75 29.67 26.23
O-SOT
O
O
O-SOT
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

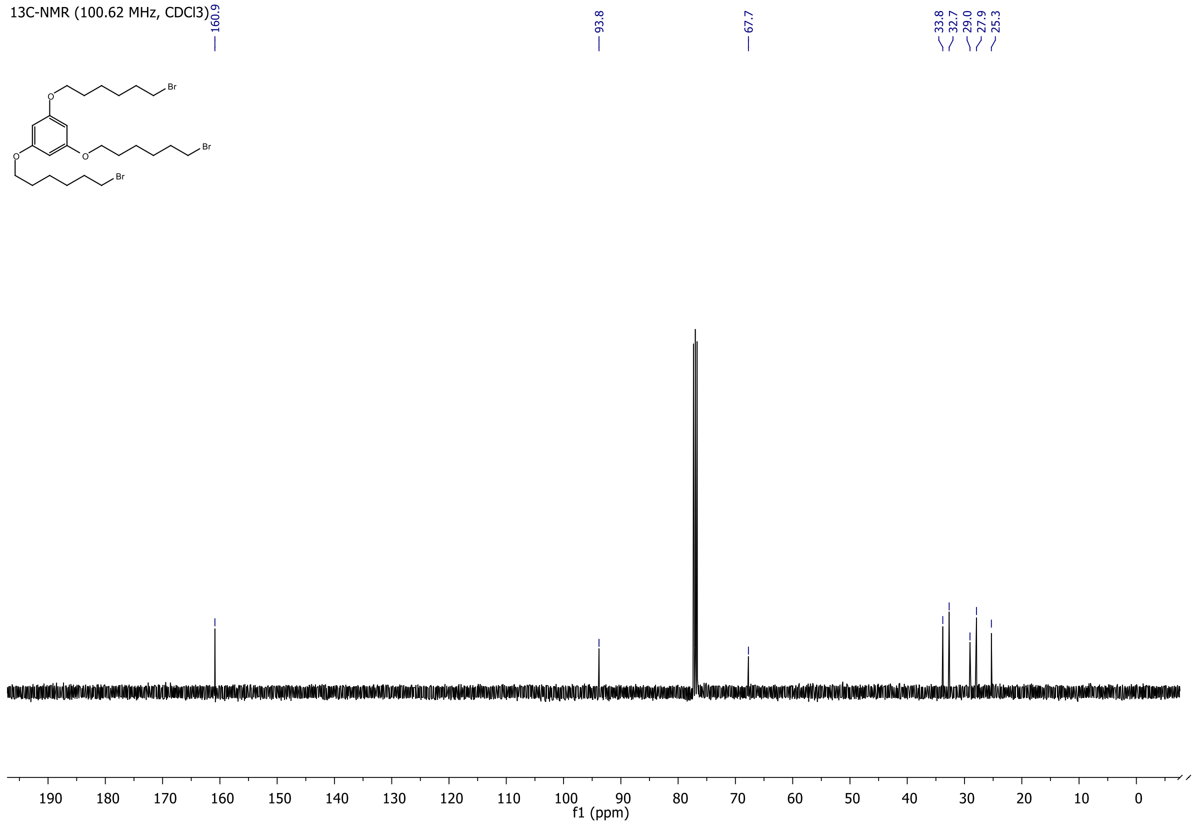

Intens.
x10^8
+M
1.0
0.8
0.6
0.4
0.2
0.0
1+
2696.18272
1+
1210.48743
1+
1292.56617
1+
1485.68536
1+
3906.68752
C178H158N8O18, M, 2695.1688
2000
1500
1000
500
0
1+
2697.17540
500
1000
1500
2000
2500
3000
3500
4000
m/


Intens.
x10^8
+MS
1.0
0.8
0.6
0.4
0.2
0.0
1+
2693.16308
1+
2694.16803
1+
2695.17905
1+
2696.18272
1+
2697.18621
1+
2698.18983
1+
2699.19336
1+
2700.19683
1+
2701.19979
Measured
C178H158N8O18, M, 2695.16886
2000
1500
1000
500
0
1+
2695.16886
1+
2696.17215
1+
2697.17540
1+
2698.17861
1+
2699.18178
1+
2700.18491
1+
2701.18802
Simulated
2693
2694
2695
2696
2697
2698
2699
2700
2701
2702
2703
m/z


SOT-D
Intensity (a.u.)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})

