

Supporting Information

Conjugated Oligomers with Alternating Heterocycles from a Single Monomer: Synthesis and Demonstration of Electroluminescence

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General Considerations

Abbreviations

aq	aqueous
ATR	attenuated total reflectance
br	broad (IR)
calcd.	calculated
δ	chemical shift in parts per million
COSY	correlated spectroscopy
DCM	dichloromethane
DSC	differential scanning calorimetry
DIPA	<i>N,N</i> -diisopropylamine
DMF	<i>N,N</i> -dimethylformamide
\bar{D}	dispersity
DEPT	distortionless enhancement by polarization transfer
d	doublet (NMR)
EI	electron impact
ESI	electrospray ionization
EtOAc	ethyl acetate
ϵ	extinction coefficient
GPC	gel permeation chromatography
GB	glovebox
HMBC	heteronuclear multiple bond coherence

HSQC	heteronuclear single quantum coherence
HOMO	highest occupied molecular orbital
HR-MS	high resolution mass spectrometry
ITO	indium tin oxide
IR	infrared spectroscopy
<i>i</i> PrOBpin	<i>i</i> sopropyl pinacol boronic ester
LUMO	lowest unoccupied molecular orbital
MALDI-TOF MS	matrix-assisted laser desorption ionization time-of-flight mass spectrometry
λ_{max}	maximum absorption wavelength
m	medium (IR)
mp	melting point
MeOH	methanol
MeOTf	methyl trifluoromethanesulfonate
m	multiplet (NMR)
<i>n</i> BuLi	<i>n</i> -butyllithium
NICS	nuclear independent chemical shift
NMR	nuclear magnetic resonance
ppm	parts per million
Ph	phenyl group
PL	photoluminescence
λ_{PL}	photoluminescence emission wavelength

PEDOT:PSS	poly(3,4-ethylenedioxythiophene) with polystyrene sulfonate
D	dispersity
OLED	Organic light emitting diode
RI	refraction index detector (GPC)
R	resolution (mass spectrometry)
R _f	retention factor
s	singlet (NMR)
SPS	solvent purification system
s	strong (IR)
THF	tetrahydrofuran
TMS	tetramethylsilane
TLC	thin layer chromatography
TGA	thermogravimetric analysis
TD-DFT	time dependent density functional theory
t	triplet (NMR)
Uv-vis	ultraviolet visible spectroscopy
w	weak (IR)

Chemicals and Solvents

All reactions were carried out using standard Schlenk techniques under a dry, inert nitrogen or argon atmosphere unless noted otherwise. Some reactions were performed in a nitrogen filled glovebox from Inert, Innovative Technology, Inc. Company (< 0.1 ppm O₂ and < 0.1 ppm H₂O). All dry solvents were taken from the solvent purification system (SPS), degassed by freeze-

pump-thaw cycles and stored under a nitrogen atmosphere unless noted otherwise. All chemicals were commercially available and were used without further purification unless noted otherwise.

Reagent	Supplier	Purity	Comments
Aluminum	Kurt J. Lesker	99.99%	
Acetonitrile	Sigma Aldrich	≥ 99.8%	
Ammonium chloride	Carl Roth	≥ 99.5%	
2-Bromophenol	ABCR	98%	
2-Bromopyridine-3-ol	Alfa Aesar	99%	
<i>n</i> BuLi	Acros Organics	N. A.	2.5 M or 1.6 M in hexanes
Carbon tetrabromide	Sigma Aldrich	99%	
<i>n</i> -Bromohexane	ABCR	97%	Degassed prior to use
Celite (SiO ₂)	Macherey Nagel		
Cesium fluoride	ABCR	99.9% (metal basis)	
DIPA	Sigma Aldrich	≥ 99.5%	Degassed prior to use
(SnMe ₃) ₂	ABCR GmbH	99%	
3- <i>n</i> -Hexylthiophene	TCI	> 98%	
Iodine	Applichem	Pure Ph. Eur.	
Iodohexane	Acros Organics Inc.	98	
<i>n</i> PrOBpin	Hoffman-La Roche	>95%	Degassed prior to use
ITO	Präzisions-Glas-Optik GmbH	Conductivity: 170 Ω, film thickness = 110 nm, Glass substrate thickness = 1.1 mm, η = 1.95	
LiF	Sigma Aldrich	99.99%	
NIS			
Magnesium sulfate	Grüssing	99%	

MeOTf	Chempur	96%	
Potassium carbonate	VWR Chemicals	≥ 99.5%	
PEDOT:PSS	Sigma Aldrich	2.8 wt % dispersion in water	Low- conductive grade
[Pd(PPh ₃) ₄]	TCI	> 97%	Stored in a freezer in a GB
[Pd(P(<i>t</i> Bu) ₃) ₂]	TCI	> 98%	Stored in a freezer in a GB
[Pd(dppf)Cl ₂]	Sigma Aldrich	n.a.	
Silver nitrate	ABCR GmbH	99%	
Sodium carbonate	VWR Chemicals	N.a.	ACS, Reag. Ph. Eur.
Sodium hydrogen carbonate	VWR Chemicals	N.a.	ACS, Reag. Ph. Eur.
Sodium chloride	Grüssing	99%	ACS, Reag. Ph. Eur.
Sodium sulfate	VWR Chemicals	N.a.	ACS, Reag. Ph. Eur.
Sodium thiosulfate	Grüssing	97%	
Tetrabutylammonium hexa-fluorophosphate.	Sigma Aldrich	≥ 99.0%	
1,3,5-trimethoxybenzene	ABCR	98%	

Table SI- 1. List of suppliers and of the purity of the chemicals used in this work.

Solvent	Comments
Acetic acid	Alfa Aesar, 99+%
Chloroform	VWR Chemicals; ACS, Reag. Ph. Eur.
Chloroform deuterated	Eurisotop
Dichloromethane	VWR Chemicals; for HPLC; dry from the SPS
Diethyl ether	VWR Chemicals; for HPLC; dry, distilled from sodium / benzophenone
<i>N,N</i> -Dimethylformamide	Extra dry from Acros Organics; 99.8%
Ethyl acetate	VWR Chemicals; ACS, Reag. Ph. Eur.
<i>n</i> -Hexane	VWR Chemicals; ACS, Reag. Ph. Eur.
Hydrochloric acid	VWR Chemicals; ACS, Reag. Ph. Eur.
Methanol	VWR Chemicals; ACS, Reag. Ph. Eur.
Tetrahydrofuran	VWR Chemicals; for HPLC; dry from the SPS and degassed
Toluene	VWR Chemicals; for HPLC; dry, from the SPS and degassed

Table SI- 2. List of suppliers and purity of used solvents.

Analyses

^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, $^{11}\text{B}\{^1\text{H}\}$ NMR and $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker Avance Neo 500 (for isolated compounds and reaction monitoring experiments) All ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR were referenced against the solvent residual proton signals (^1H), or the solvent itself (^{13}C). $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectra were calculated based on the ^1H NMR spectrum of TMS. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were referenced against $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CDCl_3 . All chemical shifts δ are given in parts per million (ppm) and all coupling constants J in Hz. The exact elucidation of the compounds was proved by ^1H , ^{13}C DEPT and two-dimensional NMR spectroscopy such as ^1H COSY, $^{13}\text{C}\{^1\text{H}\}$ HSQC or $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ HMBC when possible.

Electron impact (EI) ionization mass spectra were recorded on the double focusing mass spectrometer MAT 95+ or MAT 8200 from FINNIGAN mat. Samples were measured by direct inlet or indirect inlet method with a source temperature of 200° C. The ionization energy of the electron impact ionization was 70 eV. All signals were reported with the quotient from mass to charge m/z . Accurate masses were determined via the peak-matching method. The resolution

(R) of the peak-matching performance was 10 000. The calculated isotopic distribution for each ion agreed with experimental values.

High-resolution accurate-mass electrospray ionization (ESI) spectra were recorded on a Bruker Daltonics microTOF II mass spectrometer. High resolution accurate-mass MALDI mass spectra and MALDI MS analysis of the oligomers **O1** and **O2** were recorded on a Bruker Daltonics ultrafleXtreme TOF/TOF mass spectrometer using graphite as the matrix.

IR spectra were recorded on a NICOLET Thermo IS10 SCIENTIFIC IR spectrometer with a diamond-ATR-unit. The resolution was 4 cm⁻¹. Relative intensities of the IR bands were described by s = strong, m = medium or w = weak.

All melting points were measured with a BÜCHI Melting Point M-560 using a heating ramp of 5 K / min.

Thin layer chromatography (TLC) was carried out on aluminum plates coated with silica gel 60 F₂₅₄ with a layer thickness of 0.2 mm from Fluka or Macherey-Nagel. All bands were detected by using a fluorescent lamp (254 nm and 366 nm). Column chromatography was carried out by using the column machine PuriFlash 4250 from Interchim. Silica gel columns of the type PF-15SiHP-F0012, PF-15SiHP-F0025, PF-50SiHP-JP-F0080, PF-50SiHP-JP-F0120, and PF-50SiHP-JP-F0220 were used. The injection of the sample was made via dry load. The column material of the dry load was Celite 503 from Macherey-Nagel.

The molecular weight and molecular weight distribution of all synthesized polymers were determined using a PSS GPC/SEC system 1260/1290. The system was equipped with three PSS-SDV high combination columns (styrene-divinylbenzene copolymer network) with a molecular range from 100-3000 kDa, a refractive index detector (SECurity RID Article Nr. 404-0106), a diode array detector (SECurity DAD Article Nr. 404-0110), a viscometer detector (DVD 1260 Article Nr. 404-0025) and a Light Scattering Detector with 3D spectra option (SECcurity Multichrom SLD 1000 Article Nr. 404-0196). The columns were heated at 35 °C with a column thermostat (SECcurity TCC6000). THF (HPLC grade without stabilizer) was used as an eluent. The measurements were recorded at 35° C under an eluent flow of 1 mL/min. The apparatus was calibrated using polystyrene standards (PSS) under a conventional calibration.

The electrochemical studies were carried out under argon using an Eco Chemie Autolab PGSTAT 30 potentiostat for cyclic voltammetry with the three-electrode configuration: the working electrode was a platinum disk; the reference electrode was a saturated calomel electrode and the counter-electrode was a platinum wire. All potentials were

internally referenced to the ferrocene / ferrocenium couple. For the measurements, concentrations of 10^{-3} M of the electroactive species were used in freshly distilled and degassed dichloromethane and 0.2 M tetrabutylammonium hexafluorophosphate as the electrolyte.

Uv-vis measurements were recorded on a Jasco spectrometer model V-630, with dichloromethane as a solvent. Extinction coefficients were deduced from Uv-vis spectra measured at six different concentrations for each oligomer. The concentration was calculated based on the molecular weights calculated by MALDI measurements.

The solid state Uv-vis spectra of **O2** were recorded with a resolution of 0.1 nm on a UV-2700v- from Shimadzu with a double monochromator.

Fluorescence measurements were recorded on a Photon Technology International spectrometer with a lamp power supply LPS-220B, Motor Driver MD-5020 and 1 Photomultiplier 814. Dichloromethane was used as a solvent.

TGA measurements were performed on a Mettler Toledo DSC 3/TGA + STAR system using aluminum crucibles and under a flow of nitrogen of 20 mL/min with a temperature ramp of 10 K/min.

DSC measurements were performed on a Mettler Toledo DSC 3+ STAR system using aluminum pans, under nitrogen atmosphere and a temperature ramp of 10 K/min.

Microwave Apparatus

All microwave irradiation reactions were carried out on a Biotage® Initiator+ SP Wave synthesis system, with continuous irradiation power from 0 to 300 W. All reactions were carried out in 5 or 20 mL oven-dried Biotage microwave vials sealed with an aluminum/Teflon® crimp top, which can be exposed to a maximum of 250 °C and 20 bar internal pressure. The reaction temperature was measured by an IR sensor on the outer surface of the process vial.

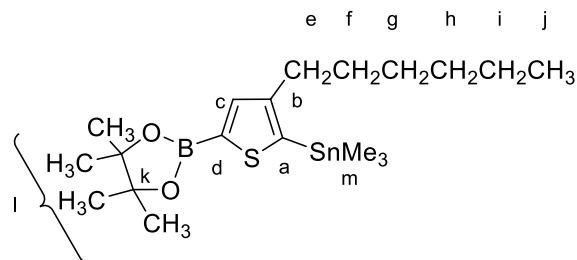
Characterizations of the OLED-type devices

The I-V characterization of the OLEDs was performed with Keithley 2400 Source measurement unit, a calibrated photodiode and an Avantes AvaSpec-2048 USB spectrometer.

The absorption spectra of the OLED-type devices were recorded on a PerkinElmer Lambda 650 spectrometer and the photoluminescence spectra were recorded on an Avantes AvaSpec-2048 USB spectrometer.

Syntheses

(3-Hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylstannane (7)



This procedure was adapted from the literature.^[1]

In a GB, a solution of 2-(4-hexyl-5-iodothiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (848 mg, 2.02 mmol), [Pd(PPh₃)₄] (120 mg, 0.10 mmol, 5 mol%,) and (SnMe₃)₂ (737 mg, 2.24 mmol) in toluene (5 mL) was transferred in a microwave vial. The mixture was heated to 120 °C in a microwave apparatus for 30 min. After allowing the mixture to cool to ambient temperature, water (10 mL) was added to the reaction mixture and it was extracted with DCM (3 x 15 mL) and washed with brine (2 x 10 mL). The combined organic layers were dried over MgSO₄, filtered, and the solvent was removed *in vacuo*. The residue was diluted in *n*-hexane (10 mL) and filtered over celite. The volatiles were removed *in vacuo* to afford an orange oil in a yield of 850 mg (92%, 1.86 mmol).

¹H NMR (500 MHz, CDCl₃) δ = 7.61 (s, 1H, c), 2.62 (dd, ³J = 10.6, 5.0 Hz, 2H, e), 1.67 – 1.54 (m, 2H, f), 1.32 – 1.28 (m, 18H, g/h/i/l), 0.94 – 0.83 (m, 3H, j), 0.37 (s, 9H, m) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃) δ = 152.3 (b), 141.2 (a), 138.9 (c), 83.9 (k), 32.3 (f), 31.9 (e), 32.2, 31.7, 29.5, 22.7 (g/h/i/l), 24.9 (k), 14.2 (j), -7.9 (l) ppm.¹

¹¹⁹Sn{¹H} NMR (187 MHz, CDCl₃): δ = -35.70 ppm.

¹¹B{¹H} NMR (160 MHz, CDCl₃): δ = 28.71 ppm.

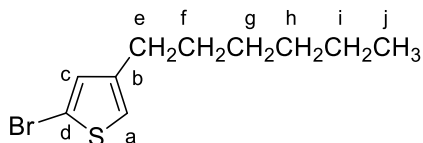
IR (ATR): ν = 2977 (w), 2926 (m), 1526 (m), 1123 (m), 1369 (m), 1322 (s), 1267 (m), 1142 (s), 982 (m), 853 (s), 771 (s), 6.65 (s), 529 (s) cm⁻¹.

HR-MS (EI, C₁₉H₃₅BO₂¹¹⁹SnS): *m/z* calcd. 458.14725, found 458.14685 (R = 10000).

¹ Carbon d was could not be identified, because of the quadrupole moment from the adjacent boron atom.

MS (EI, 70 eV, direct inlet, 200 °C): m/z (% relative intensity) = 458.2 (4) $[M]^+$, 443 (100) $[M-CH_3]^+$.

4-Bromo-2-*n*-hexylthiophene (**11**)



This procedure was adapted from the literature.^[2]

In a Schlenk flask, a solution of 3-*n*-hexylthiophene (5.01 g, 29.2 mmol) in THF (40 mL) was cooled to -78 °C and *n*BuLi (22.3 mL, 1.6 M in hexanes, 35.7 mmol) was added dropwise over 20 min. The solution was stirred for 3 h and this temperature. A solution of CBr₄ (11.8 g, 35.6 mmol) in THF (16 mL) was added with a syringe pump (rate = 1 mL / min) to the orange-brown suspension and the reaction was allowed to reach ambient temperature (ca. 20 °C) and it was stirred for 16 h. The reaction was quenched with water (100 mL) and the mixture was extracted with DCM (4 x 100 mL) and brine (2 x 50 mL). The combined organic layers were dried over MgSO₄, filtered, and the solvent was removed *in vacuo*. The product was purified by Kugelrohr distillation (70 °C, 9.0 x 10⁻² mbar) to afford a yellow oil in a yield of 5.35 g (74%, 21.7 mmol).

¹H NMR (500 MHz, CDCl₃): δ = 6.88 (d, ³J = 1.7 Hz, 1H, c), 6.80 (dt, ³J = 1.7, 0.9 Hz, 1H, a), 2.57 - 2.51 (m, 2H, e), 1.60 - 1.53 (m, 2H, f), 1.35 - 1.26 (m, 6H, g/h/i), 0.89 (dd, ³J = 9.3, 4.5 Hz, 3H, j).

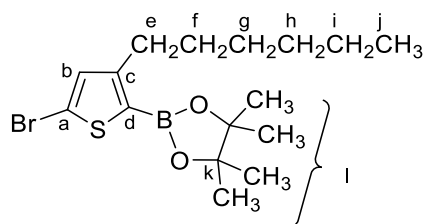
¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 142.8 (d), 129.9 (c), 120.2 (a), 110.4 (b), 29.1 (f), 29.05 (e), 30.5, 27.7, 21.5 (g/h/i), 12.9 (j).

IR (ATR): ν = 2955 (m), 2925 (s), 2855 (s), 1760 (w), 1539 (w), 1457 (m), 1412 (m), 1194 (w), 1275 (w), 1126 (m), 982 (m), 921 (w), 829 (s), 727 (s), 640 (m), 577 (w), 456 (w) cm⁻¹.

HR-MS (EI, C₁₀H₁₅⁷⁹BrS): m/z calcd. 246.0081, found 246.0078 (R = 10000).

MS (EI, 70 eV, direct inlet, 200 °C): m/z (% relative intensity) = 245.9 (22) $[M]^+$, 248.0 (34) $[M+2]^+$, 177.9 (100) $[M+2-C_5H_{11}]^+$, 175.9 (77) $[M-C_5H_{11}]^+$.

2-(5-Bromo-3-*n*-hexylthiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)



This procedure was adapted from the literature.^[3]

In a Schlenk flask, a solution of DIPA (1.04 g, 10.3 mmol) in THF (33 mL) was cooled to -78 °C and *n*BuLi (4.0 mL, 2.6 M in hexanes, 10.3 mmol) was added dropwise over 20 min. The mixture was warmed to 0 °C over the course of 30 min, cooled to -78°C and stirred for 5 min. A solution of **4** (2.54 g, 10.3 mmol) in THF (33 mL) was added with a syringe pump over the course of 20 min (rate = 0.5mL / min) and the mixture was stirred for 1 h at this temperature. A solution of *t*PrOBPin (1.82 g, 9.78 mmol) in THF (5 mL) was added with a syringe pump (rate = 1 mL / min) to the orange-green suspension. The reaction mixture was allowed to reach ambient temperature and was stirred for further 16 h. Afterwards the reaction was quenched with methanol (100 mL) and all volatiles were removed *in vacuo*. The residue was diluted in DCM (50 mL) and washed with water (2 x 100 mL), brine (2 x 100 mL) and dried over MgSO₄. After filtration, the volatiles were removed *in vacuo* and the mixture was purified by flash chromatography (*n*-hexane : EtOAc, 9: 1; R_f = 0.20) to afford an orange oil in a yield of 3.23 g (86%, 8.83 mmol).

¹H NMR (500 MHz, CDCl₃): δ = 6.94 (s, 1H, b), 2.85 - 2.77 (m, 2H, e), 1.59 - 1.50 (m, 2H, f), 1.33 - 1.27 (m, 18H, g/h/i/l), 0.88 (dd, ³J = 9.5, 4.5 Hz, 3H, j) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 155.1(c), 133.0 (b), 118.01 (a), 83.6 (k), 31.4 (f), 30.2 (e), 28.7, 24.6, 22.5 (g/h/i), 31.5 (l), 14.0 (j) ppm.²

¹¹B{¹H} NMR (160 MHz, CDCl₃): δ = 28.40 ppm.

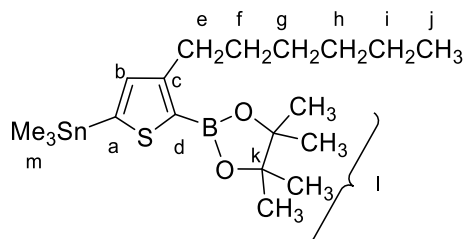
IR (ATR): $\tilde{\nu}$ = 2978 (w), 2956 (w), 2926 (m), 2857 (w), 1755 (w), 1534 (m), 1427 (s), 1370 (m), 1336 (s), 1304 (s), 1270 (m), 1140 (s), 1097(w), 1040 (s), 957 (m), 853 (s), 668 (w), 645 (m), 578 (m), 520 (w) cm⁻¹.

HR-MS (EI, C₁₈H₂₇¹¹B⁷⁹BrO₂S): *m/z* calcd. 373.1006, found 373.1006 (R = 10000).

² Carbon d could not be identified because of the quadrupole moment from the adjacent boron atom.

MS (EI, 70 eV, direct inlet, 200 °C): m/z (% relative intensity) = 373.10 (17) $[M]^+$, 259.19 (100) $[M-C_8H_{19}]^+$.

(4-Hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylstannane (13)



In a GB, a solution of **5** (752 mg, 2.02 mmol), $[Pd(PPh_3)_4]$ (116 mg, 0.10 mmol, 5 mol%), and $(SnMe_3)_2$ (661 mg, 2.02 mmol) in toluene (5 mL) was transferred in a microwave vial. The mixture was heated to 120 °C in a microwave apparatus for 30 min. After allowing the mixture to cool to ambient temperature, water (10 mL) was added to the reaction mixture and it was extracted with DCM (3 x 15 mL) and brine (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The residue was diluted in *n*-hexane (10 mL) and filtered over celite. The volatiles were removed *in vacuo* to afford an orange oil in a yield of 830 mg (89%, 1.80 mmol).

1H NMR (500 MHz, $CDCl_3$): δ = 7.09 (s, 1H, a), 2.92 – 2.87 (m, 2H, e), 1.64 – 1.53 (m, 2H, f), 1.37 – 1.28 (m, 18H, g/h/i/l), 0.89 (t, $^3J = 7.0$ Hz, 3H, j), 0.35 (s, 9H, m) ppm.

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ = 155.6 (c), 145.3 (a), 138.6 (b), 83.6 (i), 32.1 (f), 29.3 (e), 31.8, 30.1, 22.8, 24.63 (l), 14.28 (j), -8.19(m) ppm.³

$^{119}Sn\{^1H\}$ NMR (187 MHz, $CDCl_3$): δ = -28.40 ppm.

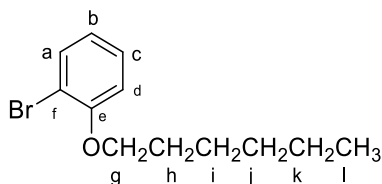
$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ = 28.91 ppm.

IR (ATR): $\tilde{\nu}$ = 2977(w), 2956(w), 2924(m), 2856(w), 1523 (w), 1425 (s), 1370 (m), 1327 (s), 1270 (m), 1192(w), 1141 (s), 1041 (m), 953 (w), 855 (m), 770(s), 695 (m), 647 (m), 531 (s), 512 (m) cm^{-1} .

ESI-MS ($[M+Na]$, $C_{19}H_{35}^{11}BO_2Na^{119}SnS$): m/z = Calcd. 481.1374 ; found 481.1370.

³ It was not possible to identify carbon d because the quadrupole moment of the adjacent boron atom.

1-Bromo-2-(*n*-hexyloxy)benzene (15)



This procedure was adapted from the literature.^[4]

To a solution of 2-bromophenol (2.80 g, 16.2 mmol) in acetonitrile (50 mL), K₂CO₃ (4.47 g, 32.4 mmol) and *n*-iodohexane (3.11 mL, 17.3 mmol) were added. The reaction mixture was stirred at 60 °C for 6 h and for 12 h at 20 °C. The reaction mixture was poured into water (70 mL). The aqueous phase was extracted with EtOAc (3 x 70 mL). The organic phase was washed with water (70 mL) and brine (70 mL). It was dried over Na₂SO₄, filtered and the filtrate concentrated under reduced pressure. The crude product was purified by column chromatography (*n*-pentane : EtOAc, 50 : 1; R_f = 0.75) to afford a colorless oil in a yield of 3.92 g (94%, 15.2 mmol).

¹H NMR (500 MHz, CDCl₃): δ = 7.53 (dd, ³J = 7.9 Hz, ⁴J = 1.6 Hz, 1H, a), 7.23 (ddd, ³J = 8.2, 7.9 Hz, ⁴J = 1.6 Hz 1H, c), 6.88 (dd, ³J = 8.2 Hz, ⁴J = 1.6 Hz, d), 6.84 – 6.79 (m, 1H, b), 4.02 (t, ³J = 6.5 Hz, 2H, g), 1.87 – 1.80 (m, 2H, h), 1.51 (ddd, ³J = 15.2, 7.2 Hz, ⁴J = 4.7 Hz, 2H, i), 1.39 - 1.33 (m, 4H, j/k), 0.96 – 0.89 (m, 3H, l) ppm.

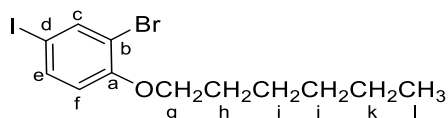
¹³C{¹H} NMR (126 MHz, CDCl₃) δ = 155.9 (e), 133.7 (a), 128.8 (c), 122.0 (b), 113.07(d), 112.7 (f), 69.6 (g), 29.5 (h), 26.1 (i), 31.9, 23.0 (j/k), 14.4 (l) ppm.

IR (ATR): $\tilde{\nu}$ = 2928 (w), 1586 (w), 1466 (m), 1442 (m), 1275 (s), 1246 (s), 1126 (w), 1050 (s), 1030 (s), 743 (s), 665 (m) cm⁻¹.

HR-MS (EI, C₁₂H₁₆O⁷⁹Br): *m/z* calcd. 256.04573, found. 256.04554 (R = 10000).

MS (EI, 70 eV, indirect inlet, 200 °C): *m/z* (% relative intensity) = 256 (100) [M]⁺.

1-Bromo-2-(*n*-hexyloxy)-5-iodobenzene (16)



This procedure was adapted from the literature.^[5]

A mixture of I₂ (3.39 g, 13.3 mmol) and AgNO₃ (1.73 g, 10.3 mmol) was gently blended in an agate mortar for 1 min, and then **10** (2.62 g, 17.3 mmol) was added. The resulting

homogeneous mixture was additionally ground for 10 min, and then after a 2-min break, the grinding was continued for an additional 1 or 1.5 h, until the mixture had a light yellow bright color. The resulting mixture was extracted with diethyl ether (2 x 100 mL), dried over MgSO₄ and filtered. The volatiles were removed *in vacuo*. The product was purified by Kugelrohr distillation (140 °C, 2.7 x 10⁻¹ mbar) to afford a yellow solid in a yield of 3.13 g (80%, 8.15 mmol).

¹H NMR (500 MHz, CDCl₃): δ = 7.82 (d, ⁴J = 2.2 Hz, 1H, c), 7.51 (dd, ³J = 8.6 Hz, ⁴J = 2.2 Hz, 1H, e), 6.63 (d, ³J = 8.6 Hz, 1H, f), 3.99 (t, ³J = 6.5 Hz, 2H, g), 1.90 – 1.76 (m, 2H, h), 1.57 – 1.40 (m, 2H, i), 1.38 – 1.29 (m, 4H, j/k), 0.91 (t, ³J = 6.7 Hz, 3H, l) ppm.

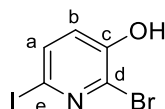
¹³C{¹H} NMR (126 MHz, CDCl₃) δ = 155.6 (a), 140.9 (c), 137.1 (e), 114.9 (f), 113.5 (b), 82.1 (d), 69.3 (g), 31.0, 22.5 (j/k), 28.9 (h), 25.6 (i), 14.0 (l) ppm.

IR (ATR): $\tilde{\nu}$ = 2925 (m), 2855 (m), 1573 (w), 1462 (s), 1377 (m), 1282(s), 1246 (s), 1152 (w), 1043 (s), 1014 (w), 813 (w), 799 (m), 687 (m), 629 (m), 544 (m) cm⁻¹.

HR-MS (EI, C₁₂H₁₆O⁷⁹BrI): *m/z* calcd. 381.9422, found 381.9429 (R = 10000).

MS (EI, 70 eV, direct inlet, 200 °C): *m/z* (% relative intensity) = 381.9 (55) [M]⁺, 384.9 (9) [M+2]⁺, 297.8 (100) [M-C₆H₁₃]⁺.

2-Bromo-6-iodo-3-pyridinol (18)



This procedure was adapted from the literature.^[6]

2-Bromopyridine-3-ol (5.00 g, 28.7 mmol) and K₂CO₃ (7.90 g, 57.5 mmol) were dissolved in water (66 mL) and I₂ (7.51 g, 29.6 mmol) was added. The reaction was stirred at 21 °C for 3 d. Excess iodine was reduced by addition of solid NaHSO₃. The pH of the solution was adjusted to -5-6 using glacial acetic acid. A solid formed during the process and was collected by filtration and dried *in vacuo* to afford a light gray solid in a yield of 8.03 g (93%, 26.8 mmol).

mp: 161.2 °C.

