Supporting information

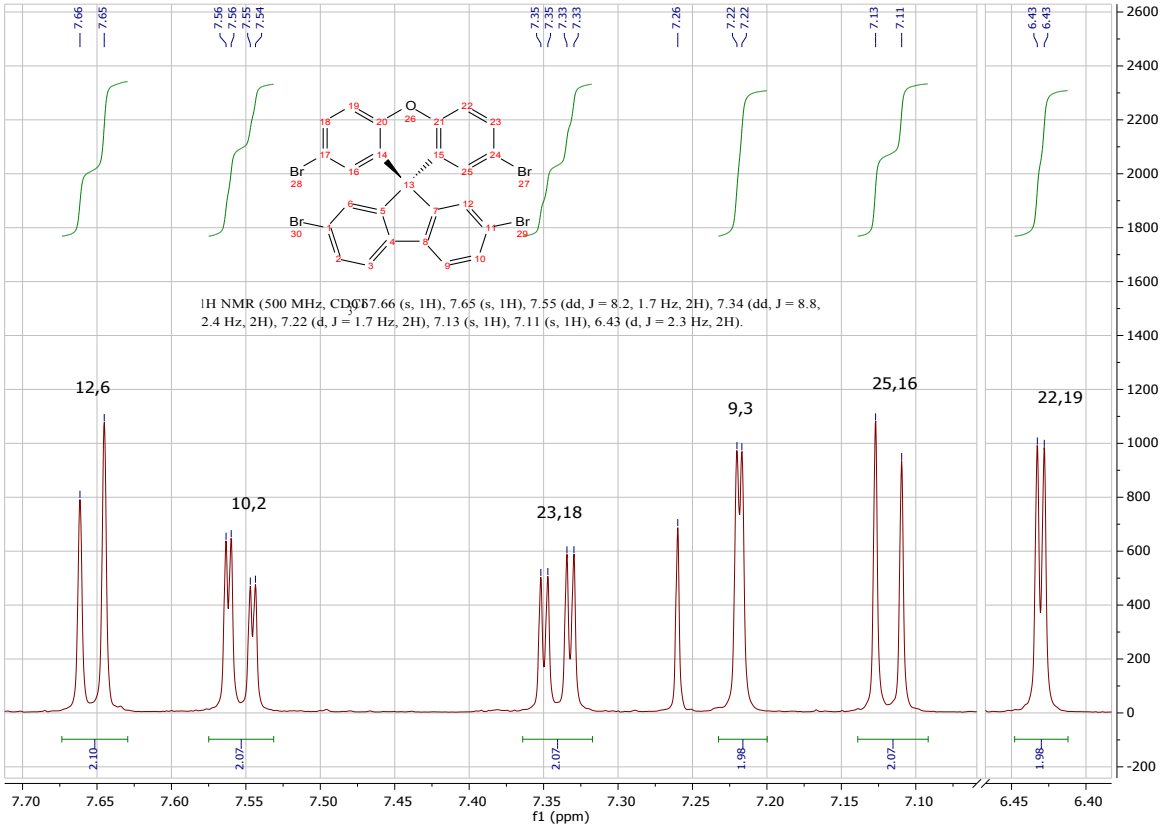
SFX as a Low-cost 'Spiro' Hole-Transport Material for Efficient Perovskite Solar Cells

Michal Maciejczyk[a], Aruna Ivaturi[a], Neil Robertson*[a]

[a]School of Chemistry and EaStCHEM, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, Scotland EH93JJ, UK

