Electronic Supplementary Material (ESI) for Polymer Chemistry.

Synthesis of Squaraine-based alternated copolymers via metal-free condensation

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[c] Institut Polytechnique de Bordeaux (IPB), Laboratoire de Chimie des Polymères Organiques (LCPO), UMR 5629, 16 Avenue Pey-Berland, 33607 Pessac Cedex, France

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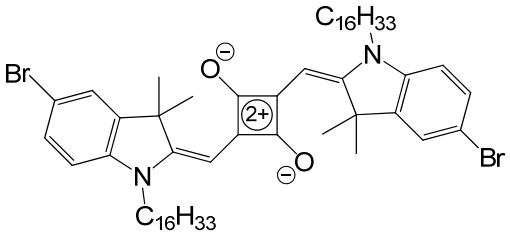
Supporting Information

^{1}H-^{13}C Heteronuclear Single Quantum Correlation (HSQC) NMR spectroscopy

The monomers and polymers were characterized by ^{1}H-^{13}C HSQC NMR spectroscopy recorded on a Bruker 400 MHz spectrometer from a deuterated chloroform ($CDCl_3$) solution with tetramethysilane (TMS) as an internal reference.

*2,5-Bis[(5-bromo-1-hexadecyl-3,3-dimethyl-2,3-dihydroindole-2-ylidene)methyl]cyclobutendiylium-1,3-diolate (**5**)*



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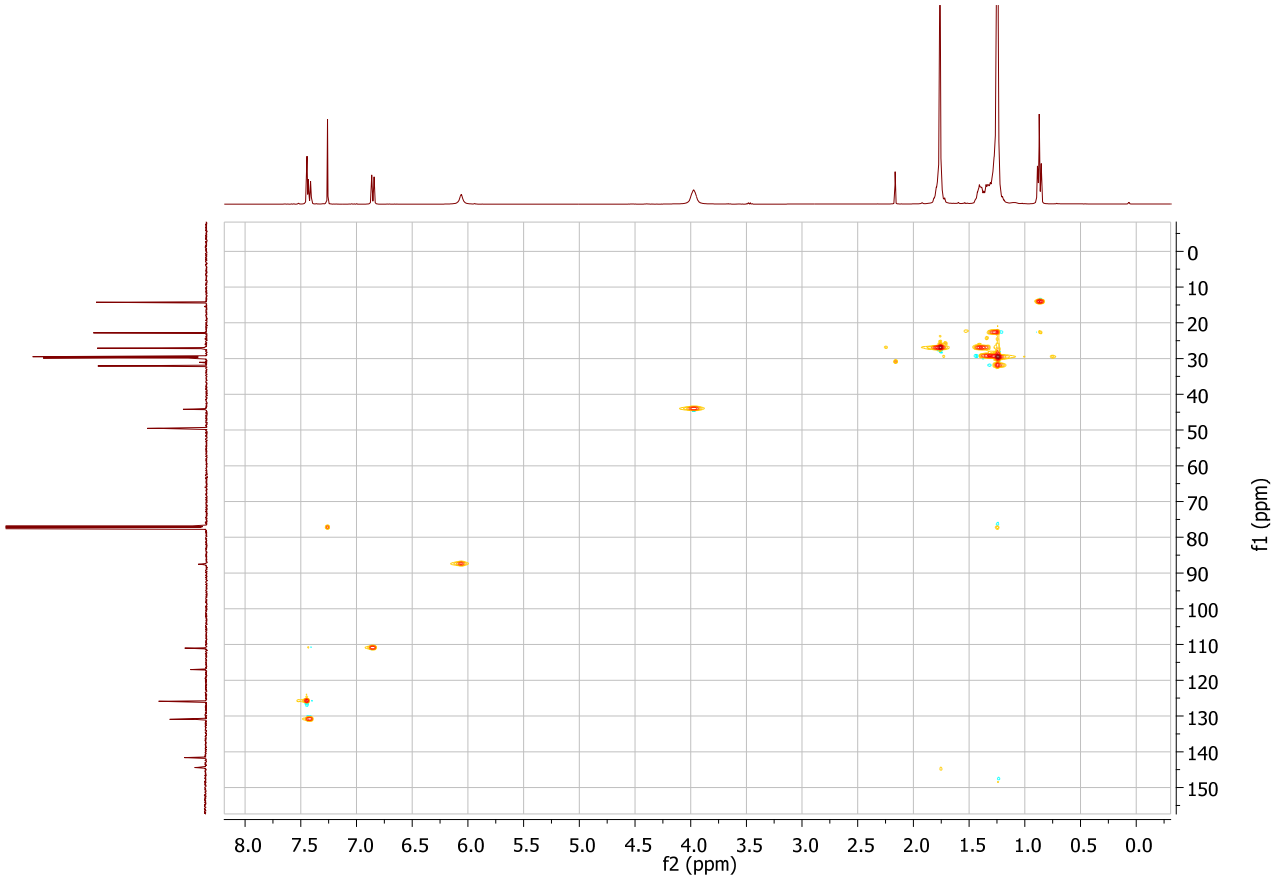
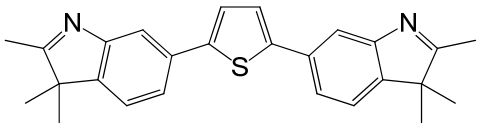


*2,5-bis(2,3,3-trimethyl-3H-indol-6-yl)thiophene (**6**)*



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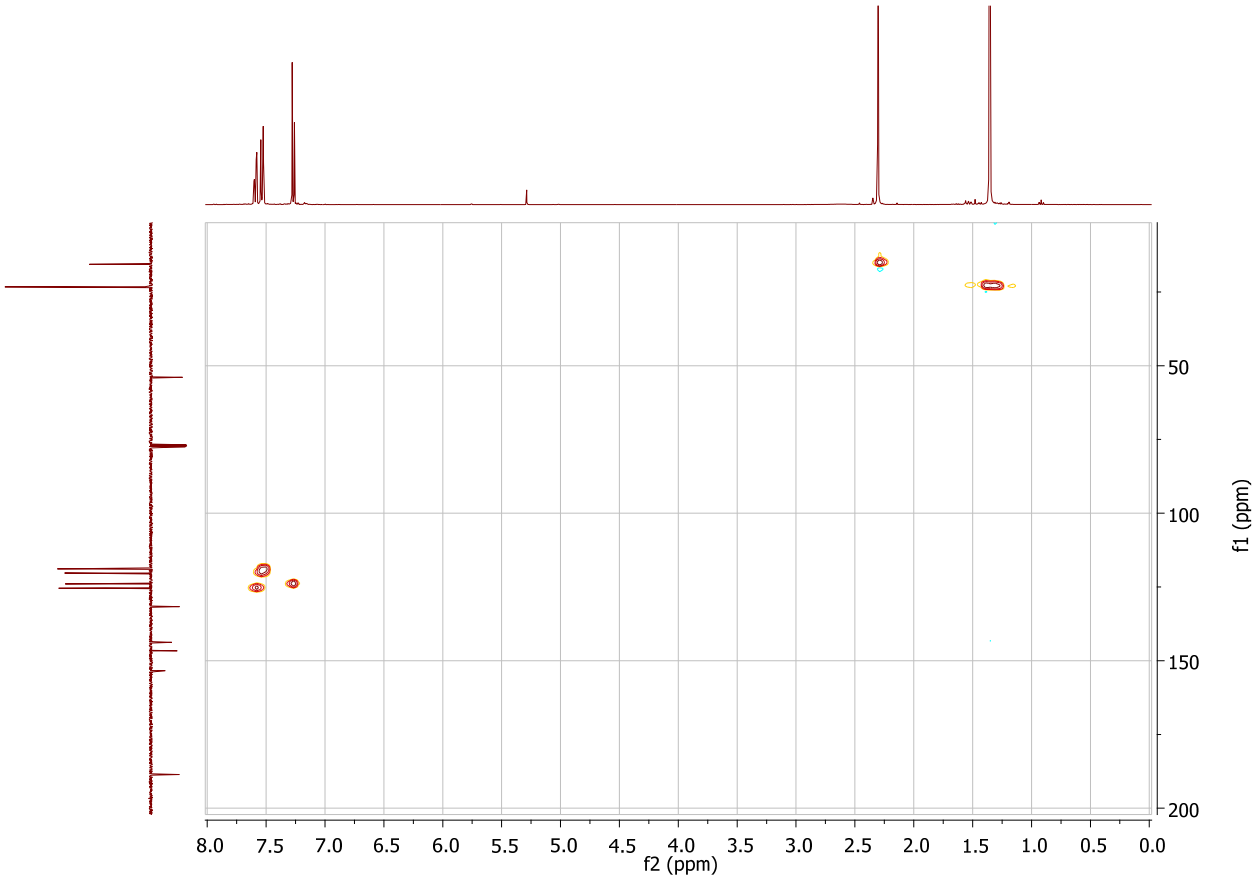
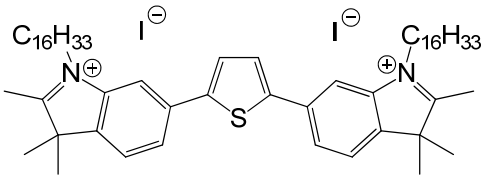


*2,5-bis(1-hexadecyl-2,3,3-trimethyl-3H-indol-6-ium)thiophene diiodide (**7**)*



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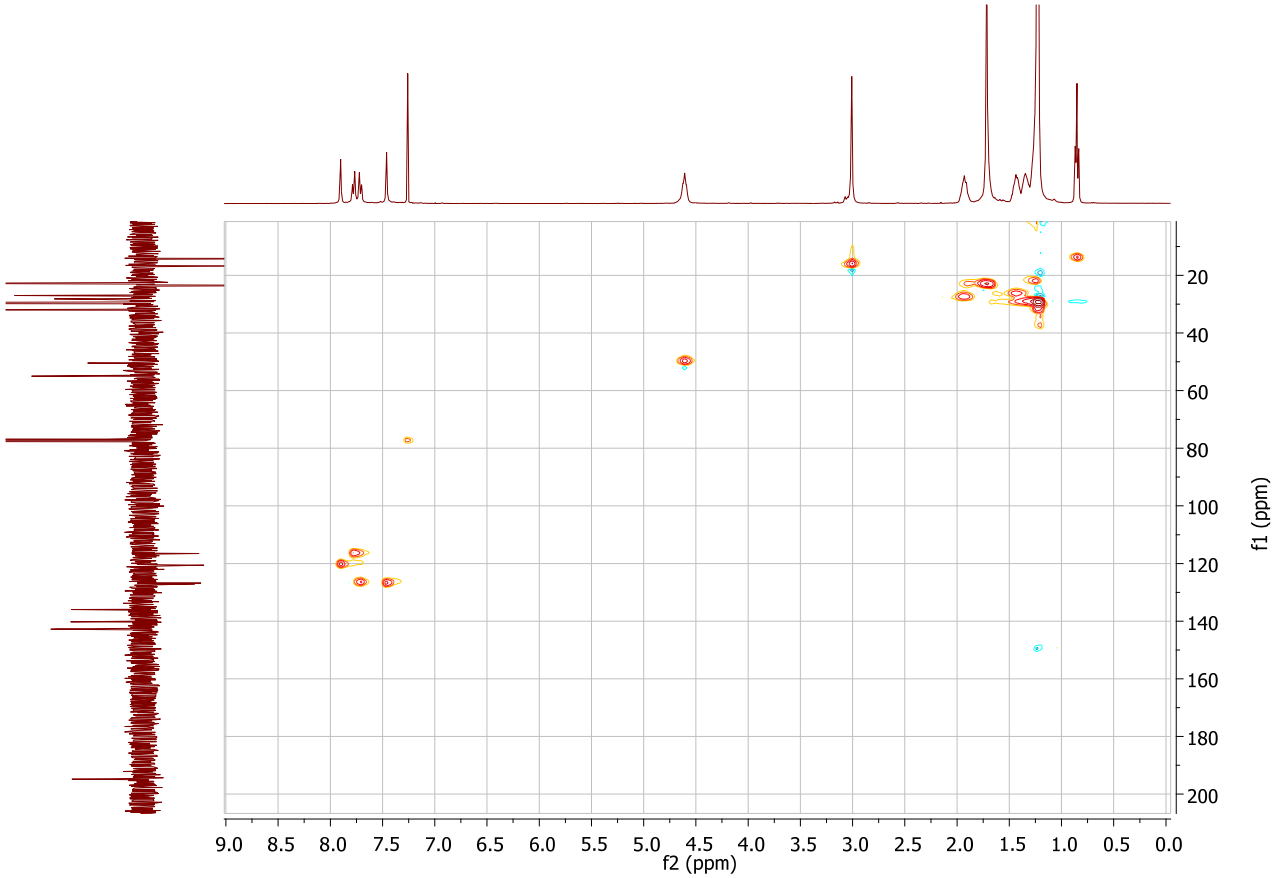
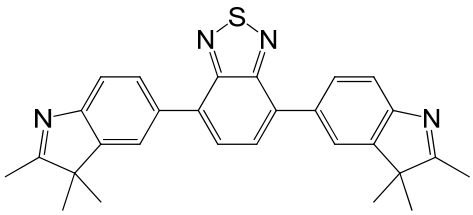