¹H NMR (500 MHz, CDCl₃): δ = 5.50 (OH), 7.0 (d, ³J = 8.2 Hz, 1H, a), 7.57 (d, ³J = 8.2 Hz, 1H, b) ppm.

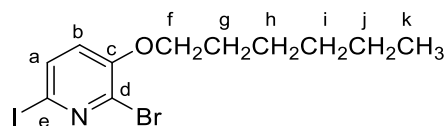
¹³C{¹H} NMR (126 MHz, CDCl₃) δ = 150.0 (e), 135.3 (d), 129.9 (c), 125.2 (a), 102.5 (b) ppm.

IR (ATR): $\tilde{\nu}$ = 3343.3 (br), 1654.0 (w), 1548 (m), 1462.2 (m), 1383.3 (s), 1287.9 (s), 1226 (s), 1132 (w), 1065 (s), 826.4 (m) cm^{-1} .

HR-MS (EI, $\text{C}_{15}\text{H}_3\text{O}^{79}\text{BrI}$): m/z calcd. 298.84344, found. 288.84344 (R = 10000).

MS (EI, 70 eV, direct inlet, 200 °C, $\text{C}_5\text{H}_3\text{O}^{79}\text{BrI}$): m/z (% relative intensity) = (299) (100) $[\text{M}]^+$.

2-Bromo-3-(hexyloxy)-6-iodopyridine (**8**)



This procedure was adapted from the literature.^[7]

To a solution of **18** (4.43 g, 14.8 mmol) in DMF (15 mL), K_2CO_3 (2.24 g, 16.2 mmol) was added, and the mixture was stirred for 30 min at 20 °C. To this mixture, *n*-bromohexane (9.26 g, 56.2 mmol) was added. The reaction mixture was stirred for 1.5 h at 100 °C. The reaction mixture was poured into ice water (70 mL) and extracted with EtOAc (3 x 70 mL). The organic phase was dried over MgSO_4 , filtered, and the volatiles were removed *in vacuo*. The product was purified by Kugelrohr distillation heating at 100 °C at 3.4×10^{-1} mbar to afford a yellow oil in a yield of 3.96 g (70%, 10.3 mmol).

^1H NMR (500 MHz, CDCl_3): δ = 7.56 (d, 3J = 8.3 Hz, 1H, a), 6.81 (d, 3J = 8.3 Hz, 1H, b), 4.00 (t, 3J = 6.4 Hz, 4H, f), 1.96 – 1.71 (m, 4H, g), 1.57 – 1.28 (m, 6H, h/i/j), 0.97 – 0.88 (m, 3H, k) ppm.

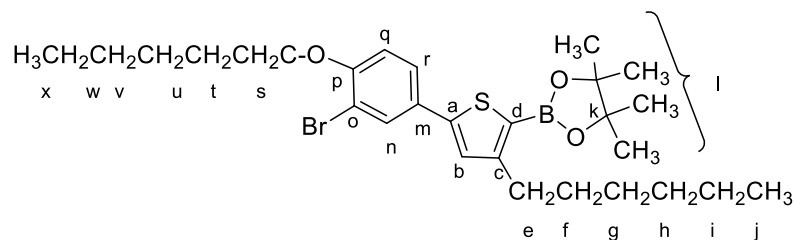
$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 152.9 (c), 134.0 (a), 121.4 (d), 101.7 (e), 69.6 (f), 28.6 (g), 31.3, 25.4, 22.4 (h/i/j), 13.9 (k) ppm.

IR (ATR): $\tilde{\nu}$ = 2928 (w), 2857 (w), 1559 (w), 1417 (s), 1383 (m), 1347 (w), 1284 (s), 1228 (m), 1136 (w), 931 (w), 817 (m), 623 (m) cm^{-1} .

HR-MS (EI, $\text{C}_{11}\text{H}_{15}\text{NO}^{79}\text{BrI}$): m/z calcd. 382.9380, found 382.9382 (R = 10000).

MS (EI, 70 eV, direct inlet, 200 °C): m/z (% relative intensity) = 382:9 (43) $[\text{M}]^+$, 385.9 (17) $[\text{C}_{11}\text{H}_{15}\text{N}^{81}\text{BrI}]^+$, 298.8 (100) $[\text{M}-\text{C}_6\text{H}_{13}]^+$.

2-(5-(4-Bromo-3-(hexyloxy)phenyl)-3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)



In a GB, a mixture of **16** (444 mg, 1.16 mmol), **13** (500 mg, 1.09 mmol) and [Pd(PPh₃)₄] (31 mg, 26 μmol, 2 mol%) in dry DMF (5 mL) was prepared in a microwave vial. The mixture was heated to 100 °C in a microwave apparatus for 12 h. After allowing the mixture to cool to ambient temperature (ca. 20 °C), water (5 mL) was added and the mixture was extracted with DCM (3 x 10 mL). The organic phase was washed with brine (3 x 5 mL) before drying the organic phase over MgSO₄. After filtration, the volatiles were removed *in vacuo*. The mixture was purified by flash chromatography (*n*-hexane : EtOAc; 70 : 30; R_f: 0.20) to afford an orange oil in a yield of 421 mg (70%, 0.77 mmol).

¹H NMR (500 MHz, CDCl₃): δ = 7.82 (d, ³J = 2.3 Hz, 1H, n), 7.49 (dd, ³J = 8.6, 2.3 Hz, 1H, r), 7.12 (s, 1H, b), 6.86 (d, ³J = 8.6 Hz, 1H, q), 4.04 (t, ³J = 6.5 Hz, 2H, s), 2.90 – 2.80 (m, 2H, e), 1.84 (dt, ³J = 14.3, 6.5 Hz, 2H, t), 1.60 (dt, ³J = 7.5, 15.0 Hz, 2H, f), 1.53 – 1.48 (m, 2H, u), 1.39 - 1.22 (m, 22H, g/h/i/l/v/w), 0.97 – 0.86 (m, 6H, j/x) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 155.9 (c), 155.3 (p), 148.2 (m), 130.9 (n), 128.6 (a), 126.2 (b), 126.2 (r), 113.3 (o), 112.7 (q), 83.7 (k), 69.5 (s), 31.6 (f), 30.6 (e), 29.1 (t), 25.9 (u), 31.8, 29.2, 24.9, 22.8 (g/h/i/l/v/w), 14.3, 14.2 (j/x) ppm.⁴

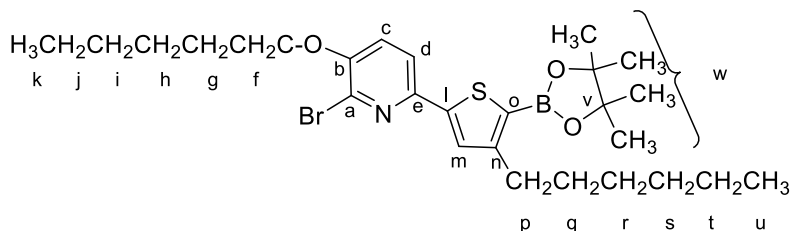
¹¹B{¹H} NMR (160 MHz, CDCl₃): δ = 28.88 ppm.

IR (ATR): $\tilde{\nu}$ = 2954 (m), 2926 (m), 2857 (m), 1599(w), 1540 (m), 1501 (w), 1451 (s), 1371(m), 1338 (s), 1287 (s), 1254 (s), 1141 (s), 1047 (s), 958 (w), 855 (s), 807 (m), 669 (w), 609 (m), 579 (w) cm⁻¹.

ESI-MS ([M+Na], C₂₈H₄₂¹¹B⁷⁹BrNaO₃S₂): *m/z* = calc. 571.2024, found = 571.2028 (R = 10000).

⁴ It was not possible to identify carbon d because the quadrupole moment of the adjacent boron atom.

2-Bromo-6-(4-*n*-hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-3-(*n*-hexyloxy)pyridine (6)



In a GB, a mixture of **19** (418 mg, 1.09 mmol), **13** (500 mg, 1.09 mmol) and [Pd(PPh₃)₄] (25 g, 22 μmol, 2 mol%) in dry DMF (6 mL) was prepared in a microwave vial. The mixture was heated to 130 °C in a microwave apparatus for 6 h. After allowing the mixture to cool to ambient temperature (ca. 20 °C), water (5 mL) was added and extracted with DCM (3 x 10 mL). The organic phase was washed with brine (3 x 5 mL) before drying over MgSO₄. After filtration, the volatiles were removed *in vacuo*. The crude mixture was purified with flash chromatography (*n*-hexane : EtOAc, 70 : 30, R_f = 0.25) to afford an orange oil in a yield of 423 mg (70%, 770 μmol).

¹H NMR (500 MHz, CDCl₃): δ = 7.48 (d, ³J = 8.4 Hz, 1H, d), 7.47 (s, 1H, m), 7.09 (d, ³J = 8.4 Hz, 1H, c), 4.04 (t, ³J = 6.5 Hz, 2H, f), 2.87 – 2.82 (m, 2H, p), 1.89 – 1.81 (m, 2H, g), 1.61 – 1.58 (m, 2H, h), 1.54 – 1.48 (m, 2H, q), 1.38 – 1.35 (m, 2H, r), 1.35 – 1.31 (m, 18H, j, s/t/w), 1.31 – 1.29 (m, 2H, i), 0.91 – 0.90 (m, 3H, u), 0.88 (t, ³J = 6.9 Hz, 3H, k) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 155.7 (n), 151.4 (b), 147.6 (l), 145.3 (e), 132.7 (a), 127.9 (m), 120.31 (c), 119.3 (d), 83.8 (v), 69.8 (f), 31.8 (i), 31.8 (r), 31.6 (h), 30.6 (p), 29.1 (g), 29.1/22.75/22.70 (j/s/t), 25.73 (q), 24.94 (w), 14.27 (k), 14.15 (u) ppm.⁵

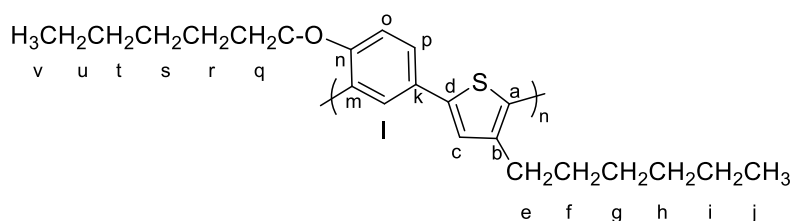
¹¹B{¹H} NMR (160 MHz, CDCl₃): δ = 29.25 ppm.

IR (ATR): $\tilde{\nu}$ = 2955 (m), 2925 (m), 2856 (m), 1526 (w), 1459 (s), 1426 (m), 1371 (m), 1337 (s), 1305 (m), 1270 (m), 1141 (s), 1045 (m), 959 (w), 854 (s), 830 (m), 668 (w), 647 (m), 578 (w), 517 (w) cm⁻¹.

ESI-MS ([M+Na], C₂₇H₄₁BBrNaO₃S₂): *m/z* = calcd. 572.1963 found 572.1981.

⁵It was not possible to identify carbon o because the quadrupole moment of the adjacent boron atom.

Poly(1,4-(3-hexyl)-thiophene-2,6-(3-hexyloxy)-phenylene) O1



Selection of the catalyst

In a Schlenk flask, **5** (69 mg, 13 μ mol) was dissolved in THF (2 mL). A suspension of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ or $[\text{Pd}(\text{dppf})\text{Cl}_2]$ 5 mol%, CsF (11 mg, 7 μ mol) in degassed water (0.5 mL) and THF (1.5 mL) were added. The mixture was heated at 60 $^\circ\text{C}$ for 24 h under a nitrogen atmosphere. The crude mixture was quenched with a solution of HCl in methanol (1 M, 1 mL) to afford a sticky yellow oil. Water was added (5 mL) and the mixture was extracted with DCM (3 x 5 mL). The organic phase was washed with brine (3 x 5 mL) before being dried over MgSO_4 . After filtration, the volatiles were removed *in vacuo*. The crude product was purified by Soxhlet extraction. First, MeOH (50 mL) was used as solvent and the system was heated at 100 $^\circ\text{C}$ for 8 h. After oligomers and small molecules were removed, the solvent was changed to chloroform and the system was heated at 80 $^\circ\text{C}$ for 4 h.

Catalyst	Mass catalyst (mg)	M_n (kDa)	\bar{D}
$[\text{Pd}(\text{tBu}_3\text{P})_2]$	3	5.8	1.35
$[\text{Pd}(\text{dppf})\text{Cl}_2]$	5	2.4	1.34

Table SI- 3. GPC measurement results from the selection of the catalyst for the oligomerization of the monomer **5**. THF was used as eluent in a concentration of 1 mg/mL, at a flow rate of 1 mL/min. Calibrated against polystyrene standards using a conventional calibration method.

Oligomer synthesis

In a Schlenk flask, **5** (300 mg, 550 μ mol) was dissolved in THF (2 mL). A suspension of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ (28 mg, 55 μ mol, 5 mol%), CsF (86 mg, 567 μ mol) in degassed water (0.5 mL) and THF (1.5 mL) were added. The mixture was heated at 60 $^\circ\text{C}$ for 24 h under a nitrogen atmosphere. The crude mixture was quenched with a solution of HCl in methanol (1 M, 1 mL) to afford a sticky yellow oil. Water was added (5 mL) and the mixture was extracted with DCM

(3 x 10 mL). The organic phase was washed with brine (3 x 5 mL) before being dried over MgSO₄. After filtration, the volatiles were removed *in vacuo*. The crude product was purified by Soxhlet extraction. First, MeOH (200 mL) was used as solvent and the system was heated at 100 °C for 8 h. After oligomers and small molecules were removed, the solvent was changed to chloroform and the system was heated at 80 °C for 4 h. The volatiles were removed *in vacuo* to afford a sticky orange oil in a yield of 87.3 mg (46%).

¹H NMR (600 MHz, CDCl₃): δ = δ 7.59 (d, ³J = 2.1 Hz, 1H, l), 7.55 – 7.52 (m, 1H, p), 7.12 (m, 1H, c), 6.97 – 6.92 (m, 1H, o), 4.02 – 3.94 (m, 2H, q), 2.54 – 2.48 (m, 2H, e), 1.76 – 1.67 (m, 2H, r), 1.65 – 1.57 (m, 2H, f), 1.43 – 1.34 (m, 4H, g/s), 1.33 – 1.18 (m, 8H, h/i/t/u), 0.89 – 0.78 (m, 4H, j/v) ppm.

¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 156.4 (n), 143.7 (d), 142.4 (a), 141.6 (b), 132.1 (k), 128.9 (p), 125.7 (o), 123.8 (c), 112.8 (l), 69.0 (q), 30.8 (f), 29.5 (e), 29.2 (r), 31.9 29.4, 25.8, 22.8 (g/h/i/s/t/u), 14.2 (j/v).

IR (ATR): $\tilde{\nu}$ = 2922 (m), 2854 (m), 1599(w), 1491 (m), 1464 (s), 1377 (w), 1248 (s), 1141 (m), 1016 (bm), 802(s), 724 (w) cm⁻¹.

λ_{max} (DCM) = 318 nm.

ε (DCM) = 8.13 x 10³ L mol⁻¹ cm⁻¹. The extinction factor was calculated from solutions of **O1**, using the molecular weight calculated by GPC (1560 g/mol), in DCM with concentration / Absorption: 1.15 μM / 0.013, 2.31 μM / 0.021, 4.62 μM / 0.043, 6.92 μM / 0.060, 9.23 μM / 0.080 and 11.5 μM / 0.097.

λ_{PL} (DCM) = 432 nm.

M_n (GPC, conventional method) = 1.56 kDa.

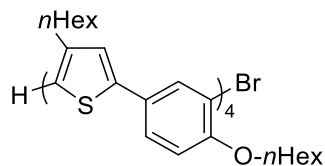
Đ = 1.12.

MALDI (graphite): m/z = 1451

DP (based on M_n from GPC measurements) = 4.

DP (based on MALDI measurements) = 4.

Proposed structure with end groups based on MALDI analysis:



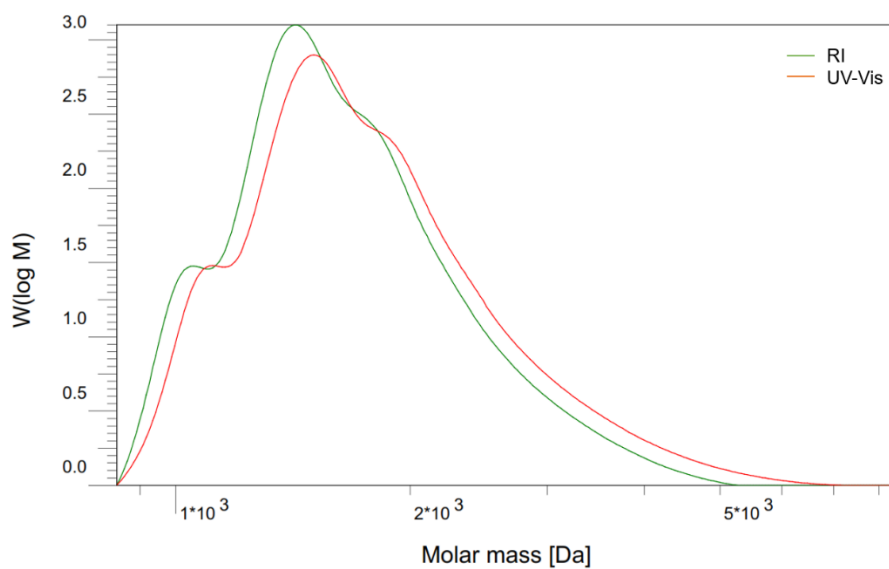


Figure SI- 1. GPC measurement result of **O1** using THF as eluent in a concentration of 1 mg/mL, at a flow rate of 1 mL/min. Calibrated against polystyrene standards using a conventional calibration method. Signals from the refraction index (RI) and Uv-vis detectors are shown.

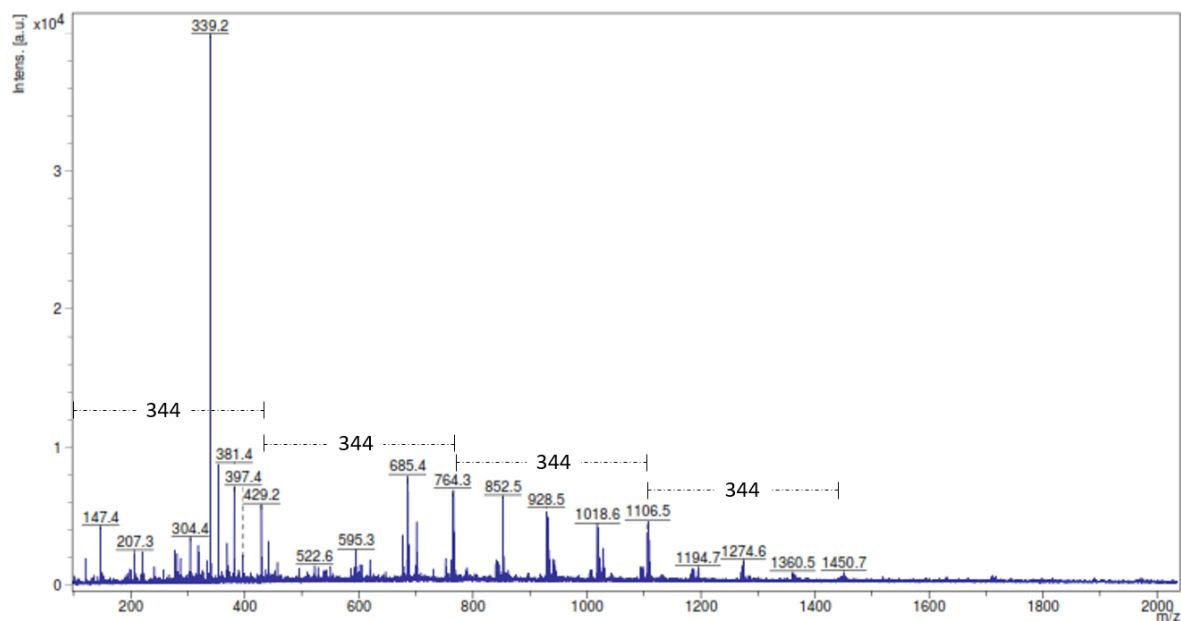


Figure SI- 2. MALDI (graphite) spectra of **O1**, with the mass of the repeating unit indicated in the picture.

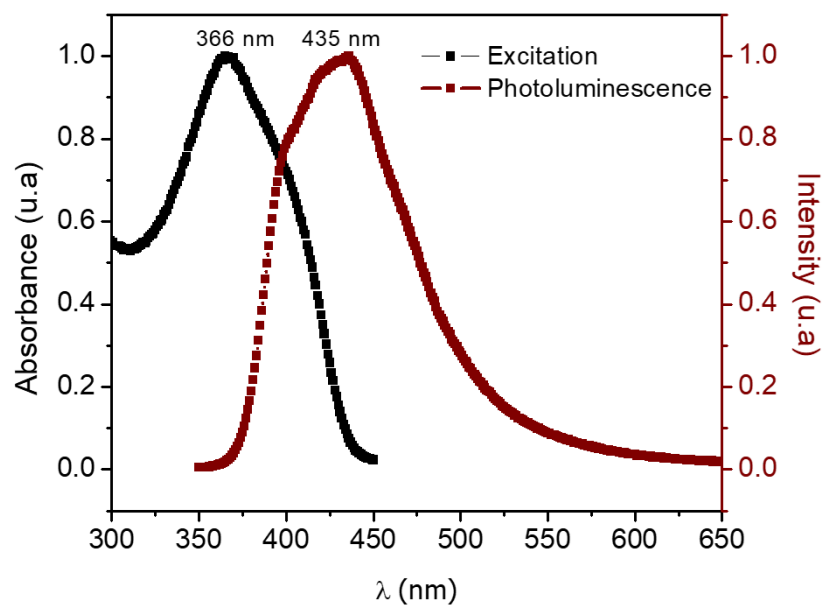


Figure SI- 3. Excitation and photoluminescence spectra ($\lambda_{\text{exc}} = 340$ nm) of a solution of **01** in DCM (6.34×10^{-6} M).

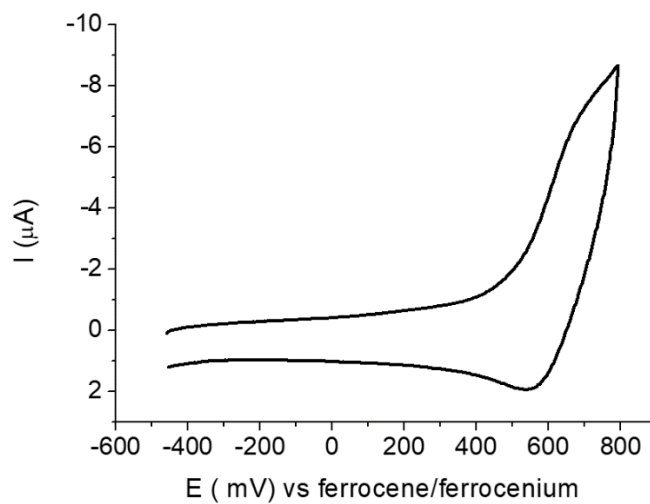


Figure SI- 4. Cyclic voltammogram of a solution of **01** (1×10^{-3} M) using Bu_4NPF_6 as electrolyte in DCM (0.2 M).

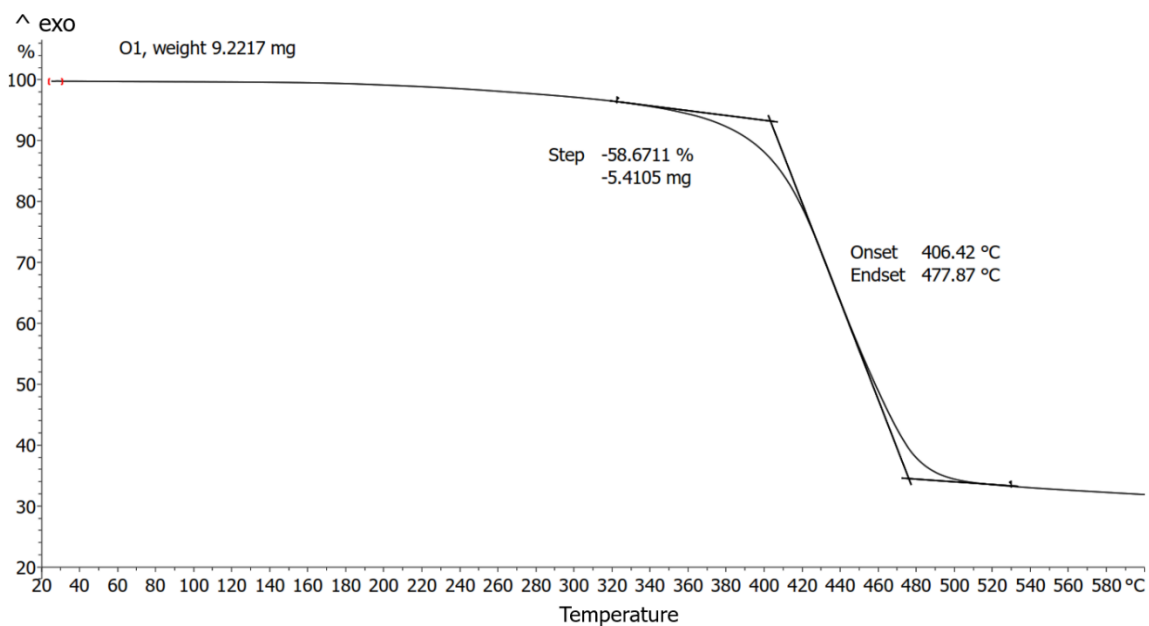


Figure SI- 5. TGA curve of **O1**. Heating rate 10 K/min, Al crucible, under a nitrogen gas flow of 20 mL/min.

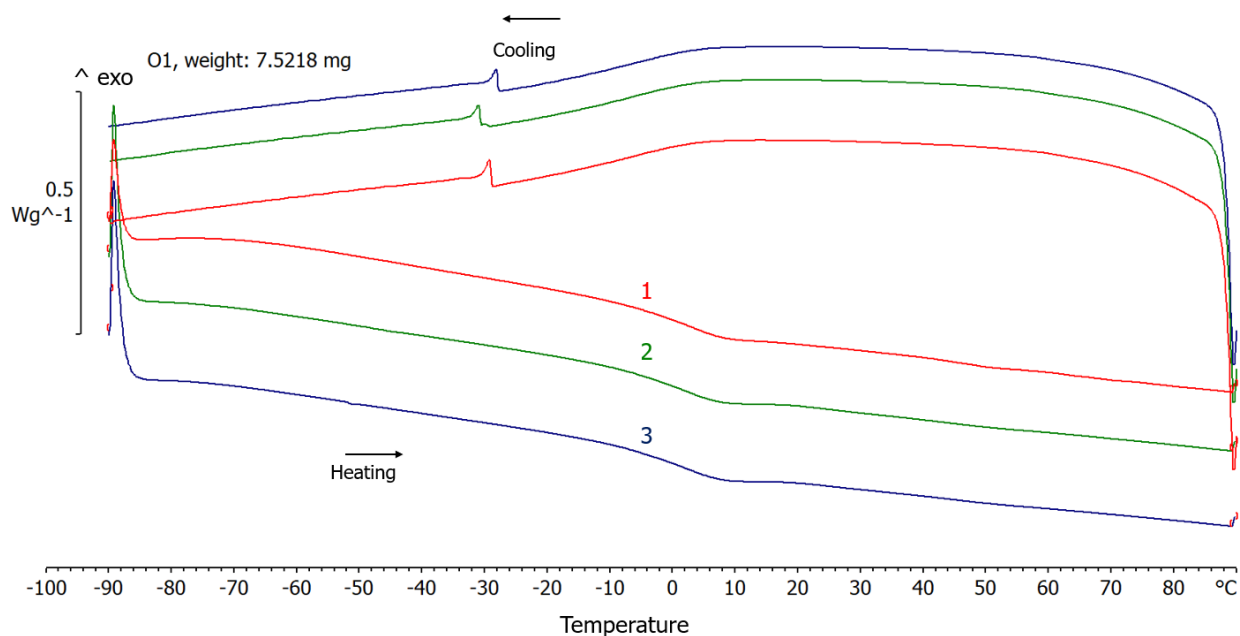


Figure SI- 6. DSC curve of **O1** Heating rate 10 K/min, Al crucible, 20 mL/min nitrogen gas, 3 cycles (-90 to +90 °C).