Contents

NMR spectra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7.13
7.11
6.43
6.43
Br
Br
Br
O
1H NMR (500 MHz, CDCl3) δ 7.66 (s, 1H), 7.65 (s, 1H), 7.55 (dd, J = 8.2, 1.7 Hz, 2H), 7.34 (dd, J = 8.8, 2.4 Hz, 2H), 7.22 (d, J = 1.7 Hz, 2H), 7.13 (s, 1H), 7.11 (s, 1H), 6.43 (d, J = 2.3 Hz, 2H).
12,6
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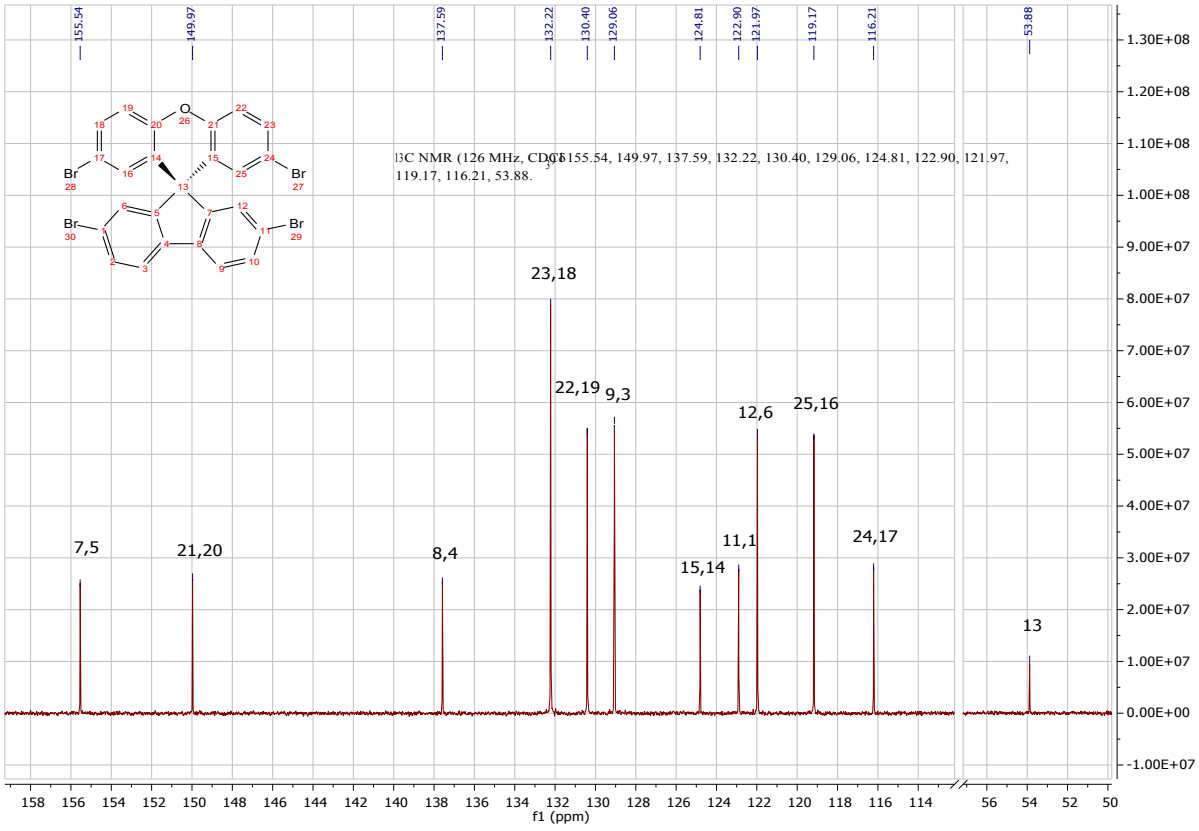
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Br
Br
O
13C NMR (126 MHz, CDCl3) δ 155.54, 149.97, 137.59, 132.22, 130.40, 129.06, 124.81, 122.90, 121.97, 119.17, 116.21, 53.88.
23,18
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21,20
8,4
15,14
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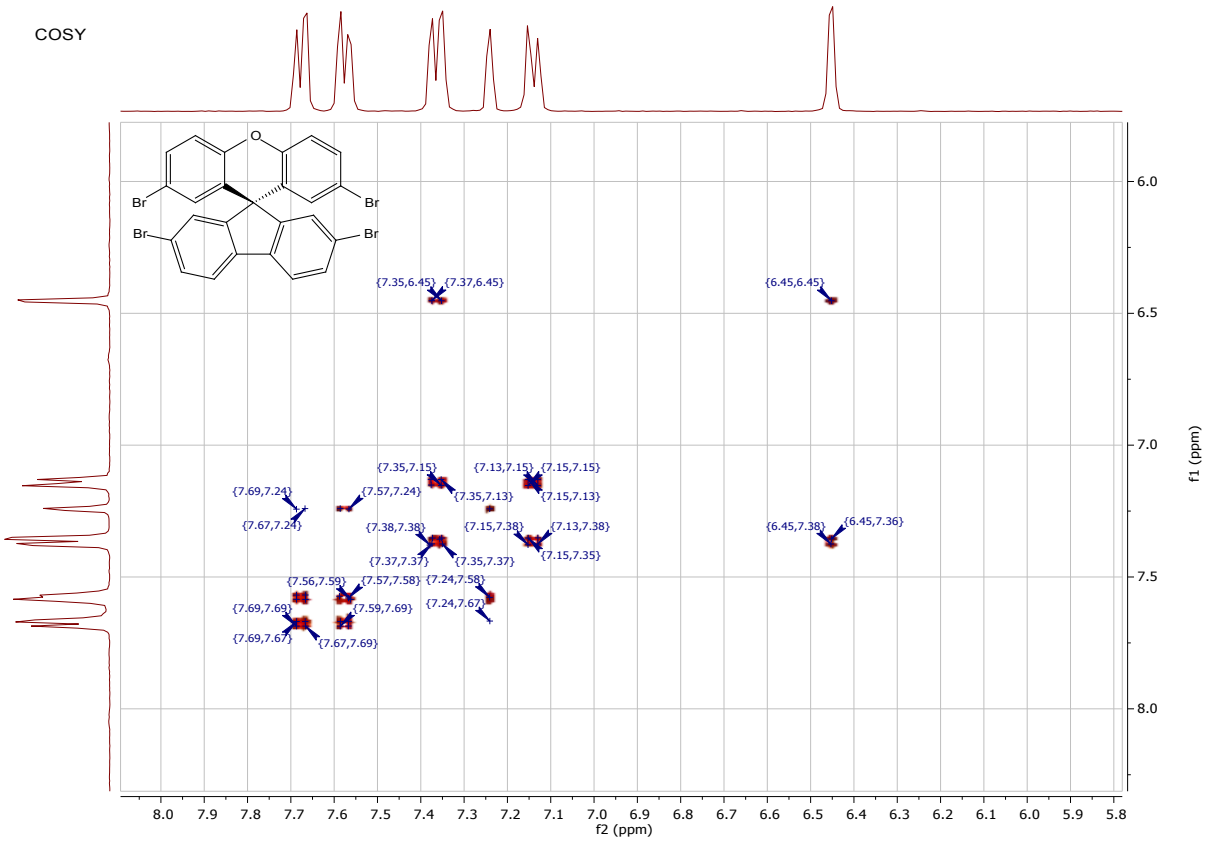
13
f1 (ppm)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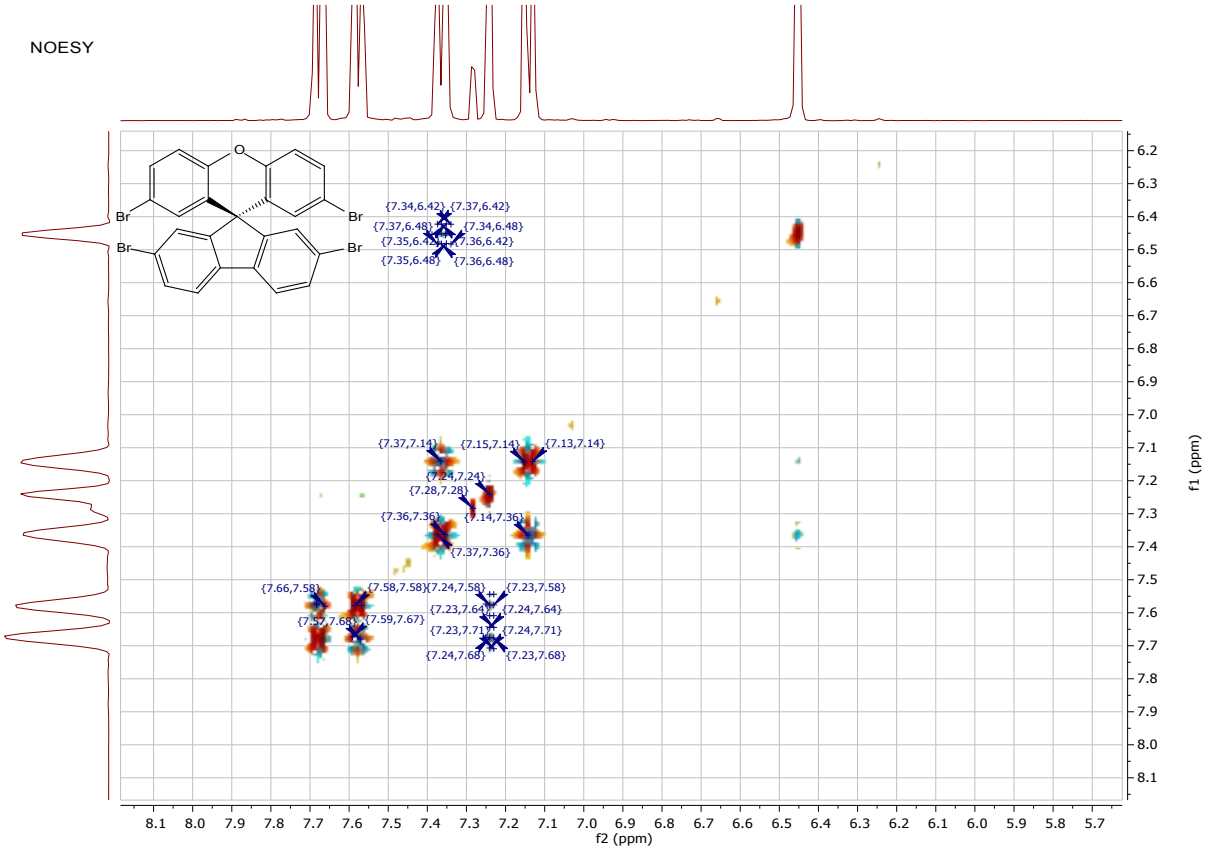
f1 (ppm)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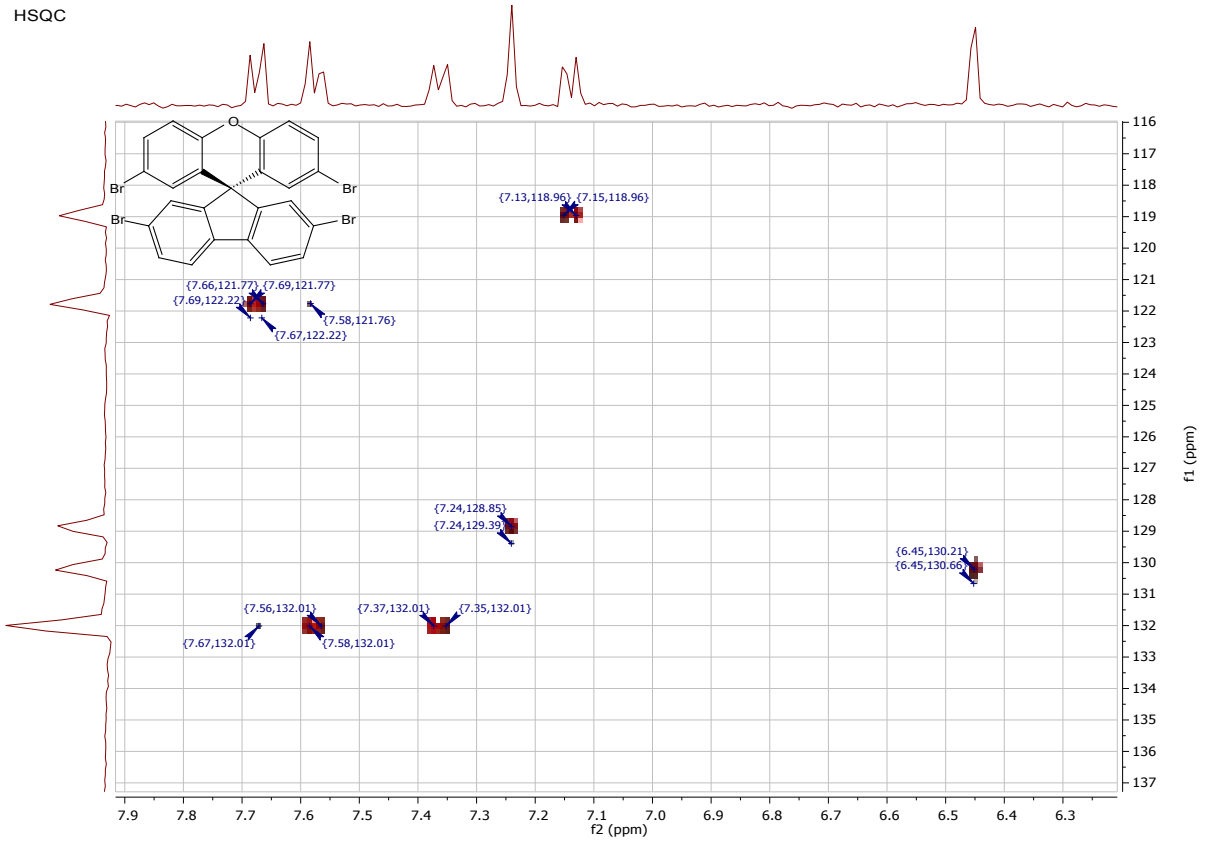
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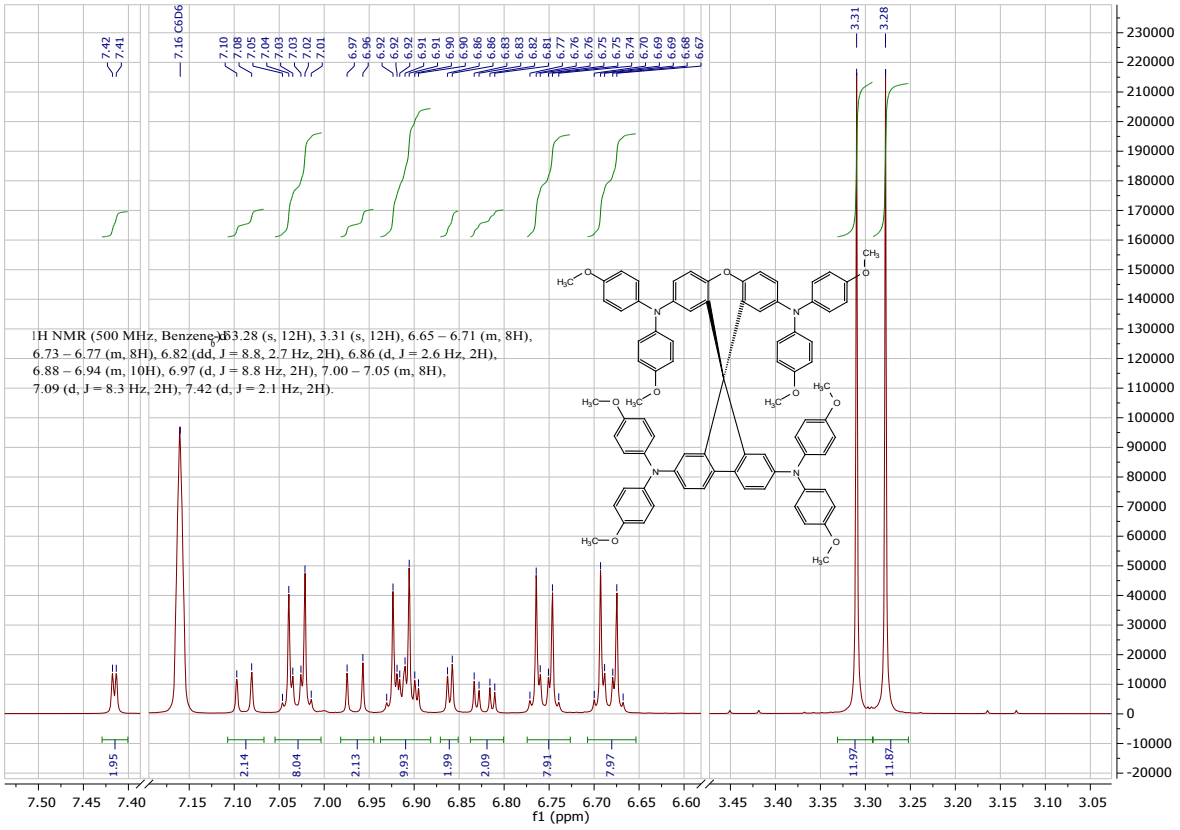
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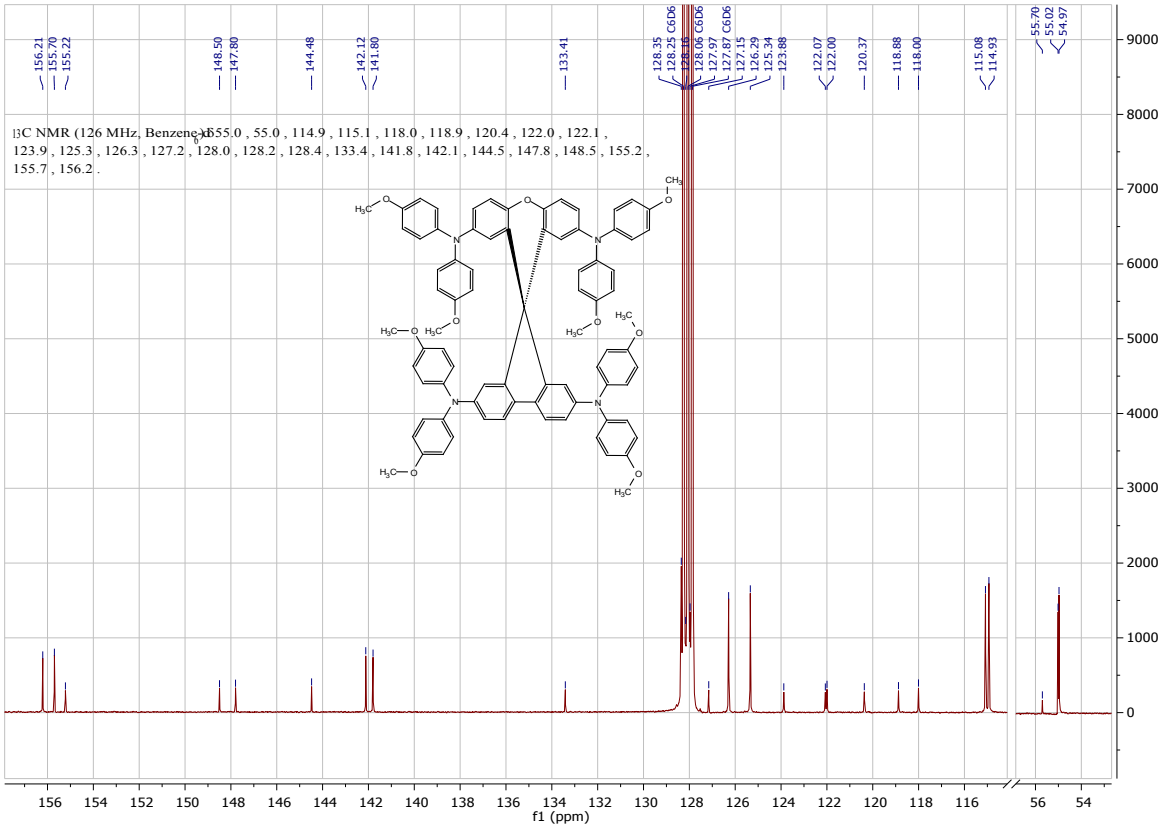
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127.87 C6D6
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118.88
118.00
115.08
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55.70