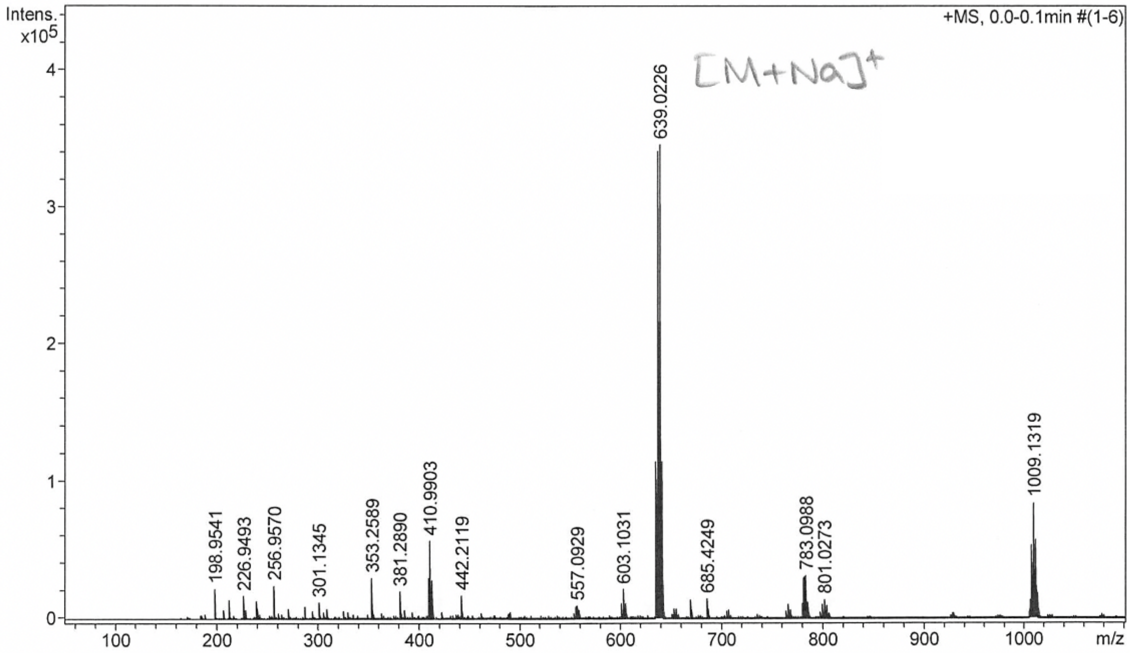
Compound **10**


1H-NMR (400.13 MHz, CDCl3)

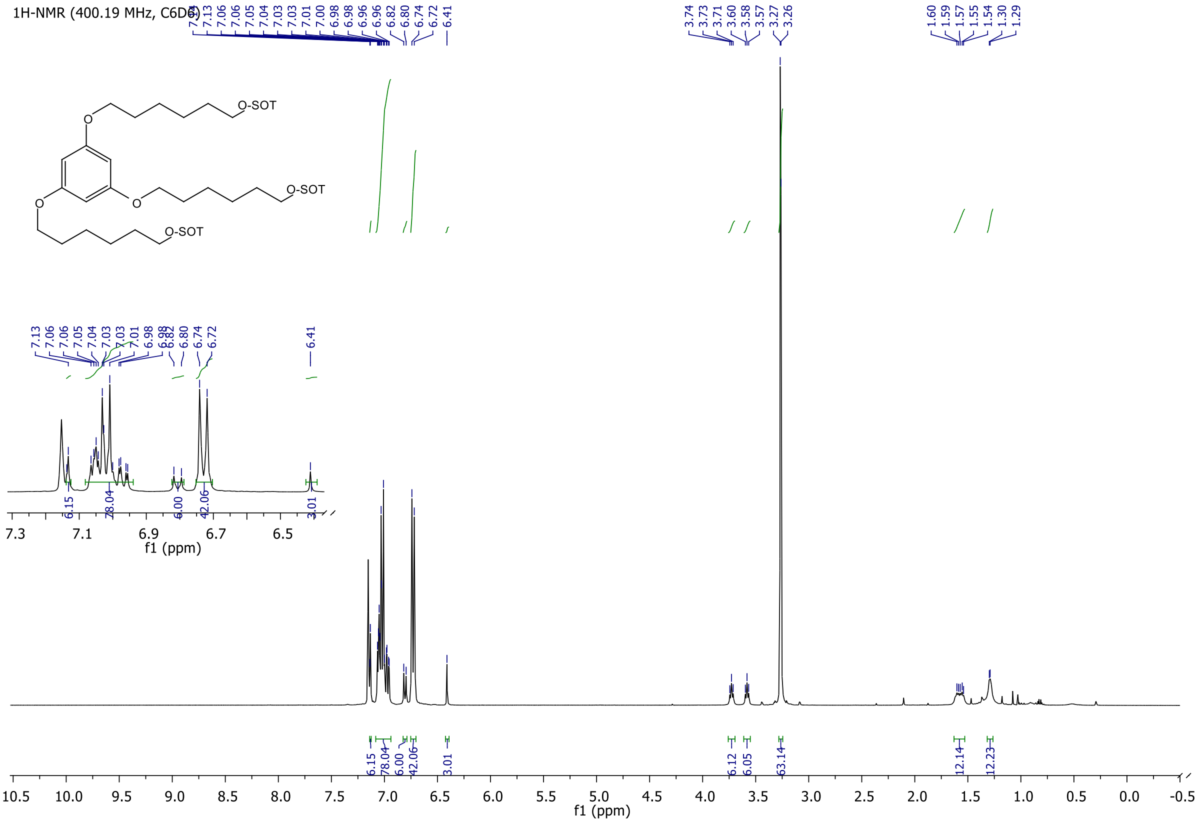

13C-NMR (100.62 MHz, CDCl3)