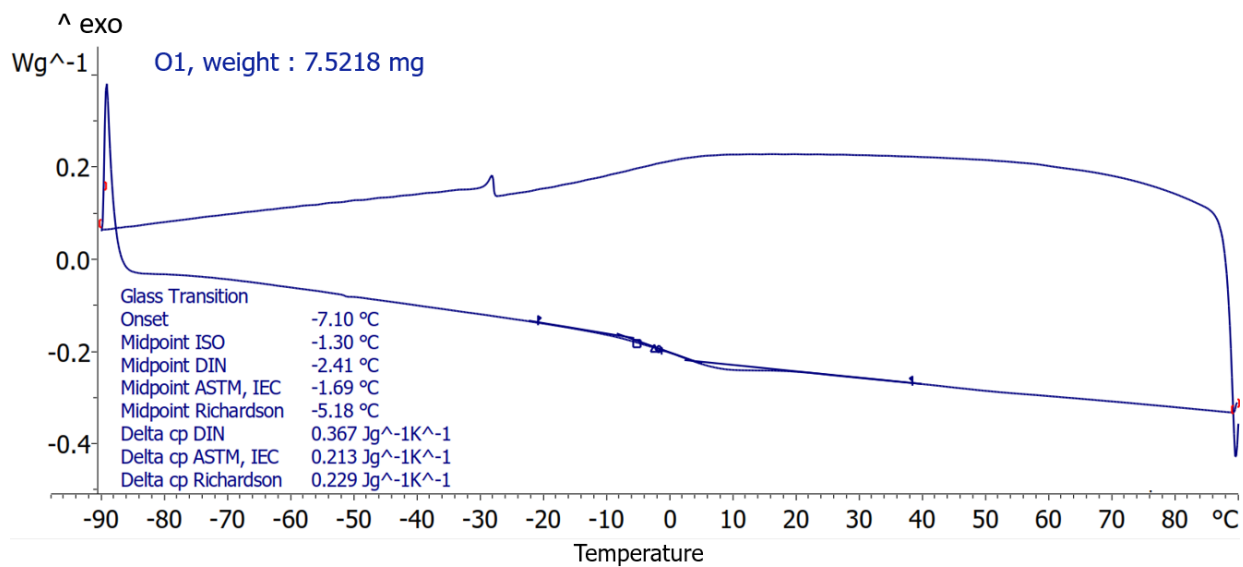
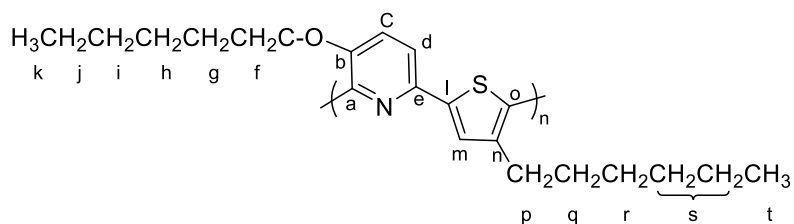


Figure SI- 7. DSC curve of **O1** Heating rate 10 K/min, Al crucible, 20 mL/min nitrogen gas, cycle 3 of 3 (-90 to +90 °C).

Poly(2,6-(3-*n*-hexyloxy)-pyridine-1,4-(3-*n*-hexyl)-thiophene) O2



Selection of the catalyst

In a Schlenk flask, **6** (55 mg, 10 μ mol) was dissolved in THF (2 mL). A suspension of [Pd(*t*Bu₃P)₂] or [Pd(dppf)Cl₂] 5 mol%, CsF (20 mg, 13 μ mol) in degassed water (0.5 mL) and THF (1.5 mL) were added. The mixture was heated at 60 °C for 24 h under a nitrogen atmosphere. The crude mixture was quenched with a solution of HCl in methanol (1 M, 1 mL) to afford a sticky yellow oil. Water was added (5 mL) and the mixture was extracted with DCM (3 x 5 mL). The organic phase was washed with brine (3 x 5 mL) before being dried over MgSO₄. After filtration, the volatiles were removed *in vacuo*. The crude product was purified by Soxhlet extraction. First, MeOH (100 mL) was used as solvent and the system was heated at 100 °C for 8 h. After oligomers and small molecules were removed, the solvent was changed to chloroform and the system was heated at 80 °C for 4 h.

Catalyst	Mass catalyst (mg)	M _n (kDa)	Đ
[Pd(<i>t</i> Bu ₃ P) ₂]	2	2.3	1.35
[Pd(dppf)Cl ₂]	3	2.3	1.48

Table SI- 4. GPC measurement results from the selection of the catalyst for the oligomerization of the monomer **6**. THF was used as eluent in a concentration of 1 mg/mL, at a flow rate of 1 mL/min. Calibrated against polystyrene standards using a conventional calibration method.

Oligomer synthesis

In a Schlenk flask, **6** (300 mg, 546 μ mol) was dissolved in THF (2 mL). A suspension of [Pd(*t*Bu₃P)₂] (14 mg, 27 μ mmol, 5 mol%), CsF (108 mg, 710 μ mol) in degassed water (0.5 mL) and THF (1.5 mL) were added. The mixture was heated at 50 °C for 24 h under a nitrogen

atmosphere. The crude mixture was quenched with a solution of HCl in methanol (1 mL, 1 mmol, 1 M) to afford a greenish yellow solid. Water was added (5 mL) and the reaction mixture was extracted with DCM (3 x 10 mL). The organic phase was washed with brine (3 x 5 mL) before being dried over MgSO₄. After filtration, the volatiles were removed *in vacuo*. The crude product was purified by Soxhlet extraction. First MeOH (200 mL) was used as solvent and the system was heated at 100 °C for 8 h. After oligomers and small molecules were removed, the solvent was changed to chloroform (100 mL) and the system was heated at 80 °C for 4 h. The volatiles were removed *in vacuo* from the receiver flask to afford a greenish, fluorescent solid in a yield of 131 mg (70%).

¹H NMR (500 MHz, CDCl₃): δ = 7.51 (d, ³J = 8.4 Hz, 1H, c), 7.47 (s, 1H, m), 7.24 (d, ³J = 8.4 Hz, 1H, d), 4.13 – 3.94 (m, 2H, f), 3.11 – 2.99 (m, 2H, p), 1.94 – 1.81 (m, 2H, g), 1.80 – 1.67 (m, 2H, q), 1.58 – 1.41 (m, 4H, h/r), 1.41 – 1.14 (m, 12H, s/l/j), 0.88 – 0.70 (m, 6H, k/t) ppm.
¹³C{¹H} NMR (126 MHz, CDCl₃): 151.2 (b), 145.0 (e), 144.7 (l), 132.6 (a), 127.1 (c), 120.3 (d), 118.6 (m), 69.4 (f), 31.5 (q), 30.5 (p), 29.0 (g), 25.6 (h/r), 22.6, 29.5, 31.7, 31.9 (i/j/s/t), 14.0 (k/u) ppm.

IR (ATR): $\tilde{\nu}$ = 2921 (m), 2851 (m), 1565 (w), 1435 (s), 1379 (w), 1272 (m), 1130 (m), 1071 (w), 816 (m) cm⁻¹.

λ_{max} (DCM) = 390 nm.

λ_{PL} (DCM) = 442 nm.

ε (DCM) = 7.10 × 10⁴ L mol⁻¹ cm⁻¹. The extinction factor was calculated from solutions of **02**, using the molecular weight calculated by GPC (5390 g/mol), in DCM with concentration / Absorption : 0.13 μM / 0.014, 0.27 μM / 0.023, 0.54 μM / 0.043, 0.81 μM / 0.064, 1.09 μM / 0.087 and 1.36 μM / 0.096.

λ_{max} (solid state) = 300 nm.

M_n (GPC, conventional method) = 5.39 kDa.

Đ = 1.83.

MALDI (graphite) = *m/z*. 2059.

DP (based on GPC measurements) = 16.

DP (based on MALDI measurements) = 6.

Proposed structure with end groups based on MALDI analysis

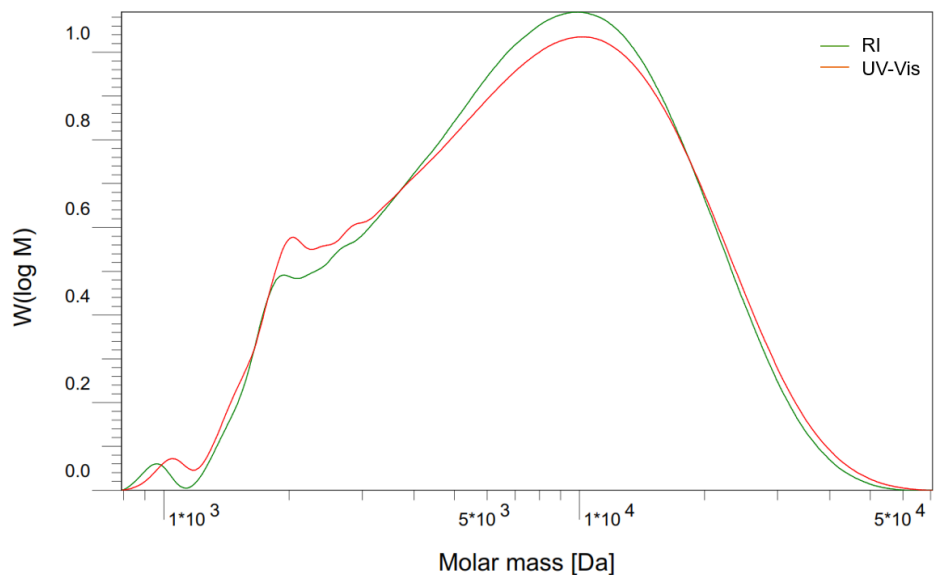
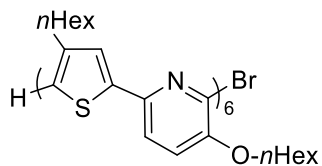


Figure SI- 8. GPC measurement result of **O2** using THF as eluent in a concentration of 1 mg/mL, at a flow rate of 1 mL/min. Calibrated against polystyrene standards using a conventional calibration method. Signals from the RI and Uv-vis detectors are shown.

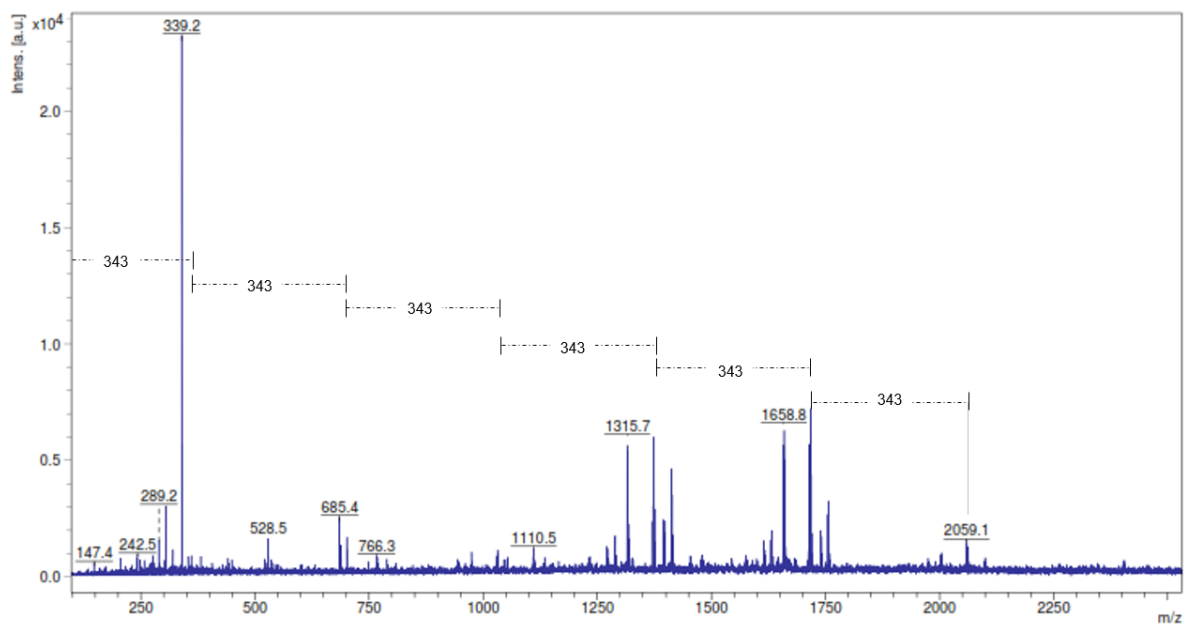


Figure SI- 9. MALDI (graphite) spectrorgam of **O2**. With the mass of the repeating unit indicated in the picture.

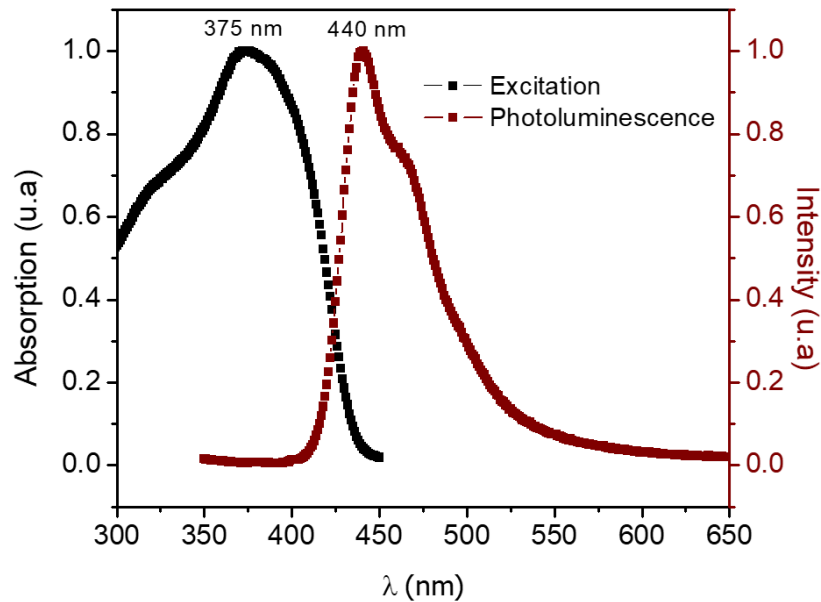


Figure SI- 10. Excitation and photoluminescence spectra ($\lambda_{exc} = 340$ nm) of a solution of **O2** in DCM (1.13×10^{-5} M).

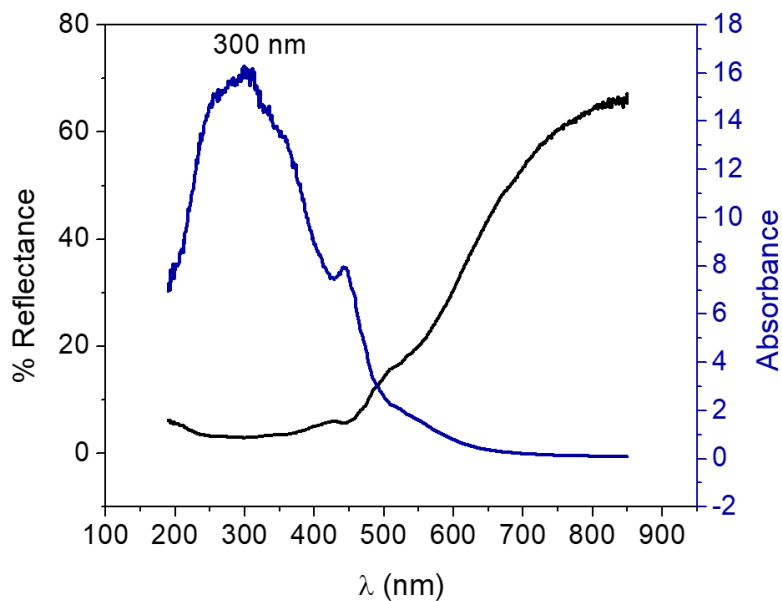


Figure SI- 11. Solid state absorption (blue) and reflection spectra (black) of **O2**.

With the reflectance spectrum it is possible to determine if the polymer has an indirect or direct band gap.

The expression proposed by Tauc, Davis and Mott it is used to calculate the band gap:^[8]

$$(h\nu\alpha)^{1/n} = A (h\nu - E_g) \quad (1)$$

where: h : Planck's constant, ν : frequency of vibration, α : absorption coefficient, E_g : band gap, A : proportional constant. The value of n denotes the nature of the sample transition. The most common ones are: $n = 1/2$ for direct allowed transition and $n = 2$ for indirect allowed transition.

The absorption coefficient α is proportional to the diffuse reflectance ($F(R_\infty)$) and the Tauc function (eq. 1) is converted into the Kubelka-Munk function (2). [9]

$$(h\nu F(R_\infty))^{1/n} = A (h\nu - E_g) \quad (2)$$

Using expression 2, the Tauc graph was plotted using $n = 1/2$ and $n = 2$. The x intercept of the tangent from the point of inflection of the curve from the plot denotes the band gap E_g .

It is expected that the nearest band gap calculated with this plot with the one obtained from the Uv-vis spectra, predicts which type of transition the material has.

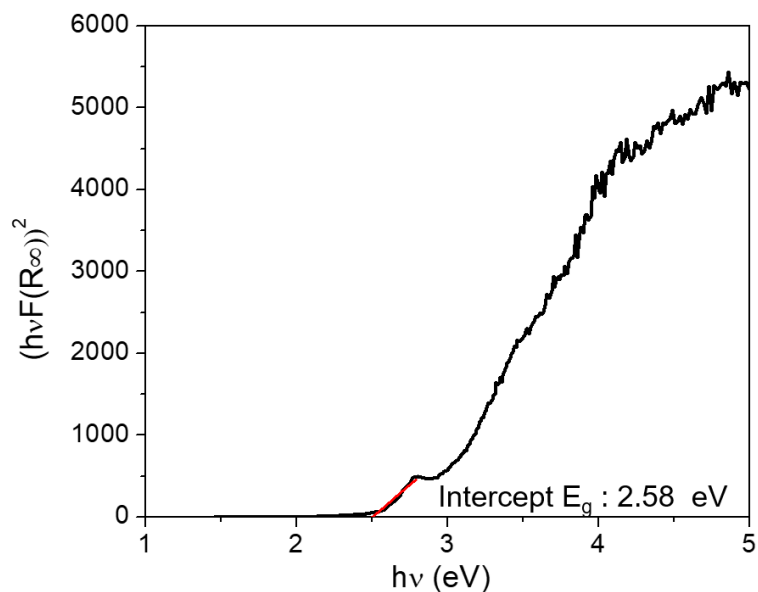


Figure SI- 12. Tauc plot of **O2** with $n = 1/2$ for direct transition.

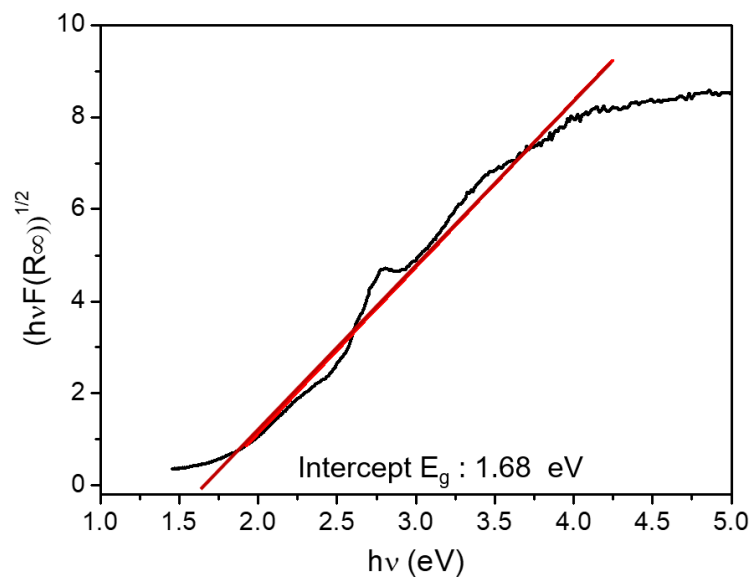


Figure SI- 13. Tauc plot of **O2** with $n = 2$ for an indirect transition.

Conclusion : **O2** showed an indirect allowed transition.

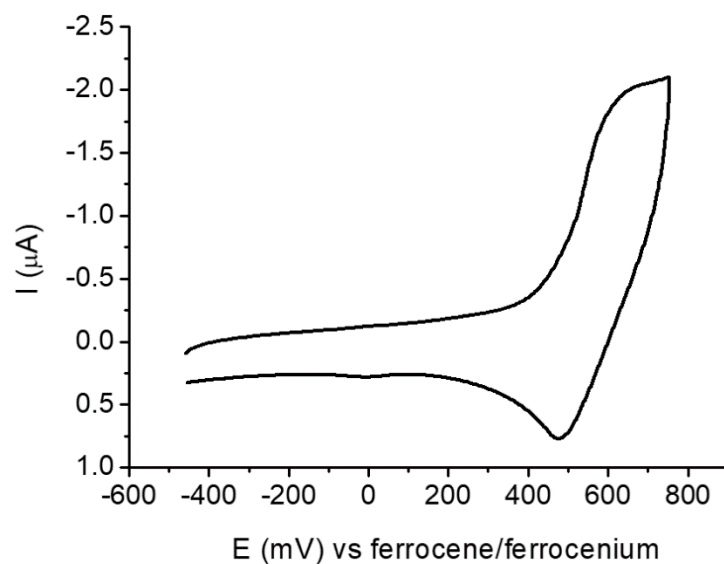


Figure SI- 14. Cyclic voltammogram of a solution of **O2** (1×10^{-3} M) using Bu_4NPF_6 as electrolyte in DCM (0.2 M).

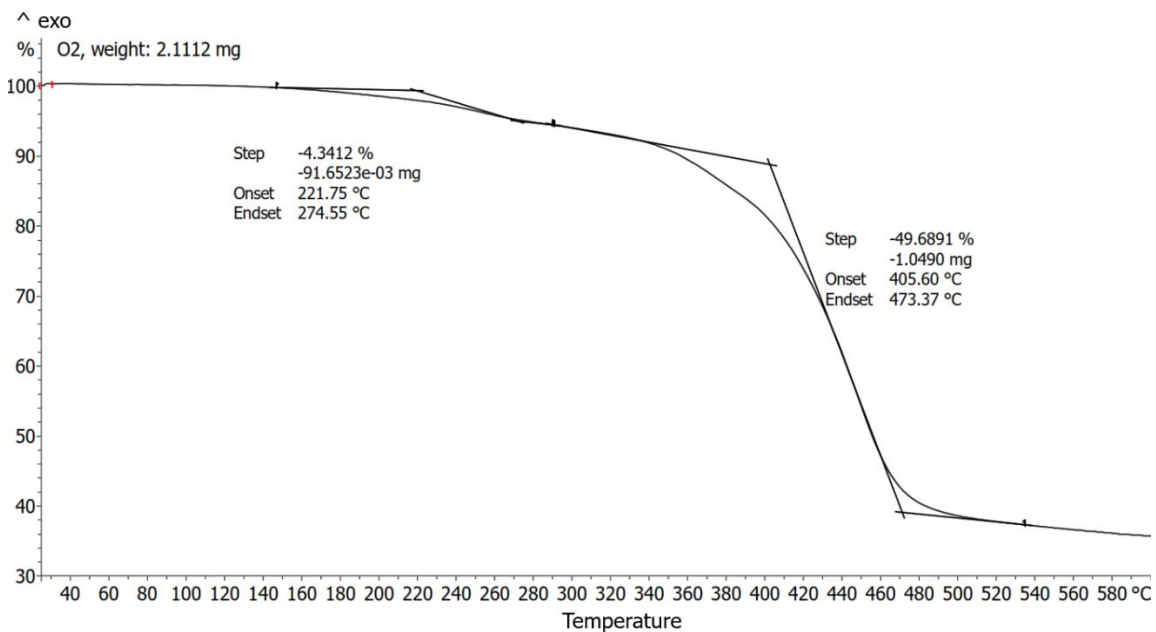


Figure SI- 15. TGA curve of **O2**. Heating rate 10 K/min, Al crucible, flow of 20 mL/min nitrogen gas.

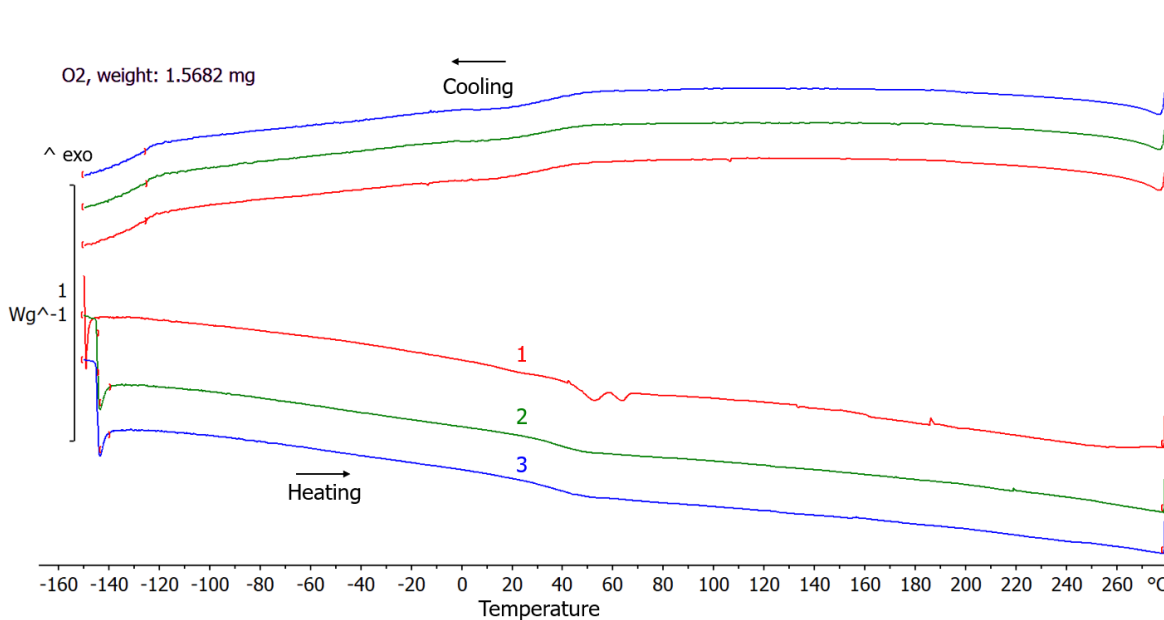


Figure SI- 16. DSC curve of **O2** Heating rate 10 K/min, Al crucible, flow of 20 mL/min nitrogen gas, 3 cycles (-150 to +250 °C).

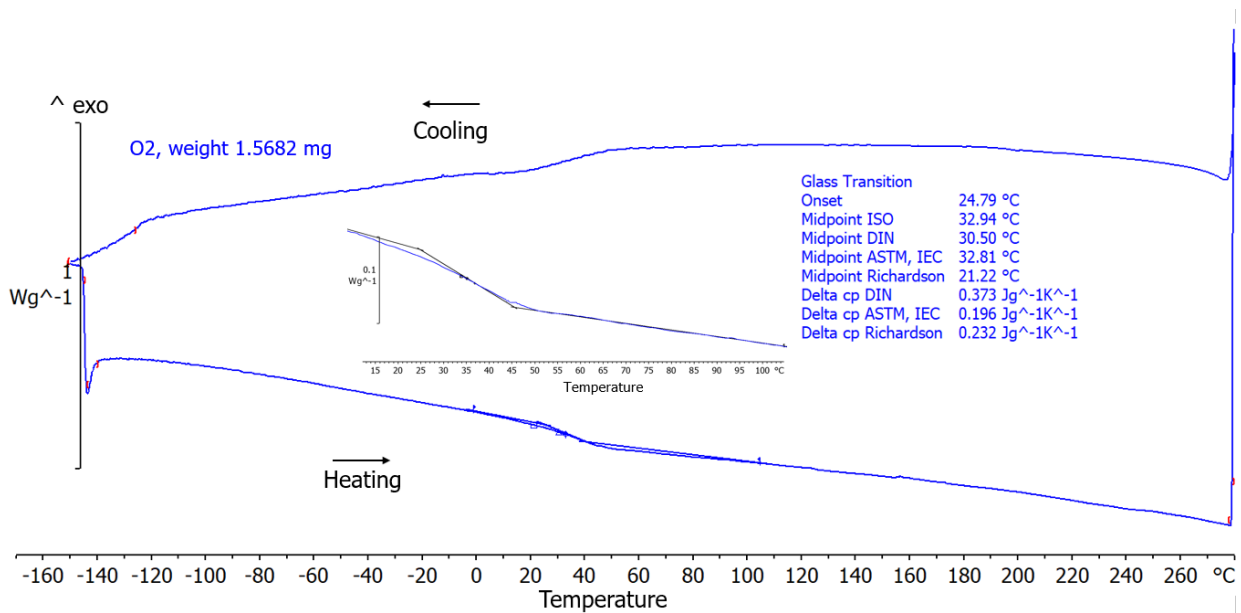


Figure SI- 17. DSC curve of **O₂** Heating rate 10 K/min, Al crucible, flow of 20 mL/min nitrogen gas, cycle 3 of 3 (-150 to +250 °C).

Reaction Monitoring

Poly(1,4-(3-*n*-hexyl)-thiophene-2,6-(3-*n*-hexyloxy)-phenylene) O1

In a Schlenk tube, a solution of **5** (103 mg, 180 μmol) and 1,3,5-trimethoxybenzene (33.8 mg, 200 μmol , used as internal standard) in THF (1 mL) was prepared and heated for 2 min at 60 °C. A first sample (0.2 mL) was taken out of from the reaction mixture (t_0). Immediately after, a suspension of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ (4.6 mg, 9 μmol , 5 mol%), CsF (37 mg, 243 μmol), water (0.5 mL) and THF (stabilizer free, 1.5 mL) was added. After 1 h, 3 h, 6 h, 12 h and 24 h reaction time, a sample was taken out of the reaction mixture.