4,7-bis(2,3,3-trimethyl-3H-indol-5-yl)benzothiadiazole ***(8)***



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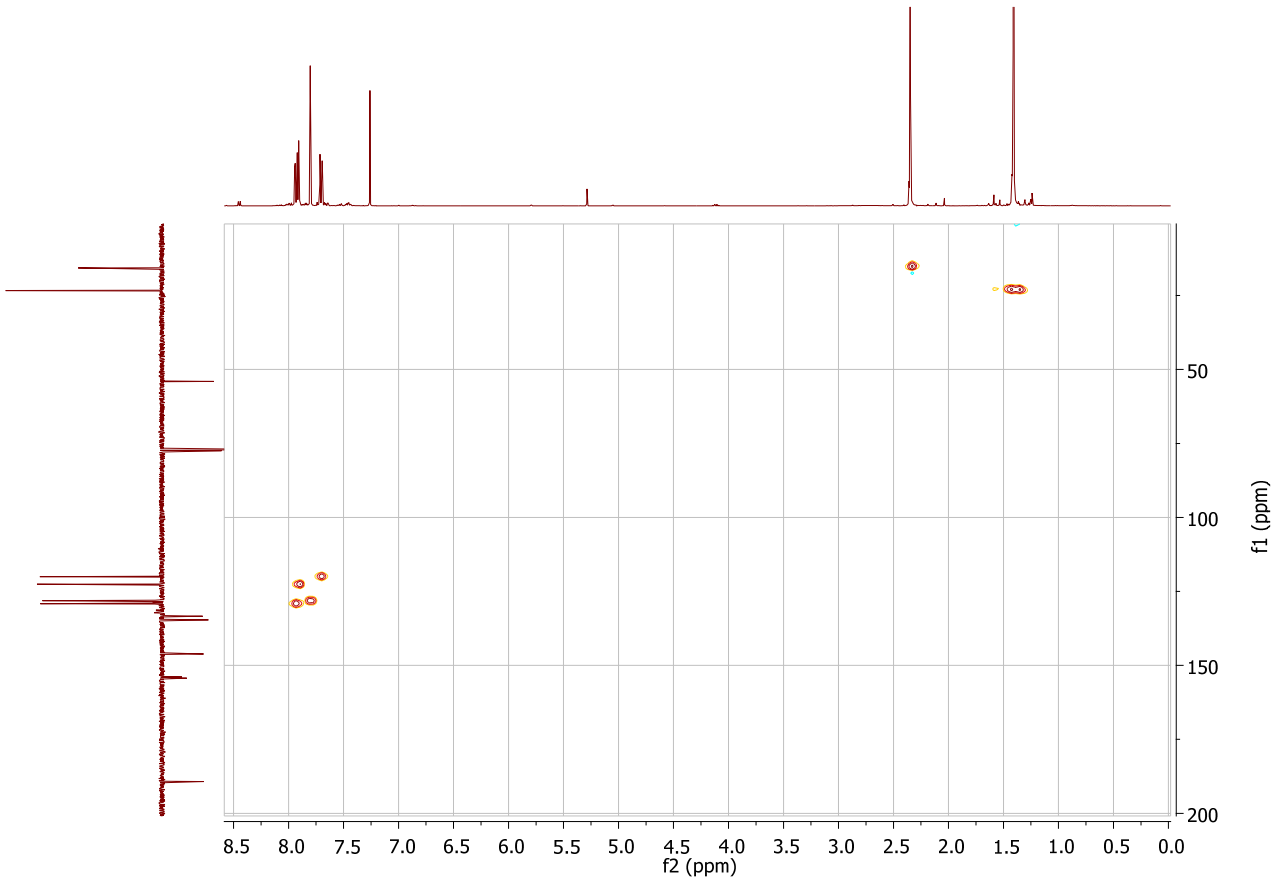
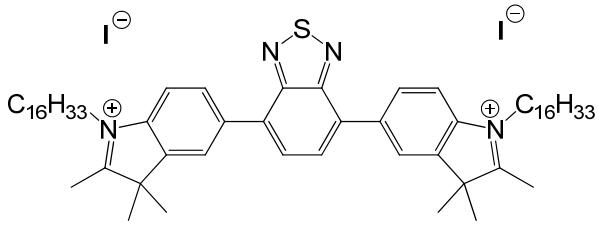


*4,7-bis(1-hexadecyl-2,3,3-trimethyl-3H-indol-5-ium)benzothiadiazole diiodide (**9**)*



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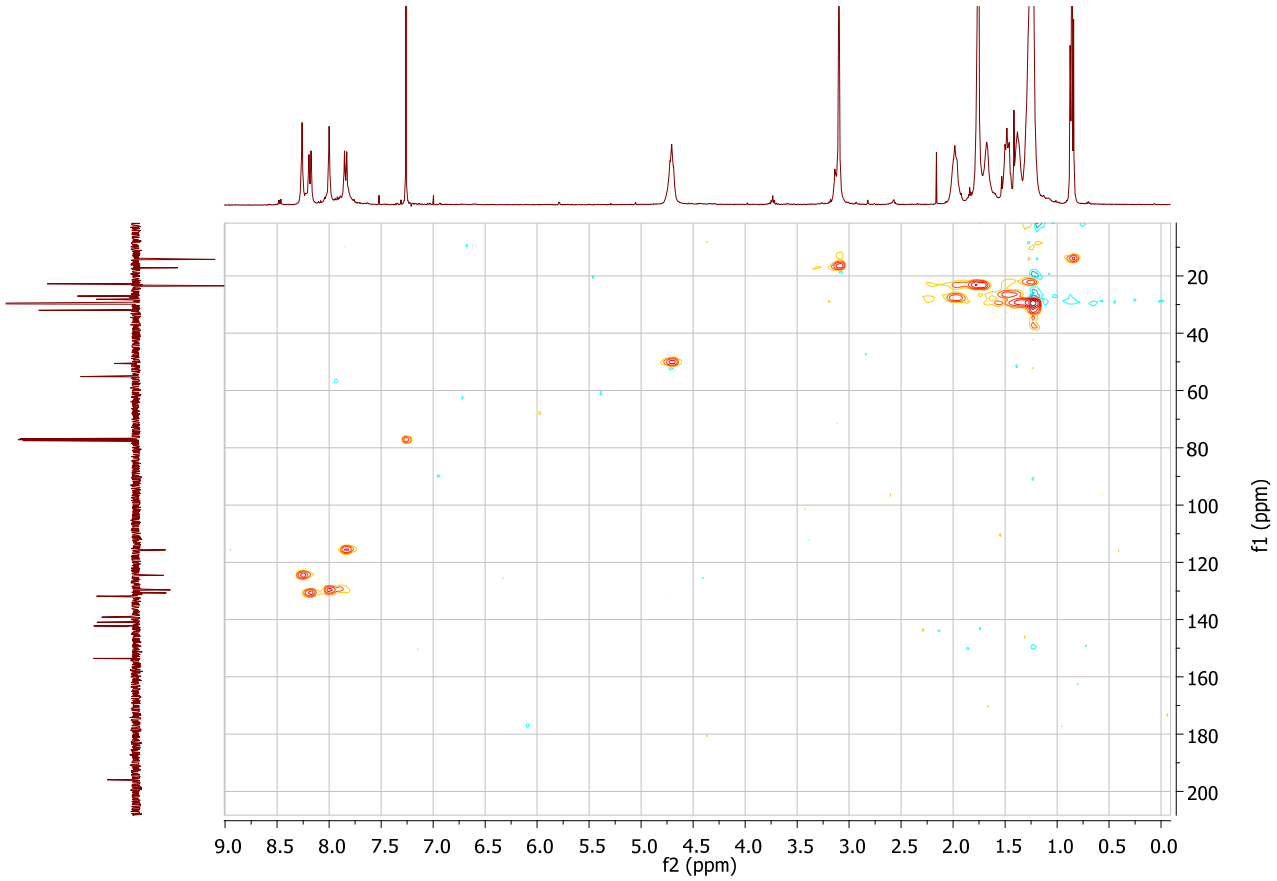
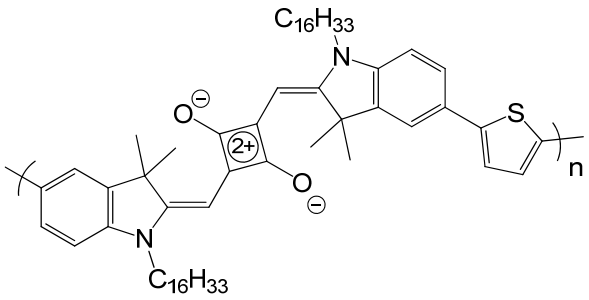
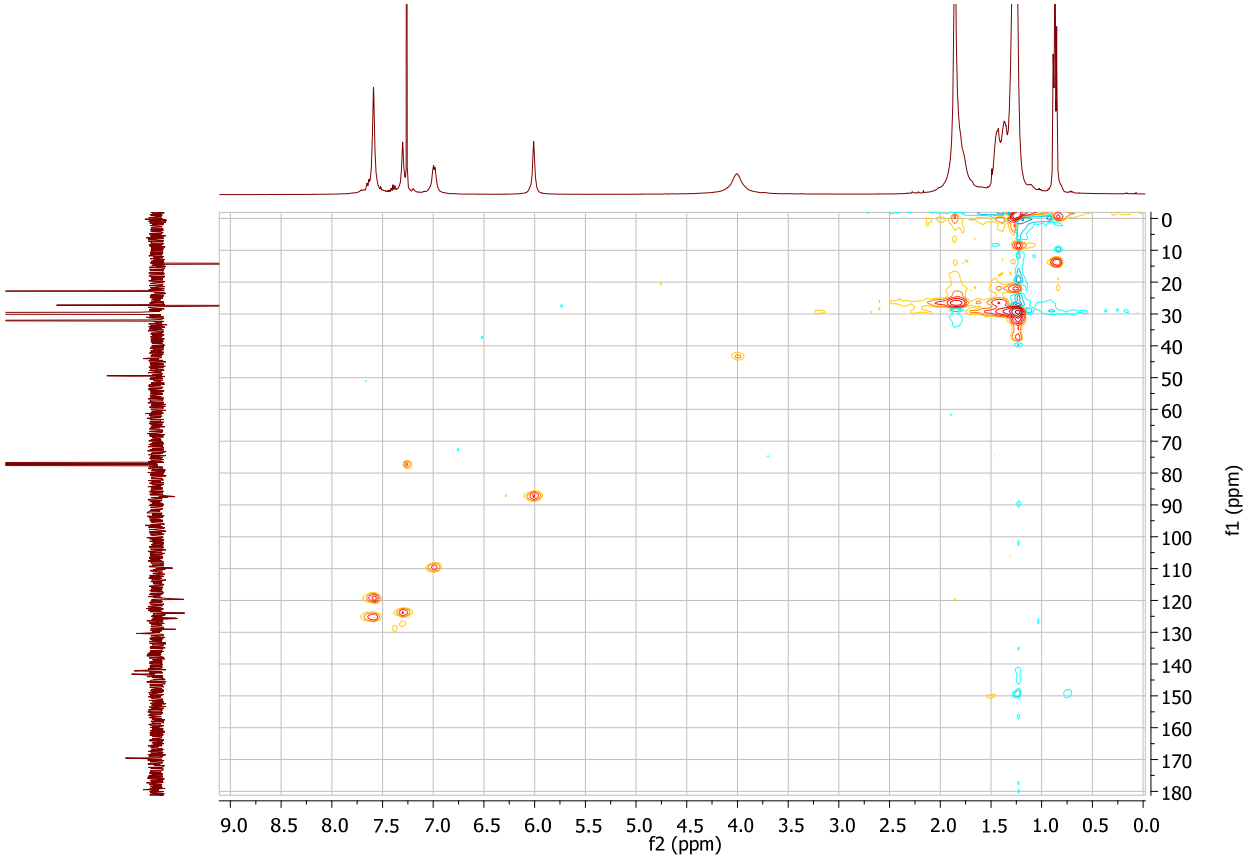