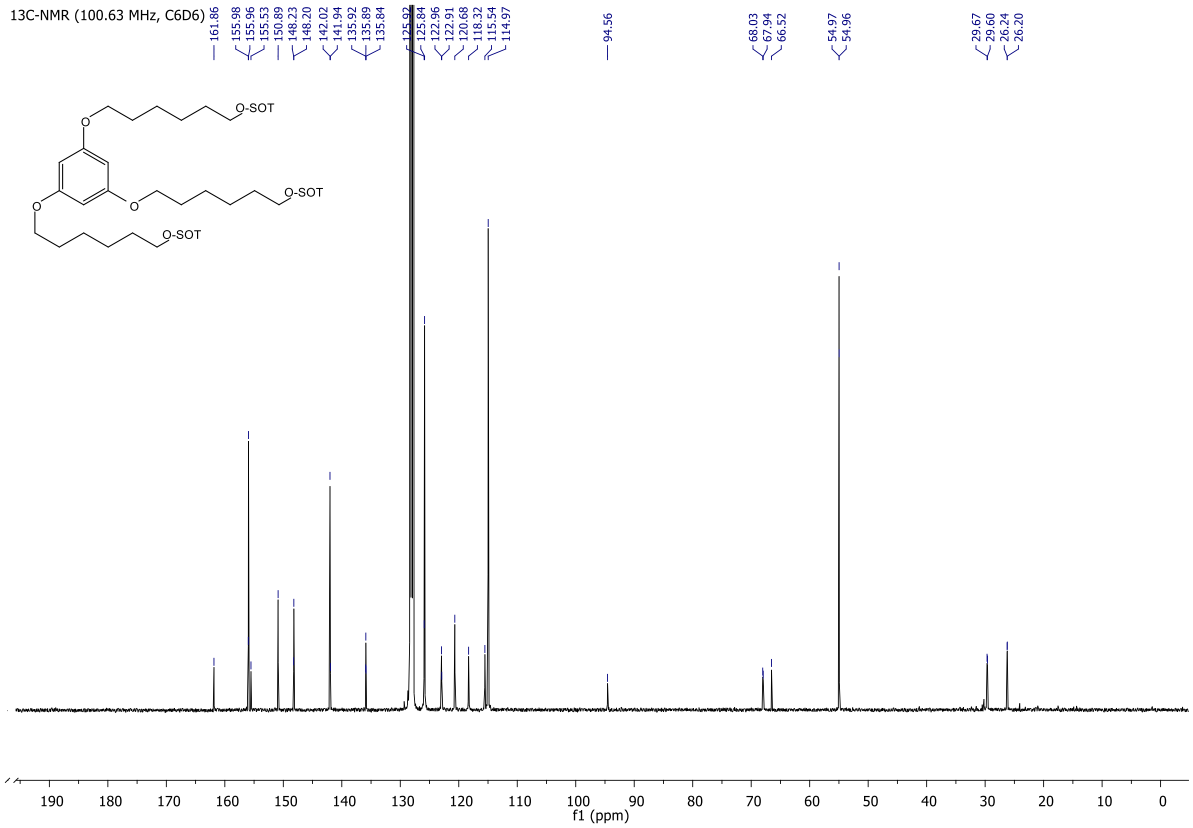
Acquisition Parameter

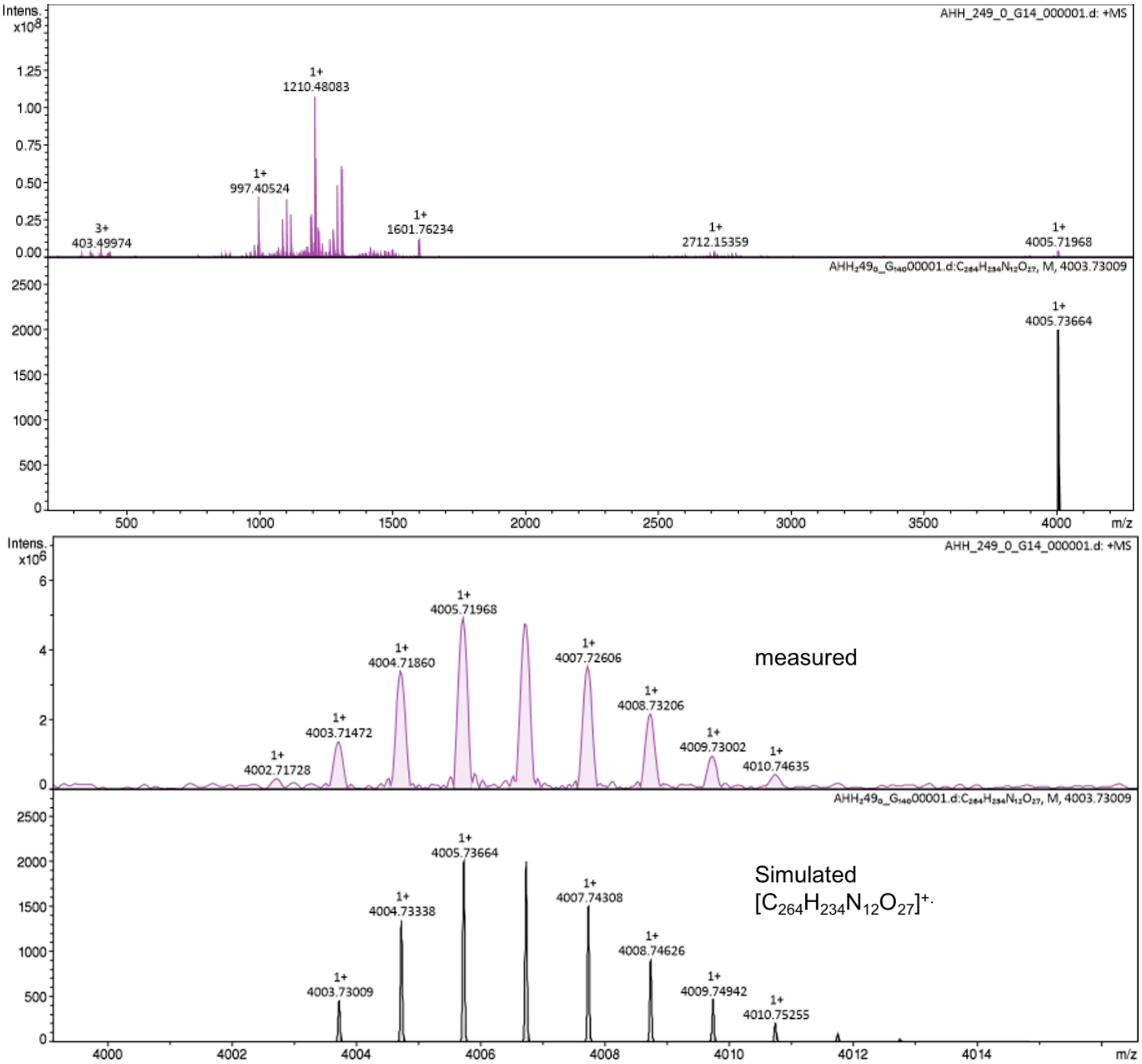
Source Type	ESI	Ion Polarity	Positive
Scan Begin	50 m/z		
Scan End	1100 m/z		