Every sample was quenched with a solution of HCl in MeOH (2,0 mL, 2 mmol, 1 M), then water (1 mL) was added and the mixture was extracted with DCM (2 x 3 mL). The organic phase was dried over MgSO_4 and filtered over a "mini column" (glass pipet filled with Celite. See Figure SI-18). The solution was split in two flasks and the solvents were removed *in vacuo*. Half of the sample was dissolved in THF for GPC analysis and the second one in CDCl_3 for ^1H NMR spectroscopic analysis.



Figure SI- 18. Picture from the filtration with the 'mini column' based on a glass pipet filled with Celite® and silica.

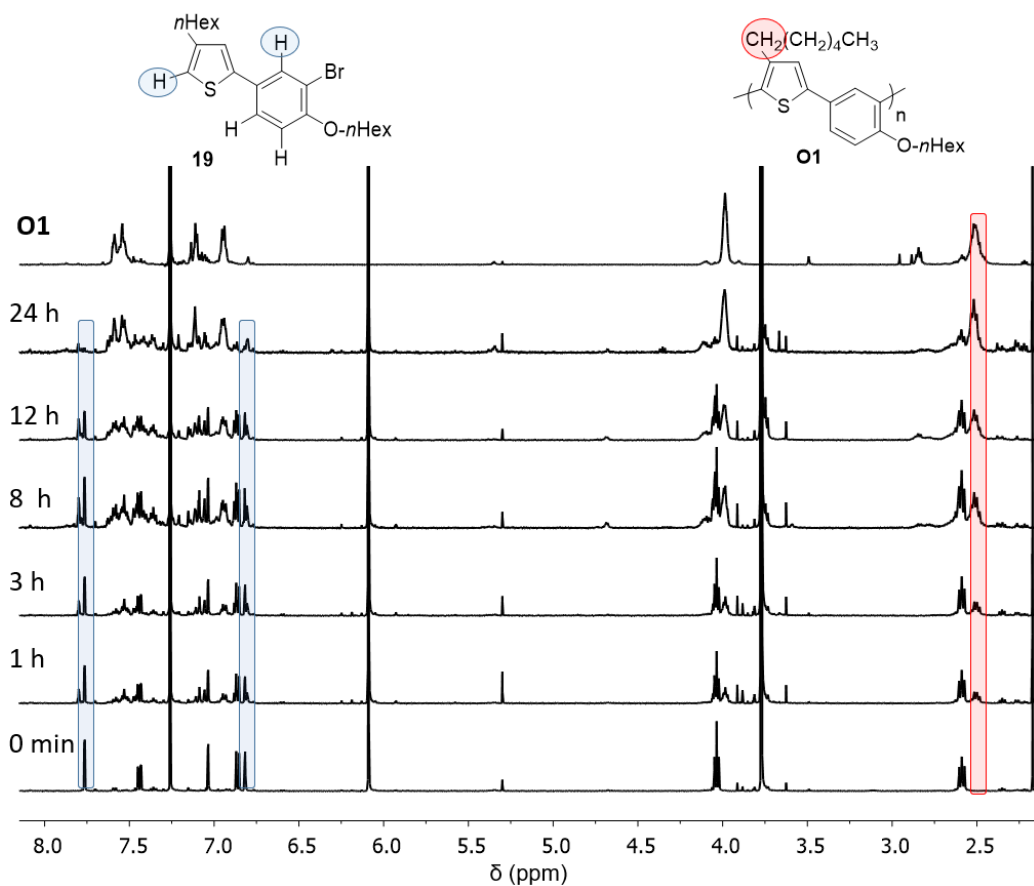


Figure SI- 19. ^1H NMR spectra (recorded at 300 K, 500 MHz in CDCl_3) of the reaction monitoring for the polymerization of **5** to produce **O1**, 1,3,5-trimethoxybenzene was used as standard. The conversion was based on the amount of compound **19** (product of the quenching of **5** with HCl/MeOH 1M).

Time (h)	% conversion	M_n (kDa)	M_w (kDa)	\bar{D}
0	0.0	0.44	0.44	1.01
1	15.0	0.99	1.06	1.07
3	16.4	1.00	1.09	1.08
8	40.5	1.50	1.65	1.10
12	37.4	1.50	1.68	1.12
24	91.6	1.58	2.60	1.65

Table SI- 5. Results from the reaction monitoring of **O1** : % conversion obtained from the ^1H NMR spectra (Figure SI-19); M_n , M_w and \bar{D} obtained from GPC measurements. The conversion was based on the amount of compound **19** (product of the quenching of **5** with HCl/MeOH 1M).

The growth behavior of **O1** was observable in the Uv-vis/elugram 2D-plot of the GPC samples (Figure SI-20). The spectra were recorded using the Win-GPC[®] software from the company PSS.

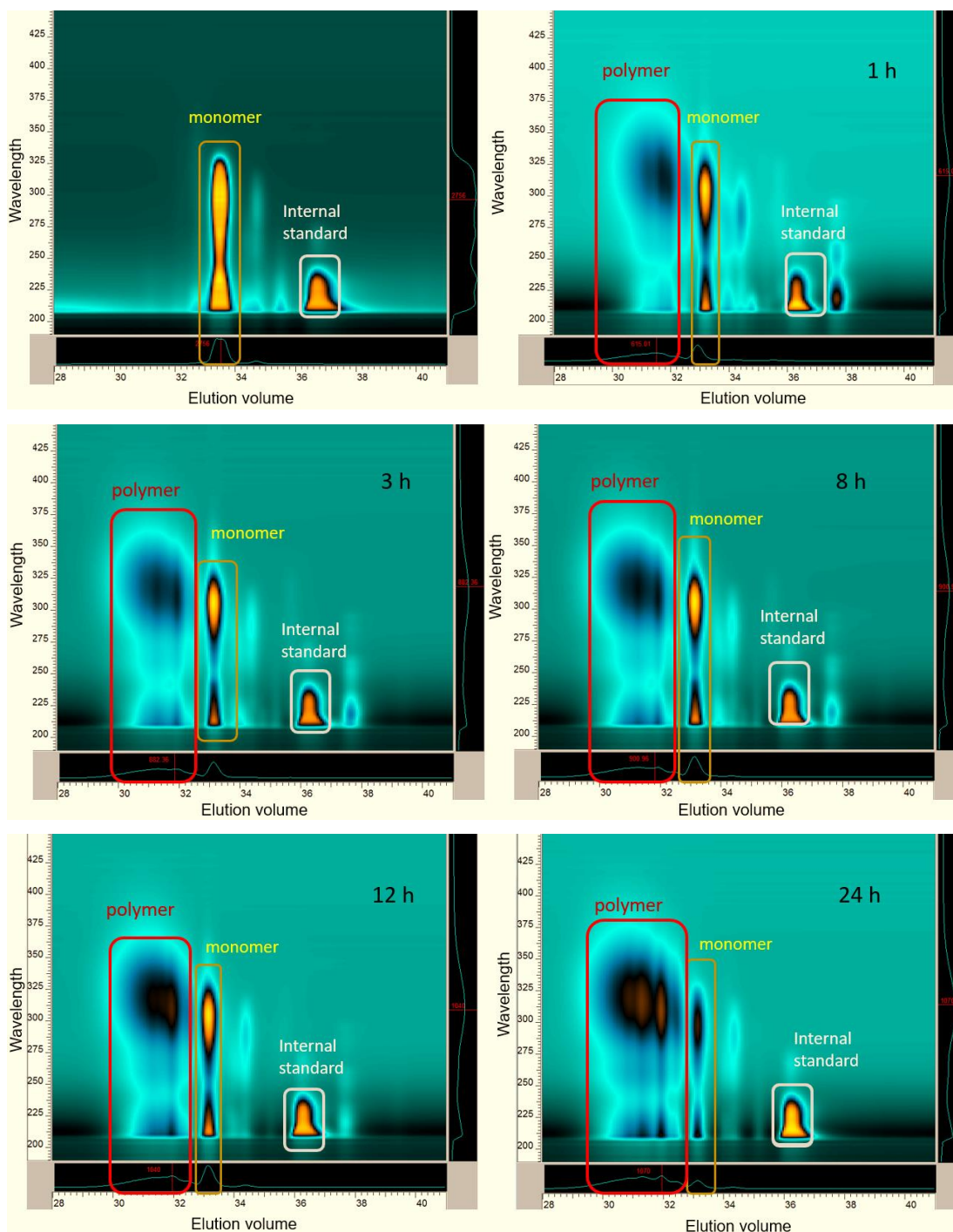


Figure SI- 20. Uv-vis spectra/ elugram 2D plots from the GPC measurements of the reaction monitoring of **O1**. The intensity (Z) of the yellow color is related to the concentration of internal standard, monomer and polymer in each sample.

The conversion of the monomer using the Uv-vis/ elution 2D-plot was based in the intensity (Z value) from the area corresponding to the monomer. The results of the time, % conversion (with respect disappearance of the monomer), M_n , M_w and \bar{D} for the polymerization of **5** are summarized in the Table SI-4.

Time (h)	% conversion	M_n (Da)	M_w (Da)	\bar{D}
0	0.0	0.44	0.44	1.01
1	36.7	0.99	1.06	1.07
3	48.7	1.00	1.09	1.08
8	51.3	1.50	1.65	1.10
12	62.0	1.50	1.68	1.12
24	100.0	1.58	2.60	1.65

Table SI- 6. Results from the reaction monitoring study of **01** : % conversion obtained from the Uv-vis/ elugram 2D- plot (Figure SI-20); M_n , M_w and \bar{D} obtained from GPC measurements.

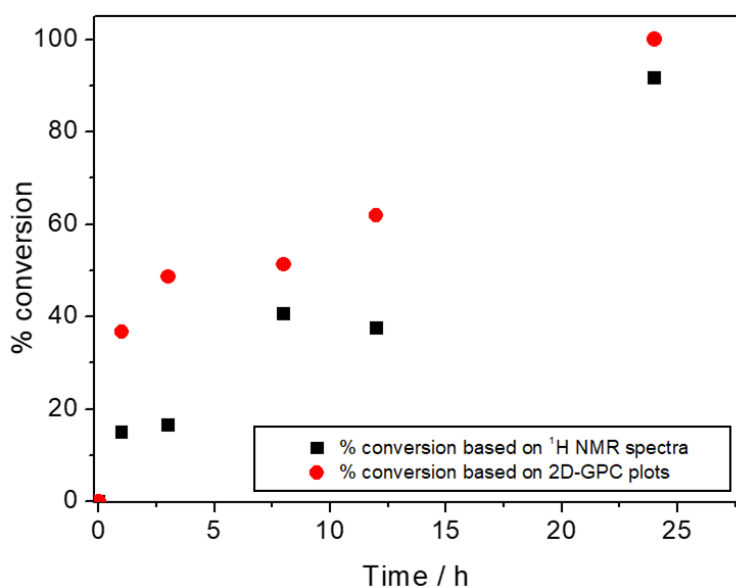


Figure SI- 21. Plots of % conversion vs. time. Calculated by the two detectors (^1H and 2D-plots GPC) for the polymerization of **5** with 5 mol% of $[\text{Pd}(\text{tBu}_3\text{P})_2]$, 1.2 eq. CsF in THF at 50 °C. The conversion was defined as amount of compound **19** consumed observed by the ^1H NMR spectra and 2D-GPC plots.

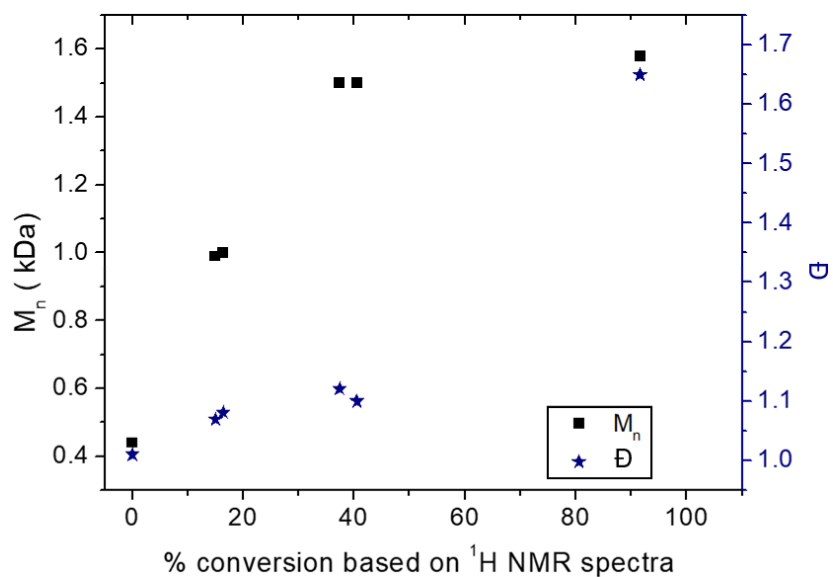


Figure SI- 22. Plot of the % conversion calculated by ^1H NMR spectra vs. M_n and \bar{D} for the polymerization of **5** with 5 mol% of $[\text{Pd}(\text{tBu}_3\text{P})_2]$, 1.2 eq. CsF in THF at 50 °C. The conversion was defined as amount of compound **19** consumed observed by the ^1H NMR spectra.

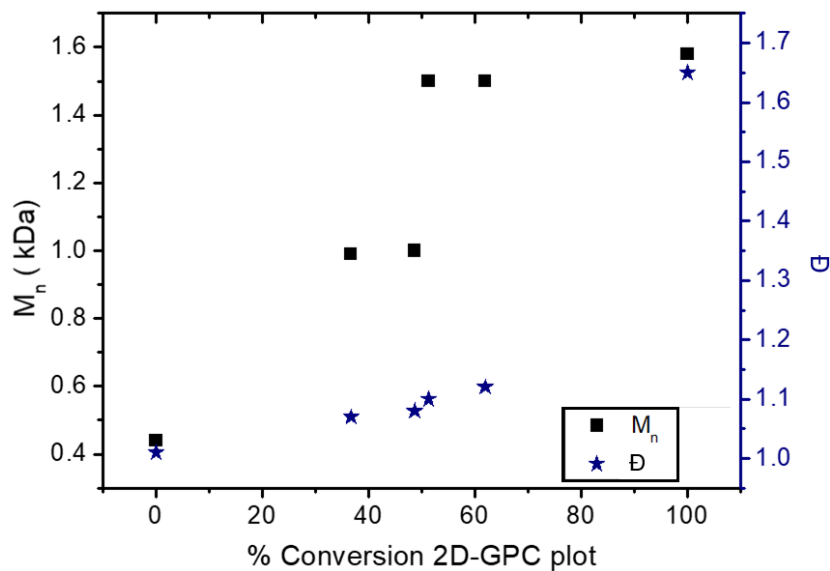


Figure SI- 23. Plot of % conversion calculated by 2D-GPC plot vs. M_n and \bar{D} for the polymerization of **5** with 5 mol% of $[\text{Pd}(\text{tBu}_3\text{P})_2]$, 1.2 eq. CsF in THF at 50 °C. The conversion was defined as amount of compound **19** consumed observed by the 2D-GPC plots.

Poly(2,6-(3-*n*-hexyloxy)-pyridine-1,4-(3-*n*-hexyl)-thiophene) **O2**

In a Schlenk tube, a solution of **6** (173 mg, 315 μmol) and 1,3,5-trimethoxybenzene (52.2 mg, 310 μmol , used as internal standard) in THF (1 mL) was prepared and heated for 2 min at 60 °C. A first sample (0.2 mL) was taken out of the reaction mixture (t_0). Immediately after, a suspension of $[\text{Pd}(\text{tBu}_3\text{P})_2]$ (7.9 mg, 15 μmol , 5 mol%), CsF (61 mg, 401 μmol), water (0.5 mL) and THF (stabilizer free, 1.5 mL) was added. After 1 h, 3 h, 6 h, 12 h and 24 h of reaction, a sample was taken from the reaction mixture.

Every sample was quenched with a solution of HCl in MeOH (2.0 mL, 2 mmol, 1 M), then water (1 mL) was added and the mixture was extracted with DCM (2 x 3mL). The organic phase was dried over MgSO_4 and filtered over a 'mini column' (glass pipet filled with Celite® and silica. See Figure SI-18). The solution was split in two flasks and the solvents were removed *in vacuo*. Half of the sample was dissolved in THF for GPC analysis and the second one in CDCl_3 for ^1H NMR spectral analysis.

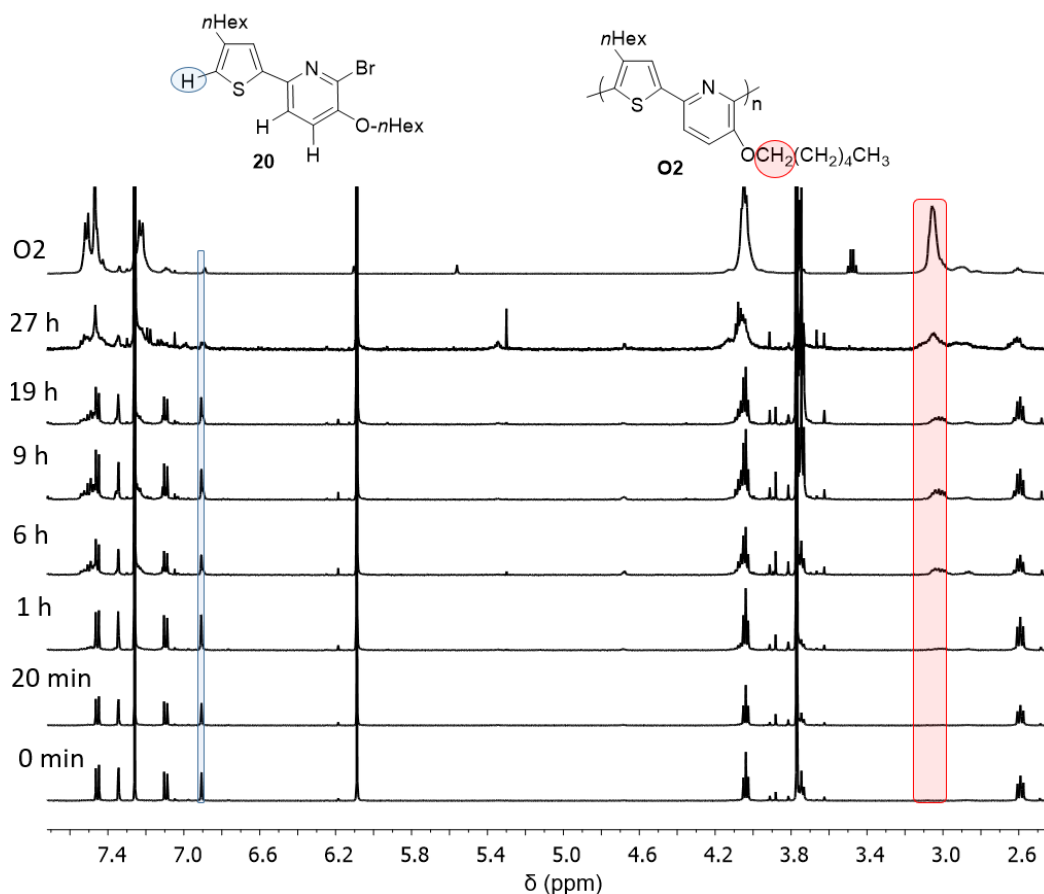
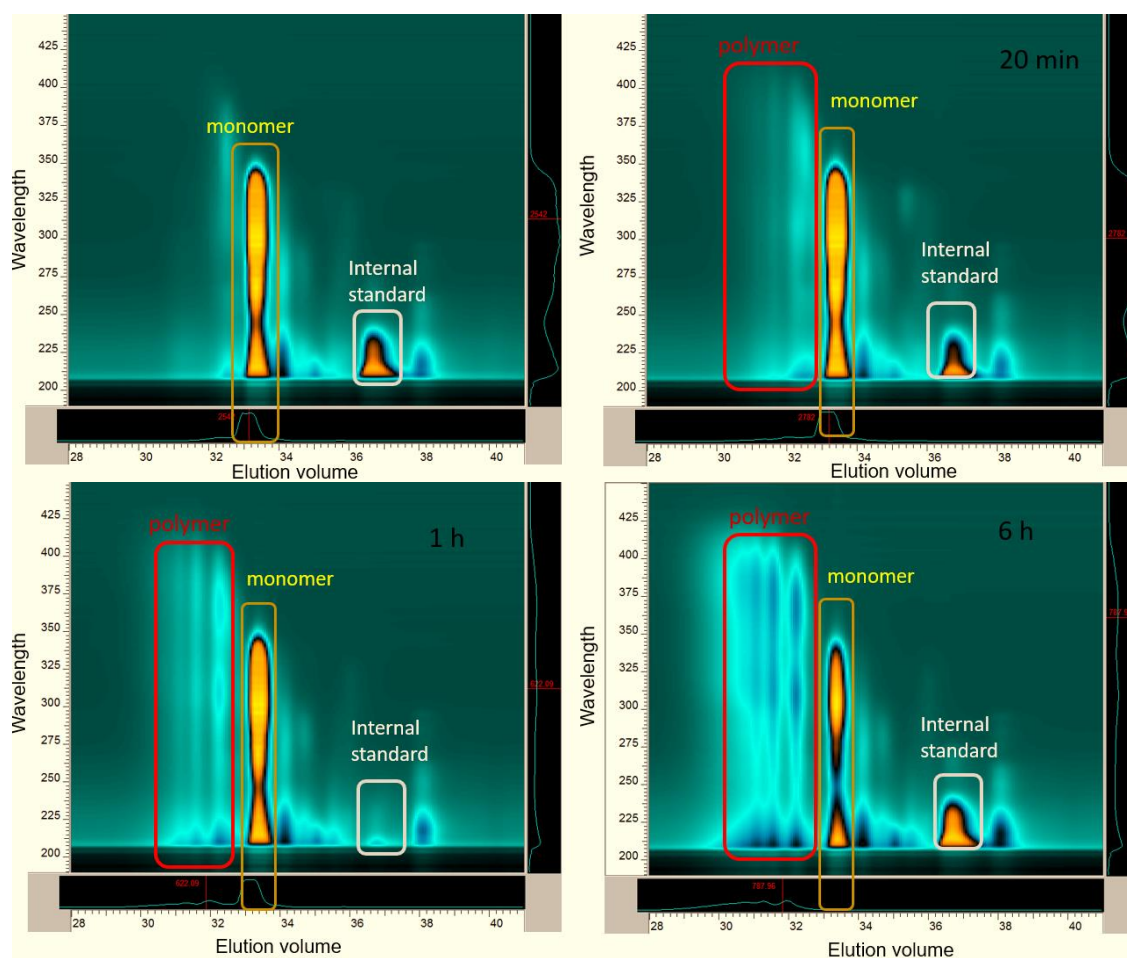


Figure SI- 24. ^1H NMR spectra (recorded at 300 K, 500 MHz in CDCl_3) of the reaction monitoring for the polymerization of **6** to produce **O2**, 1,3,5-trimethoxybenzene was used as standard. The conversion was based on the amount of compound **20** (product from the quenching of **6** in HCl/MeOH 1M).

Time (h)	% conversion	M _n (Da)	M _w (Da)	Đ
0	0.0	441.3	457.7	1.04
1	34.6	1051.9	1144.8	1.09
6	52.2	1423.1	1706.1	1.20
9	60.0	1404.8	1703.1	1.21
19	66.7	1290.3	1500.9	1.16
27	100.0	1454.0	1770.1	1.22

Table SI- 7. Results from the reaction monitoring study of **O2**: % conversion obtained from the ¹H NMR spectra (Figure SI-24); M_n, M_w and Đ obtained from GPC measurements. The conversion was based on the amount of compound **20** (product from the quenching of **6** in HCl/MeOH 1M).

The growth behavior of **O2** was observable in the Uv-vis/elugram 2D-plot of the GPC samples (Figure SI-25). The spectra were recorded using the Win-GPC[®] software from the company PSS.



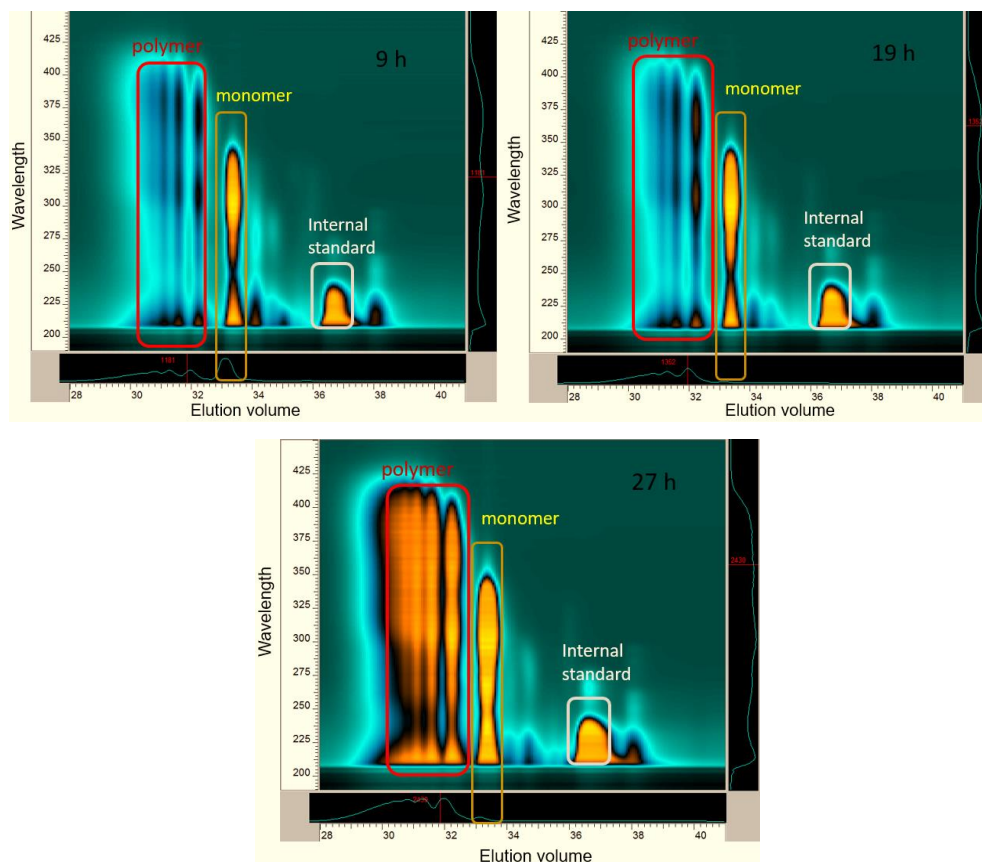


Figure SI- 25. Uv-vis spectra/ elugram 2D plots from the GPC measurements of the reaction monitoring of **O2**. The intensity (Z) of the yellow color is related to the concentration of internal standard, monomer and polymer in each sample.

The conversion of the monomer using the Uv-vis/ elution 2D-plot was based in the intensity (Z value) from the area corresponding to the monomer. The results of the time, % conversion (with respect disappearance of the monomer), M_n , M_w and \bar{D} for the polymerization of **6** are summarized in the Table SI-6.

Time (h)	% conversion	M_n (Da)	M_w (Da)	\bar{D}
0	0.0	0.44	0.46	1.04
0.33	34.3	0.45	0.49	1.09
1	40.4	1.05	1.14	1.09
6	48.3	1.42	1.71	1.20
9	65.0	1.40	1.70	1.21
19	68.1	1.29	1.50	1.16
27	100.0	1.45	1.77	1.22

Table SI- 8. Results from the reaction monitoring study of **O2**: % conversion obtained from the Uv-vis/ elugram 2D-plot (Figure SI-25); M_n , M_w and \bar{D} obtained from GPC measurements.