55.02
54.97
13C NMR (126 MHz, Benzene-d6) δ 55.0 , 55.0 , 114.9 , 115.1 , 118.0 , 118.9 , 120.4 , 122.0 , 122.1 , 123.9 , 125.3 , 126.3 , 127.2 , 128.0 , 128.2 , 128.4 , 133.4 , 141.8 , 142.1 , 144.5 , 147.8 , 148.5 , 155.2 , 155.7 , 156.2 .
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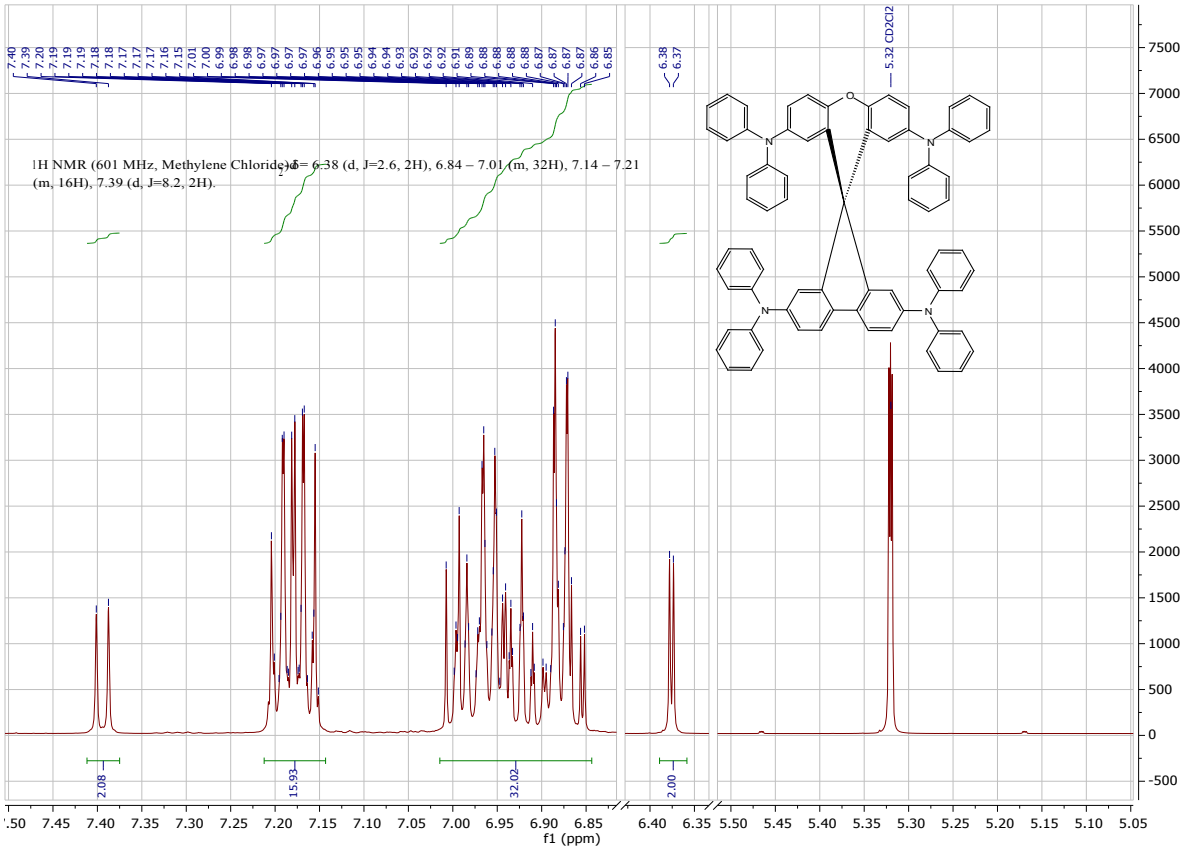
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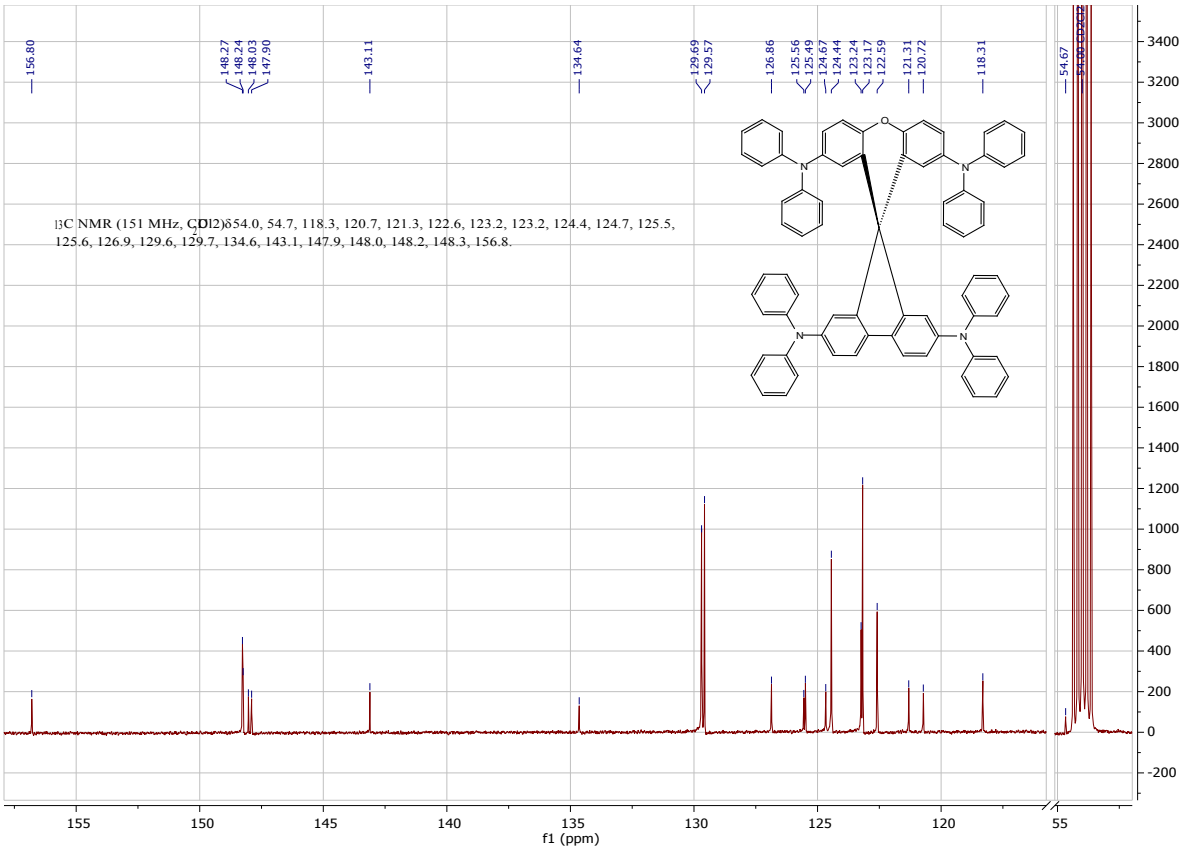
2.00
f1 (ppm)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124.44
123.24
123.17
122.59
121.31
120.72
118.31
54.67
54.00
CD2Cl2
13C NMR (151 MHz, CD2Cl2) δ 54.0, 54.7, 118.3, 120.7, 121.3, 122.6, 123.2, 123.2, 124.4, 124.7, 125.5, 125.6, 126.9, 129.6, 129.7, 134.6, 143.1, 147.9, 148.0, 148.2, 148.3, 156.8.
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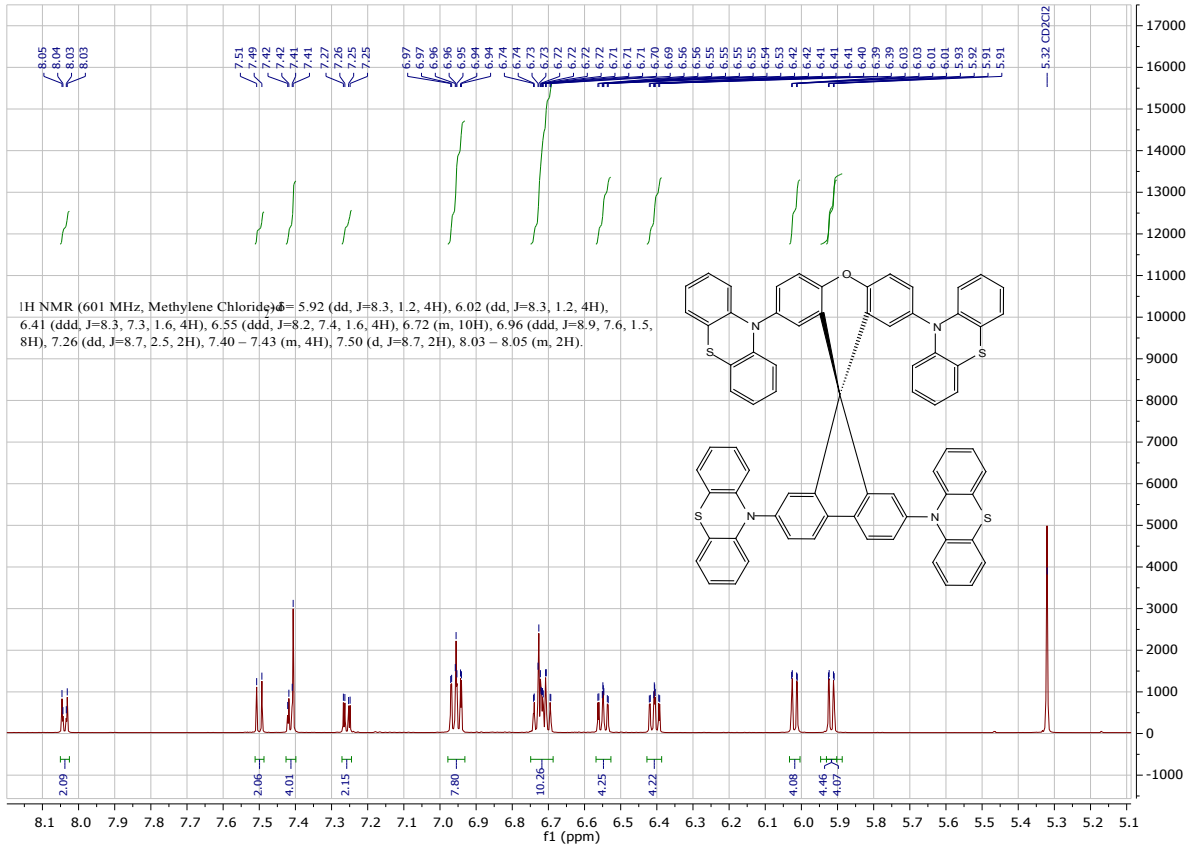
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6.03
6.01
6.01
5.93
5.92
5.91
5.91
5.32
CD2Cl2
1H NMR (601 MHz, Methylene Chloride-d2) δ 5.92 (dd, J=8.3, 1.2, 4H), 6.02 (dd, J=8.3, 1.2, 4H), 6.41 (ddd, J=8.3, 7.3, 1.6, 4H), 6.55 (ddd, J=8.2, 7.4, 1.6, 4H), 6.72 (m, 10H), 6.96 (ddd, J=8.9, 7.6, 1.5, 8H), 7.26 (dd, J=8.7, 2.5, 2H), 7.40 – 7.43 (m, 4H), 7.50 (d, J=8.7, 2H), 8.03 – 8.05 (m, 2H).
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4.08
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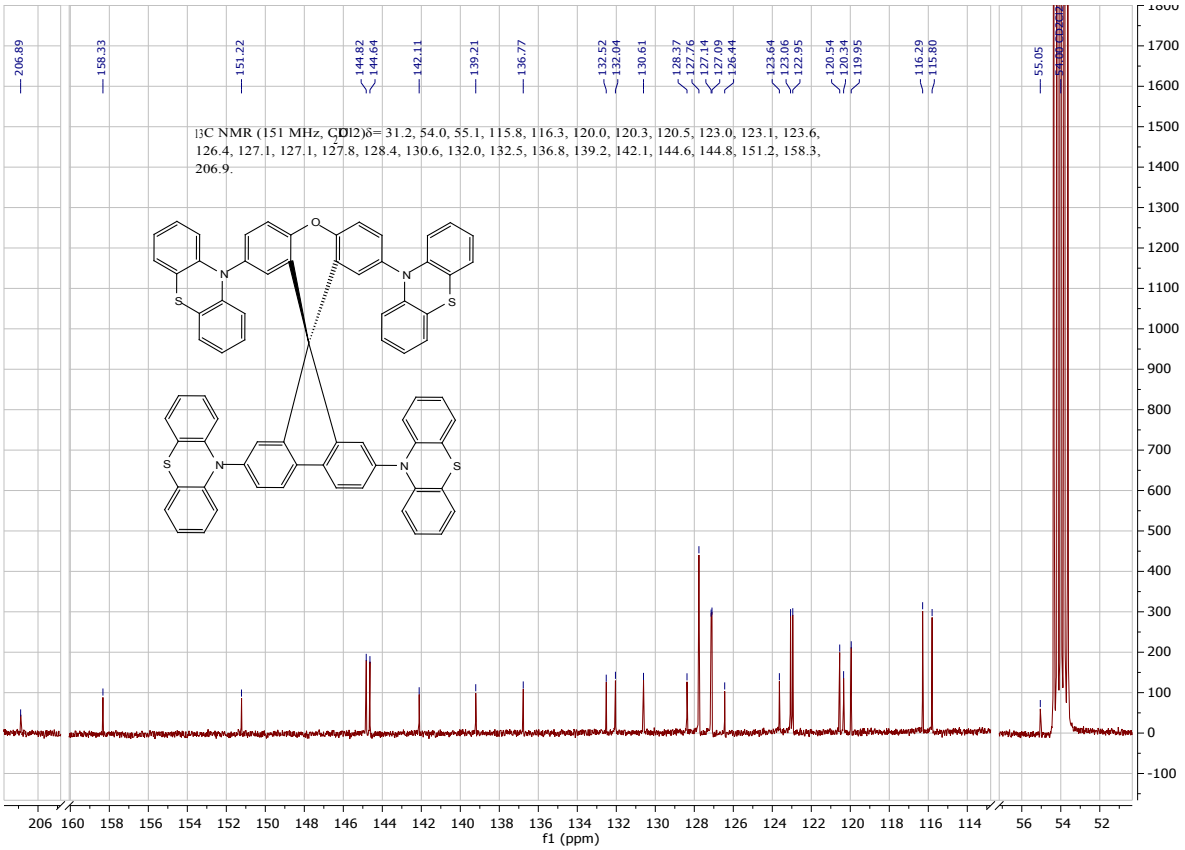