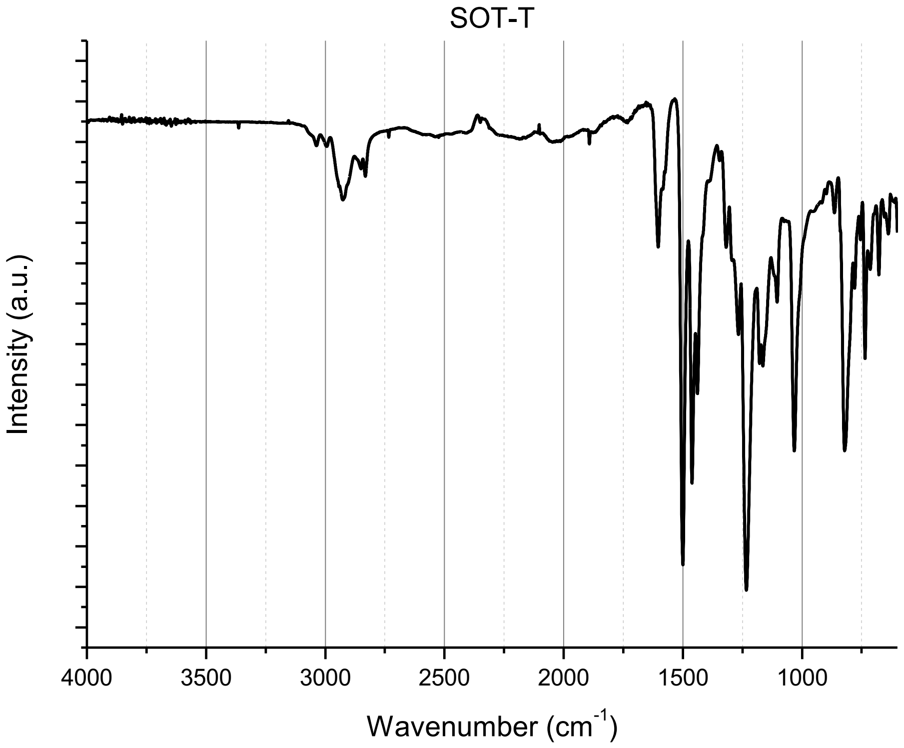


SOT-T


1H-NMR (400.19 MHz, C6D6)
7.13
7.13
7.06
7.06
7.05
7.04
7.03
7.03
7.01
7.00
6.98
6.98
6.96
6.96
6.82
6.80
6.74
6.72
6.41
3.74
3.73
3.71
3.60
3.58
3.57
3.27
3.26
1.60
1.59
1.57
1.55
1.54
1.30
1.29
O-SOT
O-SOT
O-SOT
O
O
O
6.15
78.04
6.00
42.06
3.01
6.12
6.05
63.14
12.14
12.23
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
7.3
7.1
6.9
6.7
6.5
f1 (ppm)


13C-NMR (100.63 MHz, C6D6)
161.86
155.98
155.96
155.53
150.89
148.23
148.20
142.02
141.94
135.92
135.89
135.84
125.92
125.84
122.96
122.91
120.68
118.32
115.54
114.97
94.56
68.03
67.94
66.52
54.97
54.96
29.67
29.60
26.24
26.20
O-SOT
O-SOT
O-SOT
O
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Intens.
x10^8
AHH_249_0_G14_000001.d: +MS
3+
403.49974
1+
997.40524
1+
1210.48083
1+
1601.76234
1+
2712.15359
1+
4005.71968
AHH249_0_G14_000001.d:C264H234N12O27, M, 4003.73009
1+
4005.73664
m/z
Intens.
x10^6
AHH_249_0_G14_000001.d: +MS
1+
4002.71728
1+
4003.71472
1+
4004.71860
1+
4005.71968
1+
4007.72606
1+
4008.73206
1+
4009.73002
1+
4010.74635
measured
AHH249_0_G14_000001.d:C264H234N12O27, M, 4003.73009
1+
4003.73009
1+
4004.73338
1+
4005.73664
1+
4007.74308
1+
4008.74626
1+
4009.74942
1+
4010.75255
Simulated
[C264H234N12O27]+.
m/z


SOT-T
Intensity (a.u.)
Wavenumber (cm^{-1})
4000
3500
3000
2500
2000
1500
1000

3. Electrochemical properties

SWV analysis was performed on **SOT-D** and **SOT-T** and these were compared with **Spiro-OMeTAD**, under the same conditions. The square-wave voltammograms are shown in Figure S1, while a summary of the properties of the three molecules is provided in Table S3.