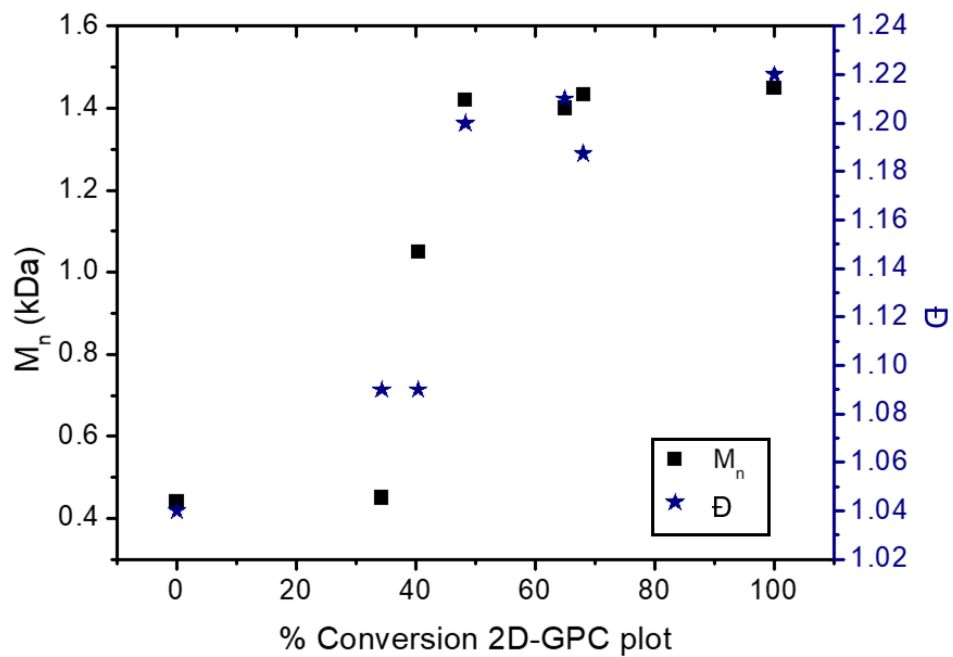
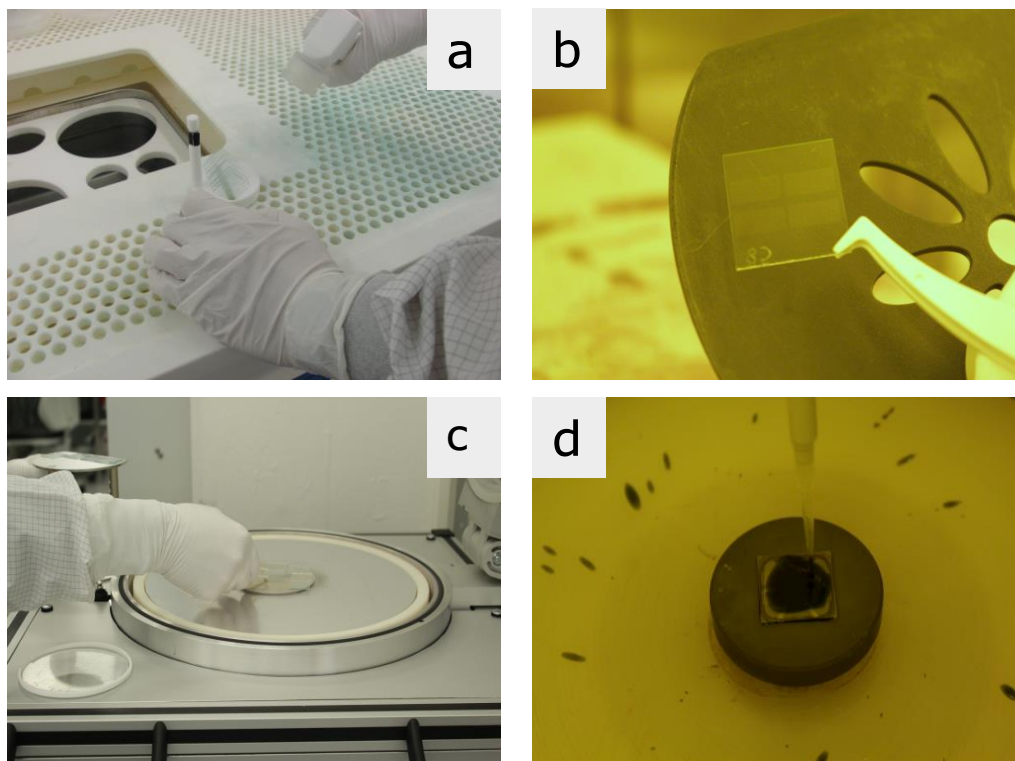


Figure SI- 26. Plot of the % conversion calculated by 2D-GPC plot vs M_n and \bar{D} for the polymerization of **6** with 5 mol% of $[\text{Pd}(\text{t-Bu}_3\text{P})_2]$, 1.2 eq. CsF in THF at 50 °C. The conversion was calculated relative to compound **20** (product from the quenching process with HCl/MeOH) based on the 2D-GPC plots.

OLED-like Device Fabrication

ITO coated glass substrates were cleaned in an ultrasonic bath of acetone and isopropanol each for 15 min. Afterwards they were dried under a nitrogen stream, heated to 160 °C for 10 min and then cleaned with an oxygen plasma with 300 W for 3 min. 200 μL of a PEDOT: PSS water suspension were spin-coated onto the substrates (3500 rpm for 60 s). The samples were then transferred into a glovebox and annealed at 150 °C for 5 min. Afterwards, they were cooled down to 50 °C over the period of 2 h. A solution of the oligomers (**O1** or **O2**) in chloroform was prepared with a concentration of 10 mg/mL. 180 μL of the polymer solutions respectively were spin coated (500 rpm for 5 s, and 1000 rpm for 60 s) on the PEDOT:PSS layer and the samples were annealed at 70 °C for 2 h. Finally, a layer of LiF (1 nm) and Al (200 nm) were deposited by thermal evaporation.



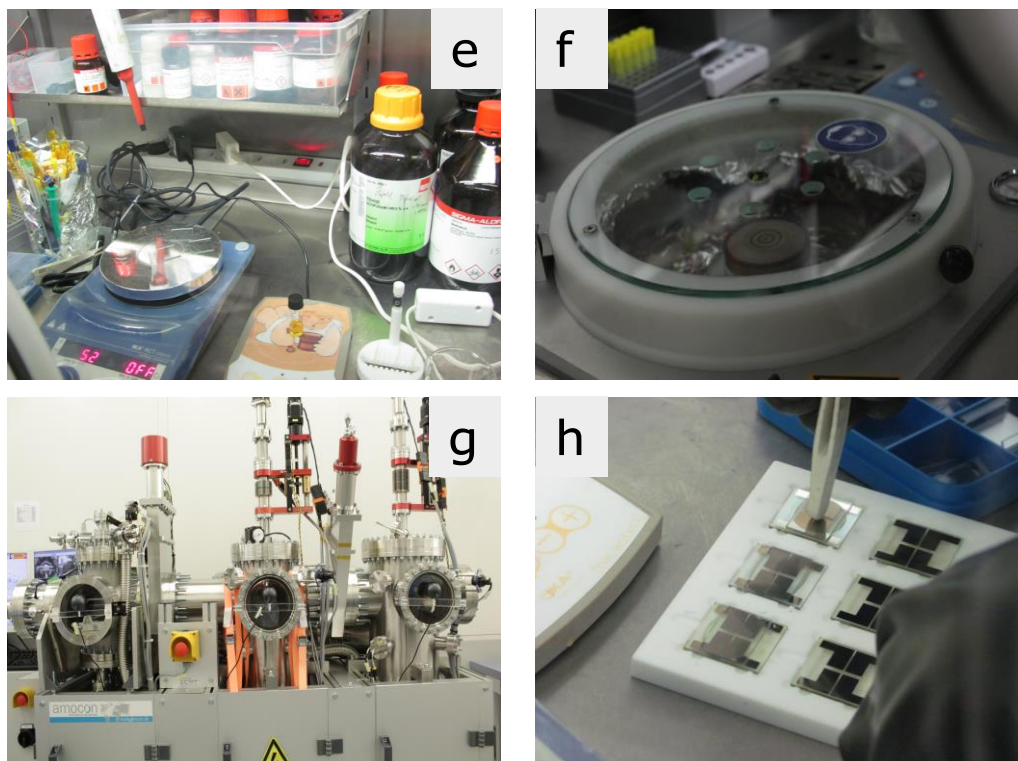


Figure SI- 27. Description of the OLED fabrication. a) Glass/ITO cleaning with acetone and isopropanol. b) Drying process of the glass/ITO. c) Glass/ITO cleaning with an oxygen plasma. d) Spin coating of a PEDOT:PSS solution over the glass/ITO. e) Annealing of the system (glass/ITO/PEDOT:PSS) inside a GB. f) Spin coating of a solution of the oligomers (**O1** or **O2**) in chloroform. g) Thermal evaporation of LiF and Al layers. h) OLED Encapsulation.

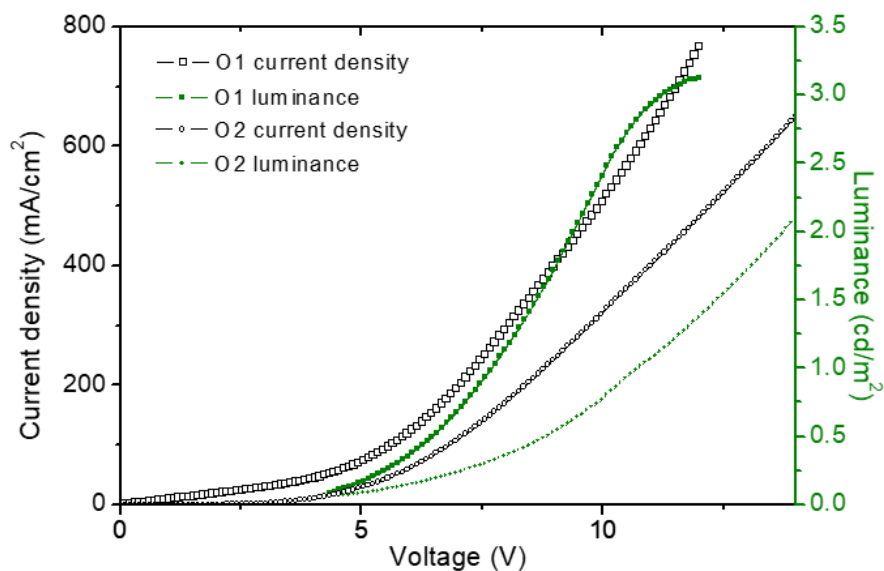


Figure SI- 28. Current density - voltage - luminance curves of the OLED-type devices with **O1** and **O2** as emissive layer.

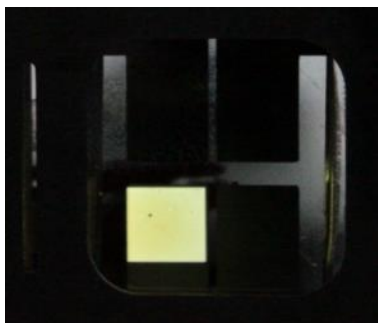


Figure SI- 29. Photo of the electroluminescence of the OLED-type device using **O2** as emissive layer. Exposure time: 1 s, which was visible to the human eye.

Device	Vol^a (V)	EQE^b (%)	CE^b (cd/A)	PE^b (lm/W)	CIE Color coordinates	Maximal brightness (cd/m²) (@ mA/cm²)
O1	7.7	3.4e ⁻⁴	4.7e ⁻⁴	1.5e ⁻⁴	0.351,0.385	3.1 (@ 750 mA/cm ²)
O2	10.7	2.6e ⁻⁴	2.6e ⁻⁴	0.8e ⁻⁴	0.379,0.381	2.1 (@ 650 mA/cm ²)

^a Voltage recorded at luminance of 1 cd/m², ^b EQE, CE and PE recorded at 500 mA/cm²

Table SI- 9. Electroluminescent performance of the OLED-type devices.

NMR Spectra

(3-Hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylstannane (7)

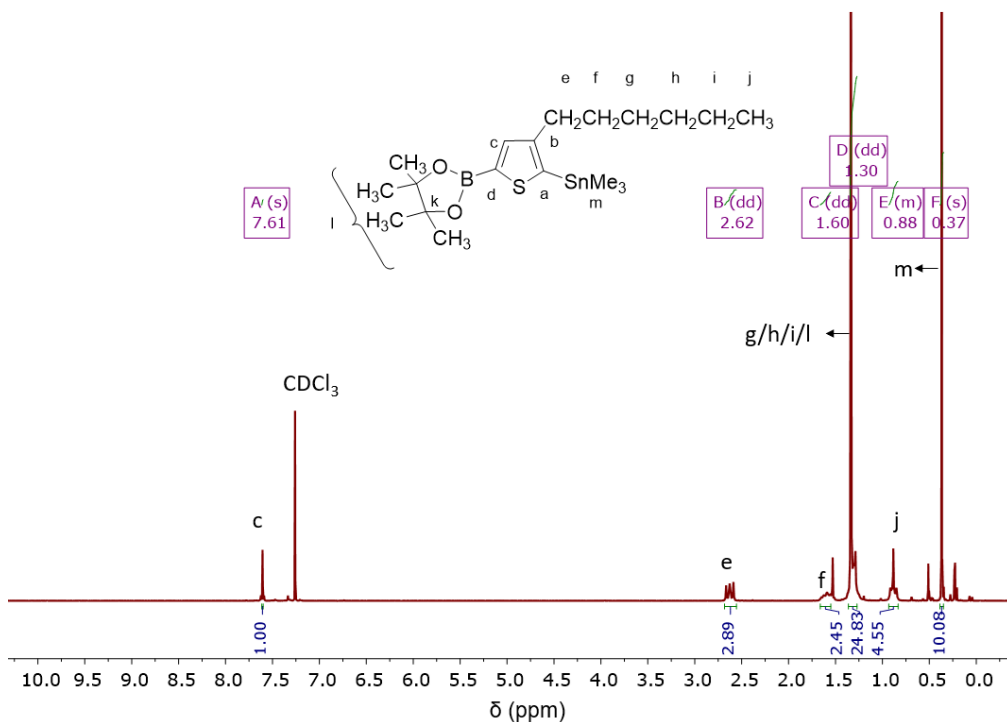


Figure SI- 30. ¹H NMR (500 MHz) spectrum of **7** in CDCl₃.

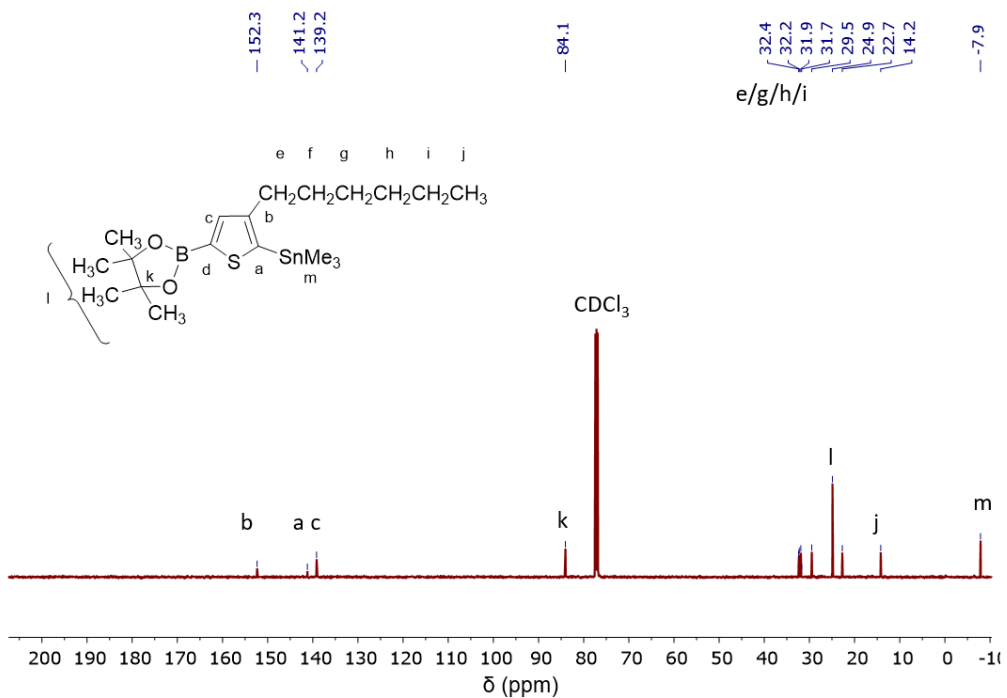


Figure SI- 31. ¹³C{¹H} NMR (126 MHz) spectrum of **7** in CDCl₃.

4-Bromo-2-*n*-hexylthiophene (**11**)

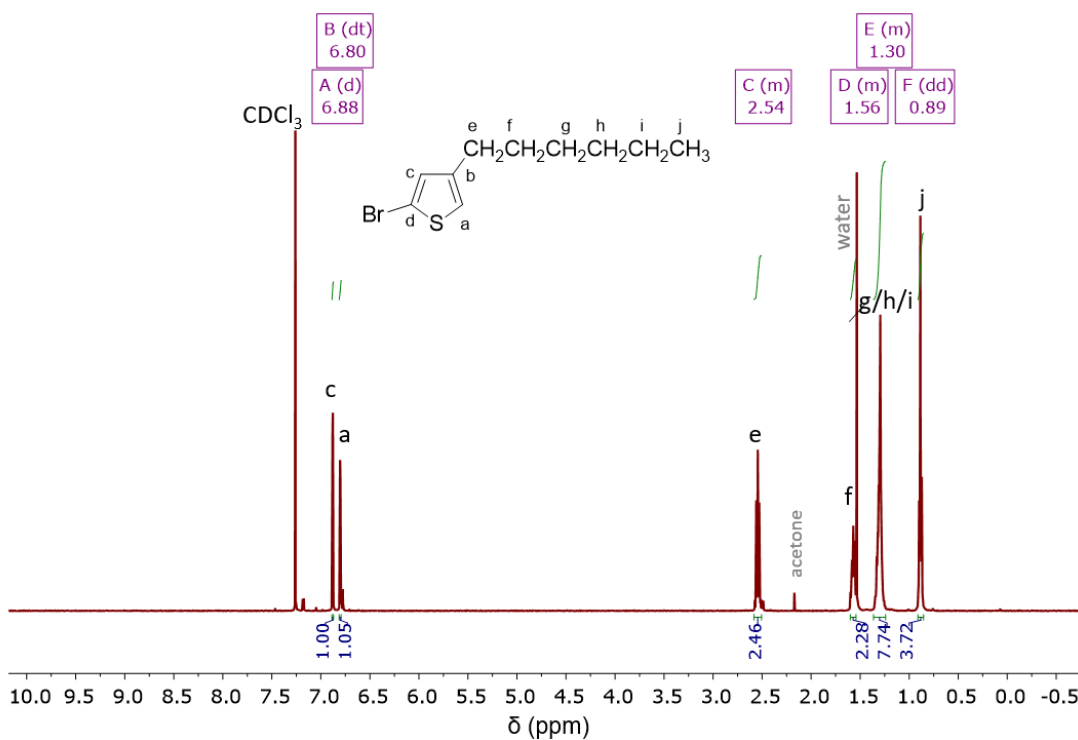


Figure SI- 32. ^1H NMR (500 MHz) spectrum of **11** in CDCl_3 .

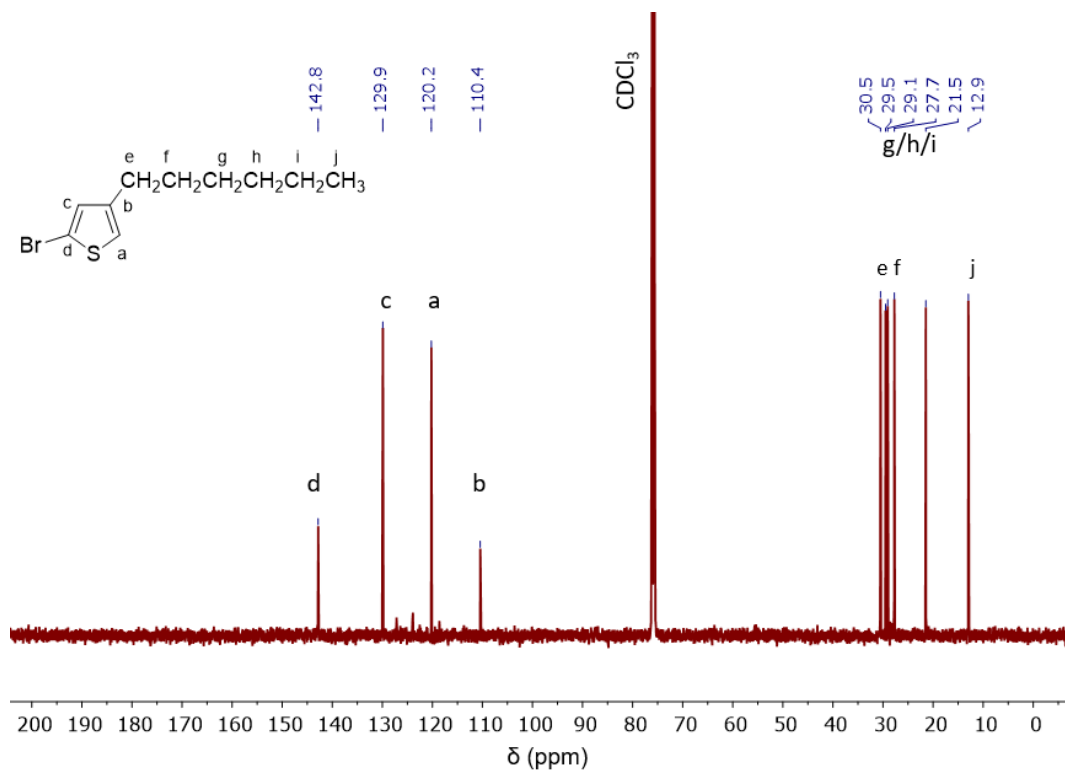
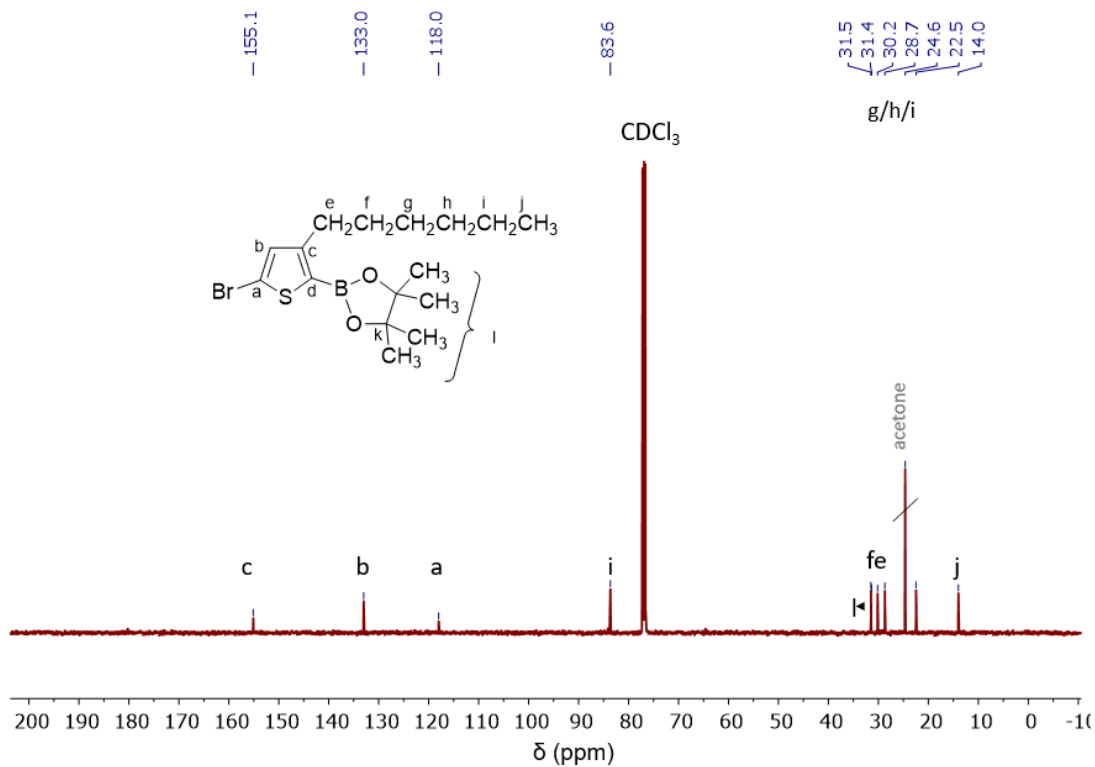
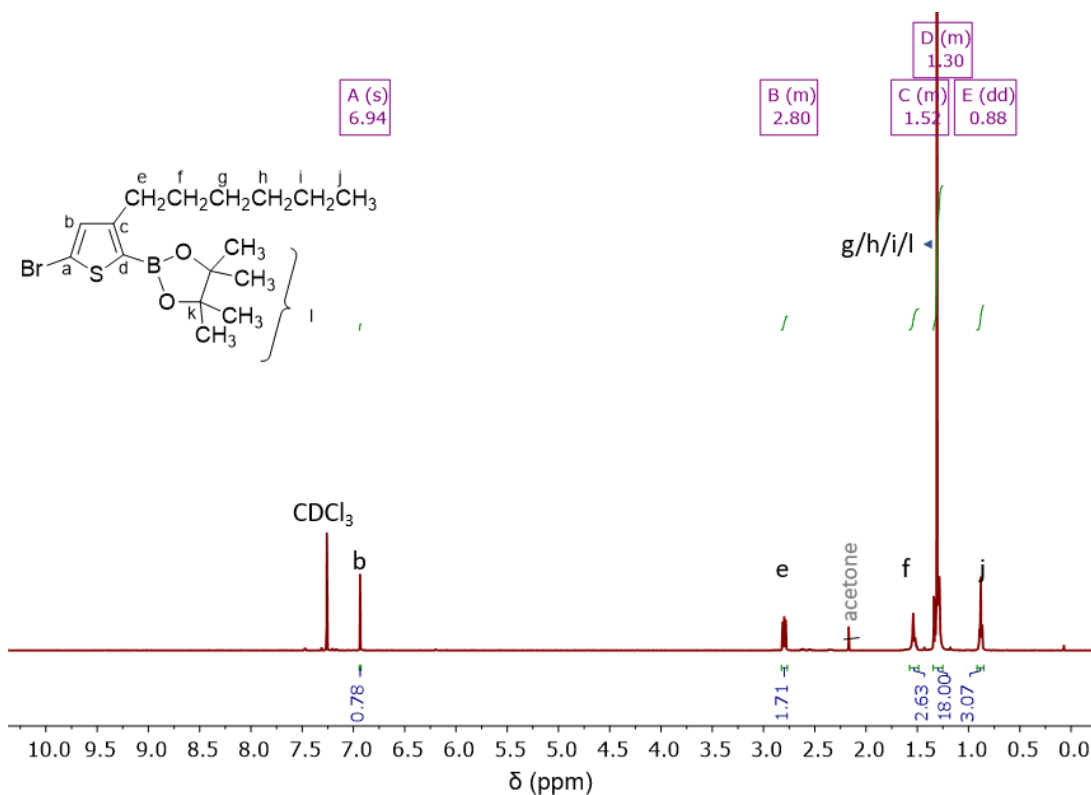


Figure SI- 33. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz) spectrum of **11** in CDCl_3 .