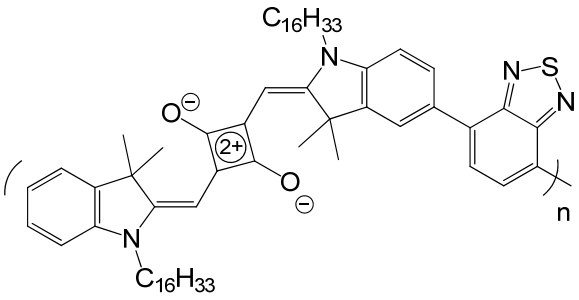
*Poly(bis(hexadecyl)squaraine-alt-thiophene) (**PSQT**) via Stille polycondensation*



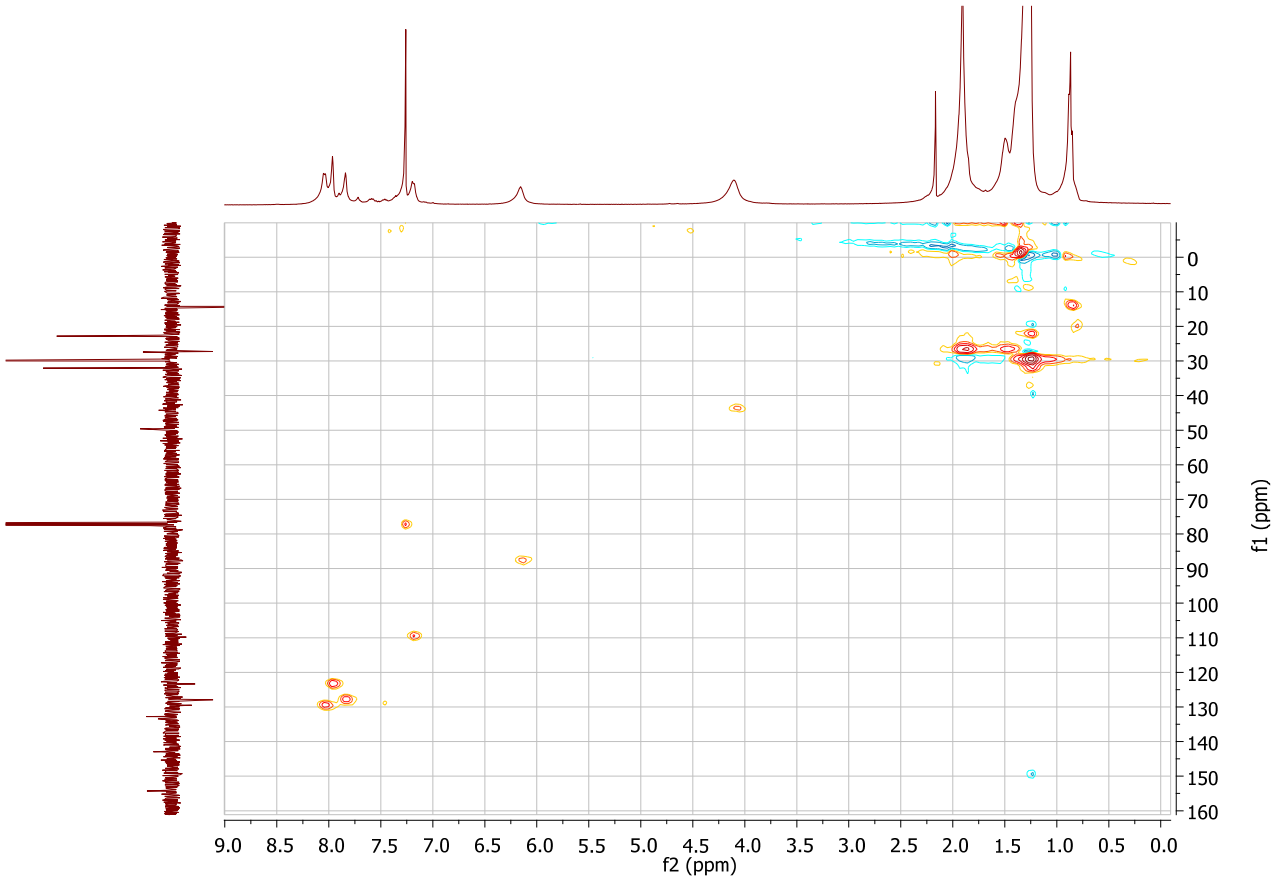
PSQT



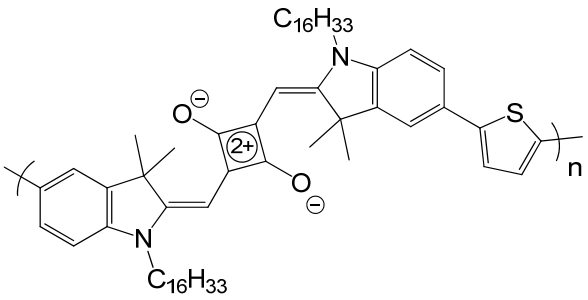
*Poly(bis(hexadecyl)squaraine-alt-benzothiadiazole) (**PSQBT**) via Suzuki polycondensation*



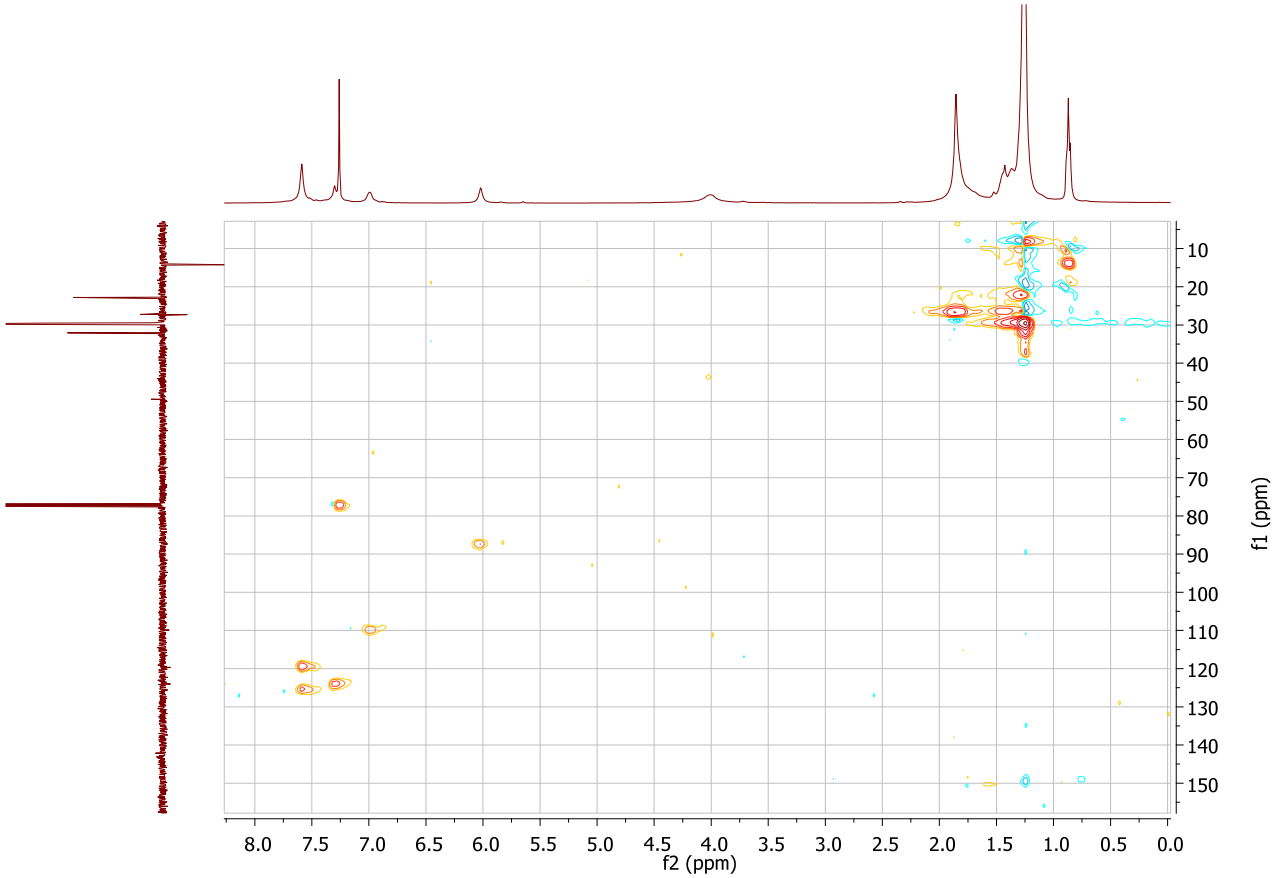
PSQBT



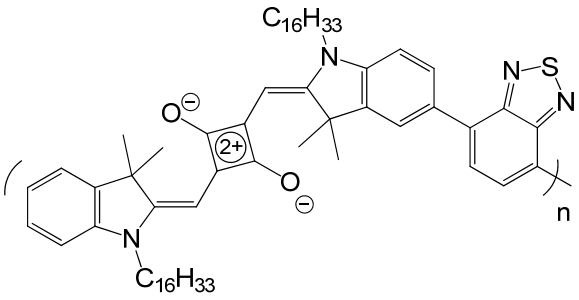
*Poly(bis(hexadecyl)squaraine-alt-thiophene) (**PSQT**) via SA polycondensation*