4.07
f1 (ppm)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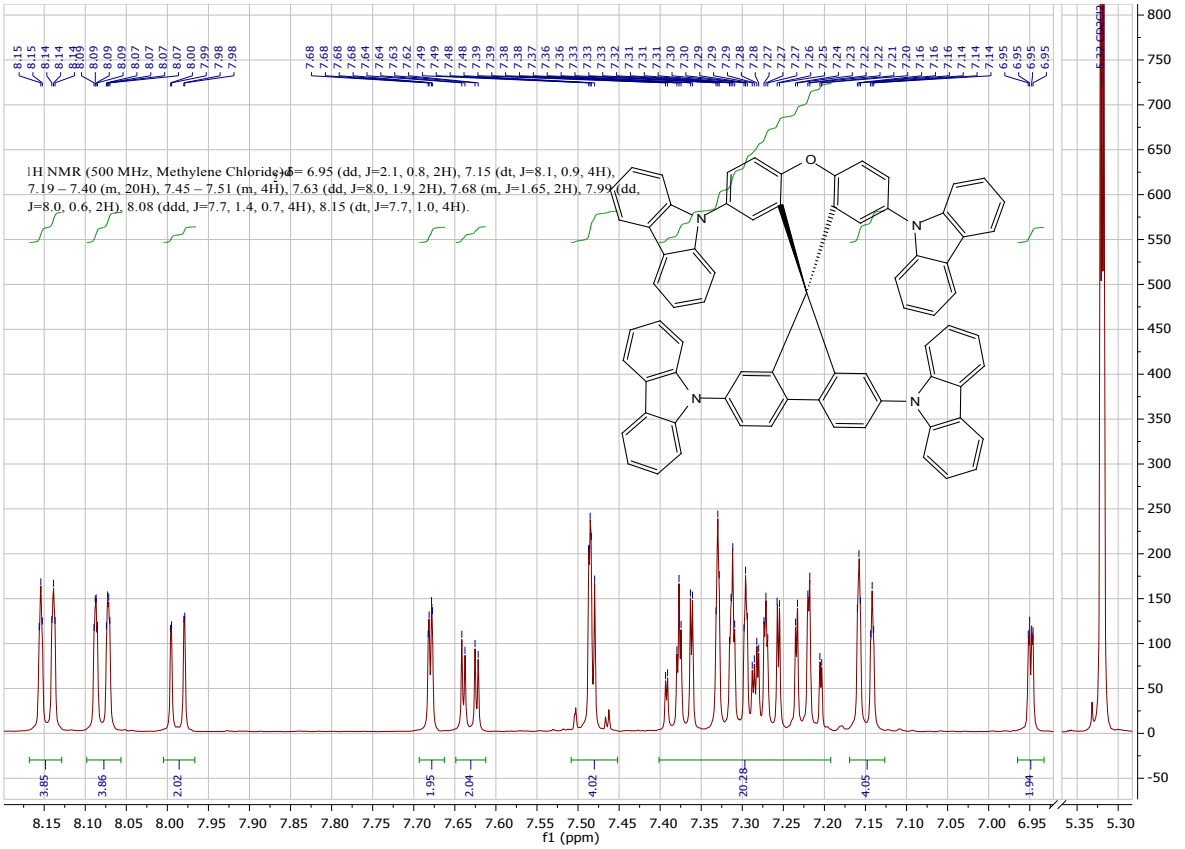
123.06
122.95
120.54
120.34
119.95
116.29
115.80
55.05
54.90
54.80
54.70
13C NMR (151 MHz, CD2Cl2) δ= 31.2, 54.0, 55.1, 115.8, 116.3, 120.0, 120.3, 120.5, 123.0, 123.1, 123.6, 126.4, 127.1, 127.1, 127.8, 128.4, 130.6, 132.0, 132.5, 136.8, 139.2, 142.1, 144.6, 144.8, 151.2, 158.3, 206.9.
f1 (ppm)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7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.16
7.14
6.95
1H NMR (500 MHz, Methylene Chloride-d2) δ= 6.95 (dd, J=2.1, 0.8, 2H), 7.15 (dt, J=8.1, 0.9, 4H), 7.19 – 7.40 (m, 20H), 7.45 – 7.51 (m, 4H), 7.63 (dd, J=8.0, 1.9, 2H), 7.68 (m, J=1.65, 2H), 7.99 (dd, J=8.0, 0.6, 2H), 8.08 (ddd, J=7.7, 1.4, 0.7, 4H), 8.15 (dt, J=7.7, 1.0, 4H).
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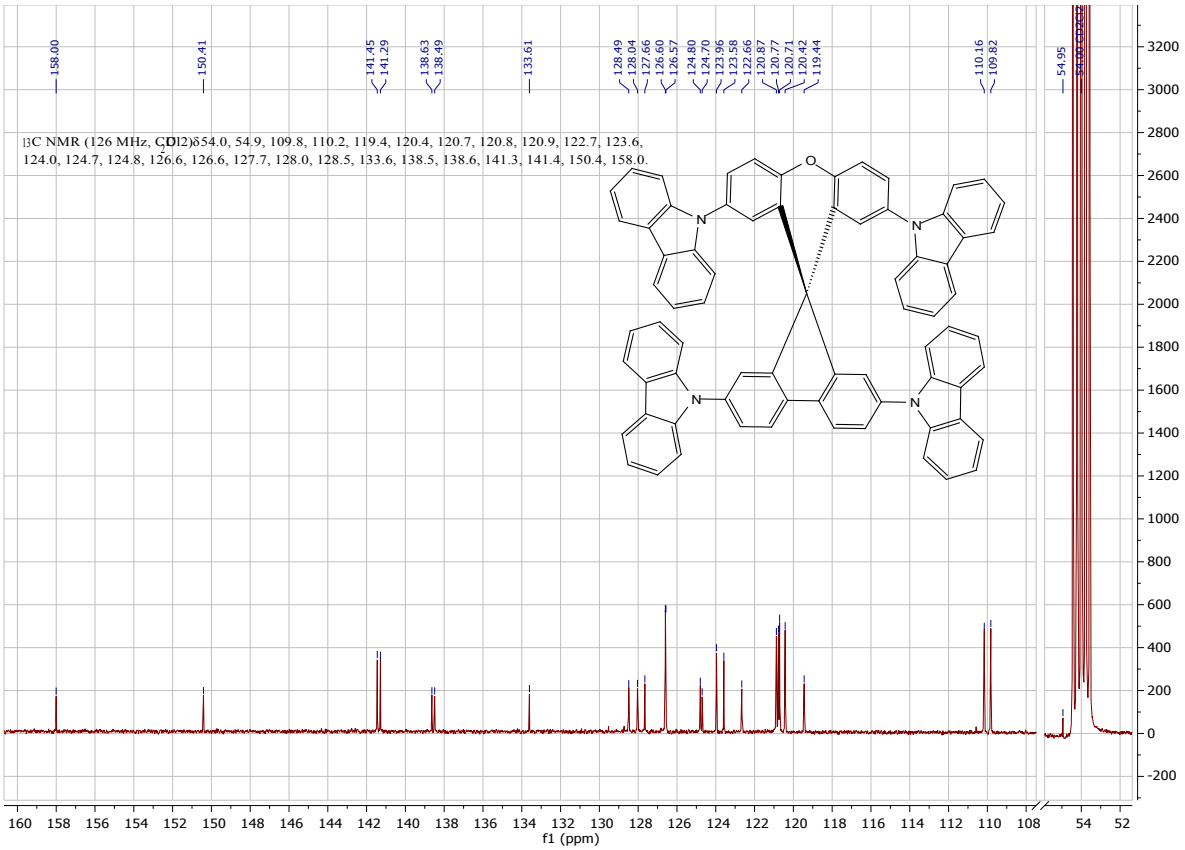
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120.77
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110.16
109.82
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54.84
54.79
13C NMR (126 MHz, CD2Cl2) δ54.0, 54.9, 109.8, 110.2, 119.4, 120.4, 120.7, 120.8, 120.9, 122.7, 123.6, 124.0, 124.7, 124.8, 126.6, 126.6, 127.7, 128.0, 128.5, 133.6, 138.5, 138.6, 141.3, 141.4, 150.4, 158.0.
O
N
N
N
N
f1 (ppm)