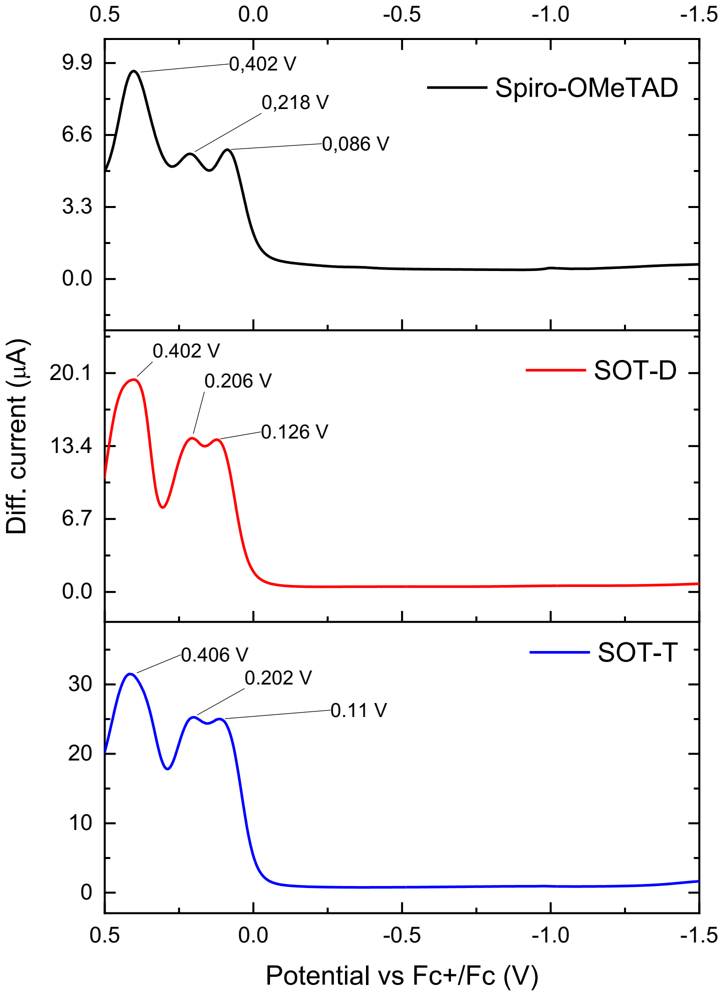


*Figure S1. Square-wave voltammetry plots of **Spiro-OMeTAD**, **SOT-D** and **SOT-T** (CH_2Cl_2, 5 × 10^{-4} M). Conditions: Pt disc working electrode, Pt wire counter electrode, Ag wire pseudo-reference electrode, 0.1 M $TBAPF_6$ electrolyte. Fc^+/Fc was used as external calibrant. Square wave amplitude: 0.025 V; potential increment: 0.004 V; frequency: 25 Hz.*

4. DFT calculations

SOT-D and **SOT-T** were modeled using Gaussian 09[11] and visualized using GaussView 5.0.9. Their geometry was optimized via DFT calculation using the B3LYP hybrid functional with the 3-21G basis set, in the gas phase. Frequency calculations were performed to ensure the absence of negative frequencies and the results were compared with **Spiro-OMeTAD**, modeled with the same conditions. The presence of elements of symmetry gives rise to nearly degenerate HOMOs and LUMOs, as shown in Table S2. The HOMO and LUMO maps are shown in Figure S2.

Table S2. DFT calculated frontier molecular orbitals of ***Spiro-OMeTAD, SOT-D*** *and* ***SOT-T****.*

	Spiro-OMeTAD		**SOT-D**		**SOT-T**	
Orbital	Energy (eV)	Gap (eV)	Energy (eV)	Gap (eV)	Energy (eV)	Gap (eV)
LUMO +5					-0,77	0,00
LUMO +4					-0,77	0,01
LUMO +3			-0,71	0,02	-0,78	0,00
LUMO +2			-0,73	0,01	-0,79	0,00
LUMO +1	-0,75	0,01	-0,74	0,02	-0,79	0,01
LUMO	-0,76	3,50	-0,76	3,51	-0,80	3,49
HOMO	-4,26	0,06	-4,27	0,04	-4,29	0,04
HOMO -1	-4,32	/	-4,31	0,02	-4,33	0,01
HOMO -2			-4,33	0,02	-4,34	0,00
HOMO -3			-4,35	/	-4,34	0,07
HOMO -4					-4,41	0,04
HOMO -5					-4,45	/