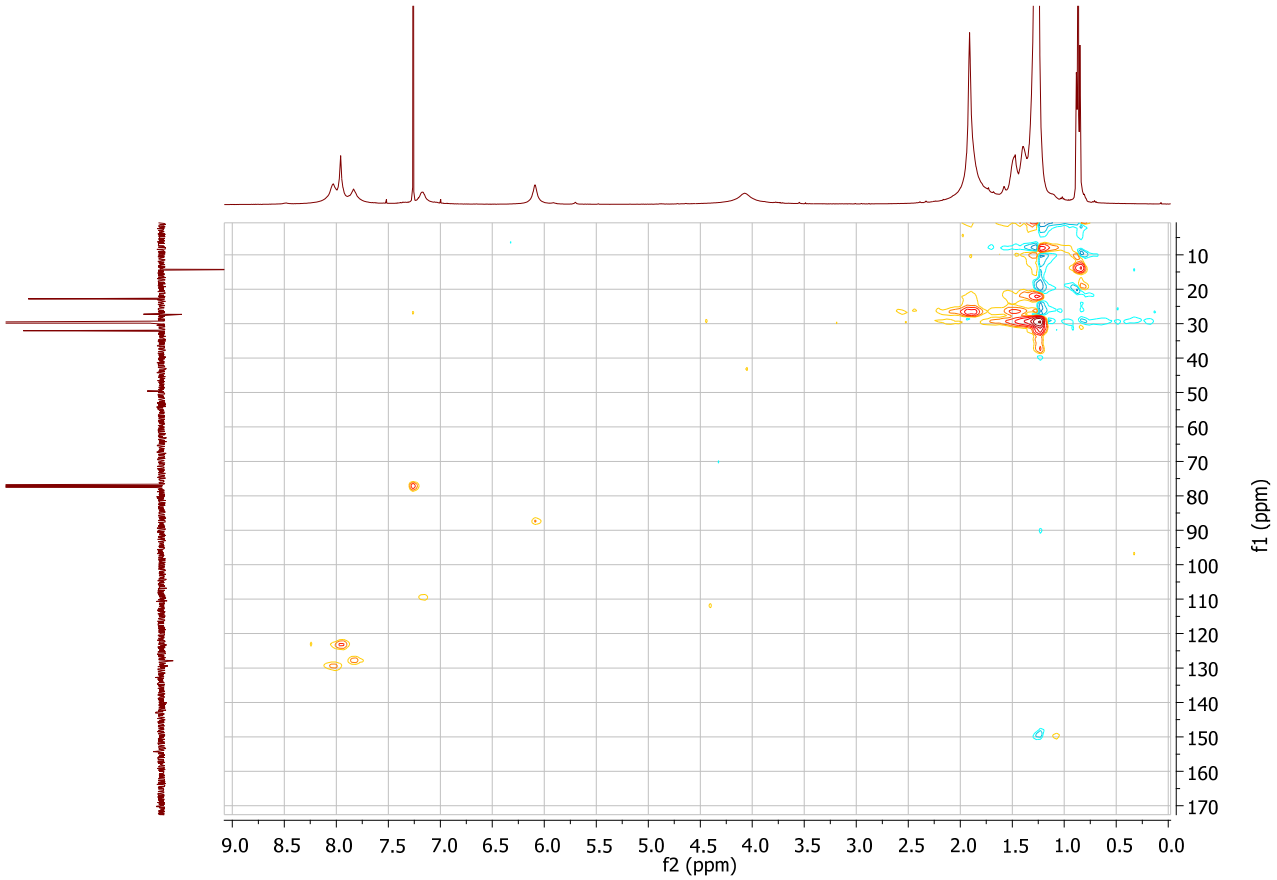
PSQT



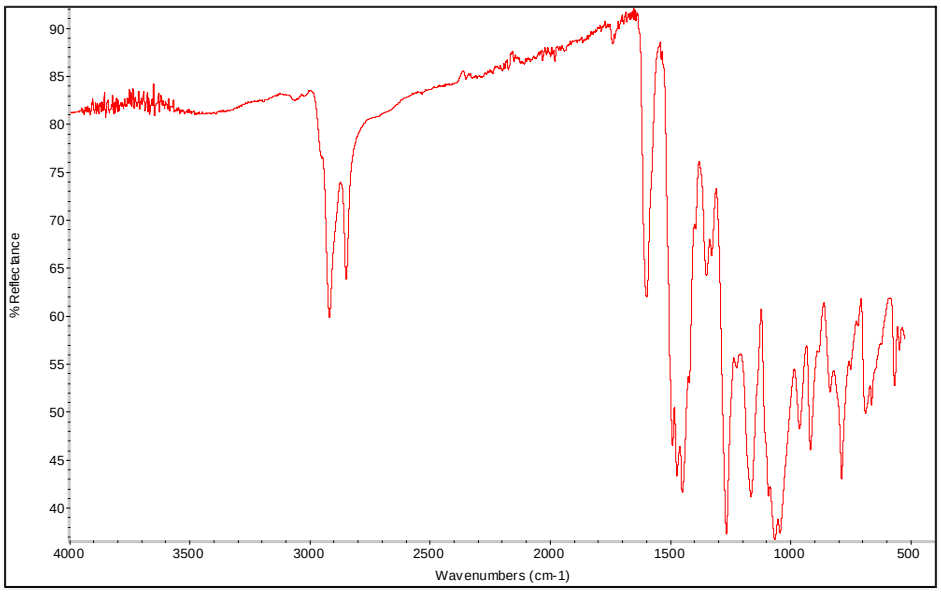
*Poly(bis(hexadecyl)squaraine-alt-benzothiadiazole) (**PSQBT**) via SA polycondensation*



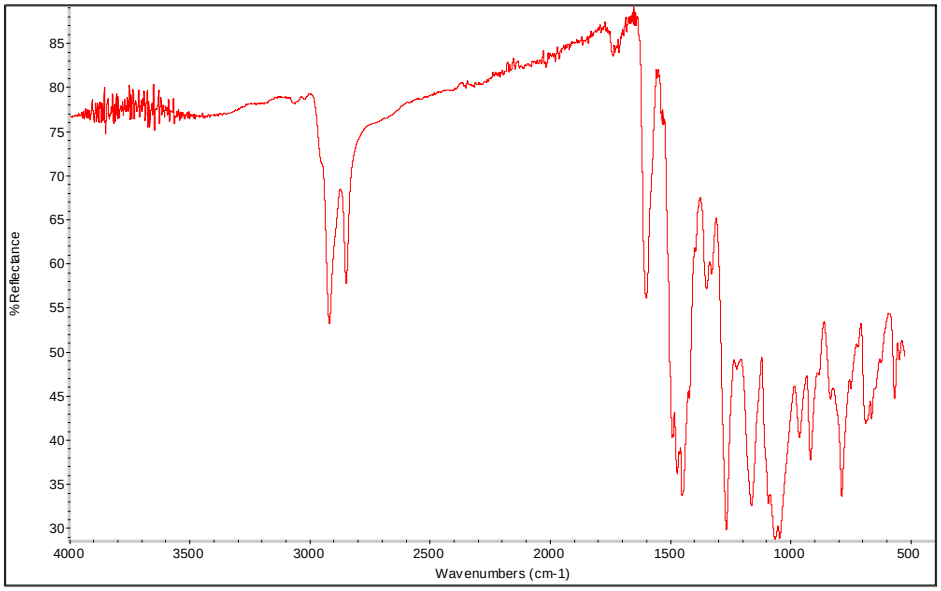
PSQBT



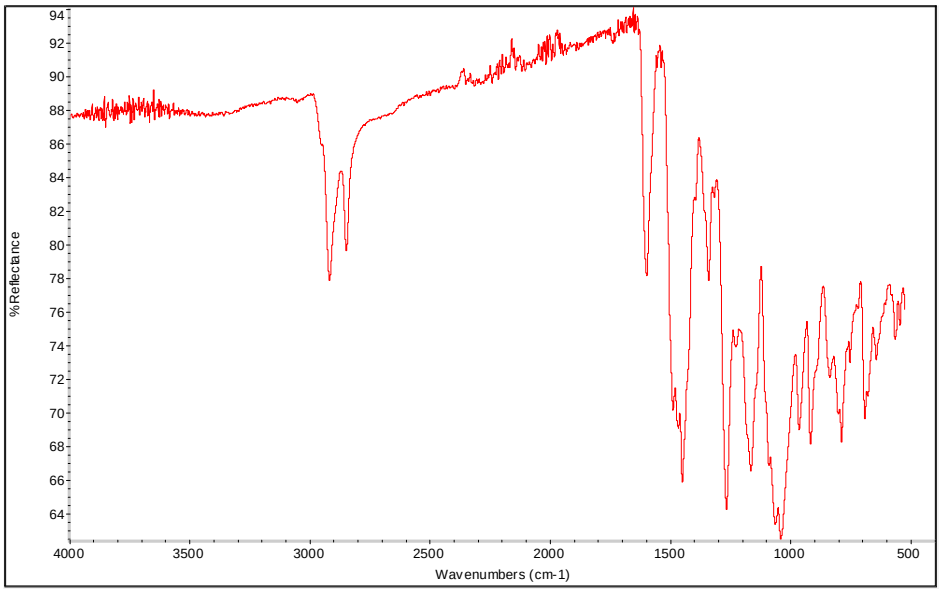
IR spectra of the polymers



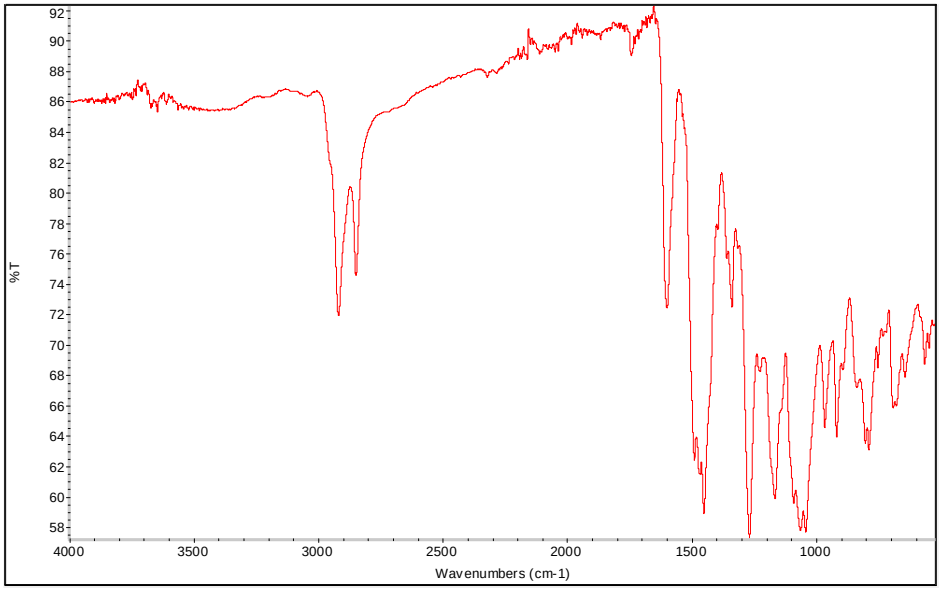
IR spectrum (ATR) of PSQT-a.



IR spectrum (ATR) of PSQT-b.



IR spectrum (ATR) of PSQBT-a.

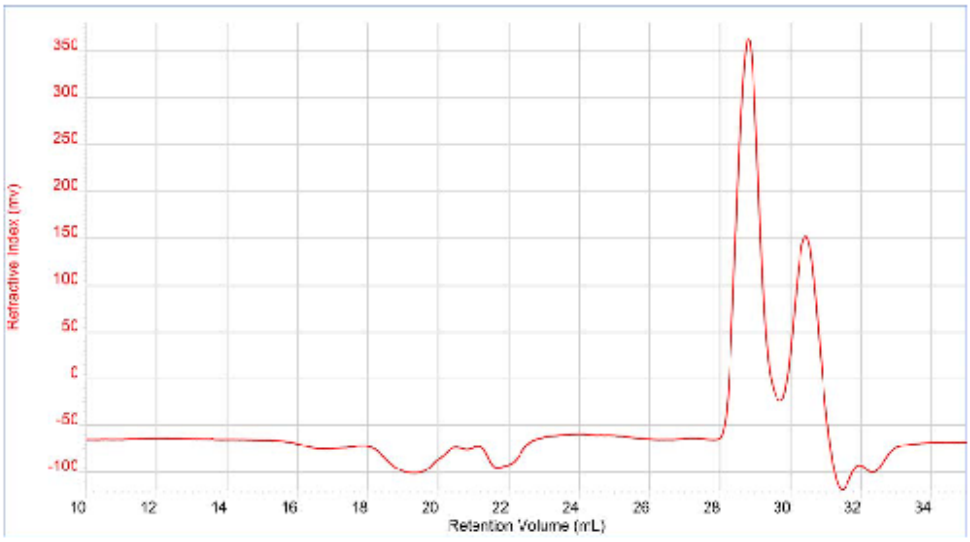


IR spectrum (ATR) of PSQBT-b.

Size Exclusion Chromatograms

PSQBT synthesized by Suzuki coupling - THF Soxhlet fraction

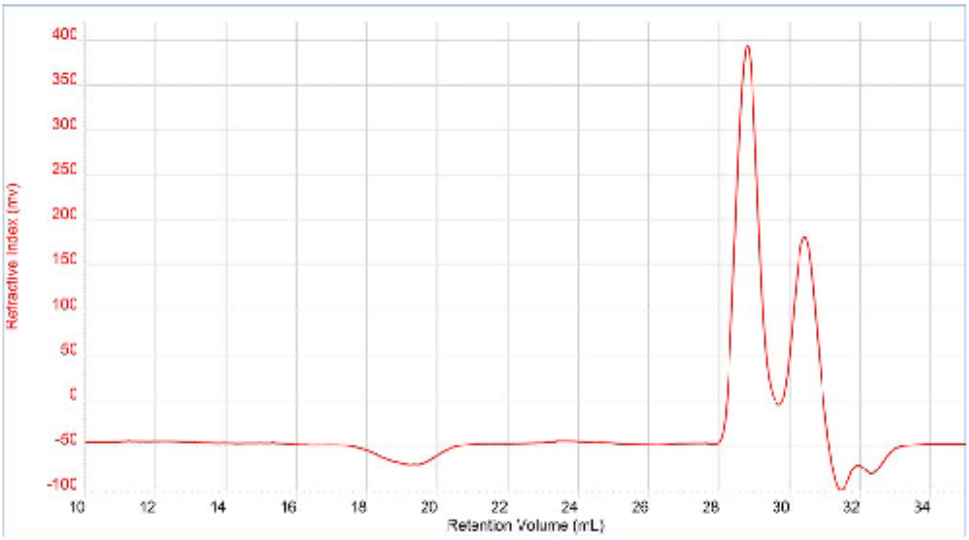
ID	JO080_THF
Method	Conv_-RI_Et3N_18-09-13-0000.vcm
Acq. Date	Sep 20, 2013 - 01:11:12
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	6.5000



Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-20_01;11;12_JO080_THF_01.vd	5 814	9 785	14 211	12 649	1.683	19.300