Cost estimation

Cost estimation of SFX-MeOTAD was adapted from Petrus et al.[1]

Table S1. Comparison of estimated materials cost for the synthesis of studied HTM and others.

HTM	Steps	Reagents ($/g)	Solvent ($/g)	Workup ($/g)	Cost ($/g)	Commercial price ($/g)
SBF	**3**				**34.83-43.88**	101.00-122.32
SFX	**1**	0.56	0	0.56	**1.09**	n/a
SFX-MeOTAD	**3**				**16.87**	n/a
Spiro-MeOTAD	6	6.14	2.06	83	91.67-108.43	170-475
EDOT-OMeTPA	4	5.73	1.42	2	9.57	n/a

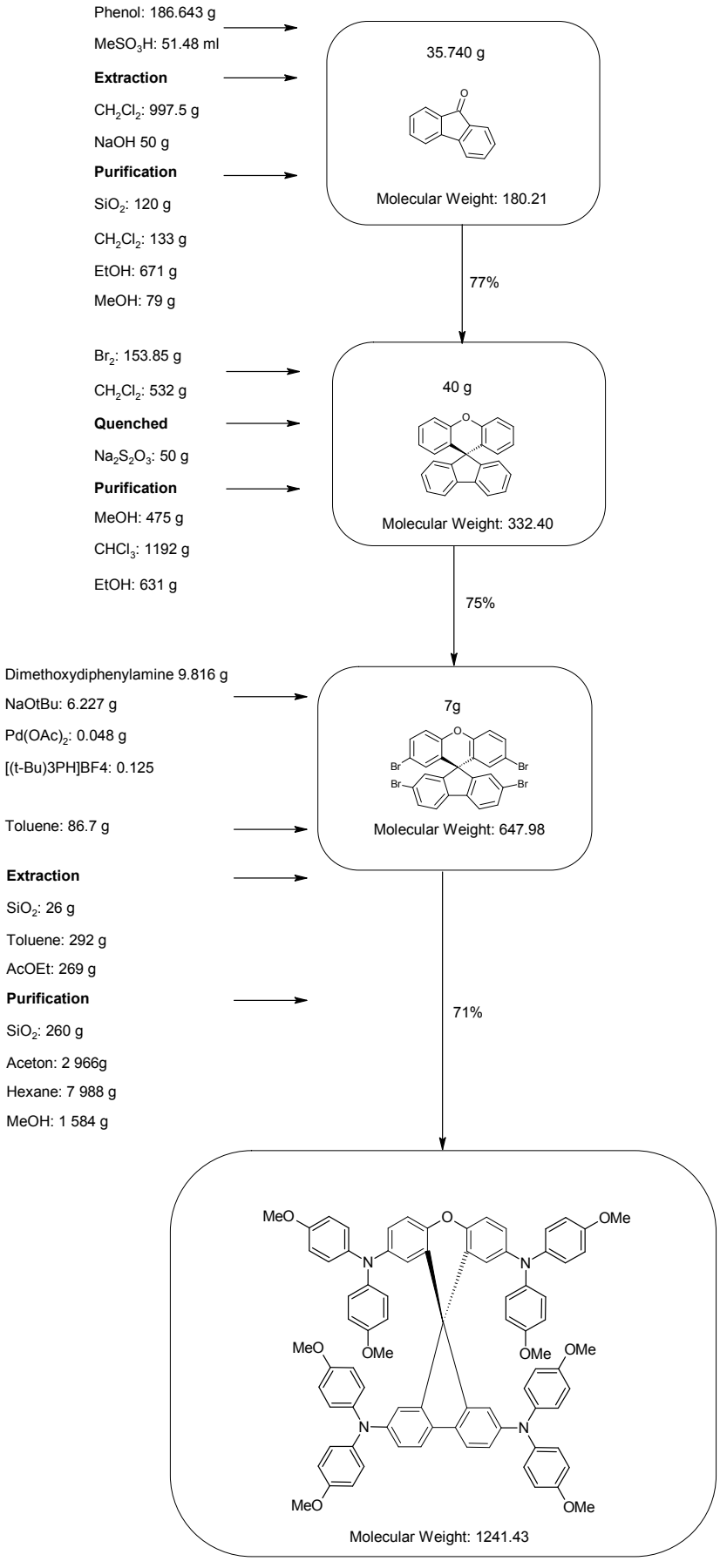

Figure S1. Flowchart describing the synthesis of 1 gram of SFX-MeOTAD.

Table S2. Materials quantities and cost for the synthesis of SFX.

Chemical name	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical ($/kg)	Material cost ($/g product)	Cost per step ($/step)
9-Fluorenone	35.740			162.72	0.11	1.09
Phenol	186.643			97.6	0.36	
$MeSO_3H$	76.190			60.50	0.09	
NaOH			50	19.42	0.019	
Dichloromethane			997.5	11.16	0.22	
Silica gel			120	66.41	0.16	
MeOH			79	2.21	0.003	
EtOH			671	9.53	0.13	

Table S3. Materials quantities and cost for the synthesis of SFXTBr.

Chemical name	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical ($/kg)	Material cost ($/g product)	Cost per step ($/step)
Bromine	153.85			44.33	0.12	0.44
Dichloromethane		532		11.16	0.10	
Na2S2O3			50	57.8	0.05	
MeOH			475	2.21	0.02	
Chloroform			1192	2.6	0.05	
Ethanol			631	9.53	0.10	

Table S4. Materials quantities and cost for the synthesis of SFX-MeOTAD.