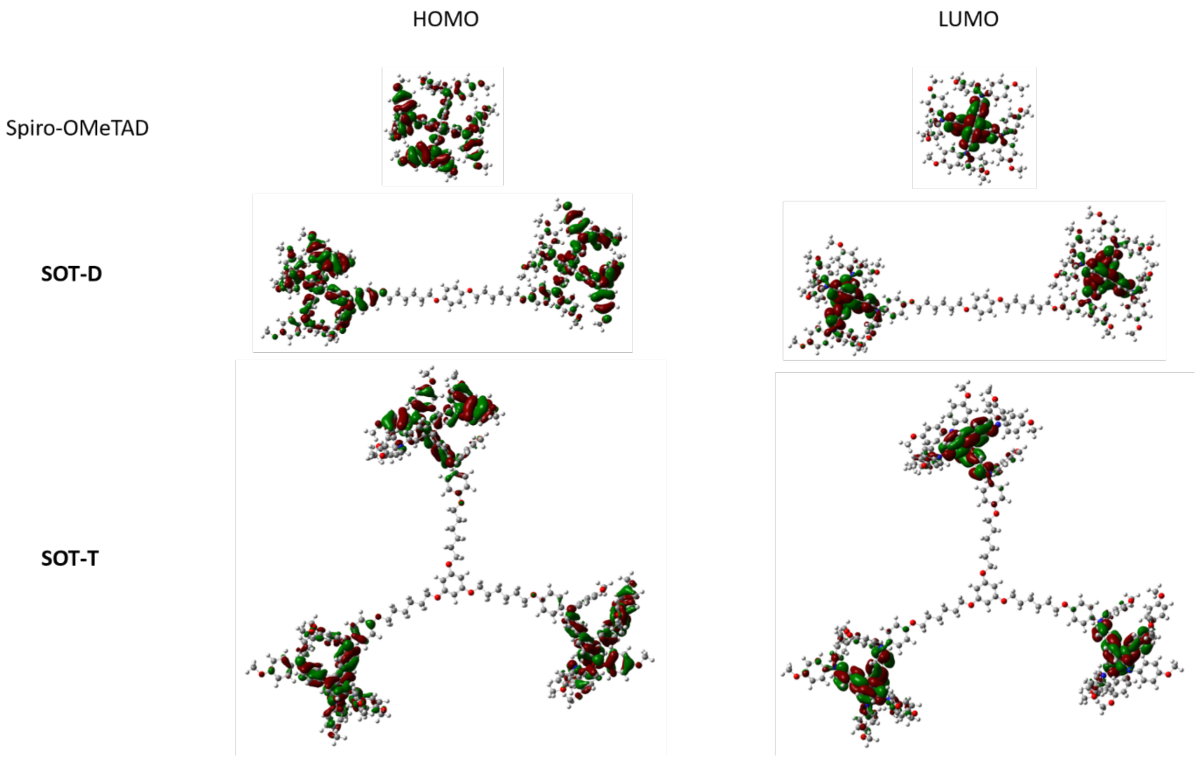


Figure S2. Calculated HOMO and LUMO spatial distribution of ***Spiro-OMeTAD****,* ***SOT-D*** *and* ***SOT-T****.*

Table S3. Summary of measured and calculated properties of ***Spiro-OMeTAD****,* ***SOT-D*** *and* ***SOT-T****.*

	$E_{g,opt}$ (eV)[a]	IP (eV)[b]	HOMO (eV)[c]	LUMO (eV)[c]	$E_{g,calc}$ (eV)[c]
Spiro-OMeTAD	2.95	–4.89	–4.26	–0.76	3.50
SOT-D	2.95	–4.93	–4.27	–0.76	3.51
SOT-T	2.95	–4.91	–4.29	–0.80	3.49

[a] estimated from UV-vis spectra: $E_{g,opt}$ (eV) = 1240/$\lambda_{cut-off}$ (nm).

[b] estimated from SWV plots: IP (eV) = – (4.8 – E_{ox}).

[c] values obtained from DFT calculations.

5. Thermal properties

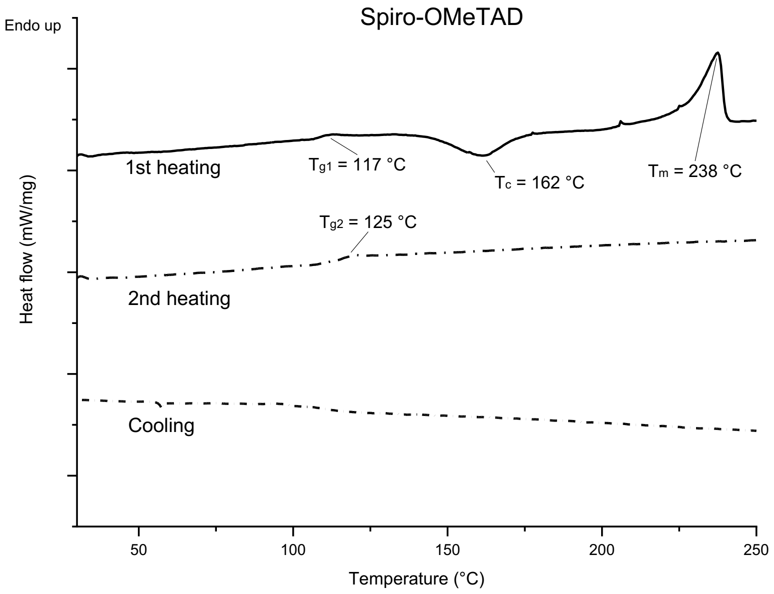


Figure S3. DSC of ***Spiro-OMeTAD****. Heat flow values were offset for better visualization.*

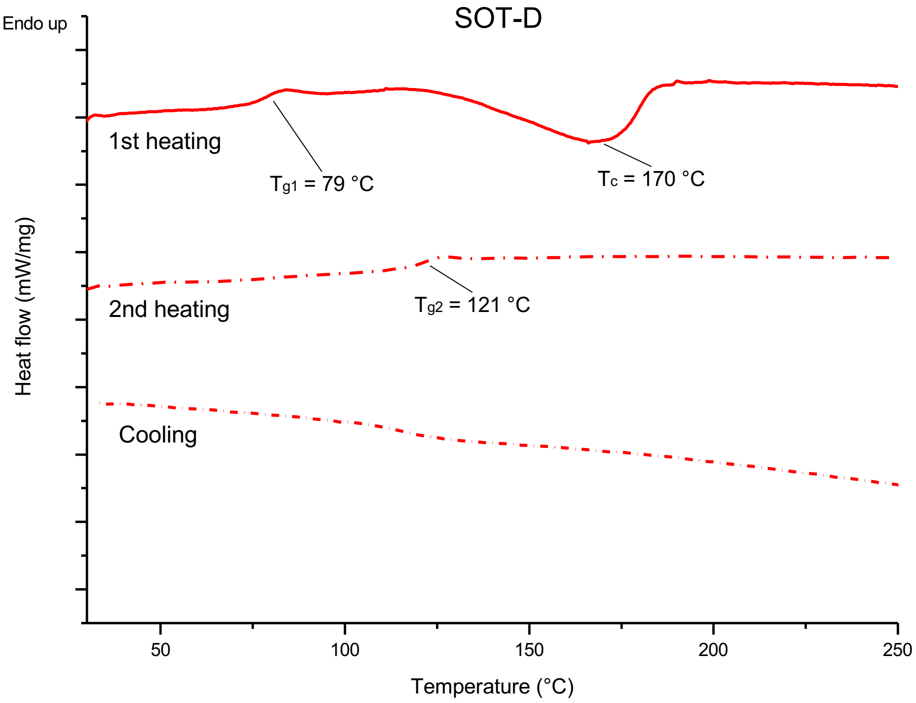


Figure S4. DSC of ***SOT-D****. Heat flow values were offset for better visualization.*