2-(5-Bromo-3-hexylthiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)



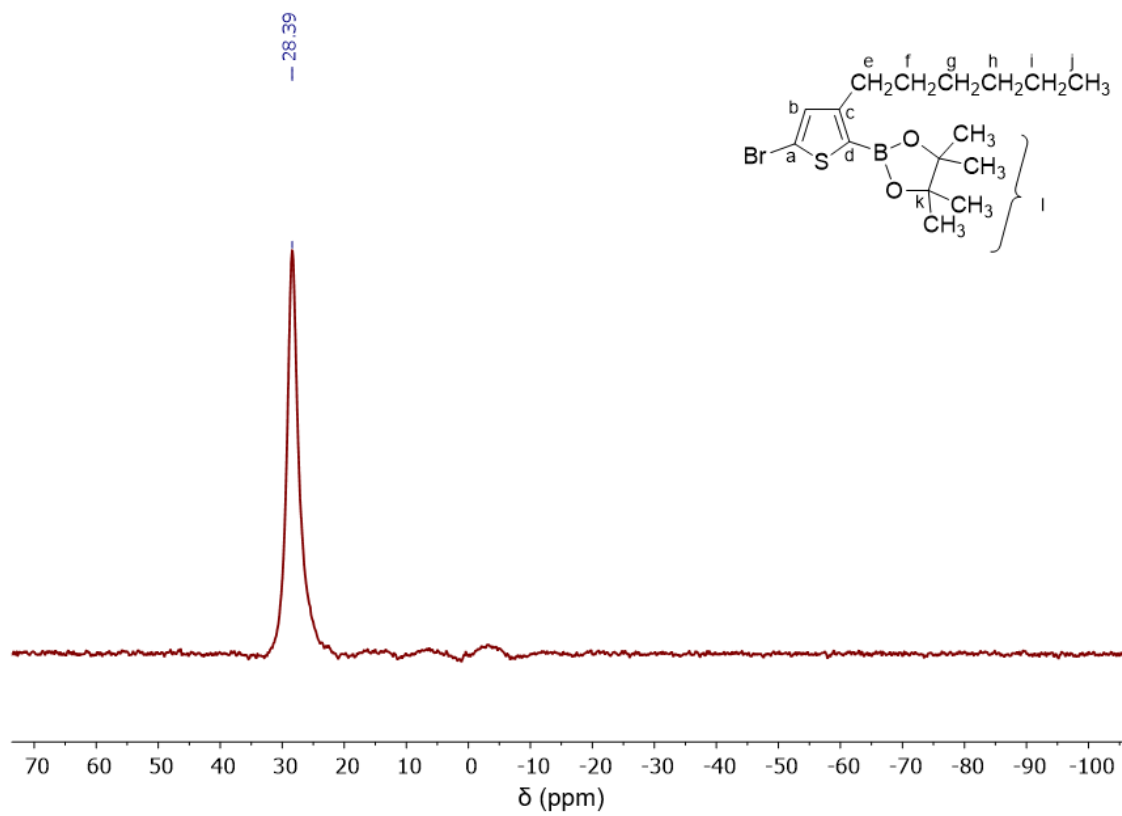
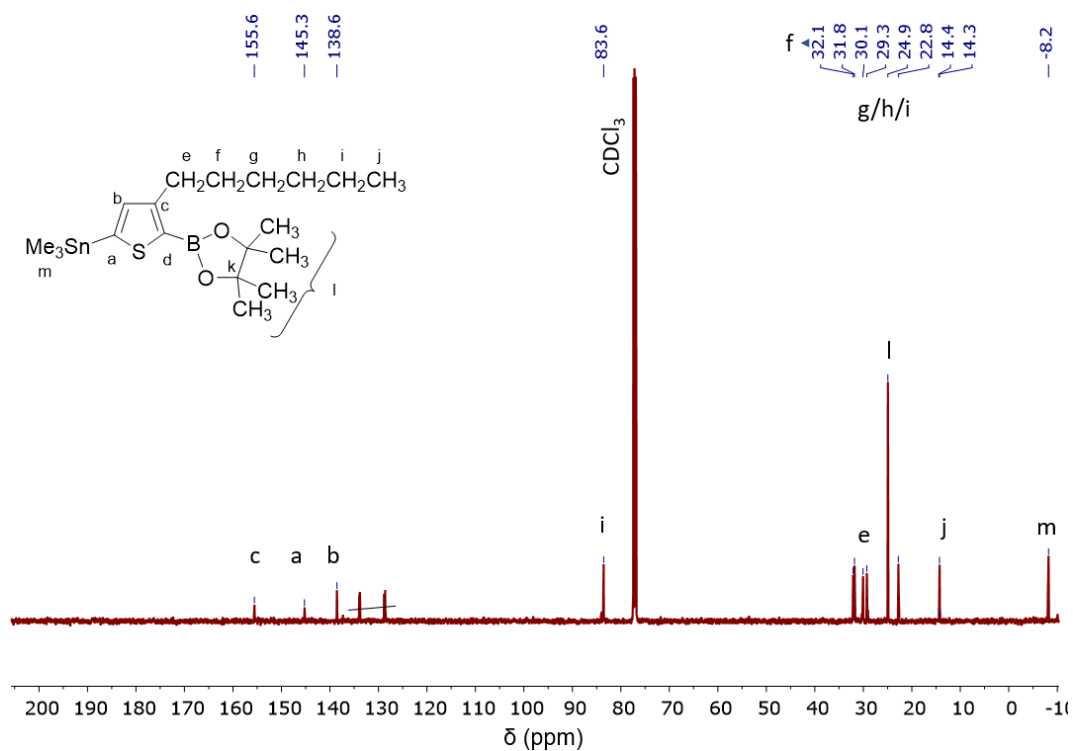
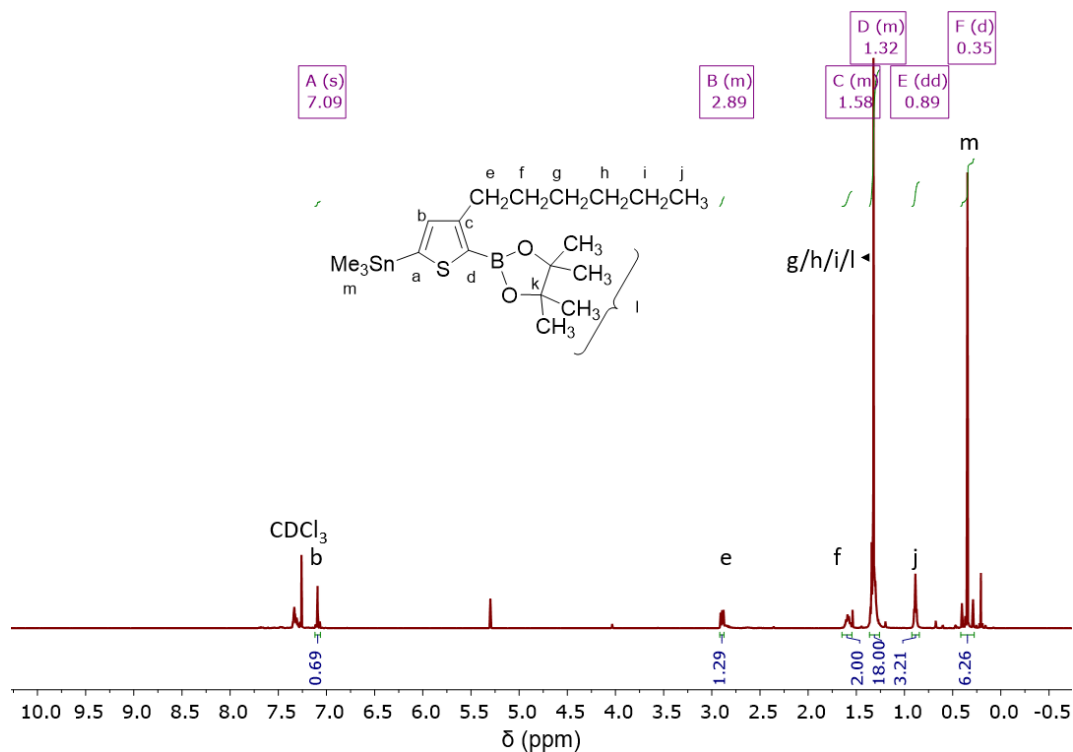


Figure SI- 36. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz) spectrum of **12** in CDCl_3 .

(4-Hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)trimethylstannane (13)



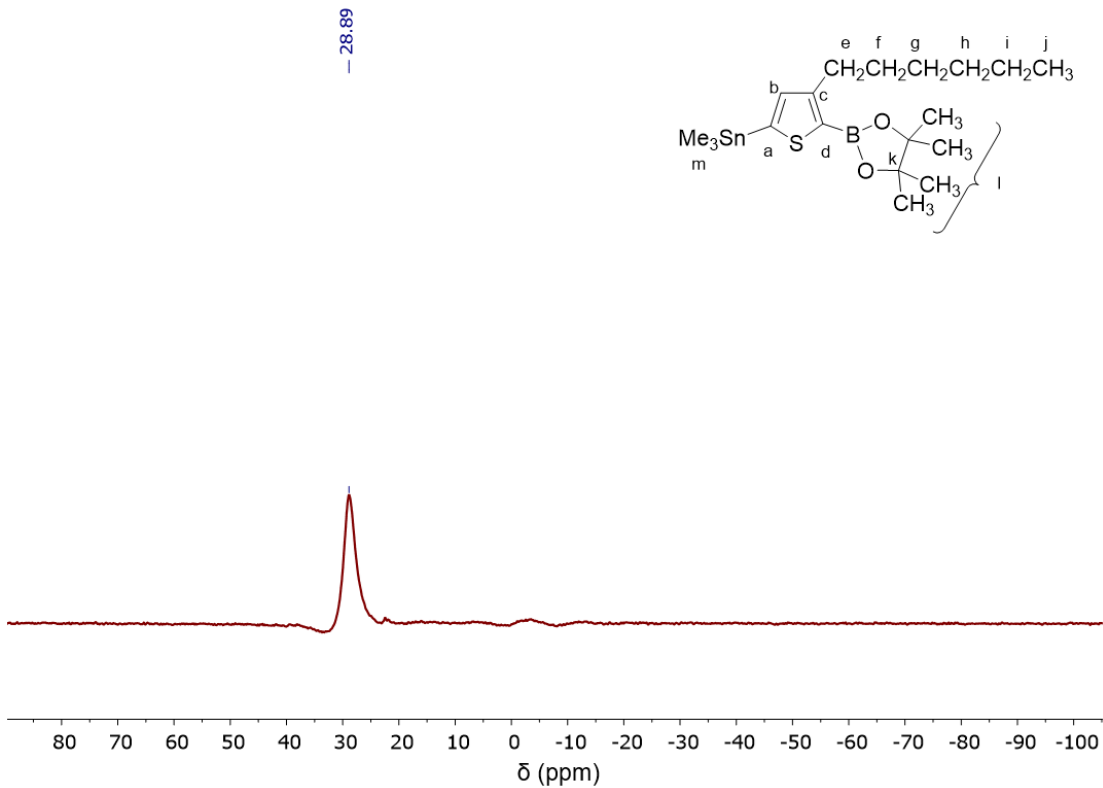


Figure SI- 39. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz) spectrum of **13** in CDCl_3 .

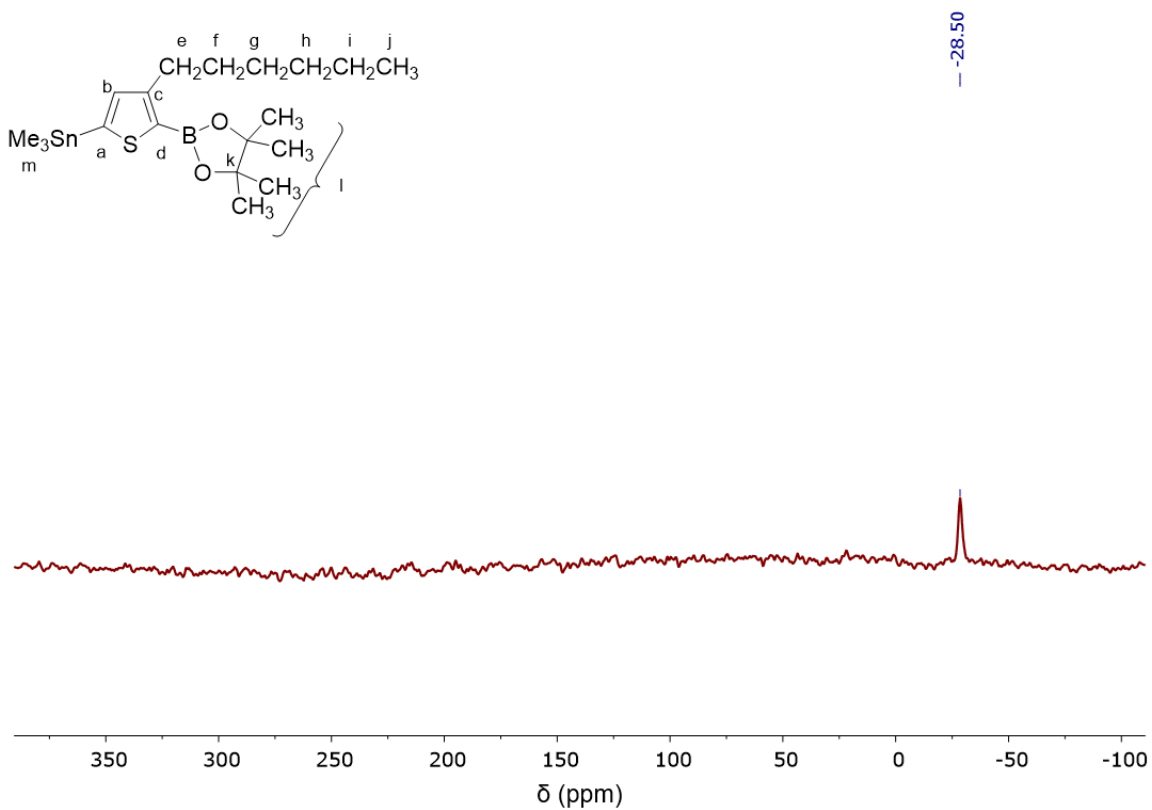


Figure SI- 40. $^{119}\text{Sn}\{^1\text{H}\}$ NMR (160 MHz) spectrum of **13** in CDCl_3 .

1-Bromo-2-(hexyloxy)benzene (**15**)

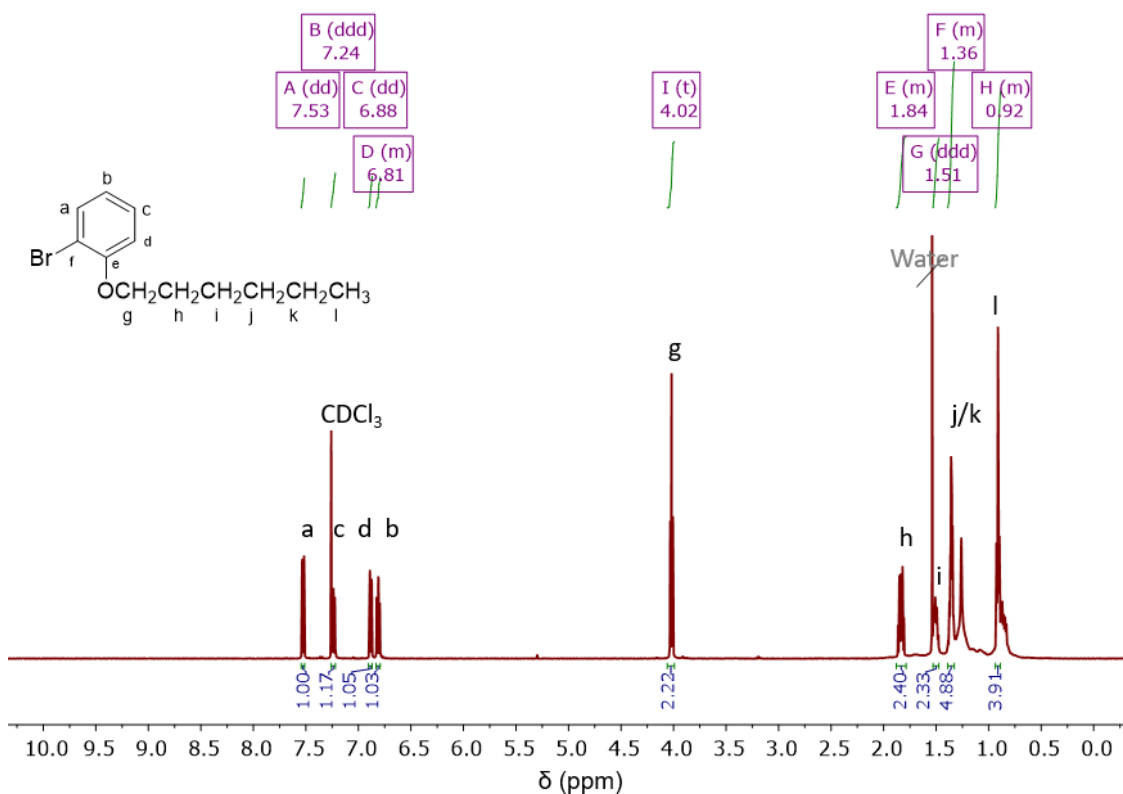


Figure SI- 41. ¹H NMR (500 MHz) spectrum of **15** in CDCl₃.

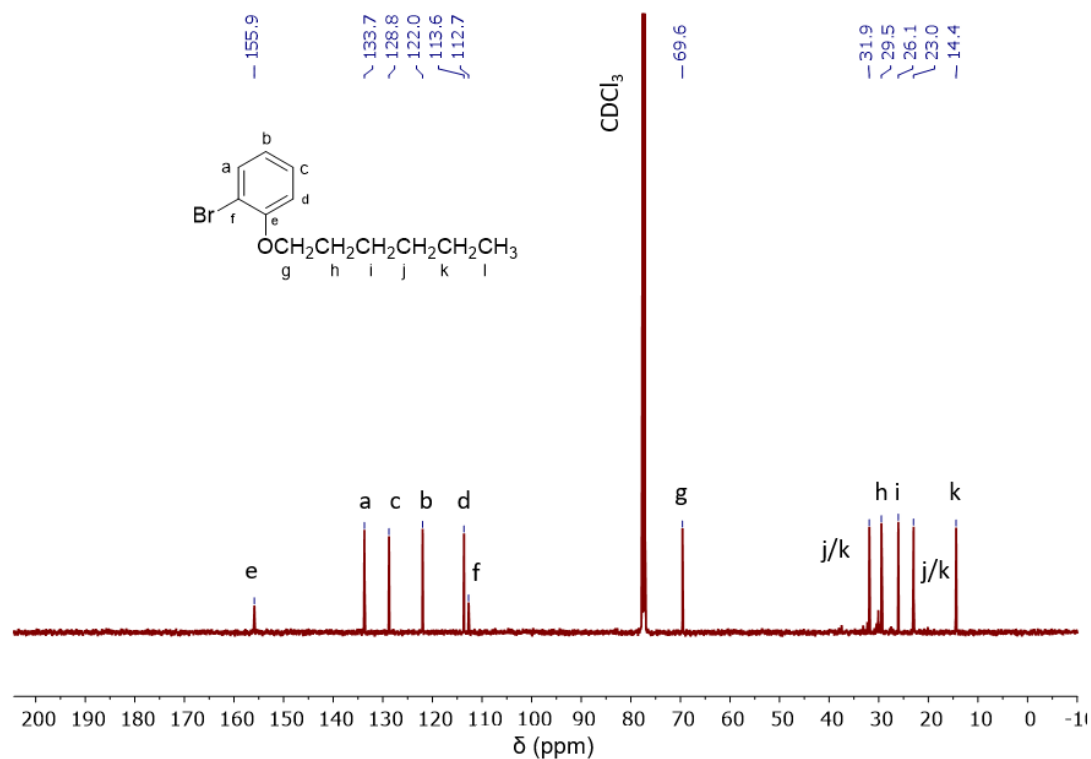


Figure SI- 42. ¹³C{¹H} NMR (126 MHz) spectrum of **15** in CDCl₃.

1-Bromo-2-(hexyloxy)-5-iodobenzene (**16**)

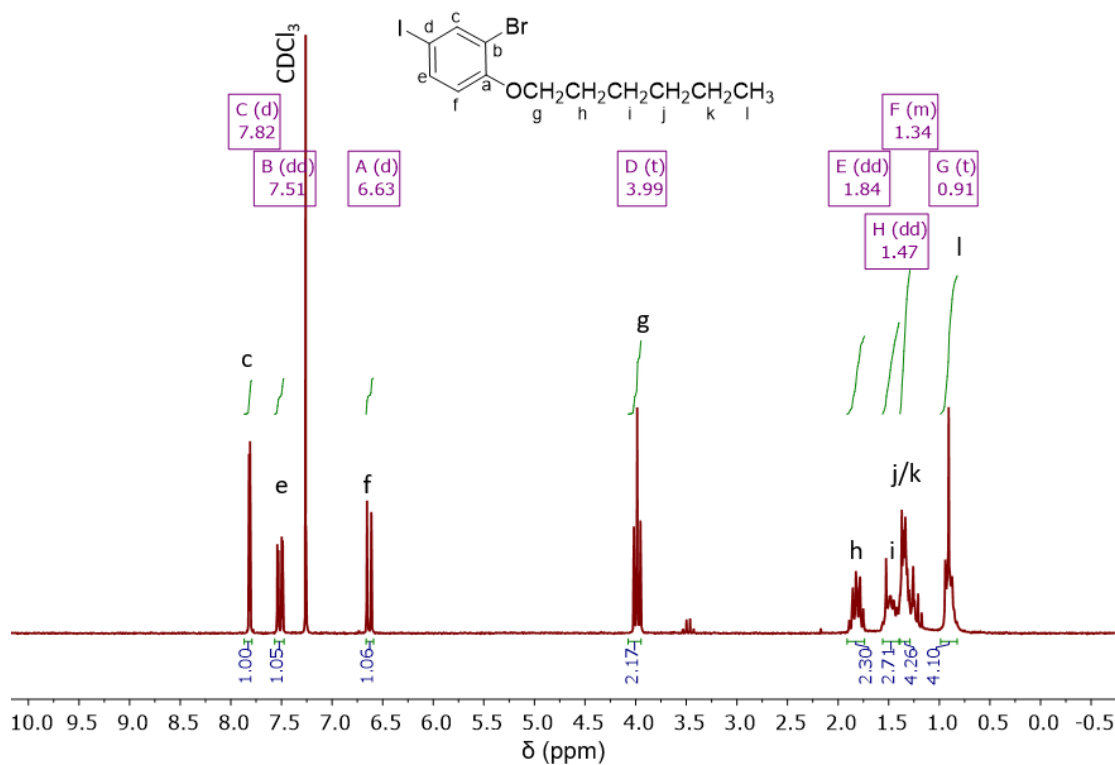


Figure SI- 43. ¹H NMR (500 MHz) spectrum of **16** in CDCl₃.

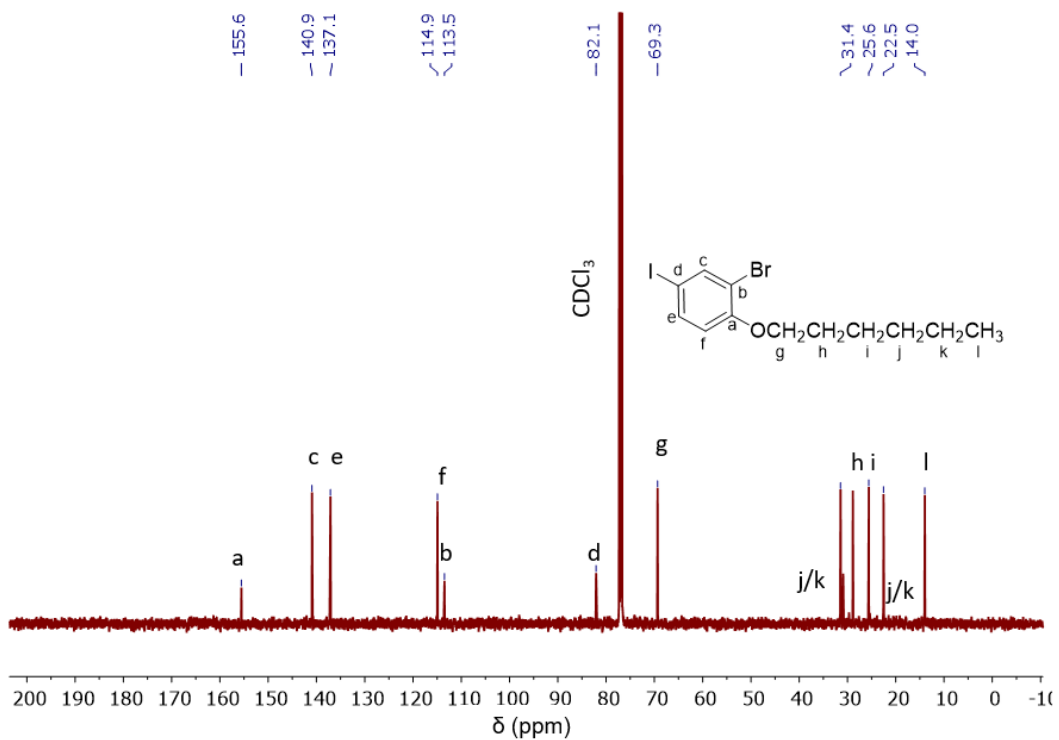


Figure SI- 44. ¹³C{¹H} NMR (126 MHz) spectrum of **16** in CDCl₃.

2-Bromo-6-iodo-3-pyridinol (**18**)

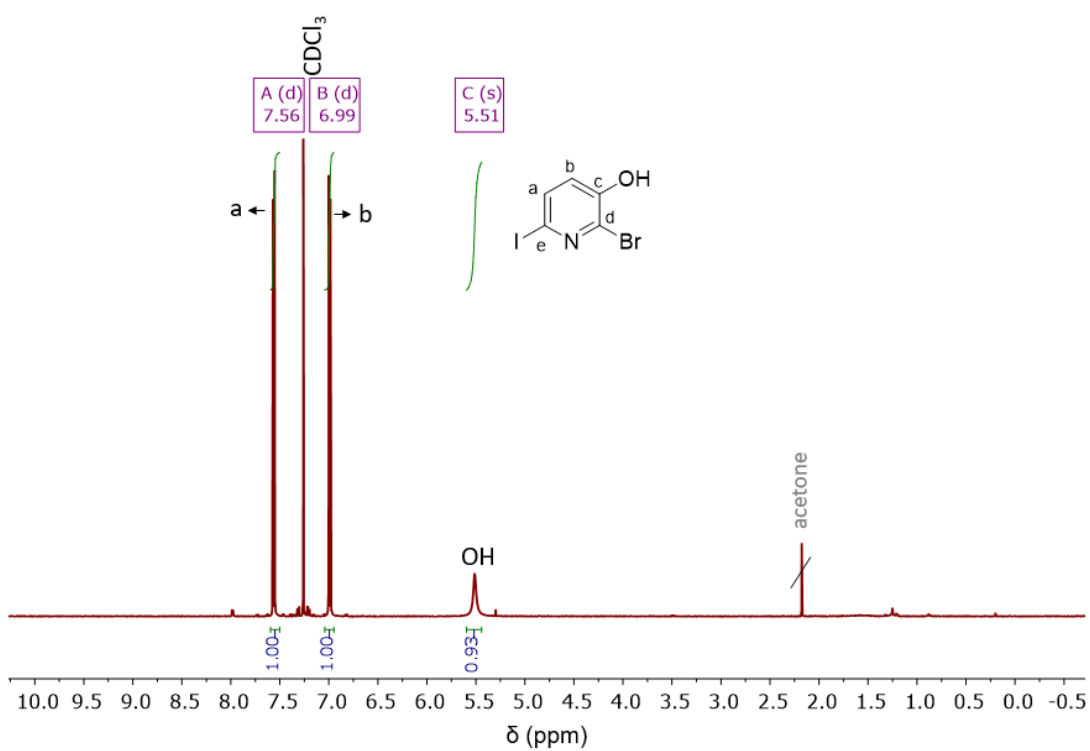


Figure SI- 45. ^1H NMR (500 MHz) spectrum of **18** in CDCl_3 .

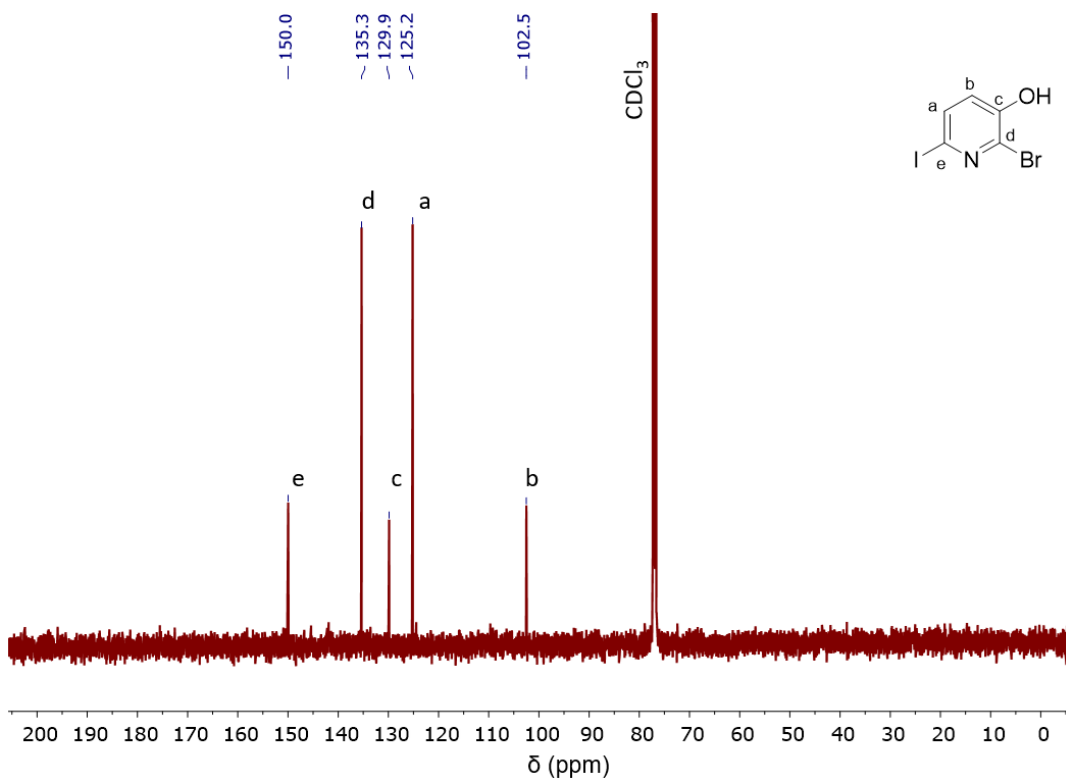


Figure SI- 46. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz) spectrum of **18** in CDCl_3 .

2-Bromo-3-(hexyloxy)-6-iodopyridine (8)

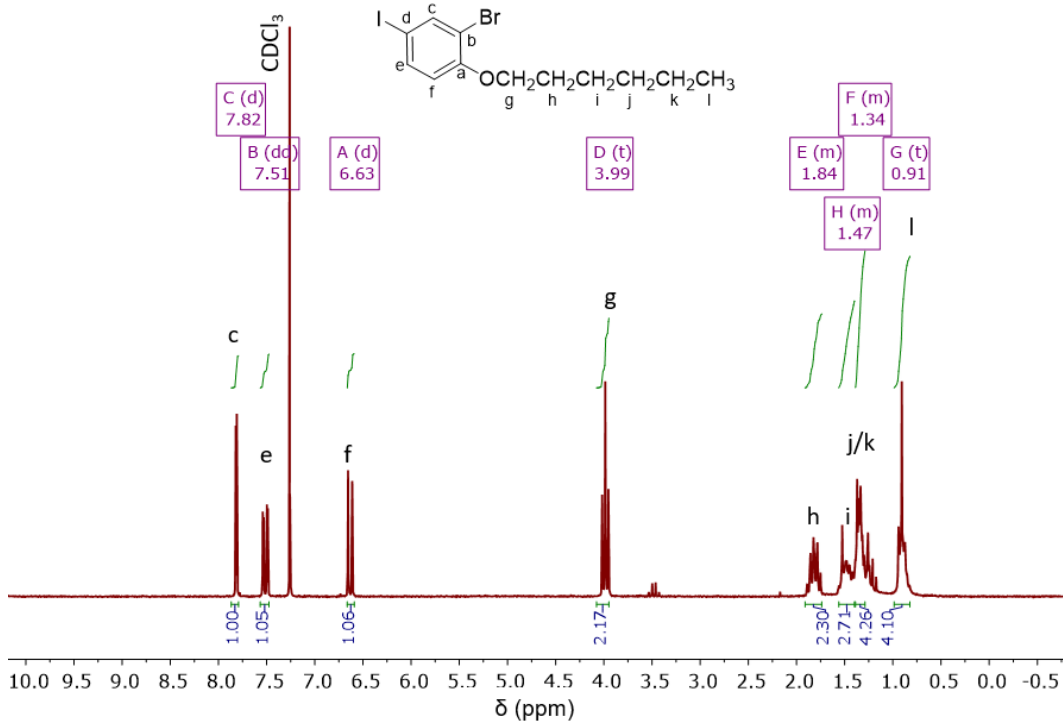


Figure SI- 47. ^1H NMR (500 MHz) spectrum of **8** in CDCl_3 .