PSQBT synthesized by Suzuki coupling - $CHCl_3$ Soxhlet fraction

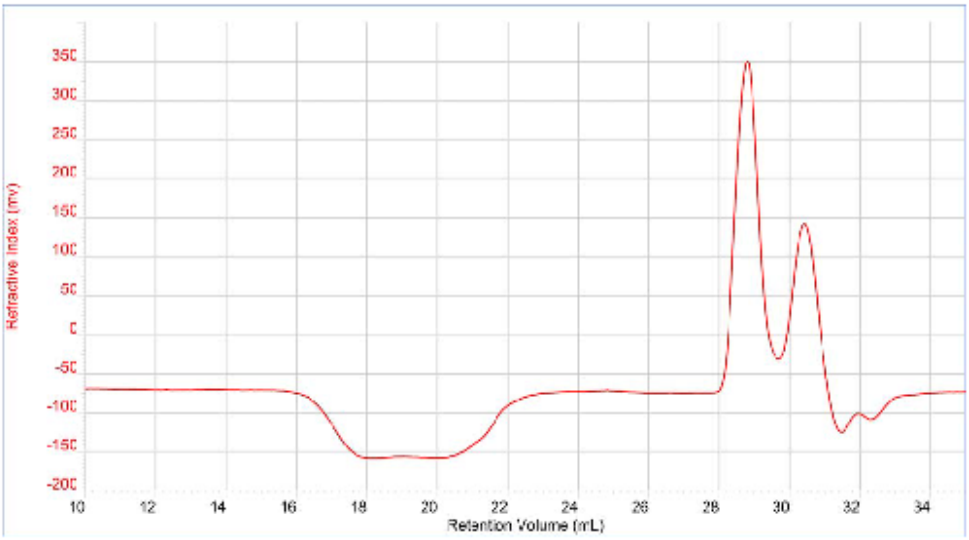
ID	JO080_CHCl3
Method	Conv_-RI_Et3N_18-09-13-0000.vcm
Acq. Date	Sep 19, 2013 - 22:52:52
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	4.0000



Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-19_22;52;52_JO080_CHCl3_01.	13 508	17 568	24 056	13 218	1.301	19.233

PSQT synthesized by Stille coupling - THF Soxhlet fraction

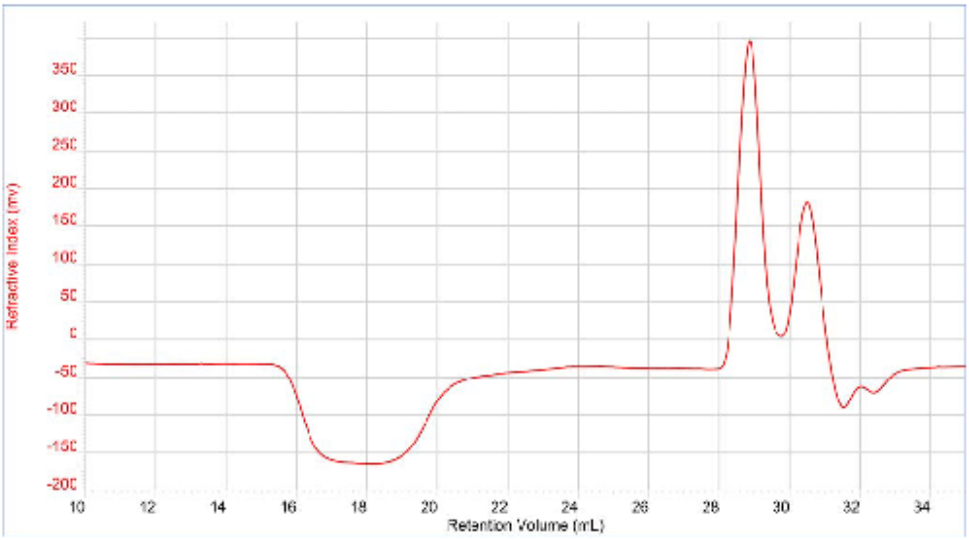
ID	JO081_THF
Method	Conv_-RI_Et3N_18-09-13-0000.vcm
Acq. Date	Sep 20, 2013 - 01:57:20
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	6.0000



Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-20_01;57;20_JO081_THF_01.vd	9 325	23 026	53 868	27 086	2.469	18.220

PSQT synthesized by Stille coupling - $CHCl_3$ Soxhlet fraction

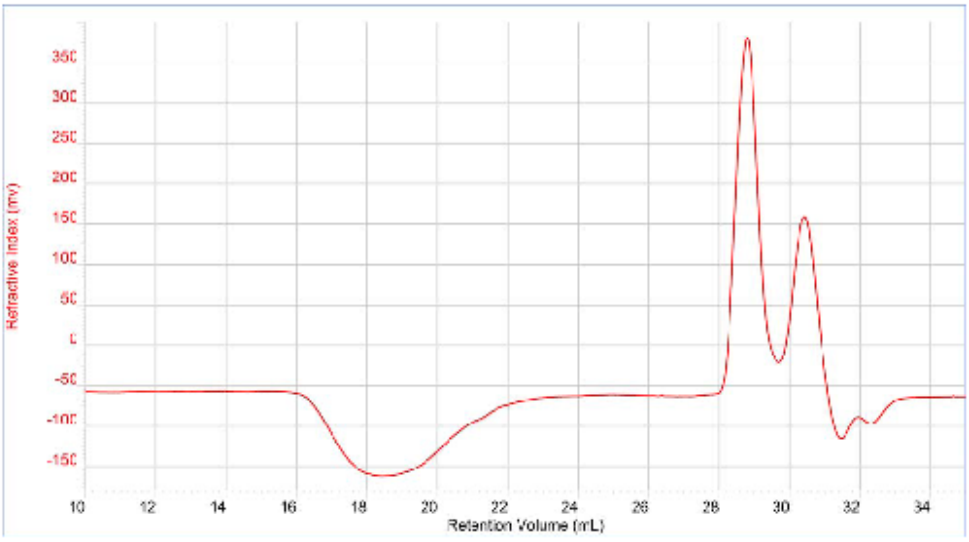
ID	JO081_CHCl3
Method	Conv_Et3N_18-09-13-0005.vcm
Acq. Date	Sep 19, 2013 - 20:34:30
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	5.0000



Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-19_20;34;30_JO081_CHCl3_01.	19 861	54 091	115 371	28 355	2.723	18.207

PSQT synthesized by squaric acid condensation - THF Soxhlet fraction

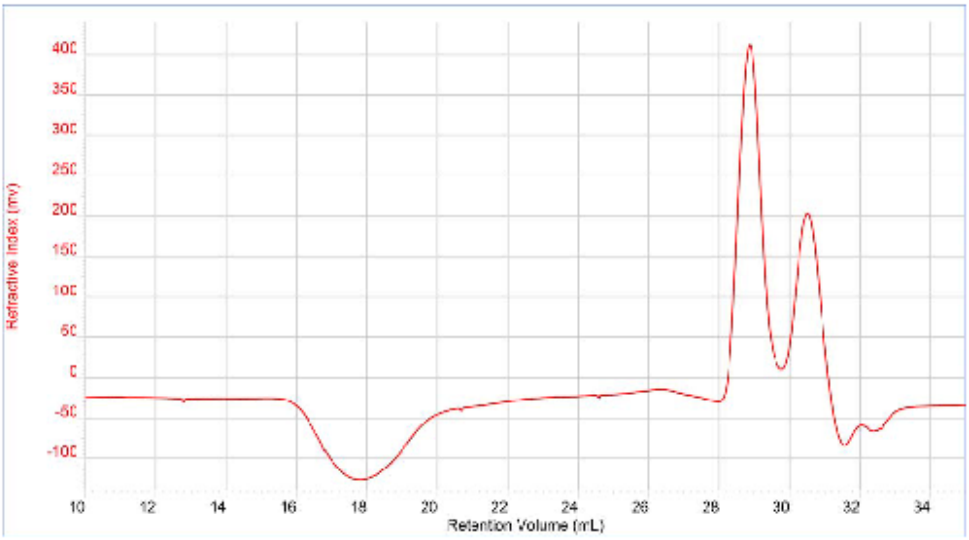
ID	JO166_THF
Method	Conv_-RI_Et3N_18-09-13-0000.vcm
Acq. Date	Sep 20, 2013 - 00:25:06
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	5.0000



Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-20_00;25;06_JO166_THF_01.vd	12 124	26 876	53 186	22 917	2.217	18.437

PSQT synthesized by squaric acid condensation - $CHCl_3$ Soxhlet fraction

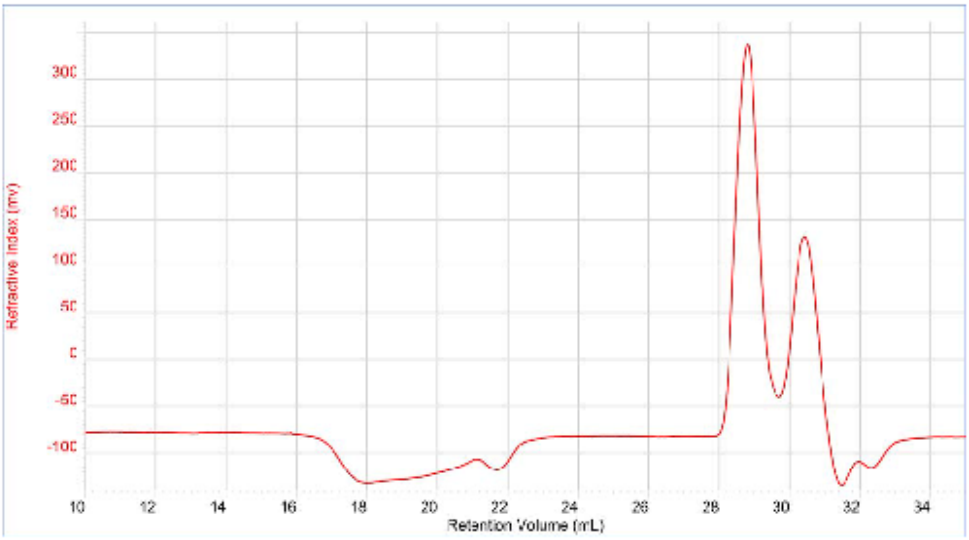
ID	JO166_CHCl3
Method	Conv_Et3N_18-09-13-0005.vcm
Acq. Date	Sep 18, 2013 - 03:41:08
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	5.0000



Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-18_03;41;08_JO166_CHCl3_01.	23 614	48 110	91 288	39 685	2.037	17.793

PSQBT synthesized by squaric acid condensation - THF Soxhlet fraction

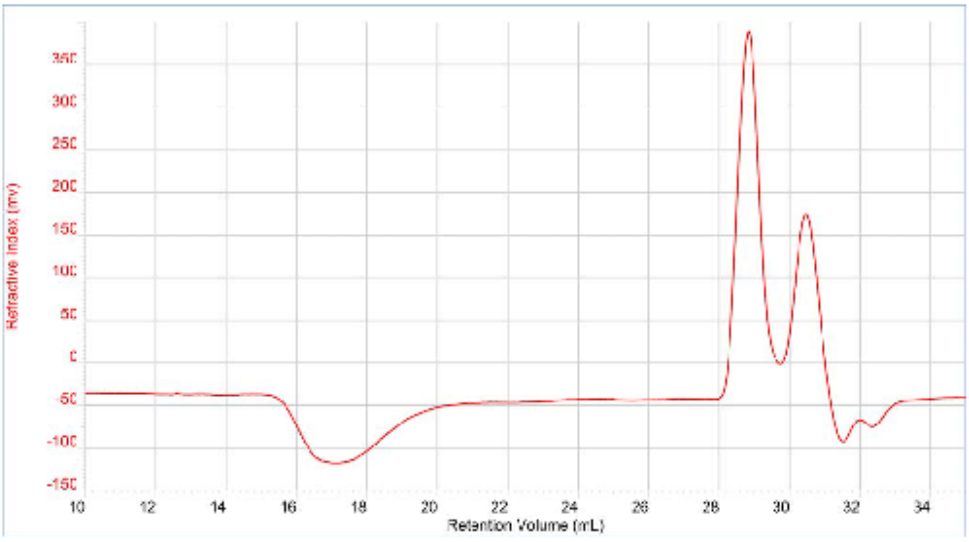
ID	JO172_THF
Method	Conv_-RI_Et3N_18-09-13-0000.vcm
Acq. Date	Sep 20, 2013 - 02:43:28
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	5.0000



Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-20_02;43;28_JO172_THF_01.vd	8 472	19 895	38 151	32 252	2.348	18.000