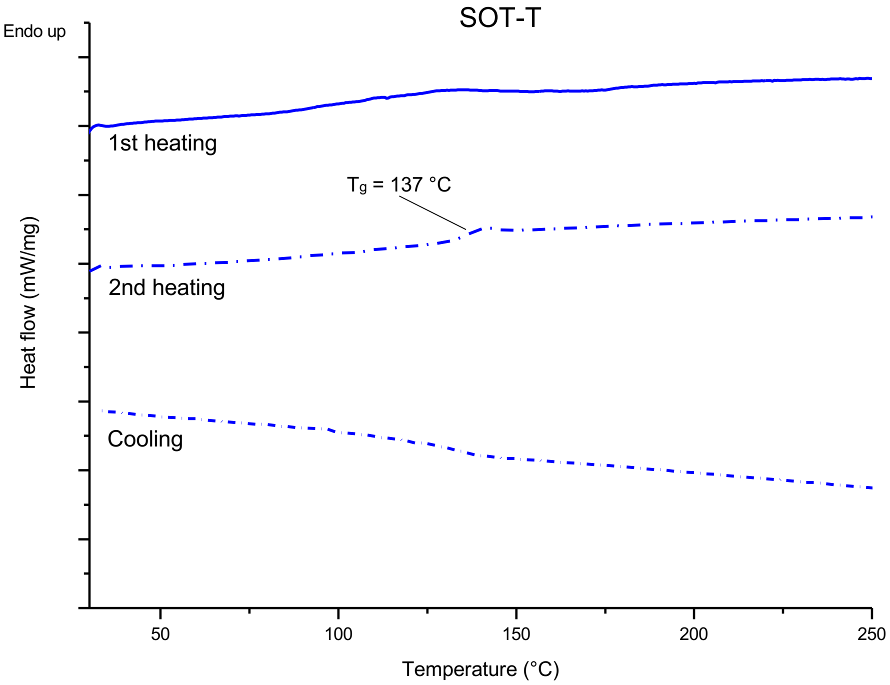


*Figure S5. DSC of **SOT-T**. Heat flow values were offset for better visualization.*

6. Absorption Spectra of the HTM films

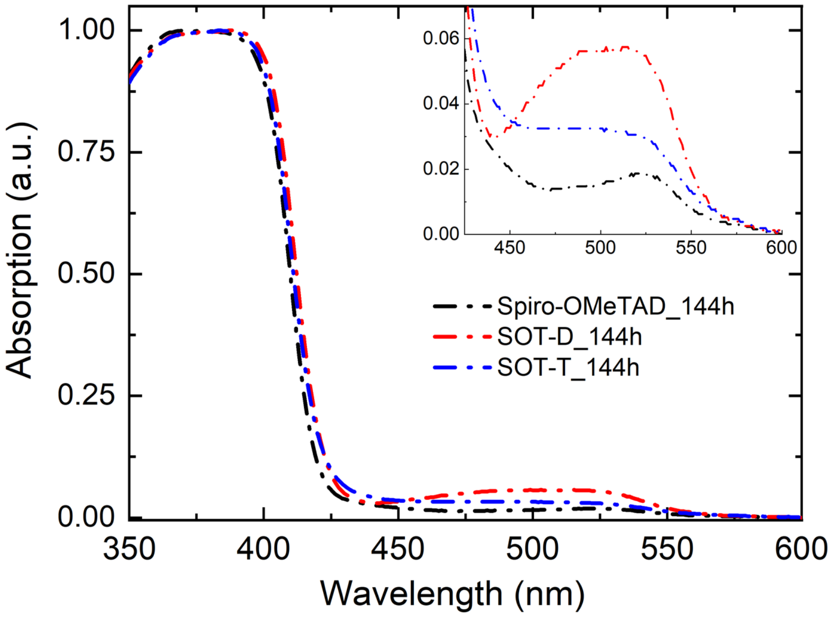
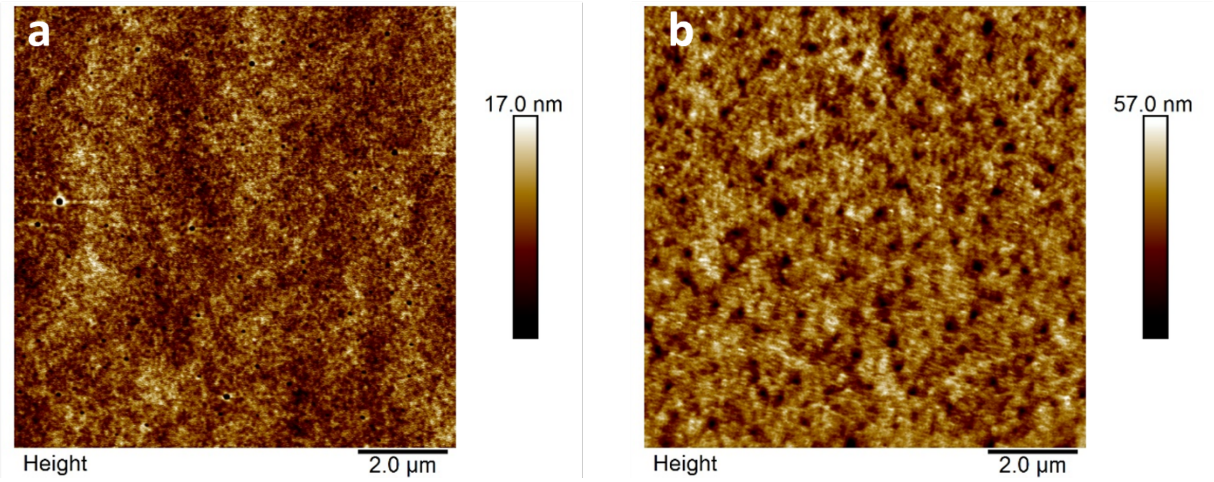