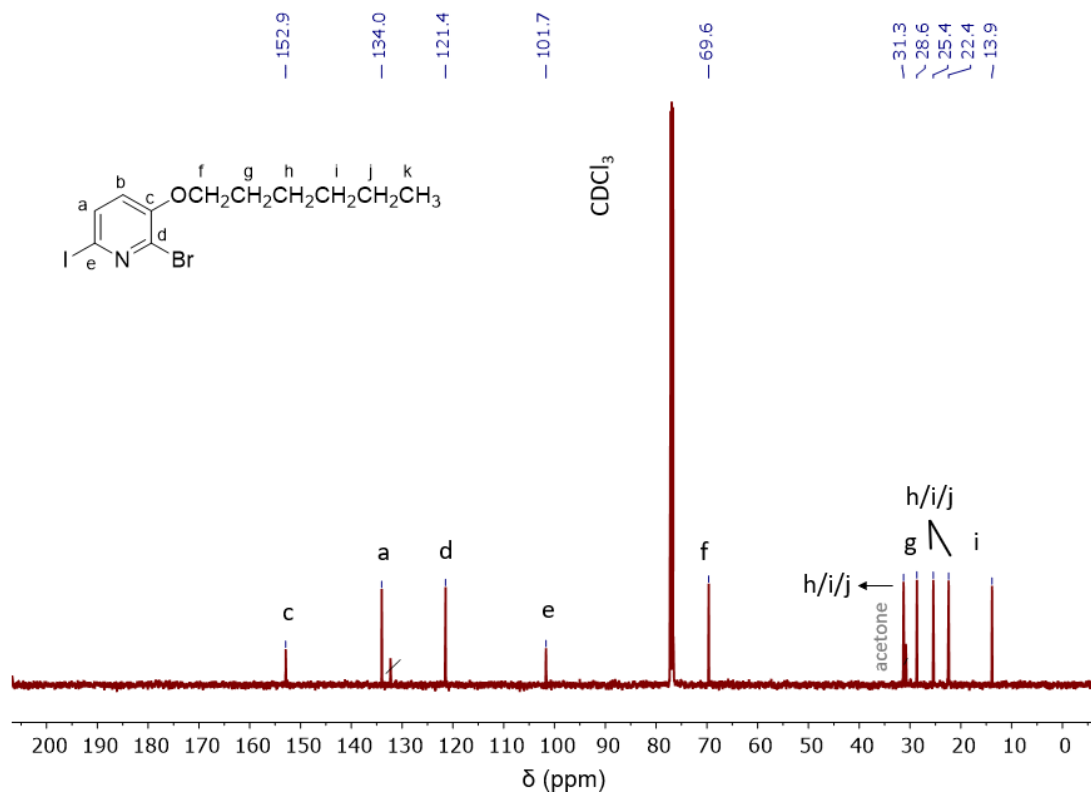


Figure SI- 48. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz) spectrum of **8** in CDCl_3 .

2-(5-(4-Bromo-3-(hexyloxy)phenyl)-3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

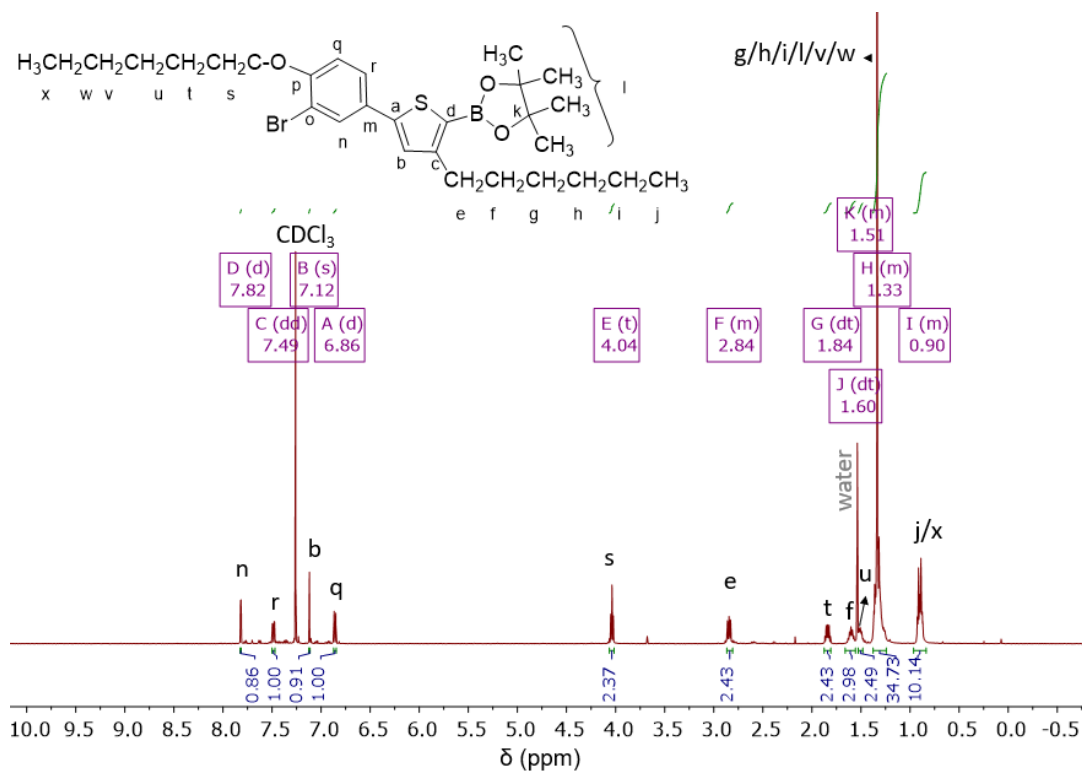


Figure SI- 49. ¹H NMR (500 MHz) spectrum of **5** in CDCl₃.

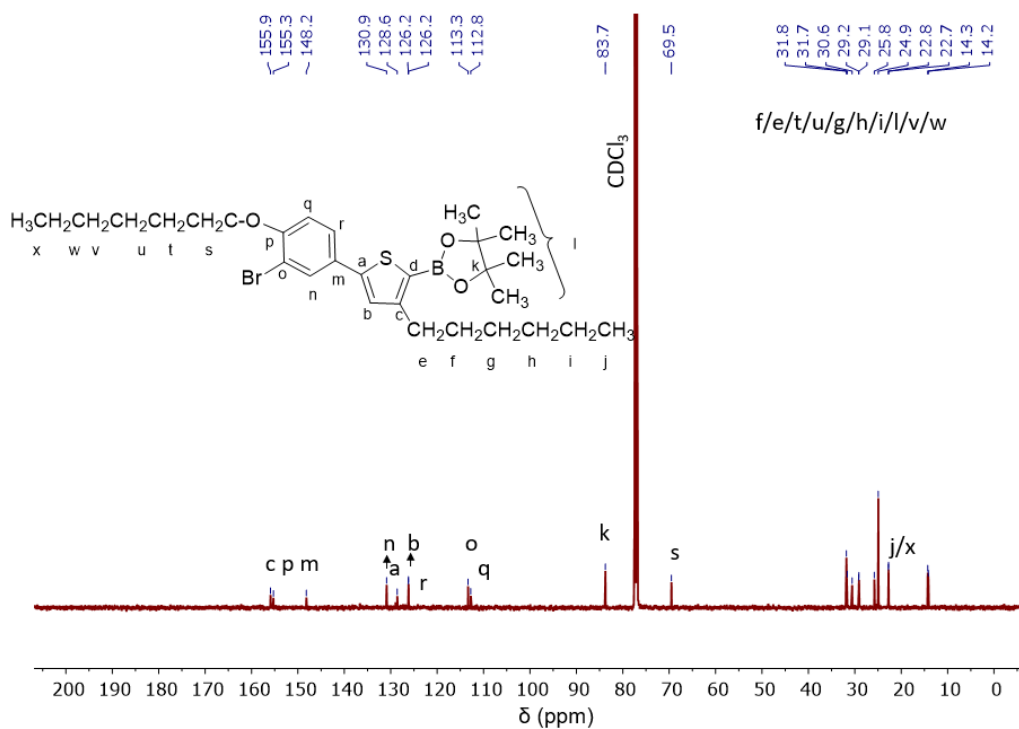


Figure SI- 50. ¹³C{¹H} NMR (126 MHz) spectrum of **5** in CDCl₃.

-28.87

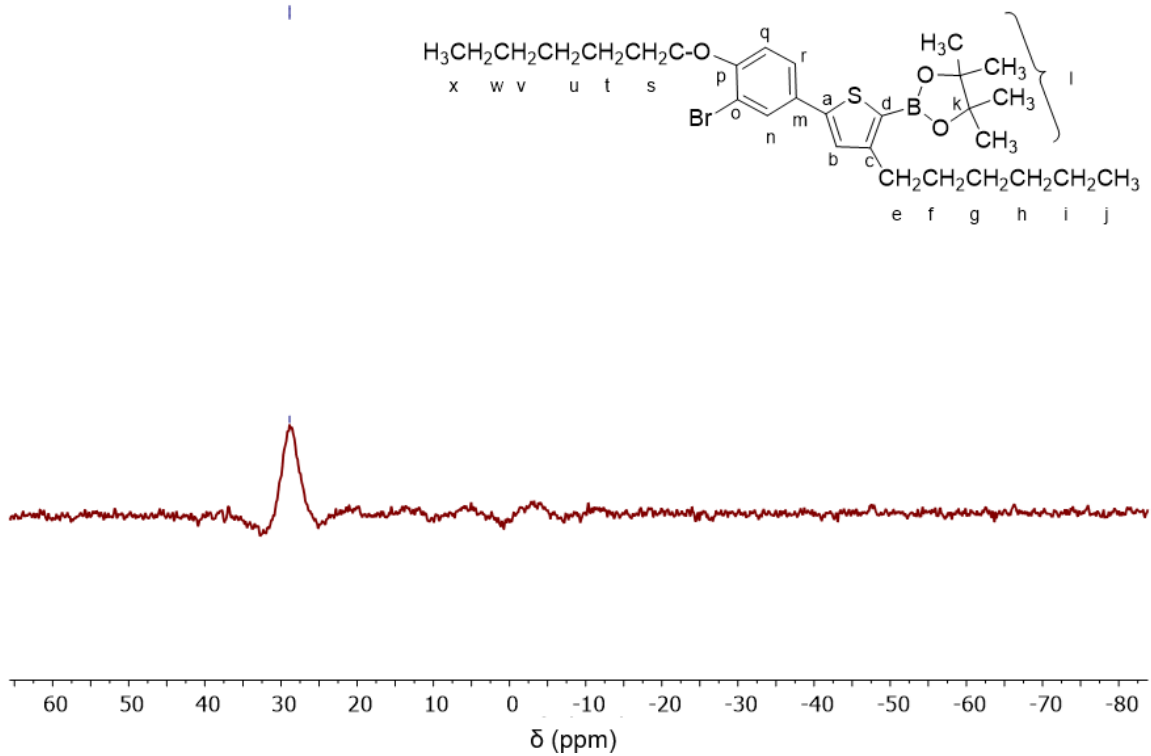


Figure SI- 51. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz) spectrum of **5** in CDCl_3 .

2-Bromo-6-(4-hexyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-3-(hexyloxy)pyridine (6)

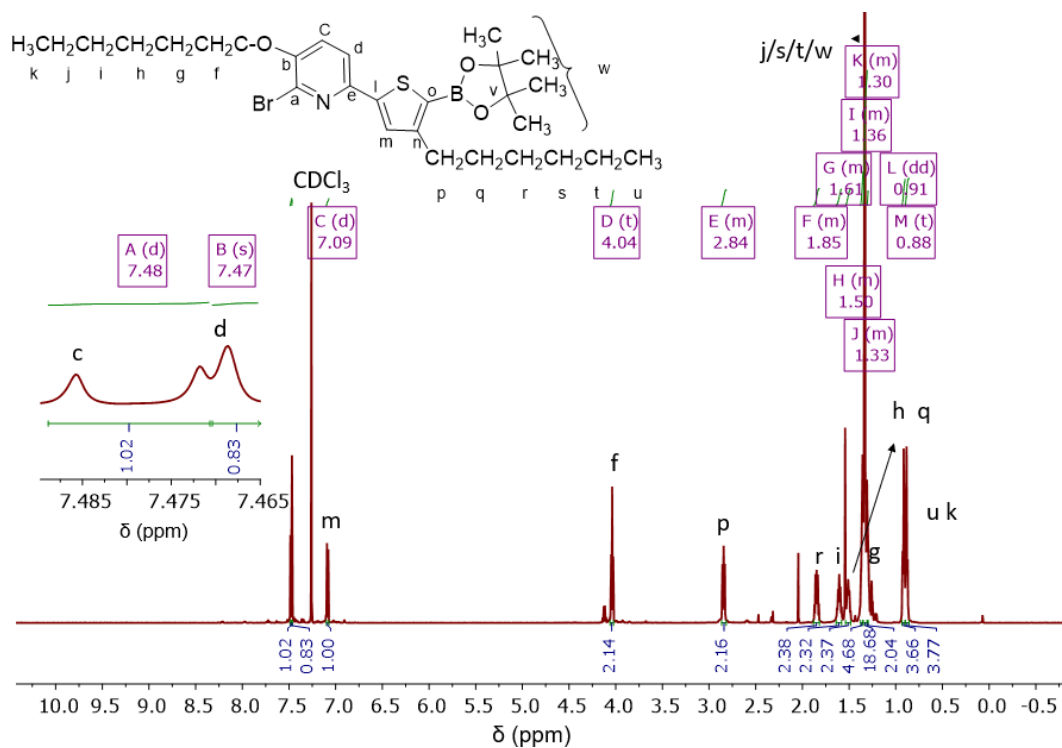


Figure SI- 52. ^1H NMR (500 MHz) spectrum of **6** in CDCl_3 .

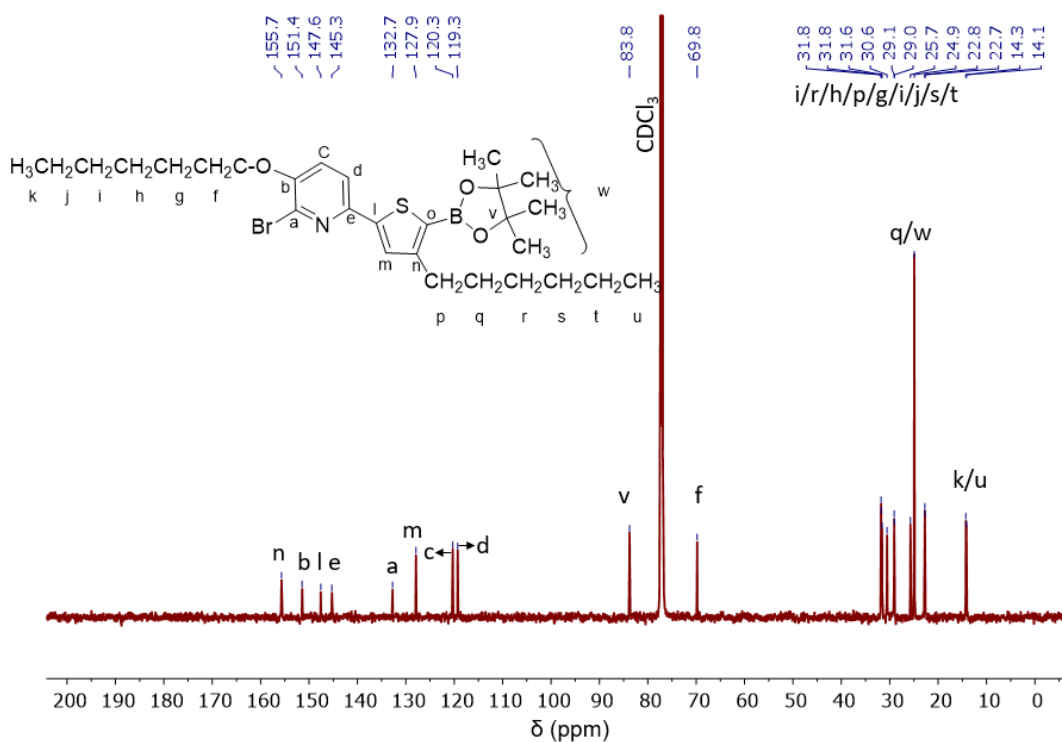


Figure SI- 53. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz) spectrum of **6** in CDCl_3 .

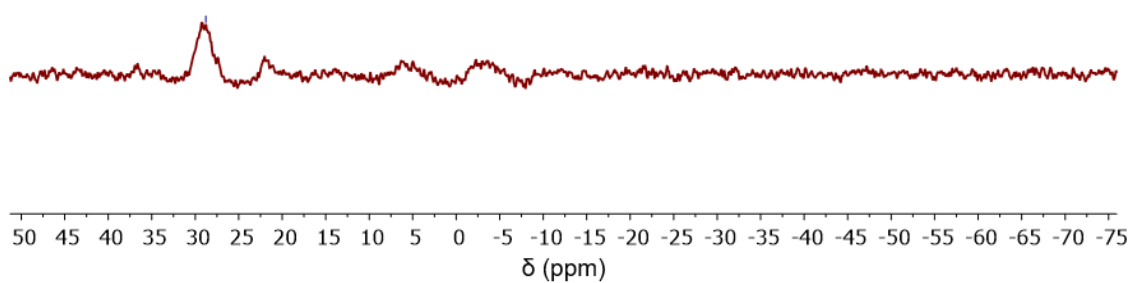
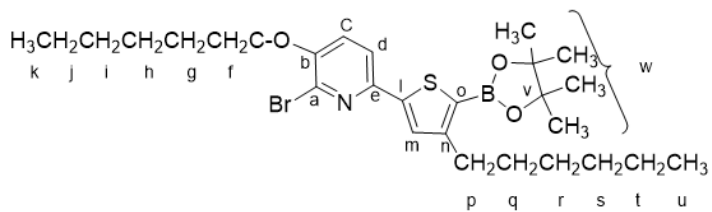


Figure SI- 54. $^{11}\text{B}\{^1\text{H}\}$ NMR (160 MHz) spectrum of **6** in CDCl_3 .

Poly-(1,4-(3-hexyl)-thiophene-2,6-(3-hexyloxy)-phenylene) O1

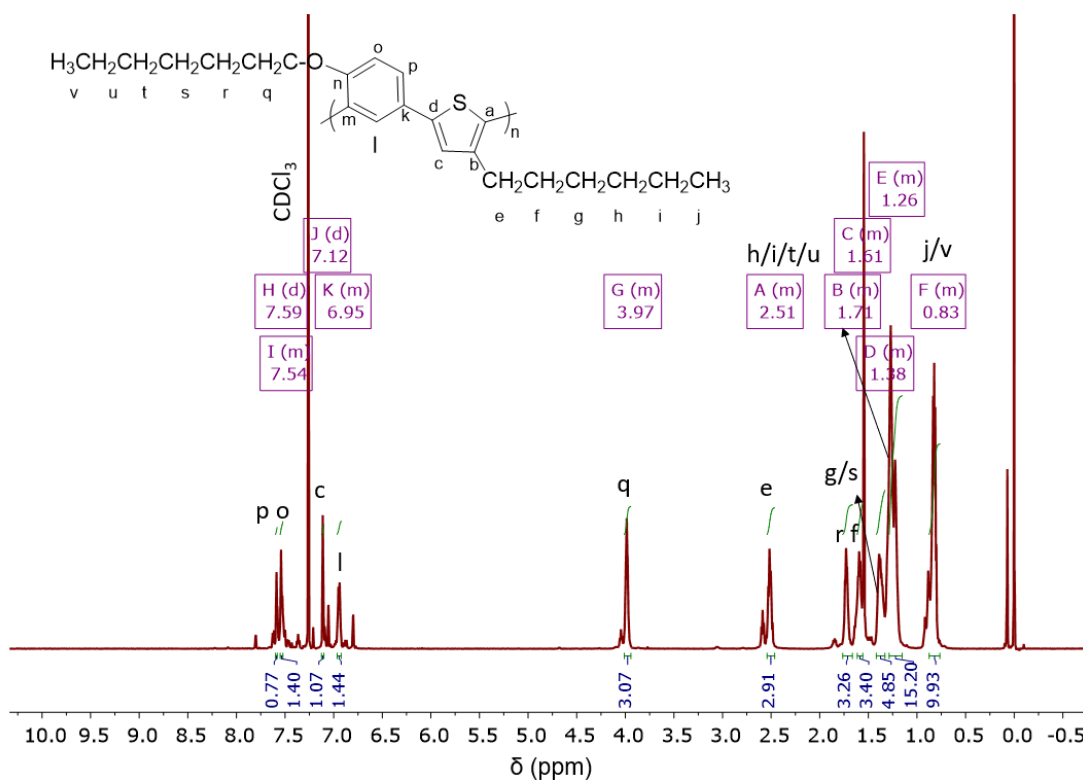


Figure SI- 55. ^1H NMR (600 MHz) spectrum of **O1** in CDCl_3 .

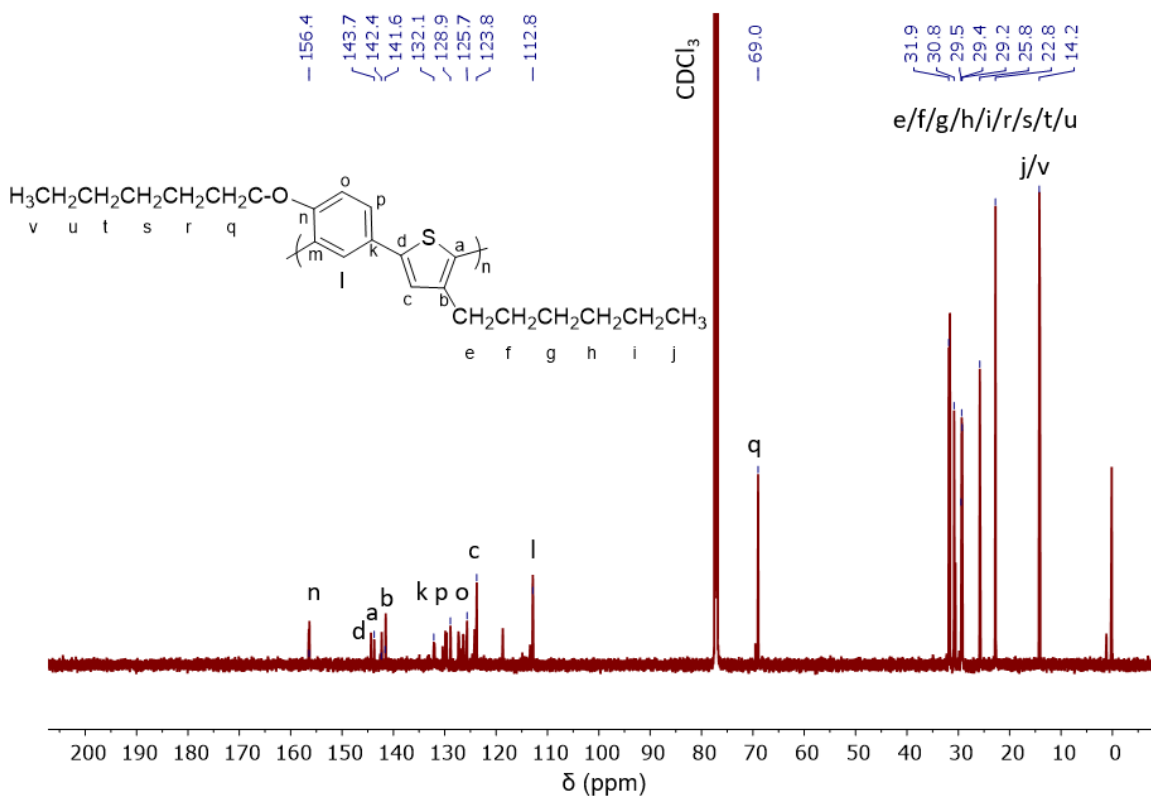


Figure SI- 56. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz) spectrum of **O1** in CDCl_3 .

Poly-(2,6-(3-hexyloxy)-pyridine-1,4-(3-hexyl)-thiophene) O2

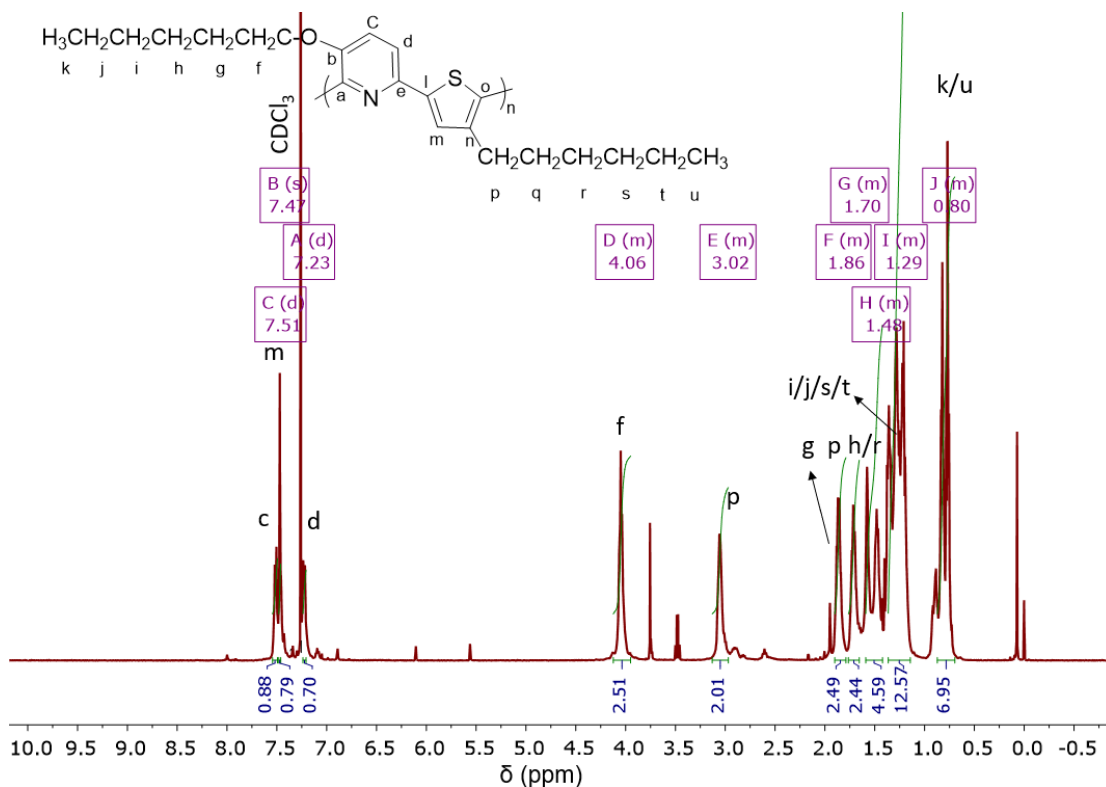


Figure SI- 57. ^1H NMR (600 MHz) spectrum of **O2** in CDCl_3 .