PSQBT synthesized by squaric acid condensation - $CHCl_3$ Soxhlet fraction

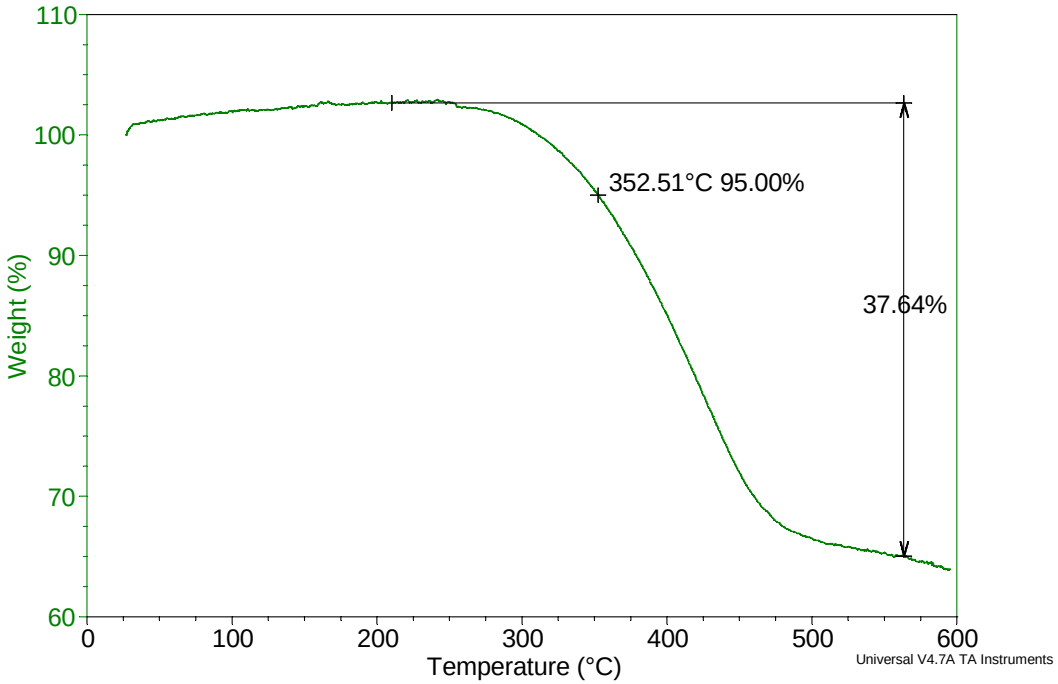
ID	JO172_CHCl3
Method	Conv_Et3N_18-09-13-0005.vcm
Acq. Date	Sep 19, 2013 - 21:20:36
Solvent	CHCl3_1%Triethylamine
Column	HxL_2000_3000_4000
Flow Rate	1.0000
Inj Vol	75.0
Col Temp	30.00
Conc	5.0000



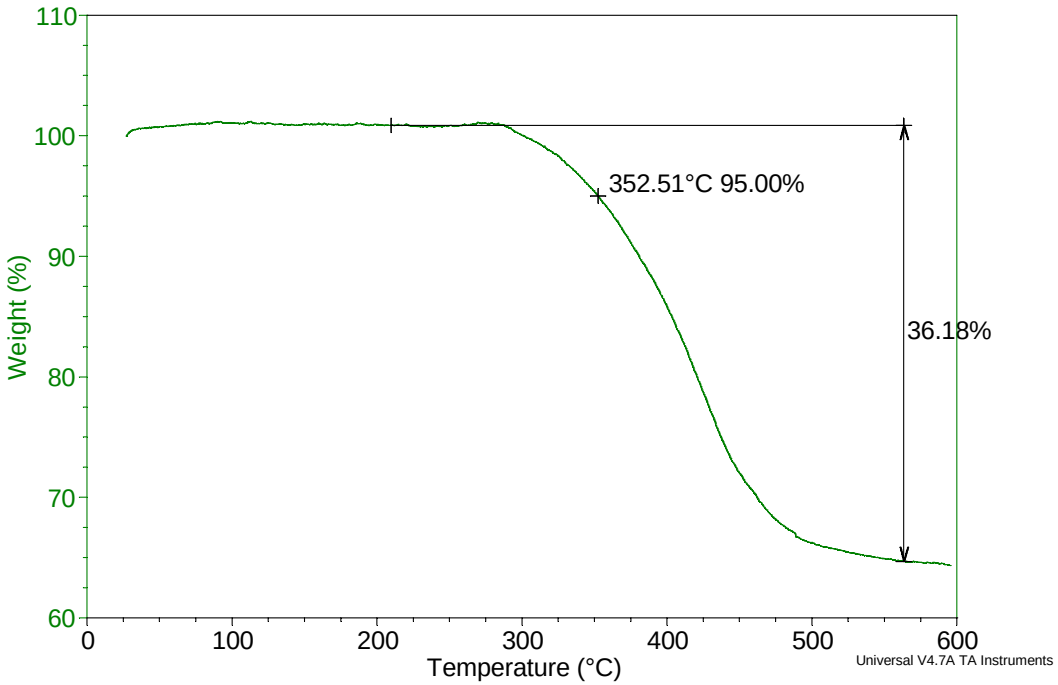
Sample	Mn	Mw	Mz	Mp	Mw/Mn	Ret Vol
2013-09-19_21;20;36_JO172_CHCl3_01.	36 529	79 001	145 201	77 765	2.163	17.017