Figure S6. *UV-Vis absorption spectra of thin films of* ***Spiro-OMeTAD***, ***SOT-D*** *and* ***SOT-T*** *on glass.*

7. Surface structure of the HTM films



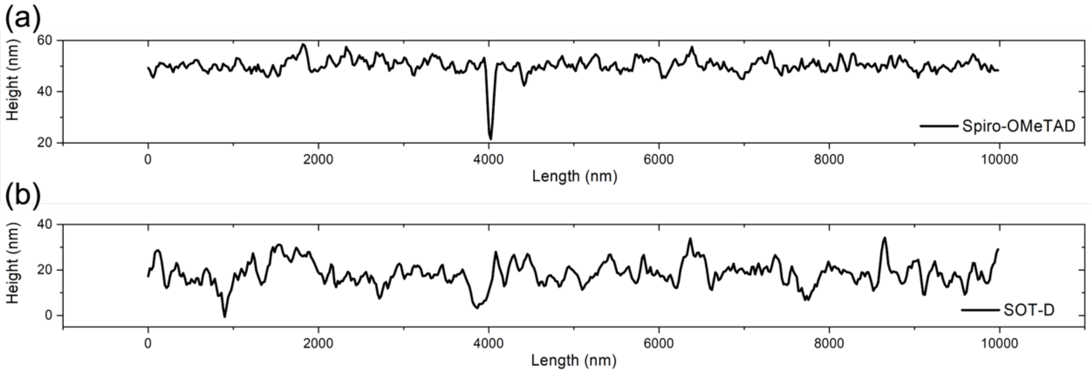


Figure S7. Examples of line plots taken from the images shown in Figure 6 for (a) ***Spiro-OMeTAD*** *and (b)* ***SOT-D.***

8. Conductivity measurements

ITO substrates (2 × 2 cm) were laser etched, with a pattern particularly designed for conductivity measurements. Then, they were treated with UV ozone for 10 minutes each, to improve the surface wettability. The substrates were transferred to the glovebox for film deposition. Solutions of the HTMs (75 mg/ml) in 1.0 ml of chlorobenzene were prepared, and to these 30 μl of a stock solution of LiTFSI (170 mg/ml in acetonitrile) and 20 μl tBP were added as dopants. The solution was spun on the substrates at 1000 rpm for 45 seconds. After deposition, the films were kept at room temperature for 15 minutes. The measurements were carried out by obtaining the current-voltage characteristics for the films, and the values were determined from the slope of the curves.

9. Device Fabrication

PSCs were fabricated in the regular device structure with FTO/SnO_2-nanoparticles(np)/FAMACs perovksite/**Spiro-OMeTAD**/Au stack. FTO glass substrates were patterned using a laser etcher and cleaned using Hellmanex III special cleaning solution/DI water, acetone, and ethanol. The substrates were then UV-Ozoned for 10 minutes. For the electron-transporting layer, SnO_2-np (Alfa Aeser) diluted with DI water (1:1) were spin-coated onto the patterned substrates at 2000 rpm for 30 seconds under air and annealed at 150 °C for 30 minutes. The substrates were then transferred to the glovebox, for deposition of perovskite and hole-transporting layer (HTL). The perovskite solution was prepared according to the following procedure: solutions of PbI_2 (1.1 M) and $PbBr_2$ (0.2 M) in a mixture of DMF/DMSO (4/1, v/v) were separately made and stirred overnight at 70 °C in the glovebox. The day after, FAI was added to the PbI_2 solution to obtain a solution of 1.0 M $FAPbI_3$. Similarly, MABr was added to the $PbBr_2$ solution in an equimolar amount to obtain $MAPbBr_3$ (0.2 M). The resulting solutions were left to stir for 5 minutes, after which, 200 μl of the $MAPbBr_3$ solutions were added to the $FAPbI_3$ solution. Finally, 50 μl of a solution of CsI (1.5

M in DMSO) were added to the mixture to get the triple cation perovskite. The solution was filtered before use. To deposit the perovskite film, the solution was dynamically spin coated on top of FTO/SnO_2 at 4000 rpm for 30 seconds. 300 µl of ethyl acetate (antisolvent) were dripped onto the spinning substrate at 15th second, and the substrate was immediately transferred to the hot plate at 100 °C. The film was annealed for 30 minutes. For the HTL, **Spiro-OMeTAD** and **SOT-D** were separately dissolved in chlorobenzene at 75 mg/ml concentration. 30 µl of a stock solution of LiTFSI (170 mg/ml in acetonitrile) and tBP (20 µl) were added to the 1 ml HTL solutions to enhance their p-type conductivity. The HTL solutions were spin-coated on top of the perovskite films at 2000 rpm for 45 seconds, and allowed to dry inside the glovebox, before transferring them to the evaporation chamber for electrode deposition. Finally, the Au electrodes were deposited (thickness ~40 nm) by thermal evaporation under vacuum (~1.0×10^{-5} Pa) on top to complete the device stack.

2. References

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