Chemical name	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical ($/kg)	Material cost ($/g product)	Cost per step ($/step)
Sodium t-butoxide	6.227			277.30	0.18	15.34
$Pd(OAc)_2$	0.048			44 499.40	0.22	
Tri-tert-butylphosphonium tetrafluoroborate	0.125			24 500.00	0.32	
Dimethoxydiphenylamine	9.816			5 584.94	5.75	
Toluene		86.7		4.08	0.04	
Ethyl acetate			269	3.63	0.10	
$MgSO_4$			10	54.24	0.06	
Aceton			2 966	2.00	0.62	
Hexane			7 988	6.79	5.68	
Silica gel			286	66.41	2.00	
MeOH			1 584	2.21	0.37	

Cyclic voltammetries of SFX derivatives

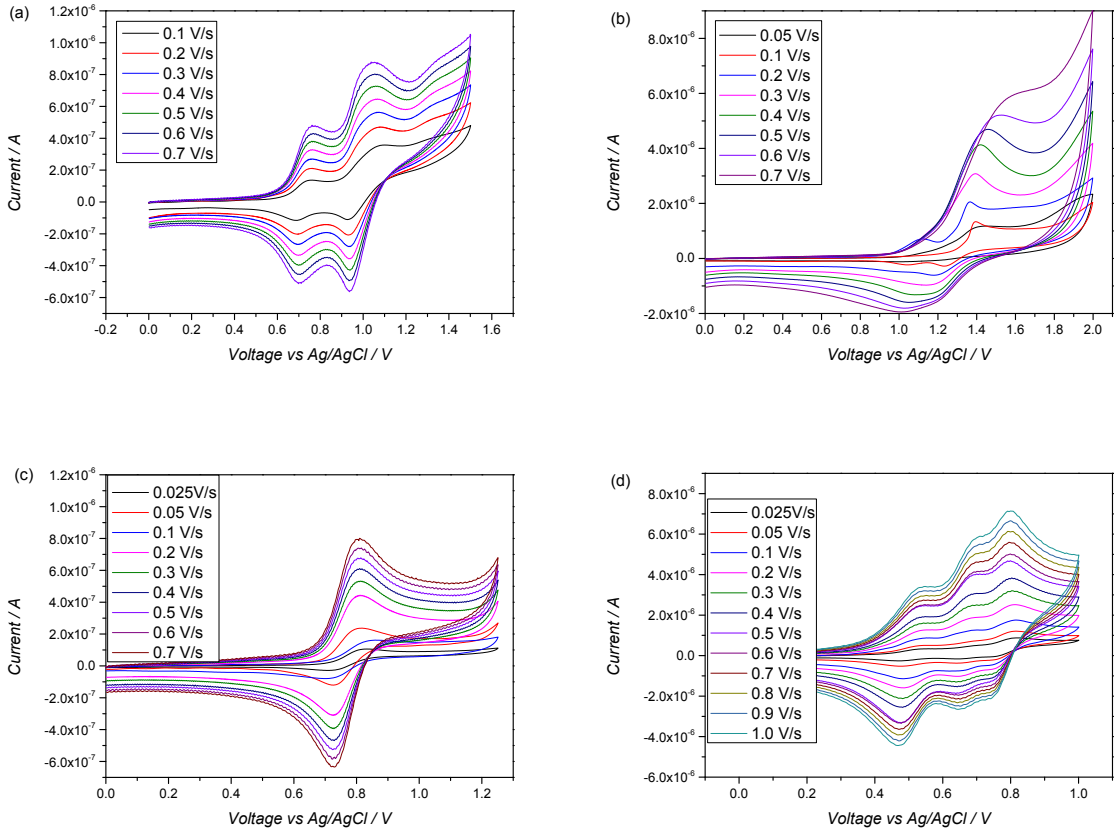

Figure S2. Cyclic voltammetry traces at different scan rates of (a) SFX-TAD, (b) SFX-TCz, (c) SFX-TPTZ and (d) SFX-MeOTAD.

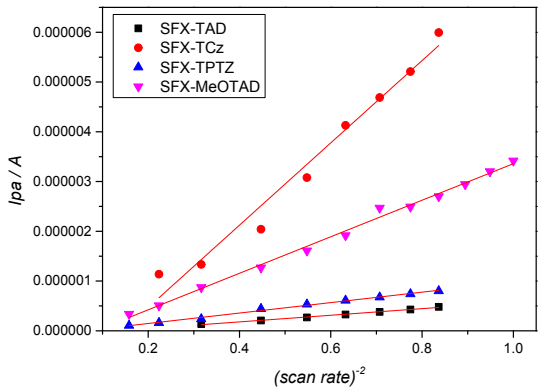

Figure S3. Plot of ipa (first) versus (scan rate)-2 for SFX-TAD (from 0.1 V/s to 0.7 V/s), SFXTCz (from 0.05 V/s to 0.7 V/s), SFX-TPTZ (from 0.025 V/s to 0.7 V/s) and SFX-MeOTAD (from 0.025 V/s to 1.0 V/s) from cyclic voltammograms.

Above plots illustrate that oxidation potentials are independent of scan rate SFX-TAD (R^2= 0.995), SFX-TCz (R^2= 0.970), SFX-TPTZ (R^2= 0.993) and SFX-MeOTAD (R^2= 0.994). Scan plots are consistent with the Radles-Sevcik; the anodic peak current increases with square root of the scan rate.

X-ray crystallography

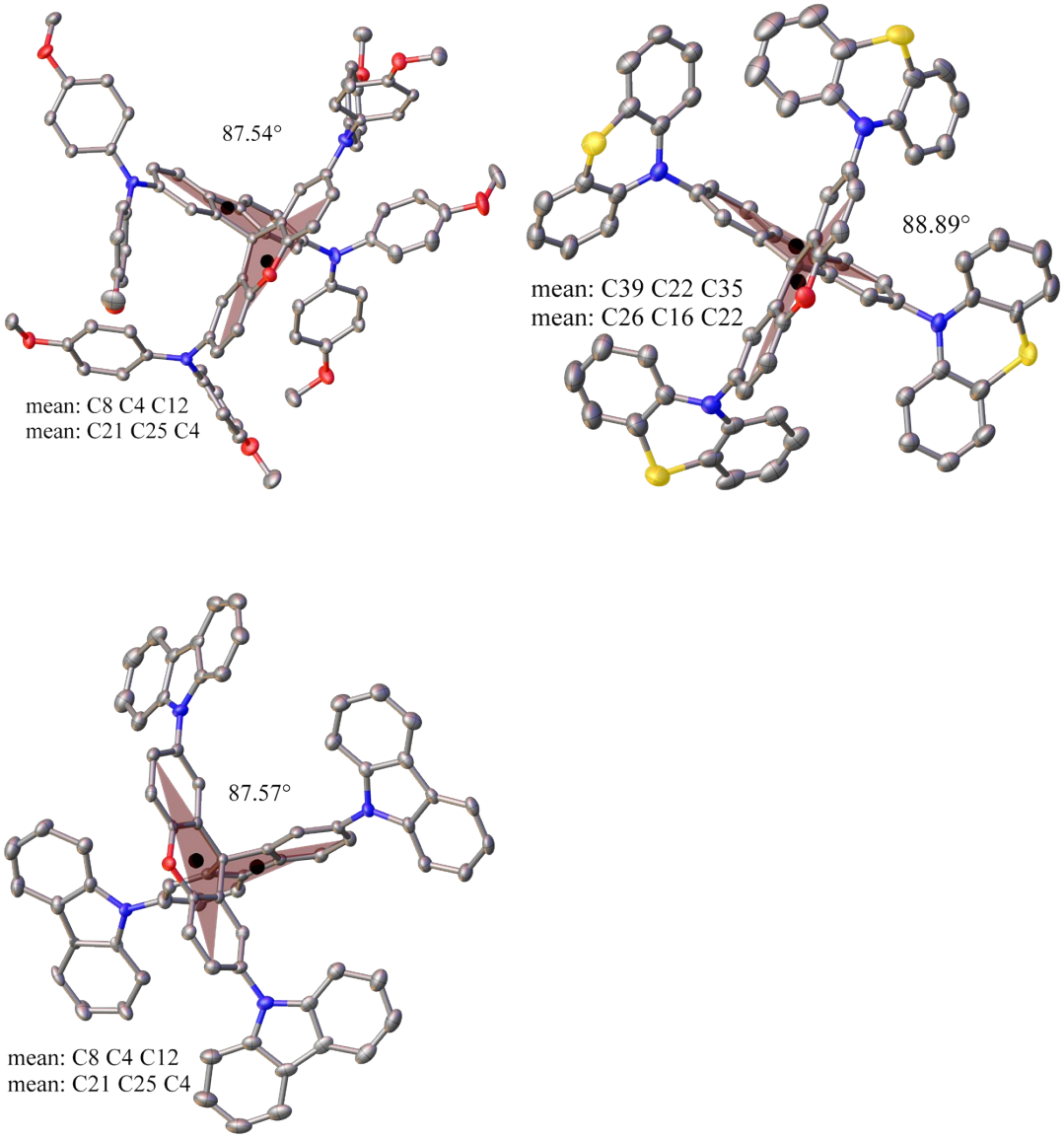

Figure S4. Dihedral angle of SFX-MeOTAD, SFX-TPTZ and SFX-TCz.

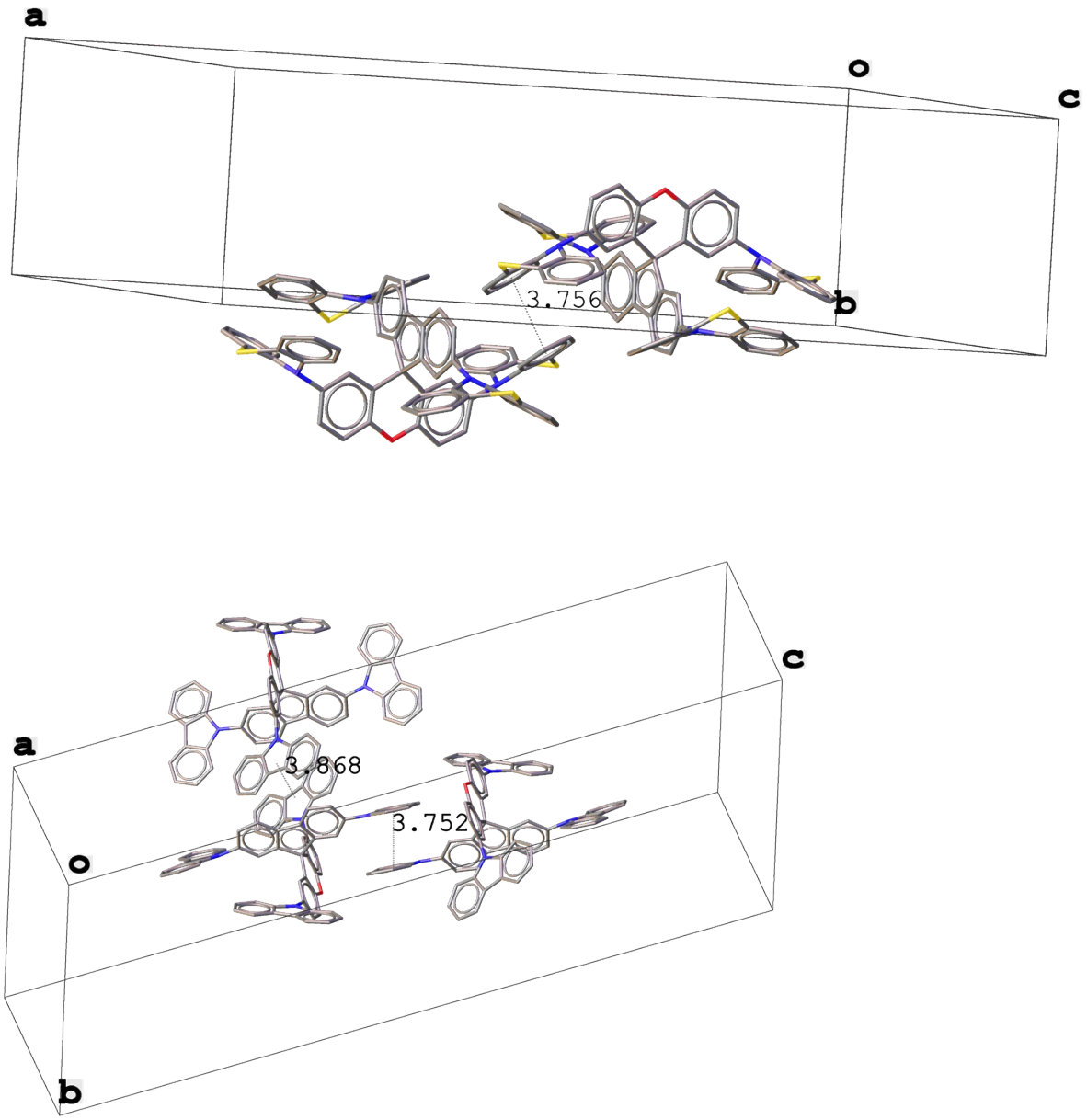

Figure S5. Crystal packing and π-π stacking of SFX-TPTZ (top) and SFX-TCz (bottom).