Thermogravimetric Analyses

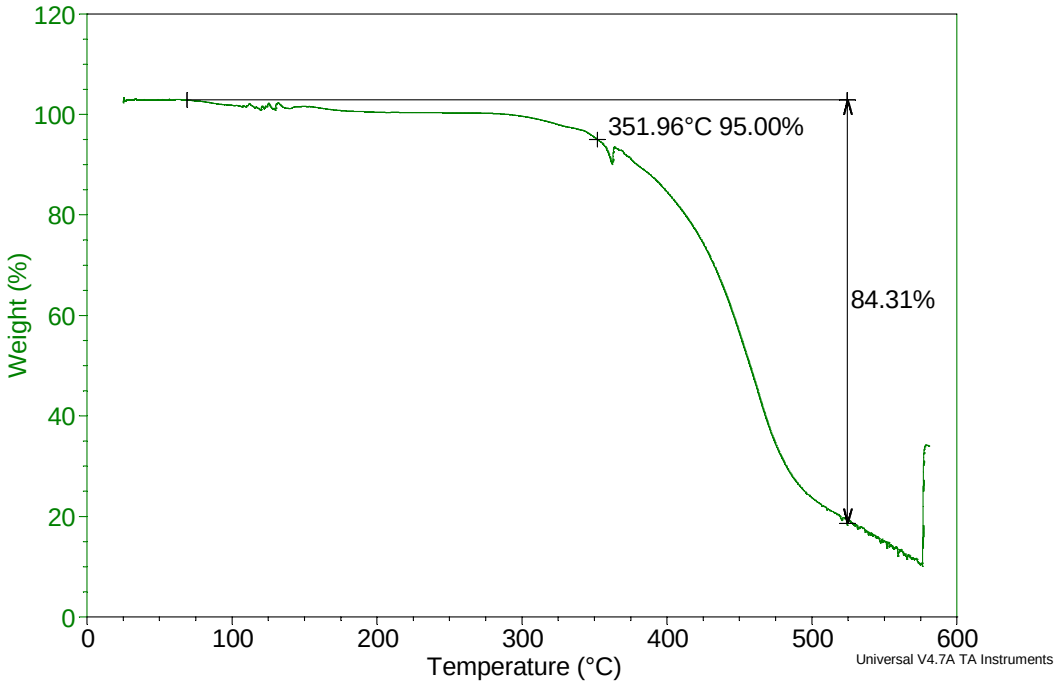
PSQT obtained by Stille coupling



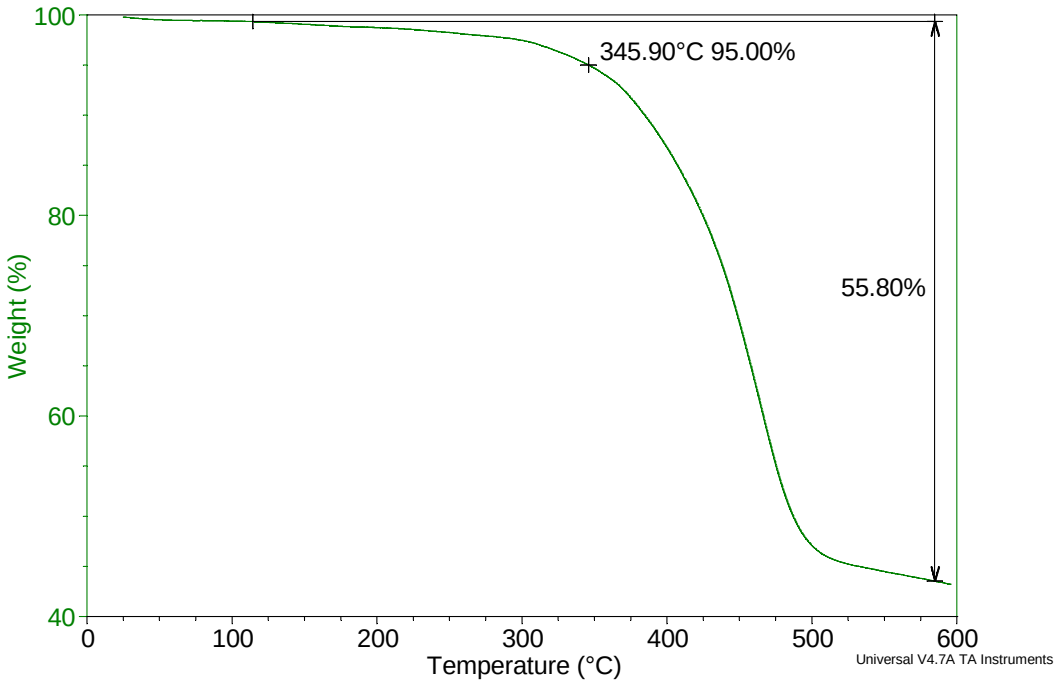
PSQBT obtained by Suzuki coupling



PSQT obtained by SA condensation

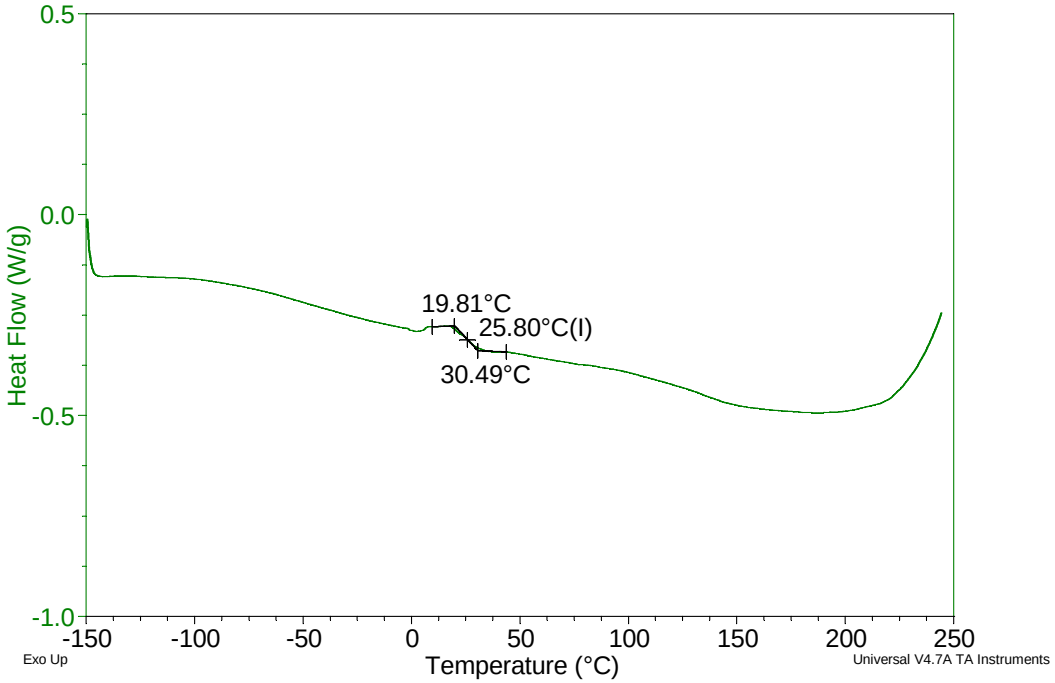


PSQBT obtained by SA condensation

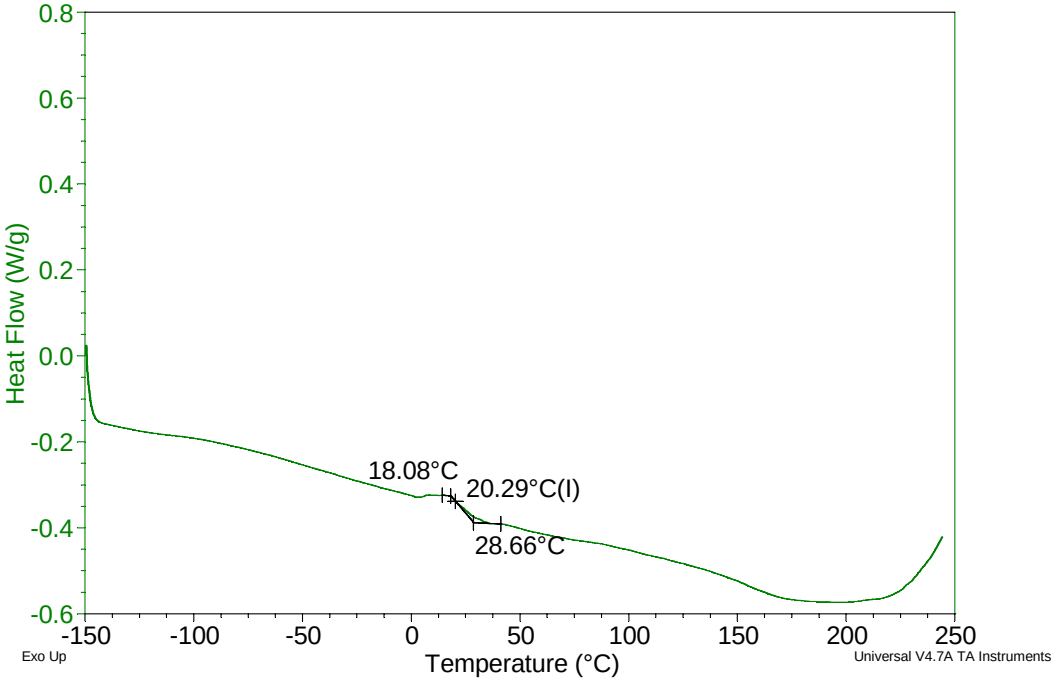


Differential Scanning Calorimetry

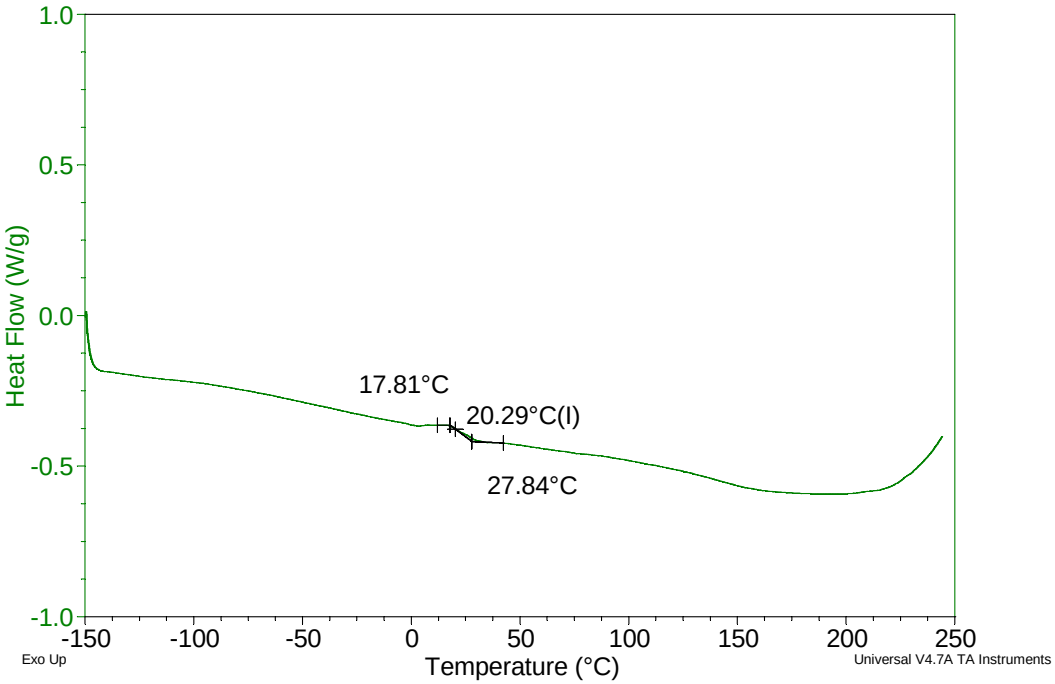
PSQT obtained by Stille coupling



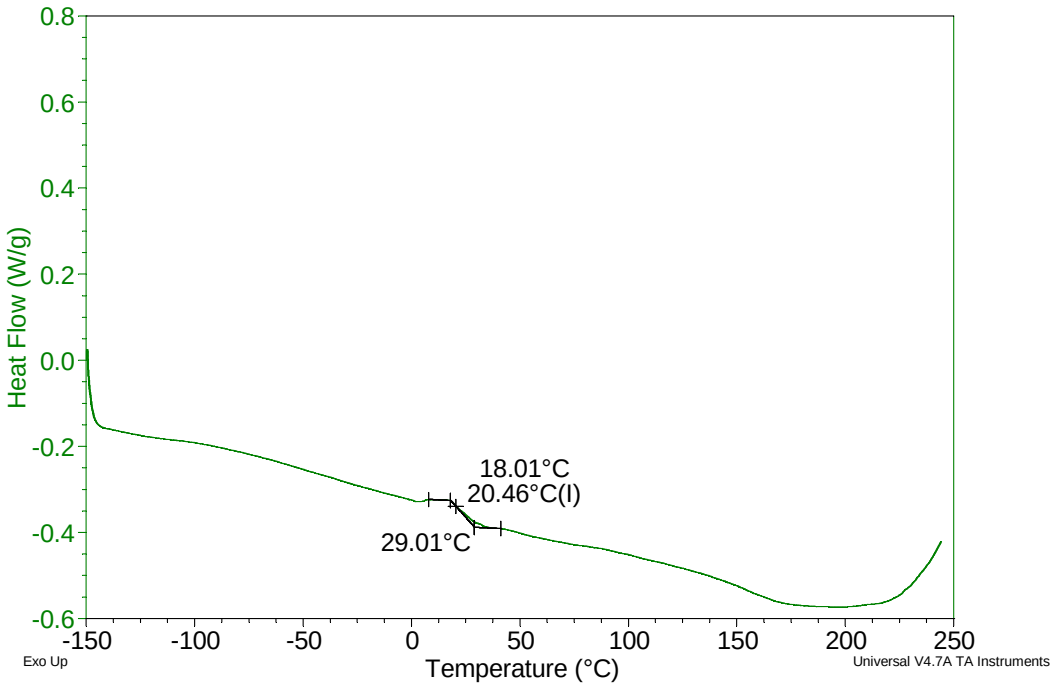
PSQBT obtained by Suzuki coupling



PSQT obtained by SA condensation

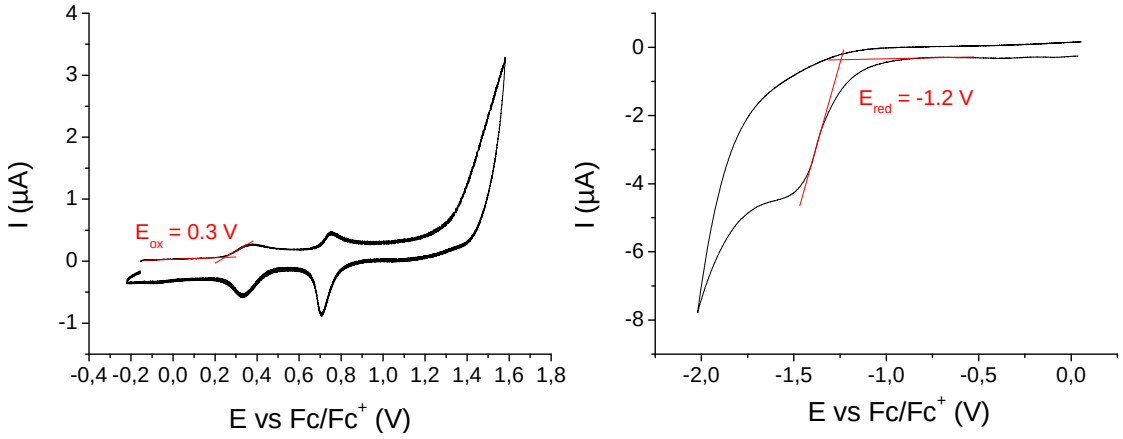


PSQBT obtained by SA condensation

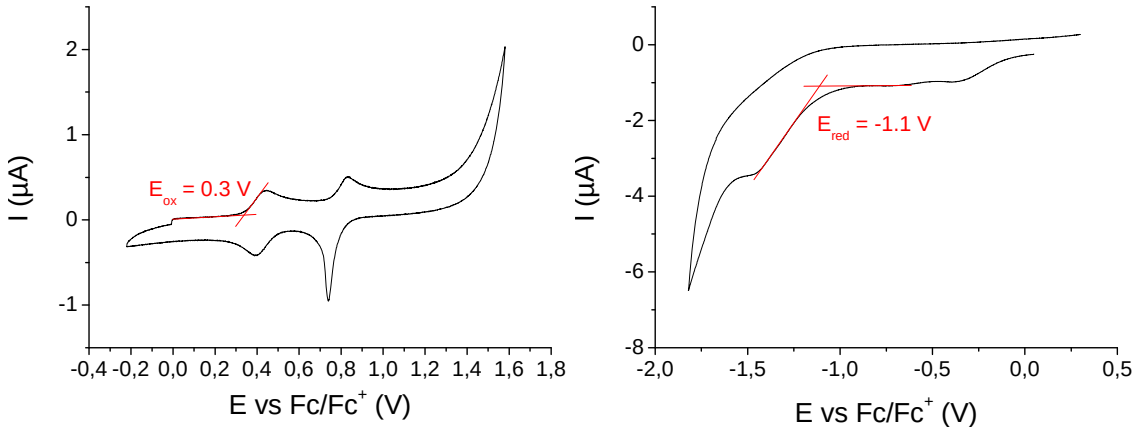


Electrochemical characterizations in $CHCl_3$ solutions (left: oxidation - right: reduction)