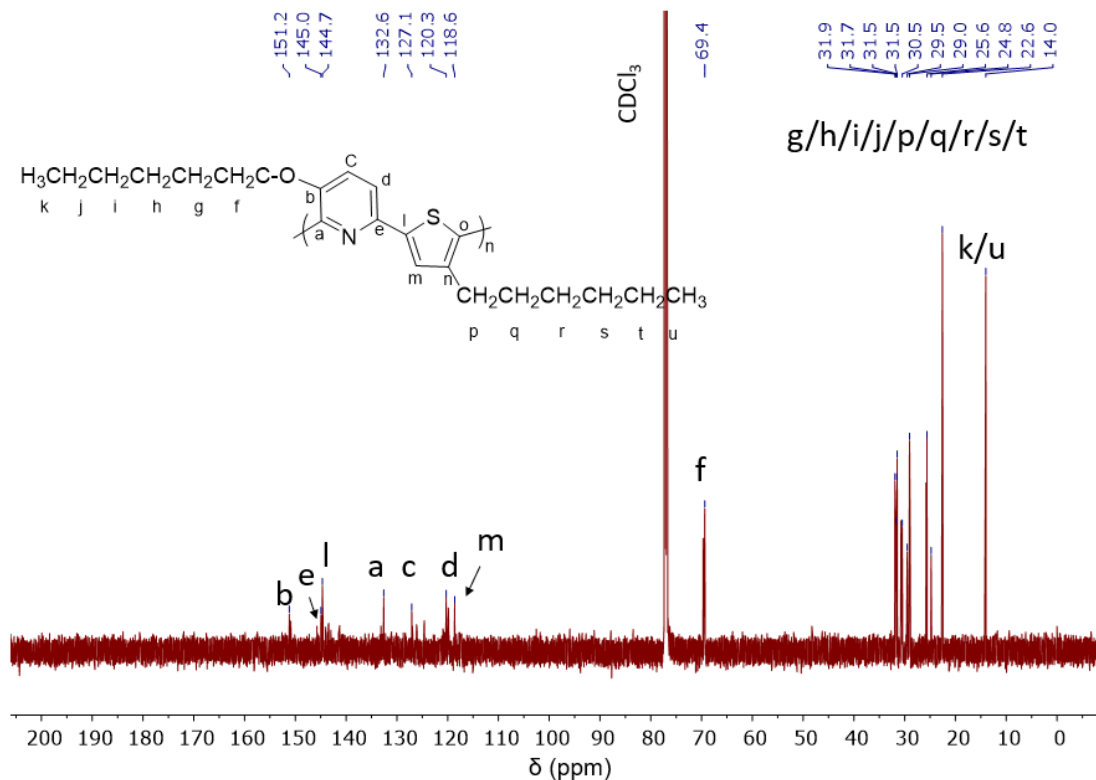


Figure SI- 58. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz) spectrum of **O2** in CDCl_3 .

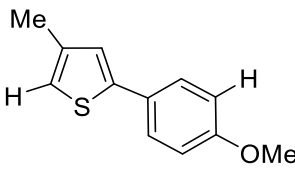
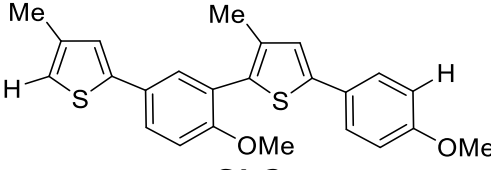
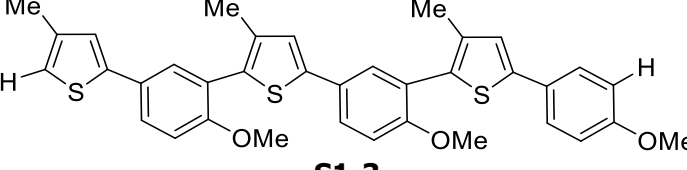
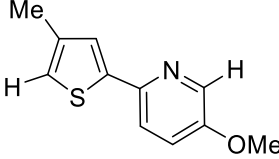
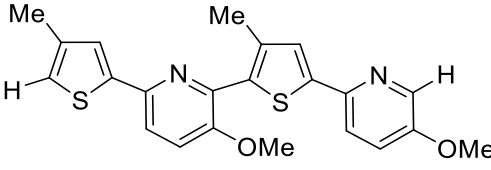
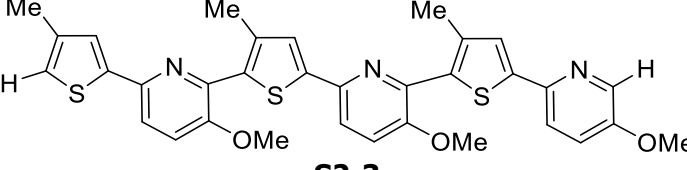
Molecule	E_{homo} (eV)	E_{lumo} (eV)	HOMO-LUMO (eV)	$UV_{\lambda_{\text{max}}}$
 <p style="text-align: center;">S1</p>	-0.66	-5.32	4.66	4.37 eV 284 nm
 <p style="text-align: center;">S1-2</p>	-1.09	-5.17	4.08	3.71 eV 334 nm
 <p style="text-align: center;">S1-3</p>	-1.22	-5.17	3.95	3.60 eV 344 nm
 <p style="text-align: center;">S2</p>	-1.01	-5.43	4.42	4.12 eV 301 nm
 <p style="text-align: center;">S2-2</p>	-1.45	-5.15	3.70	3.39 eV 366 nm
 <p style="text-align: center;">S2-3</p>	-1.57	-5.11	3.54 eV	3.14 eV 395 nm

Table SI- 10. Molecular orbital energies (HOMO, LUMO), HOMO-LUMO gaps and calculated absorption wavelength from the monomers **S1** and **S2**, dimers **S1-2**, **S2-2** and trimers **S1-3** and **S2-3**.

Molecular Orbitals

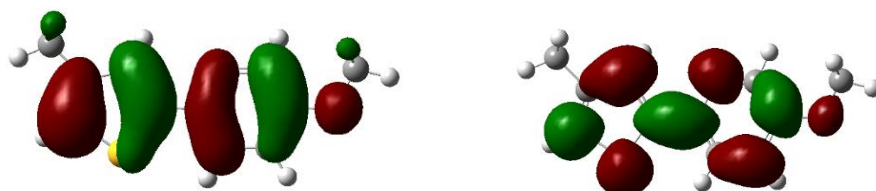


Figure SI- 59. Molecular orbitals of **S1** (displayed with an isovalue of 0.02): HOMO (left) and LUMO (right).

Symmetry = C1

B3LYP/6-31G(d)

E=-937.92384330 Ha

ATOM	SYMBOL	X	Y	Z
1	C	0.919567	-1.27171	0.406397
2	C	0.202495	-0.11965	0.026458
3	C	0.942719	1.019296	-0.3243
4	C	2.305746	-1.28042	0.435678
5	C	3.028695	-0.12825	0.092916
6	C	2.337051	1.028512	-0.28737
7	O	4.386986	-0.23991	0.159257
8	C	5.17097	0.896508	-0.16902
9	H	6.211054	0.589787	-0.04309
10	H	4.958857	1.741717	0.500202
11	H	5.010153	1.212673	-1.20889
12	C	-1.26411	-0.08968	0.000244
13	C	-2.09817	0.981374	0.214313
14	S	-2.21246	-1.52477	-0.35591
15	C	-3.4927	0.677175	0.105882
16	C	-3.70004	-0.64286	-0.19261
17	C	-4.58667	1.689834	0.310417
18	H	-4.64793	-1.14832	-0.32613
19	H	-1.72578	1.966456	0.477531
20	H	2.867164	1.93065	-0.57012

21	H	2.856642	-2.16721	0.732714
22	H	0.379007	-2.16713	0.701041
23	H	-4.50626	2.513021	-0.4107
24	H	-4.53606	2.132805	1.313026
25	H	-5.57636	1.237493	0.193371
26	H	0.419699	1.912838	-0.65257

Table SI- 11. xyz Coordinates from the DFT calculations of molecule **S1-1**.

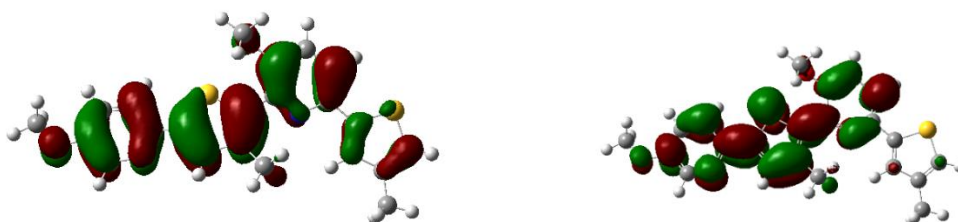


Figure SI- 60. Molecular orbitals of dimer of **S1-2** (displayed with an isovalue of 0.02): HOMO (left) and LUMO (right).

Symmetry = C1

B3LYP/6-31G(d)

E=-1874.65930957 Ha

ATOM	SYMBOL	X	Y	Z
1	C	3.731042	2.085738	-0.2582
2	C	3.613124	0.686968	-0.20421
3	C	2.339871	0.137835	0.014373
4	C	2.611913	2.893348	-0.0812
5	C	1.359116	2.333192	0.164789
6	C	1.201117	0.930374	0.220664
7	O	0.285024	3.184532	0.306807
8	C	-0.17714	3.342686	1.651613
9	H	0.609483	3.779838	2.281548
10	H	-0.49898	2.38655	2.08117
11	H	-1.03006	4.023003	1.603646

12	C	4.769996	-0.20031	-0.37253
13	C	4.965114	-1.44927	0.166722
14	S	6.14669	0.247599	-1.36493
15	C	6.207604	-2.06095	-0.19387
16	C	6.948125	-1.25221	-1.01438
17	C	6.641177	-3.41983	0.285194
18	H	7.923617	-1.45748	-1.43645
19	H	4.247525	-1.91384	0.835787
20	C	-0.10053	0.284968	0.456328
21	H	2.68957	3.975488	-0.11856
22	H	4.703265	2.542901	-0.41938
23	S	-1.54105	0.799555	-0.40522
24	C	-0.37885	-0.79078	1.280292
25	C	-2.51777	-0.43894	0.352016
26	C	-1.74783	-1.18612	1.212042
27	C	0.60748	-1.46963	2.195853
28	H	-2.15814	-1.98273	1.824591
29	C	-3.9472	-0.58294	0.059467
30	H	6.694037	-3.45706	1.380542
31	H	7.627826	-3.68472	-0.10719
32	H	5.934198	-4.19712	-0.03094
33	H	1.462242	-0.82536	2.419751
34	H	0.999293	-2.39549	1.753573
35	H	0.12683	-1.74391	3.14184
36	C	-4.5737	-1.84176	0.168892
37	C	-4.74196	0.505222	-0.33017
38	C	-6.10277	0.360646	-0.60096
39	C	-6.70565	-0.89659	-0.476
40	C	-5.92691	-1.9973	-0.08638
41	H	-4.29717	1.493601	-0.40844
42	H	-6.67741	1.230888	-0.89597
43	O	-8.02416	-1.1575	-0.70918

44	H	-6.407	-2.96756	-0.00659
45	C	-8.85728	-0.08562	-1.12366
46	H	-9.85205	-0.51427	-1.25904
47	H	-8.51627	0.347283	-2.07404
48	H	-8.90464	0.706865	-0.36421
49	H	-3.98039	-2.71067	0.437897
50	H	2.21837	-0.93936	-0.01817

Table SI- 12. xyz Coordinates from the DFT calculations of molecule **S1-2**.

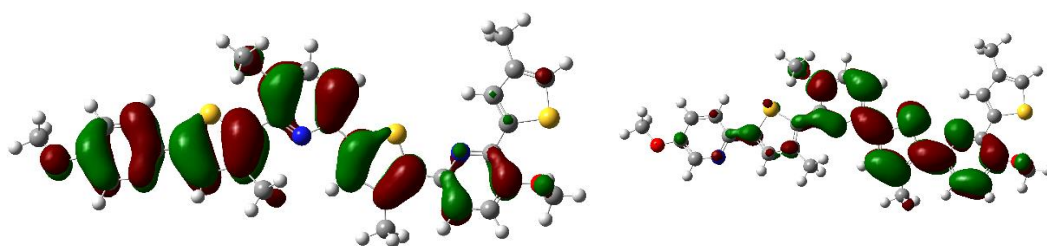


Figure SI- 61. Molecular orbitals of trimer of **S1-3** (displayed with an isovalue of 0.02): HOMO (left) and LUMO (right).

Symmetry = C1

B3LYP/6-31G(d)

E=-2811.39411966 Ha

ATOM	SYMBOL	X	Y	Z
1	C	-0.14973	2.12917	0.231239
2	C	-0.27217	0.731206	0.156165
3	C	-1.55522	0.172038	0.269528
4	C	-1.2745	2.924965	0.423375
5	C	-2.54159	2.354251	0.536371
6	C	-2.70406	0.953057	0.459961
7	O	-3.62146	3.196516	0.686578
8	C	-4.16198	3.244615	2.010709
9	H	-3.40881	3.608455	2.722758
10	H	-4.52353	2.260952	2.333247
11	H	-5.00005	3.943794	1.973248

12	C	0.889824	-0.13935	-0.0526
13	C	0.936594	-1.36959	-0.66401
14	S	2.486067	0.303268	0.513662
15	C	2.230837	-1.96955	-0.70452
16	C	3.193538	-1.1777	-0.10839
17	C	2.484256	-3.29201	-1.38097
18	C	4.634246	-1.42512	0.052607
19	H	0.065815	-1.82713	-1.1231
20	C	-4.01895	0.300647	0.576645
21	H	-1.19404	4.006159	0.4782
22	H	0.824974	2.595361	0.118626
23	S	-5.39965	0.87603	-0.34206
24	C	-4.3538	-0.81559	1.3211
25	C	-6.42932	-0.39325	0.28332
26	C	-5.7185	-1.19359	1.146234
27	C	-3.43154	-1.55177	2.258694
28	H	-6.1705	-2.01816	1.688395
29	C	-7.83906	-0.50751	-0.10294
30	H	1.839536	-3.40303	-2.2599
31	H	2.269401	-4.13737	-0.71368
32	H	3.524264	-3.38617	-1.70623
33	H	-2.58359	-0.93293	2.564558
34	H	-3.02498	-2.46082	1.795802
35	H	-3.97134	-1.86416	3.159915
36	C	-8.47855	-1.76454	-0.09977
37	C	-8.60269	0.607491	-0.4787
38	C	-9.94618	0.490541	-0.83595
39	C	-10.5633	-0.76577	-0.81435
40	C	-9.81542	-1.89329	-0.44132
41	H	-8.14807	1.594513	-0.47652
42	H	-10.497	1.380793	-1.11628
43	O	-11.8678	-1.00125	-1.13656

44	H	-10.3055	-2.86185	-0.44244
45	C	-12.6699	0.099799	-1.53547
46	H	-13.6587	-0.31112	-1.74783
47	H	-12.2749	0.580813	-2.44075
48	H	-12.7532	0.849829	-0.737
49	C	5.108984	-2.69105	0.441156
50	C	5.567232	-0.39667	-0.1447
51	C	6.950393	-0.58984	0.007004
52	C	7.386758	-1.87443	0.393183
53	C	6.473389	-2.90644	0.603501
54	H	4.405274	-3.48975	0.650327
55	H	6.855297	-3.8724	0.920008
56	O	8.727168	-2.12079	0.607422
57	C	7.871322	0.526357	-0.25051
58	C	9.429025	-2.57071	-0.556
59	H	9.020124	-3.52603	-0.91152
60	H	10.4703	-2.70366	-0.2556
61	H	9.374273	-1.82859	-1.36234
62	C	7.636978	1.611326	-1.06583
63	S	9.433851	0.697678	0.535829
64	C	9.70548	2.224959	-0.23819
65	C	8.678447	2.589344	-1.06833
66	H	6.741208	1.705663	-1.67124
67	H	10.62465	2.767866	-0.05576
68	C	8.64191	3.848866	-1.8909
69	H	9.544002	4.449577	-1.73893
70	H	7.776684	4.47075	-1.62907
71	H	8.564873	3.623532	-2.96205
72	H	5.206439	0.589332	-0.41901
73	H	-1.66984	-0.90455	0.205958
74	H	-7.90763	-2.6523	0.155709

Table SI- 13. xyz values from the DFT of Molecule **S1-3**.

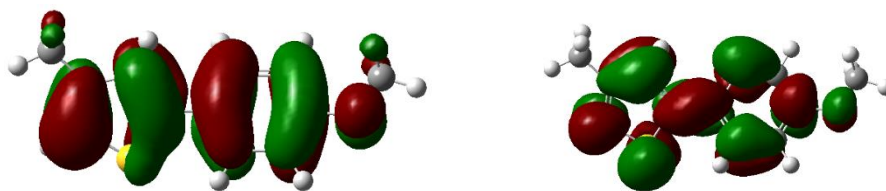


Figure SI- 62. Molecular orbitals of **S2** (displayed with an isovalue of 0.02): HOMO (left) and LUMO (right).

Symmetry = C1

B3LYP/6-31G(d)

E= -953.96099057 Ha

ATOM	SYMBOL	X	Y	Z
1	C	0.947856	-1.40437	-0.00064
2	C	0.232807	-0.18984	-6.9e-05
3	N	0.872	0.992888	0.000307
4	C	2.332228	-1.38134	-0.00064
5	C	2.993317	-0.1468	-0.00017
6	C	2.206566	1.014343	0.000228
7	O	4.35428	-0.18103	-0.00018
8	C	5.053967	1.056726	0.000464
9	H	6.11473	0.799992	0.000539
10	H	4.823161	1.649479	0.895786
11	H	4.823468	1.650221	-0.89445
12	C	-1.23392	-0.12938	-3.2e-05
13	C	-2.01257	1.002383	-0.00027
14	S	-2.24648	-1.56324	0.000529
15	C	-3.41877	0.746435	-8.9e-05
16	C	-3.68882	-0.59695	0.000347
17	C	-4.46534	1.827525	-0.00042
18	H	-4.65952	-1.07615	0.000487
19	H	-1.57185	1.992456	-0.00057
20	H	2.6608	2.001487	0.000548

21	H	2.919373	-2.29446	-0.00105
22	H	0.425336	-2.35644	-0.00113
23	H	-4.36888	2.472663	0.881699
24	H	-5.47567	1.406608	0.000075
25	H	-4.36939	2.471662	-0.88333

Table SI- 14. xyz Coordinates from the DFT calculations of molecule **S2-1**.

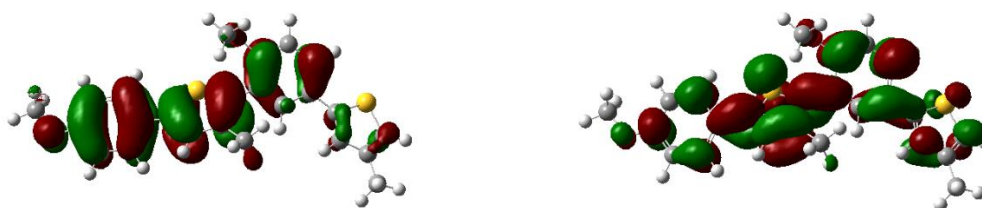


Figure SI- 63. Molecular orbitals of dimer of **S2-2** (displayed with an isovalue of 0.02): HOMO (left) and LUMO (right).

Symmetry = C1

B3LYP/6-31G(d)

E=-1906.73623146 Ha

ATOM	SYMBOL	X	Y	Z
1	C	3.733679	2.148625	-0.27105
2	C	3.562851	0.757823	-0.17116
3	N	2.348121	0.201341	-0.0349
4	C	2.605586	2.956381	-0.19884
5	C	1.352041	2.377464	-0.03628
6	C	1.245343	0.966827	0.037441
7	O	0.236105	3.183077	0.015992
8	C	-0.09177	3.638404	1.334768
9	H	0.724803	4.243038	1.750821
10	H	-0.29842	2.793074	2.002507
11	H	-0.99022	4.250453	1.234244
12	C	4.69036	-0.18295	-0.21593
13	C	4.627585	-1.55226	-0.12432
14	S	6.357365	0.337907	-0.39264

15	C	5.897624	-2.20359	-0.19296
16	C	6.92019	-1.30274	-0.33793
17	C	6.076329	-3.69555	-0.11551
18	H	7.979281	-1.51256	-0.41708
19	H	3.684001	-2.07163	-0.01028
20	C	-0.0339	0.262664	0.191374
21	H	2.675008	4.037858	-0.27028
22	H	4.717293	2.588521	-0.40295
23	S	-1.56871	1.022485	-0.22361
24	C	-0.23478	-1.05049	0.605387
25	C	-2.45829	-0.43076	0.147165
26	C	-1.60626	-1.4196	0.579998
27	C	0.825149	-2.02676	1.043478
28	H	-1.97007	-2.39622	0.876416
29	C	-3.91541	-0.52809	0.019376
30	H	5.684082	-4.09292	0.828831
31	H	7.131688	-3.97691	-0.18575
32	H	5.538325	-4.20131	-0.92683
33	H	1.584524	-1.55371	1.670474
34	H	1.35238	-2.44397	0.178381
35	H	0.366819	-2.85348	1.597038
36	N	-4.46708	-1.69911	0.414389
37	C	-4.70953	0.512364	-0.48407
38	C	-6.09078	0.352637	-0.57989
39	C	-6.65001	-0.85878	-0.16745
40	C	-5.77954	-1.85073	0.32111
41	H	-4.25819	1.44594	-0.80675
42	H	-6.70195	1.158435	-0.97045
43	O	-7.97174	-1.18052	-0.19254
44	H	-6.20172	-2.80088	0.643973
45	C	-8.88436	-0.2066	-0.67957
46	H	-9.87367	-0.66228	-0.61226

47	H	-8.67483	0.053912	-1.72605
48	H	-8.86243	0.706498	-0.06902

Table SI- 15. xyz Coordinates from the DFT calculations of molecule **S2-2**.

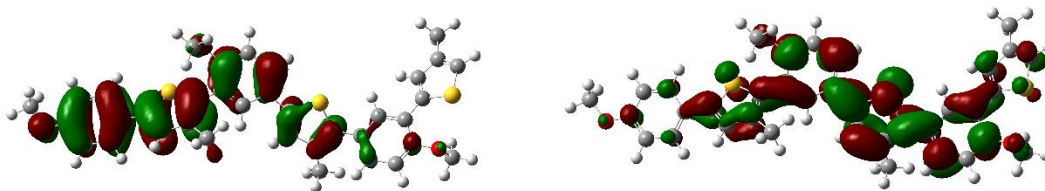


Figure SI- 64. Molecular orbitals of trimer of **S2-3** (displayed with an isovalue of 0.02): HOMO (left) and LUMO (right).

Symmetry = C1

B3LYP/6-31G(d)

E=-2859.51240006 Ha

ATOM	SYMBOL	X	Y	Z
1	C	0.062352	2.069507	0.315208
2	C	-0.13611	0.679128	0.265718
3	N	-1.36619	0.138839	0.254192
4	C	-1.056	2.891031	0.37693
5	C	-2.32674	2.326481	0.38538
6	C	-2.45993	0.917567	0.316337
7	O	-3.43243	3.146423	0.423383
8	C	-3.84162	3.515201	1.746444
9	H	-3.04609	4.072381	2.2584
10	H	-4.10669	2.629707	2.337061
11	H	-4.72127	4.1512	1.629723
12	C	0.979023	-0.27379	0.213735
13	C	0.881536	-1.64278	0.115261
14	S	2.653072	0.21938	0.263455
15	C	2.129966	-2.32199	0.084207
16	C	3.202009	-1.44371	0.165622

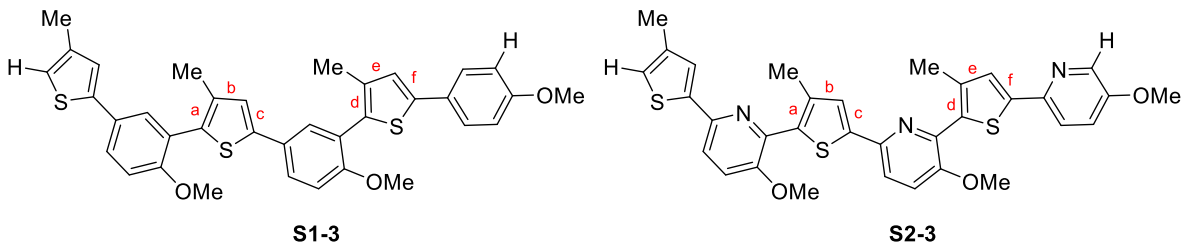
17	C	2.203381	-3.82133	-0.05372
18	C	4.650734	-1.66142	0.167702
19	H	-0.07509	-2.14726	0.056349
20	C	-3.75764	0.230568	0.309231
21	H	-0.9657	3.972738	0.412969
22	H	1.059987	2.496776	0.300157
23	S	-5.24946	1.064916	-0.11927
24	C	-4.00709	-1.11377	0.568855
25	C	-6.18584	-0.39736	0.041388
26	C	-5.38007	-1.44582	0.418842
27	C	-2.99526	-2.15569	0.967849
28	H	-5.77865	-2.43923	0.587237
29	C	-7.63358	-0.44577	-0.18333
30	H	1.224542	-4.22311	-0.3324
31	H	2.498432	-4.30724	0.885536
32	H	2.921108	-4.12612	-0.82342
33	H	-2.27367	-1.77087	1.692094
34	H	-2.4158	-2.48934	0.099862
35	H	-3.50387	-3.02652	1.39554
36	N	-8.22738	-1.64175	0.037277
37	C	-8.37877	0.665116	-0.60439
38	C	-9.75413	0.550275	-0.79832
39	C	-10.3572	-0.68781	-0.56594
40	C	-9.53425	-1.75039	-0.14892
41	H	-7.89369	1.619722	-0.7856
42	H	-10.3271	1.411035	-1.12425
43	O	-11.6803	-0.97309	-0.70512
44	H	-9.99065	-2.72171	0.034143
45	C	-12.5452	0.072487	-1.12602
46	H	-13.5442	-0.36437	-1.17137
47	H	-12.2677	0.448924	-2.12007
48	H	-12.5455	0.906907	-0.41138

49	C	5.254477	-2.92053	0.355912
50	N	5.391941	-0.5524	0.004185
51	C	6.732461	-0.6089	-0.01745
52	C	7.39785	-1.8454	0.127828
53	C	6.641475	-2.99703	0.326294
54	H	4.667449	-3.80747	0.547711
55	H	7.155196	-3.94246	0.475243
56	O	8.772562	-1.9029	0.126832
57	C	7.42149	0.673526	-0.20253
58	C	9.345937	-2.39217	-1.09142
59	H	9.001181	-3.41165	-1.30796
60	H	10.42721	-2.395	-0.94122
61	H	9.094215	-1.73479	-1.93287
62	C	6.797739	1.87296	-0.464
63	S	9.160498	0.901592	-0.10361
64	C	8.992302	2.596175	-0.42397
65	C	7.686499	2.980497	-0.59432
66	H	5.720314	1.941446	-0.55843
67	H	9.871733	3.226934	-0.46884
68	C	7.235023	4.386577	-0.88348
69	H	8.084393	5.074146	-0.94549
70	H	6.560175	4.75536	-0.10105
71	H	6.688136	4.440798	-1.83303

Table SI- 16. xyz Coordinates from the DFT calculations of molecule **S2-3**.

Bond length alternation (BLA) values

The BLA values for **S1-3** and **S2-3** were accessible by subtraction of the longer C-C bond with the shorter C=C bond in both inner thiophene rings.



S1-3									
r_a (Å)	r_b (Å)	r_c (Å)	Δr_{ba} (Å)	Δr_{bc} (Å)	r_d (Å)	r_e (Å)	r_f (Å)	Δr_{ed} (Å)	Δr_{ef} (Å)
1.38173	1.42712	1.37458	0.04539	0.05254	1.38287	1.42683	1.37493	0.04396	0.0519
S2-3									
r_a (Å)	r_b (Å)	r_c (Å)	Δr_{ba} (Å)	Δr_{bc} (Å)	r_d (Å)	r_e (Å)	r_f (Å)	Δr_{ed} (Å)	Δr_{ef} (Å)
1.38826	1.42157	1.37598	0.03331	0.04559	1.39171	1.42050	1.37514	0.02879	0.04536

Table SI-17. Bond lengths for C-C/C=C units and BLA values for **S1-3** and **S2-3**.

Trimer	δr_{ba} (Å)	δr_{bc} (Å)	δr_{ed} (Å)	δr_{ef} (Å)
S1-3	0.04539	0.05254	0.04396	0.0519
S2-3	0.03331	0.04559	0.02879	0.04536

Table SI-18. BLA values for **S1-3** and **S2-3** in direct comparison.

Comparing the BLA values of **S1-3** and **S2-3** lead to the conclusion that the thiophene rings in **S2-3** represent a more quinoidal structure than in **S1-3** since the bond length of the central C-C unit is shorter than expected as has a tendency to form a C=C unit.

Literature

- [1] A. C. J. Heinrich, University of Kiel (Kiel), **2014**.
- [2] X. Liu, J. Long, G. Wang, Y. Pei, B. Zhao, S. Tan, *Dyes Pigm.* **2015**, *121*, 118-127.
- [3] A. C. J. Heinrich, B. Thiedemann, P. J. Gates, A. Staubitz, *Org. Lett.* **2013**, *15*, 4666-4669.
- [4] J. Y. Hwang, L. A. Arnold, F. Zhu, A. Kosinski, T. J. Mangano, V. Setola, B. L. Roth, R. K. Guy, *Journal of Medicinal Chemistry* **2009**, *52*, 3892-3901.
- [5] M. S. Yusubov, E. N. Tveryakova, E. A. Krasnokutskaya, I. A. Perederyna, V. V. Zhdankin, *Synthetic Communications* **2007**, *37*, 1259-1265.
- [6] M. Gao, M. Wang, Q.-H. Zheng, *Bioorg Med Chem Lett* **2016**, *26*, 3694-3699.
- [7] A. K. Parhi, A. Xiang, J. D. Bauman, D. Patel, R. S. Vijayan, K. Das, E. Arnold, E. J. Lavoie, *Bioorg Med Chem* **2013**, *21*, 6435-6446.

- [8] J. Tauc, R. Grigorovici, A. Vancu, *physica status solidi (b)* **1966**, *15*, 627-637.
- [9] a) J. H. Nobbs, *Review of Progress in Coloration and Related Topics* **1985**, *15*, 66-75; b) E. A. Davis, N. F. Mott, *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics* **1970**, *22*, 0903-0922.
- [10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Wallingford, CT, **2016**.