Table S5. Summary of X-ray crystallographic data for SFX-MeOTAD, SFX-TPTZ and SFX-TCz.

	SFX-MeOTAD	**SFX-TPTZ**	**SFX-TCz**
Chemical formula	$C_{81}H_{68}N_4O_9$	$C_{76}H_{51}N_4OS_4$	$C_{73}H_{44}N_4O$
Formula weight	1241.39	1164.44	993.12
Data collection	CrysAlisPro	CrysAlisPro	CrysAlisPro
Structure refinement	ShelXL	CrysAlisPro	CrysAlisPro
Colour, habit	colourless, block	colourless, block	colourless, prism
Crystal size (mm)	0.40×0.08×0.03	0.41×0.09×0.04	0.19×0.16×0.10
Space group	P-1	C2/c	Pbca
a (Å)	10.5201(3)	35.5400(14)	9.5612(2)
b (Å)	16.2972(4)	9.8814(2)	23.4614(4)
c (Å)	20.9582(6)	36.3474(14)	46.6024(10)
α (°)	68.652(2)	90	90
β (°)	80.004(2)	119.018(5)	90
γ (°)	71.759(2)	90	90
V (Å^3)	3171.31(16)	11162.3(8)	10453.8(4)
Z	2	8	8
ρ(calc.)(g cm^{-3})	1.300	1.386	1.262
μ (mm^{-1})	0.678	1.988	0.075
N° of rflen/unique	51866/13172	118201/11573	13284/13284
Θ range (°)	3.0 to 76.2	3.723 to 76.119	1.7 to 20.8
Compl. to Θ_{max} (%)	100	100	95.5
R_1	0.0609	0.0698	0.0916
wR_2	0.1668	0.1817	0.2673
GooF	1.037	1.042	1.039

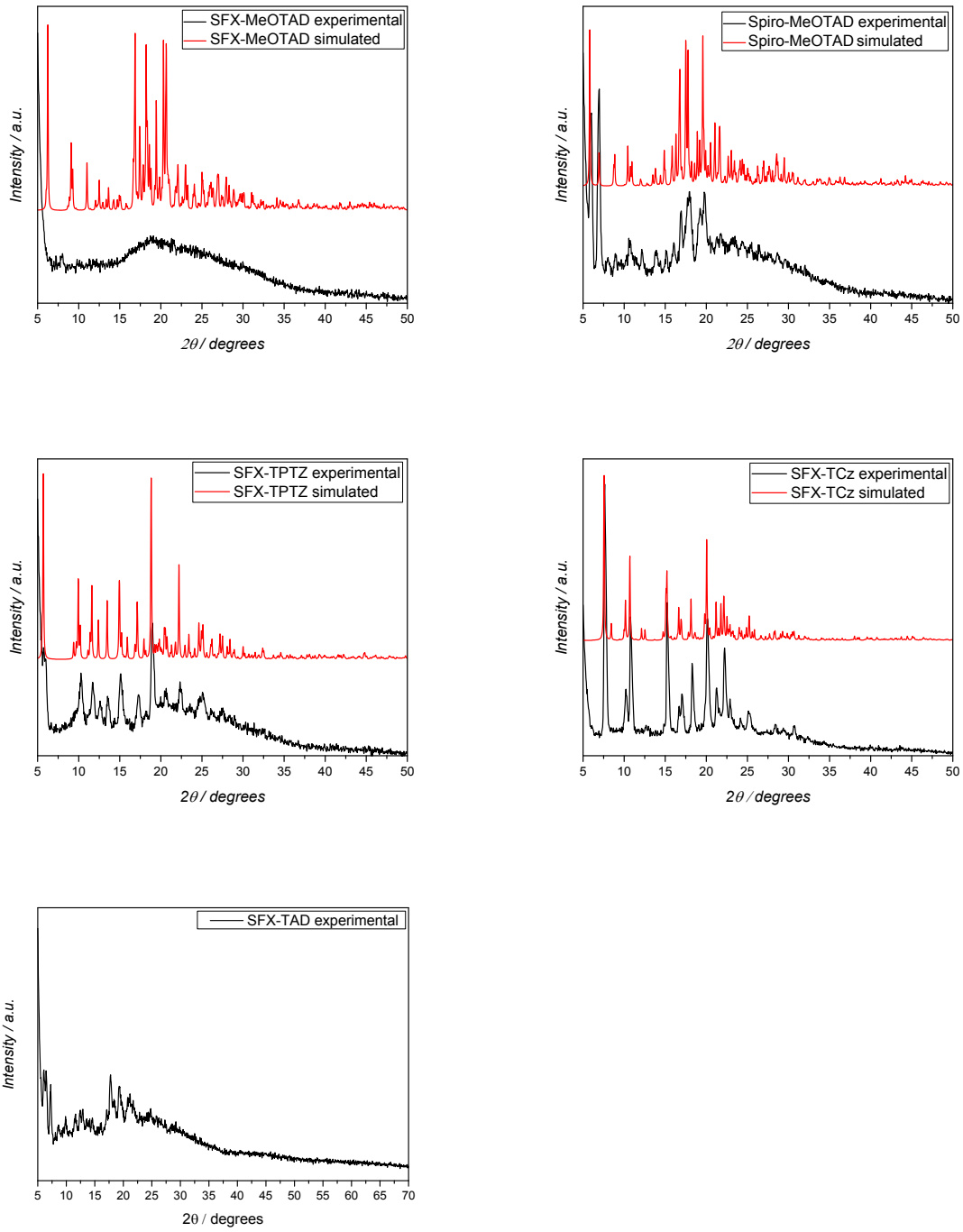

Figure S6. XRD powder patterns: simulated from single-crystal structures (red) and experimental (black).

Thermal properties

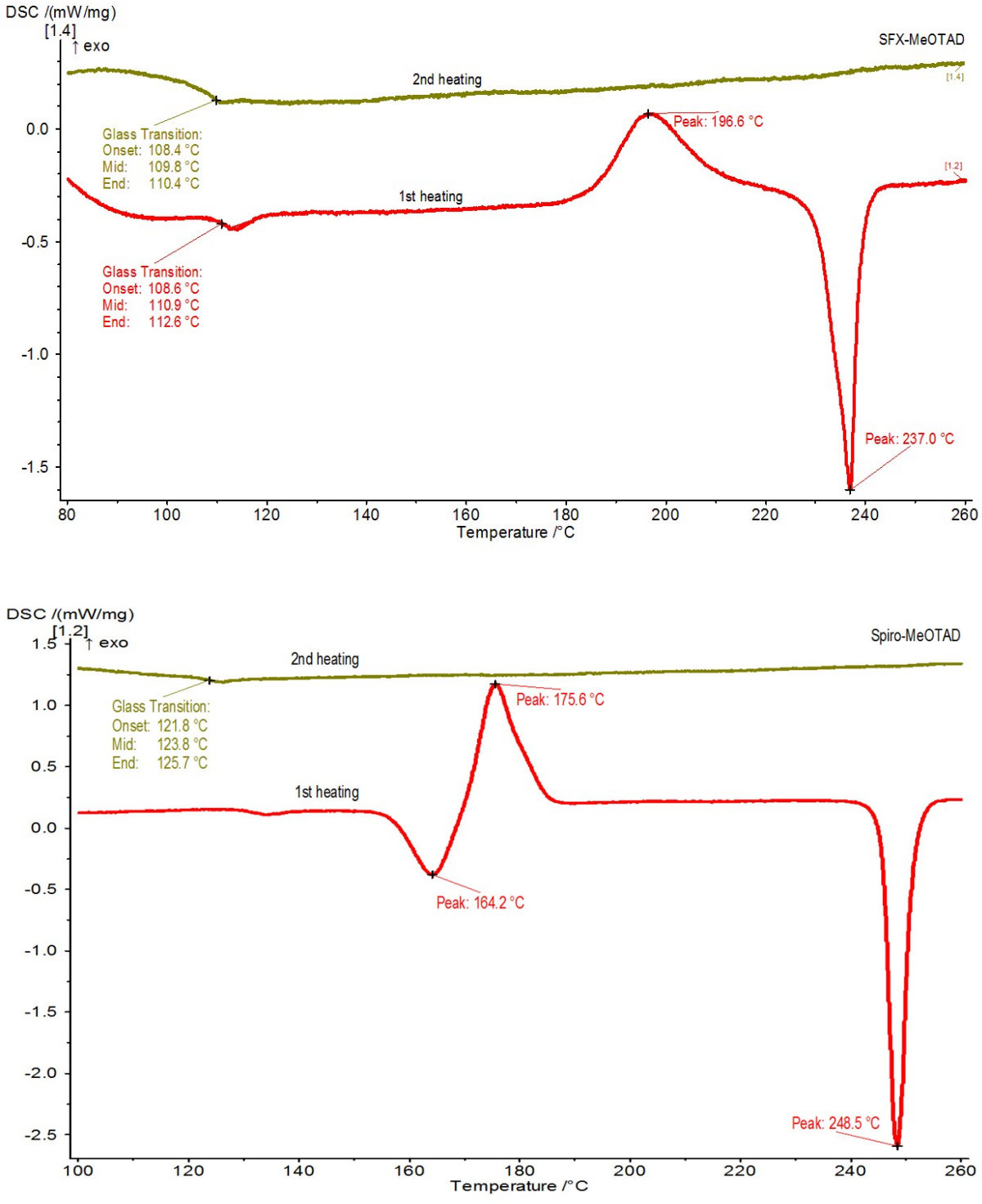

Figure S7. Differential scanning calorimetry of SFX-MeOTAD (top) and Spiro-MeOTAD (bottom).