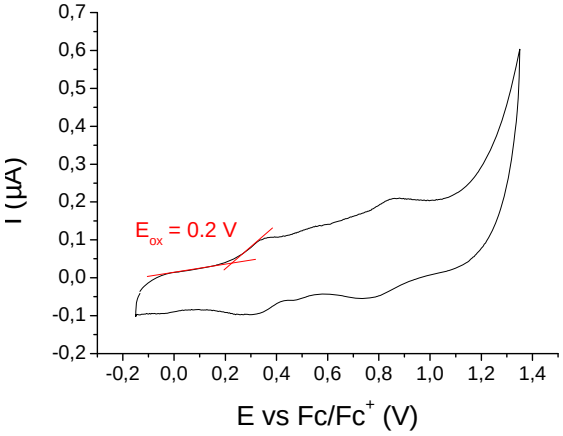
PSQT obtained by Stille coupling

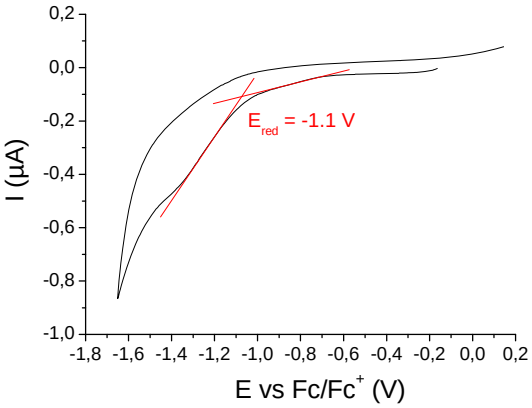


PSQBT obtained by Suzuki coupling

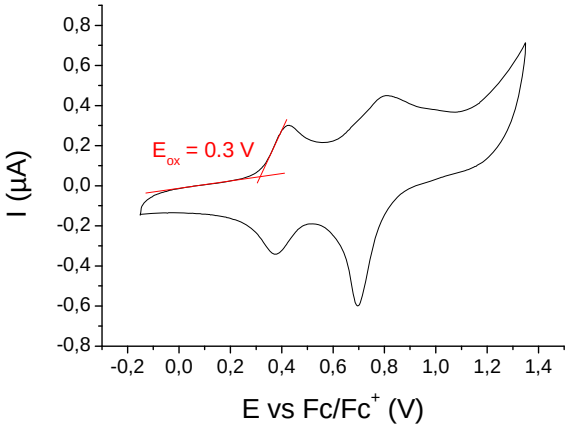


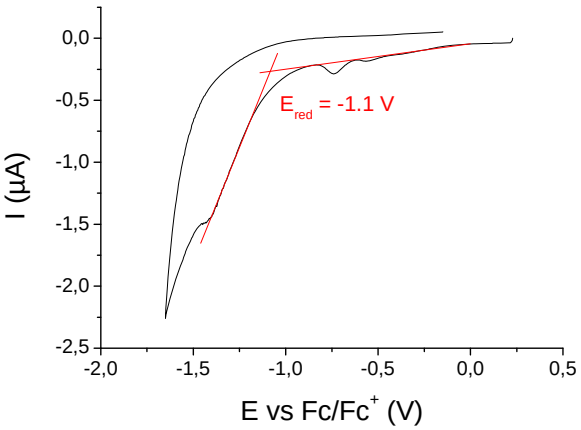
PSQT obtained by SA condensation





PSQBT obtained by SA condensation

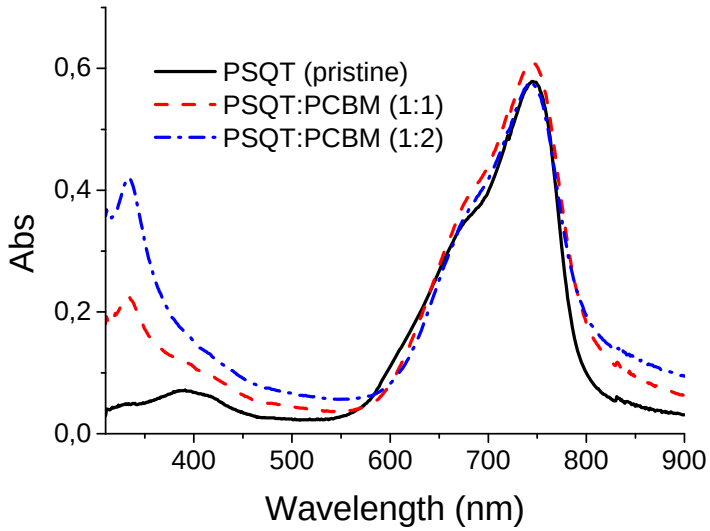


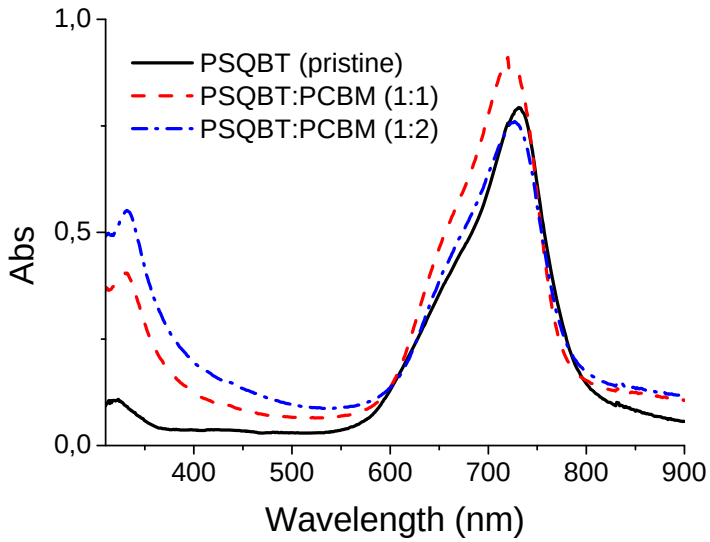


Preliminary studies for photovoltaic characterizations

The polymers obtained by Pd-catalyzed couplings were solubilized with $PC_{60}BM$ at different ratios in ODCB, and subsequently spin-casted onto a glass substrate coated with a PEDOT-PSS layer, simulating conditions similar to the active layer in a typical direct-architecture BHJ solar cell.

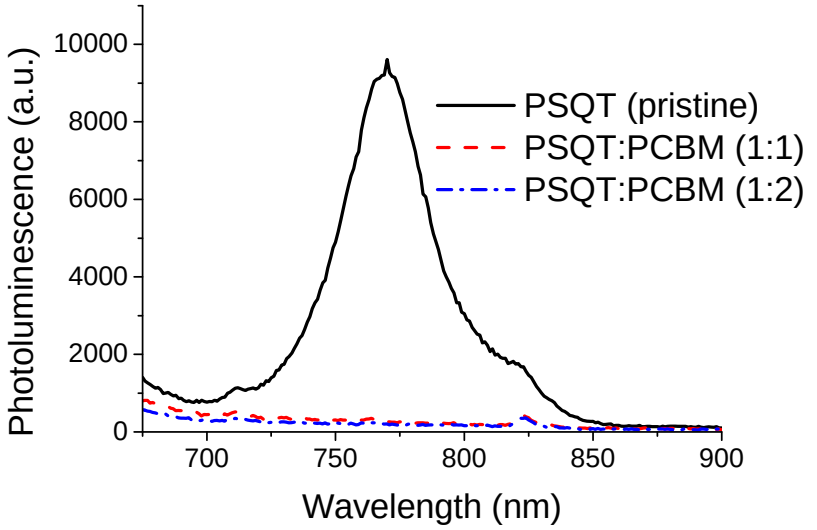
Optical Absorption of the polymers:PCBM blends in film

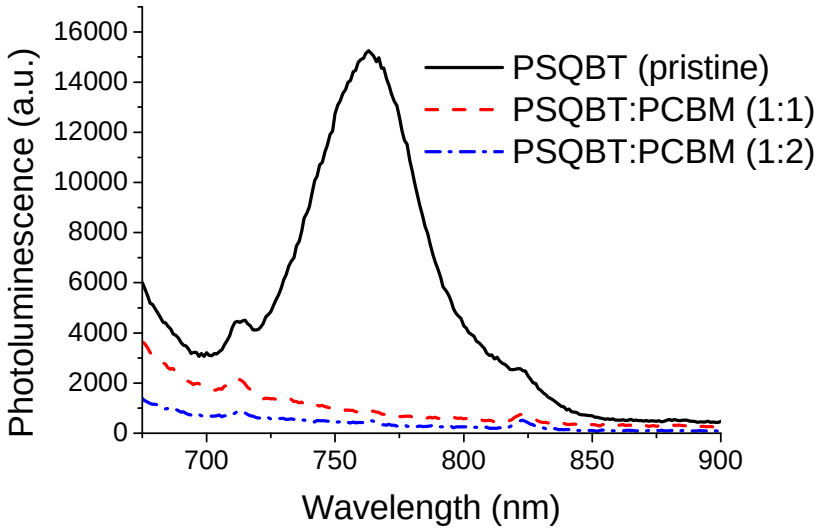




Photoluminescence of the polymers:PCBM blends in film

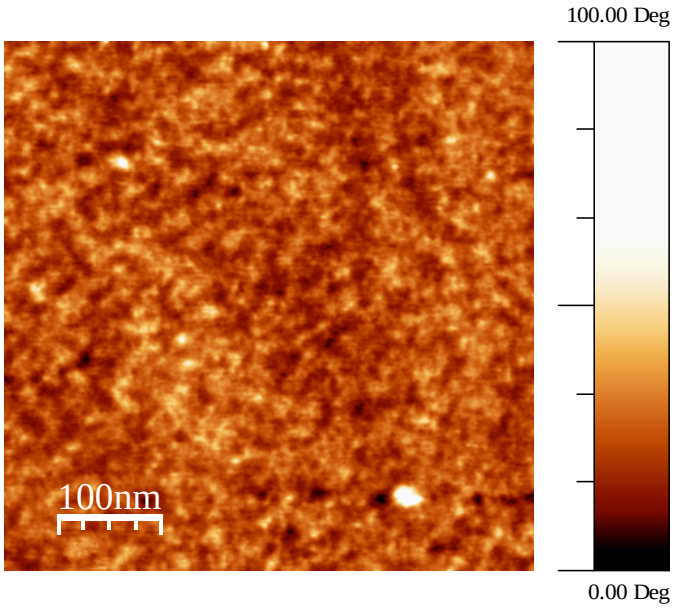
The previously obtained films were then excited at 650 nm to induce the photoluminescence of the polymers.



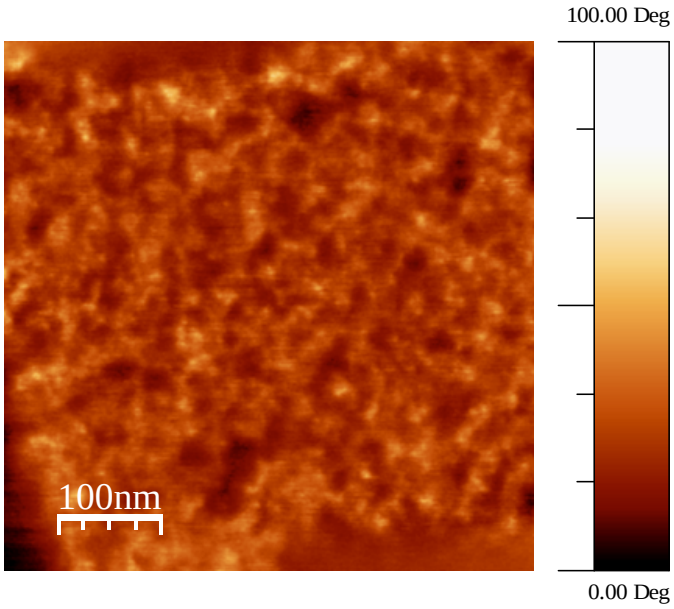


AFM images (phase) of the polymers:PCBM blends (1:1 ratio) in film

PSQT:PCBM (1:1)



PSQBT:PCBM (1:1)



Photovoltaic performance of PSQBT-PCBM blends

The devices were fabricated by using the previously prepared PSQBT-a polymer blended with [6,6]-phenyl-C61 butyric acid methyl ester (PSQBT:PCBM).

Substrates (glass coated with ITO) were cleaned in an ultrasonic bath in methanol and isopropanol. After drying the substrate a thin layer (~50 nm) of PEDOT-PSS was spin-coated at 4000 rpm and dried at 110 °C under rotary pump vacuum for 1 h. All procedures after PEDOT:PSS deposition were performed in an inert-atmosphere glovebox of nitrogen (O2 and H2O<0.1 ppm). Different blend ratio of PSQBT and PCBM were prepared by making 24 mg/mL solutions in o-dichlorobenzene (o-DCB). The photoactive layer (PCBT:PCBM 1:1 wt%) was spin-coated on the top of the PEDOT-PSS layer from o-dichlorobenzene (o-DCB) solutions at 50 °C. The thickness of the photoactive layer was typically in the range of 80 nm. The aluminium cathode was thermally deposited (100 nm) through a shadow mask with a base pressure of 10-7 mbar. The active areas of the devices were ca. 8.4 mm^2. An annealing treatment was performed at 120°C after the cathode deposition during 20 minutes. The current density-voltage (J-V) characteristics were measured with a Keithley 4200 SCS under an illumination of 100 mW/cm^2 from a K.H.S. Solar Celltest 575 solar simulator with AM1.5 filters and in the dark.

Results are presented in the table below.

%w Polymer in active layer	Annealing	V_{OC} (V)	J_{SC} (mA/cm²)	FF	PCE (%)
90	none	0.343	0.057	0.25	0.005
	120°C 20min	0.401	0.055	0.25	0.006
80	none	0.251	0.732	0.26	0.048
	120°C 20min	0.271	0.479	0.25	0.033
70	none	0.274	0.683	0.27	0.050
	120°C 20min	0.264	1.047	0.30	0.084
60	none	0.249	1.470	0.31	0.115
	120°C 20min	0.261	1.025	0.31	0.084
50	none	0.259	1.967	0.34	0.172
	120°C 20min	0.261	1.315	0.34	0.117
40	none	0.261	2.015	0.33	0.176
	120°C 20min	0.254	1.336	0.35	0.120
30	none	0.254	1.804	0.33	0.150
	120°C 20min	0.254	1.592	0.38	0.152
20	none	0.287	2.384	0.35	0.241
	120°C 20min	0.269	2.146	0.39	0.226
10	none	0.113	2.735	0.27	0.083
	120°C 20min	0.322	3.029	0.40	0.395