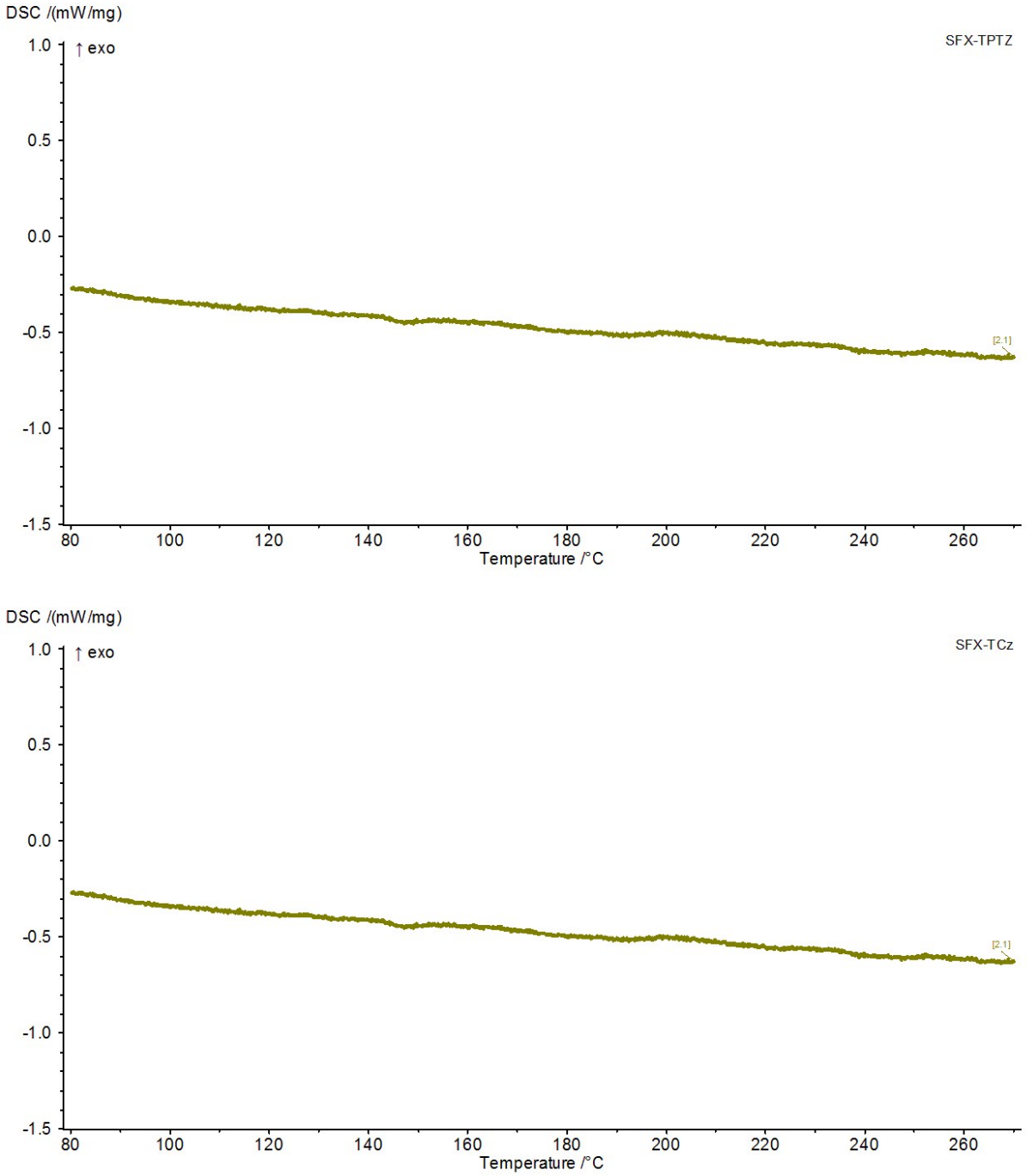

Figure S8. Differential scanning calorimetry curves of SFX-TPTZ (top) and SFX-TCz (bottom).

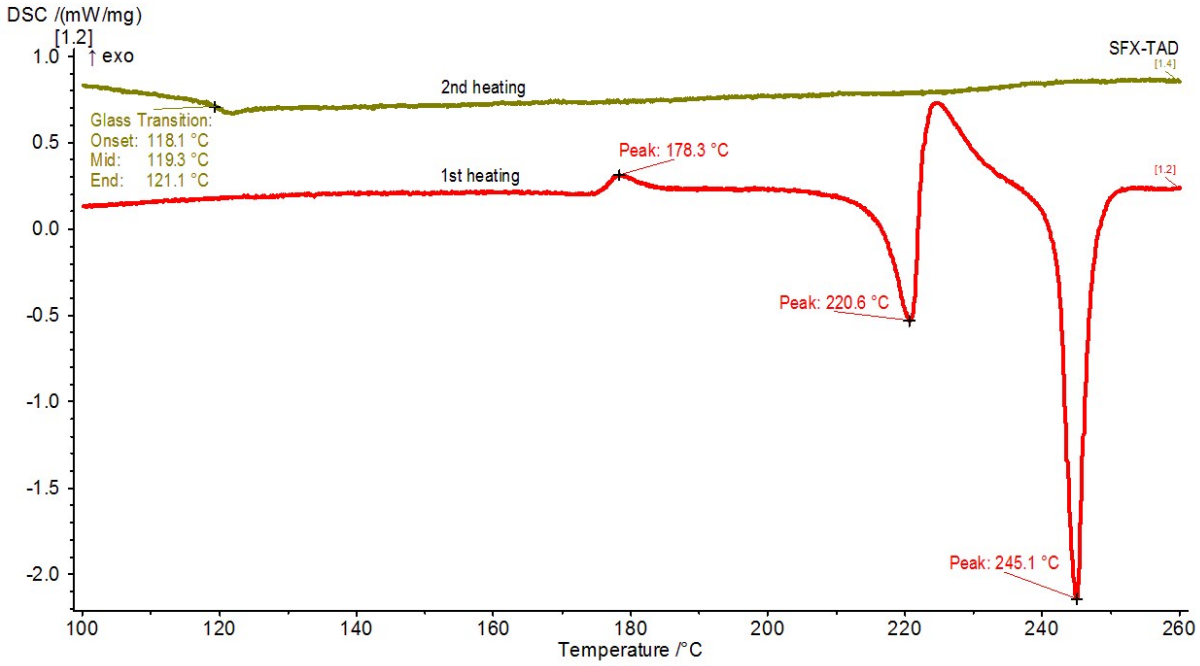

Figure S9. Differential scanning calorimetry curves of SFX-TAD.

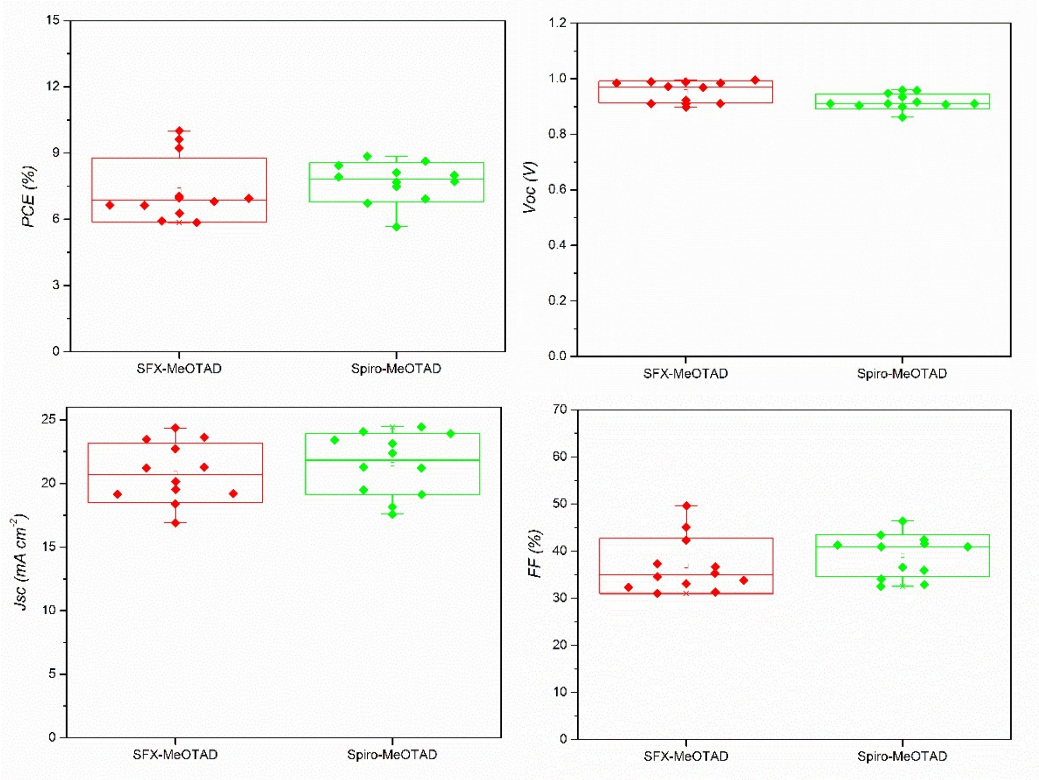
PCE (%)
Voc (V)
Jsc (mA cm^{-2})
FF (%)
SFX-MeOTAD
Spiro-MeOTAD

Figure S10. Box plot of photovoltaic parameters of PSCs with SFX-MeOTAD (left), and Spiro-MeOTAD (right) HTMS recorded using 0.05Vs-1 from short circuit to forward bias.

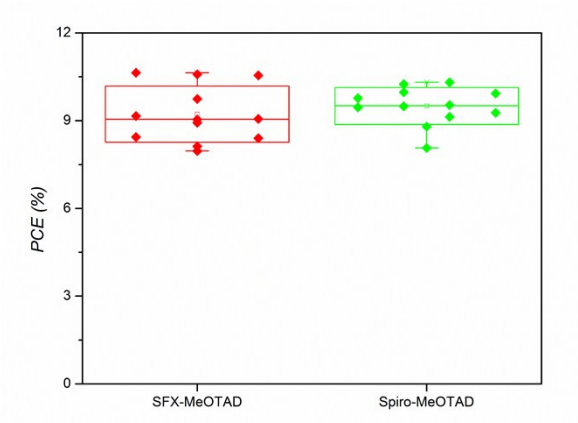

Figure S11. Box plot of average PCE (forward and reverse direction) of PSCs with SFX-MeOTAD (left), and Spiro-MeOTAD (right) HTMS recorded using 0.05Vs^{-1} scan speed.

Bibliography

1 M. L. Petrus, T. Bein, T. J. Dingemans and P. Docampo, *J. Mater. Chem. A*, 2015, **3**, 12159–12162.