Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Highly functionalisable polythiophene phenylenes

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	TMeThP **P5**	TTGThP **P6**	PTGThP **P2**	TMeThP-Hex **P8**	TMeThP-Sty **P14**
Mn	3525	8051	6255	6004	7729
Mw	24800	36150	19550	17880	42630
Mw/Mn	7.038	4.490	3.554	5.729	16.70

Table S1: GPC result for TMeThP **P5**, TTGThP **P6,** PTGThP **P1**, TMeThP-Hex **P8** and TMeThP-Sty **P9** determined in DMF on the basis of a linear polystyrene calibration. **P2** did not fully dissolve.

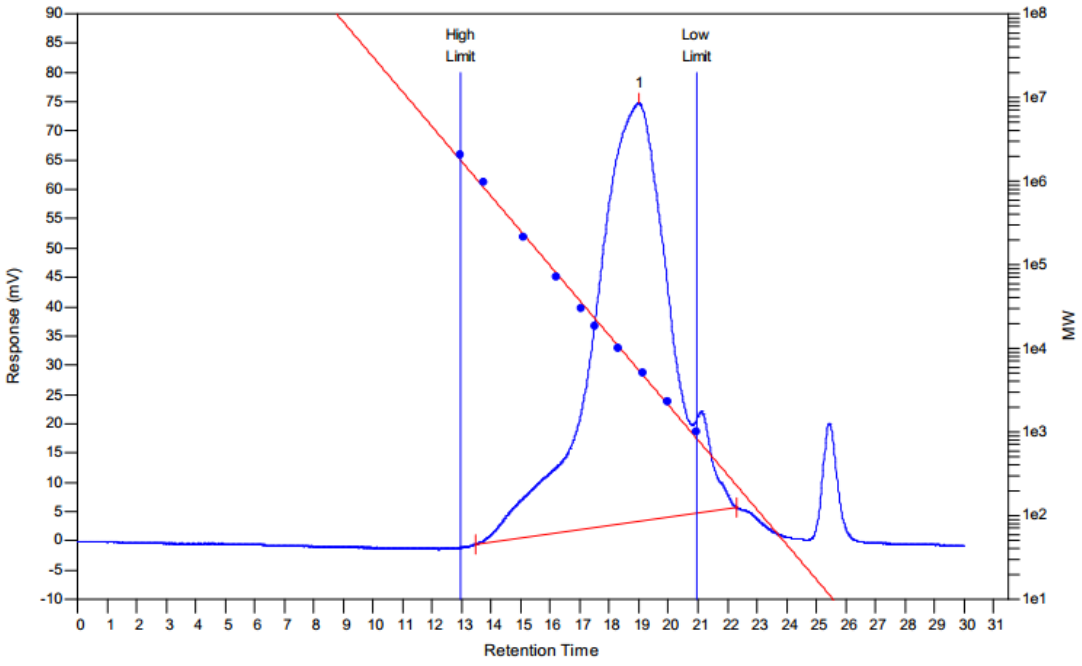


Figure S1: GPC trace of TMeThP **P5**

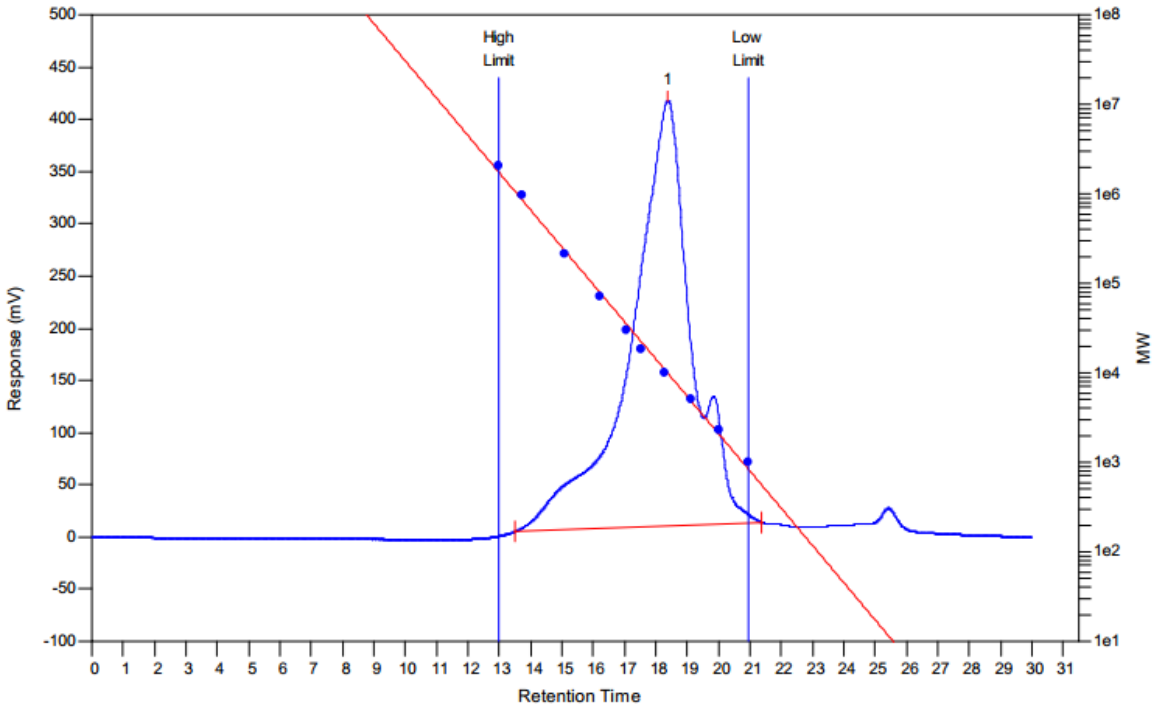


Figure S2: GPC trace of TTGThP **P6**

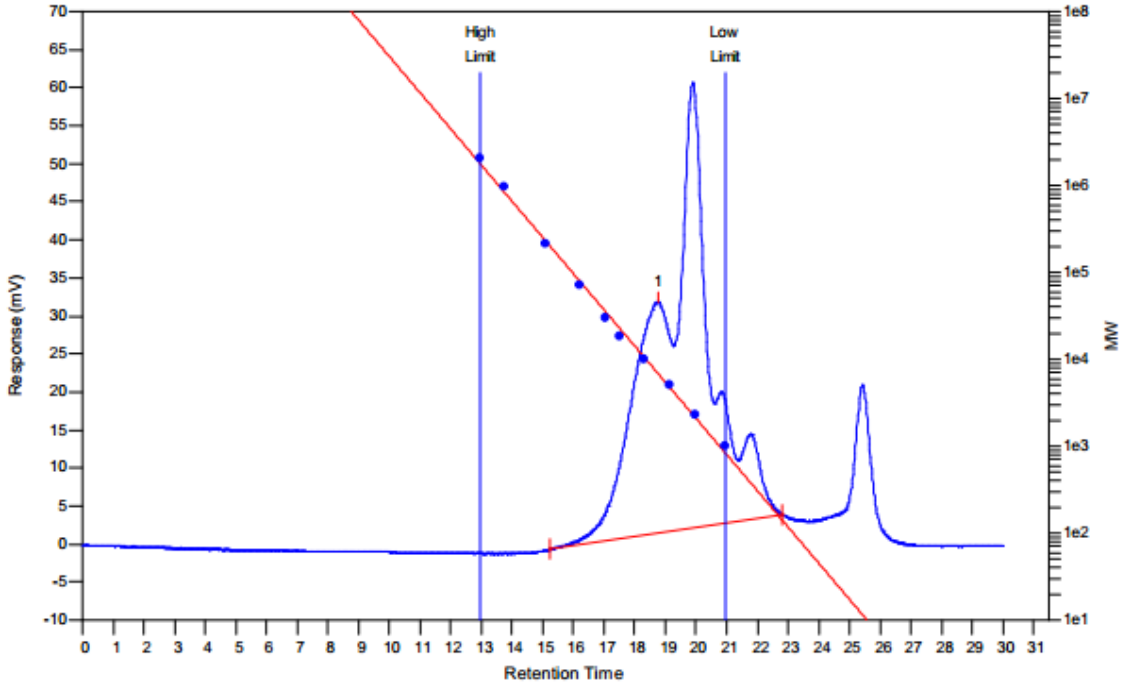


Figure S3: GPC trace of PTGThP **P2**

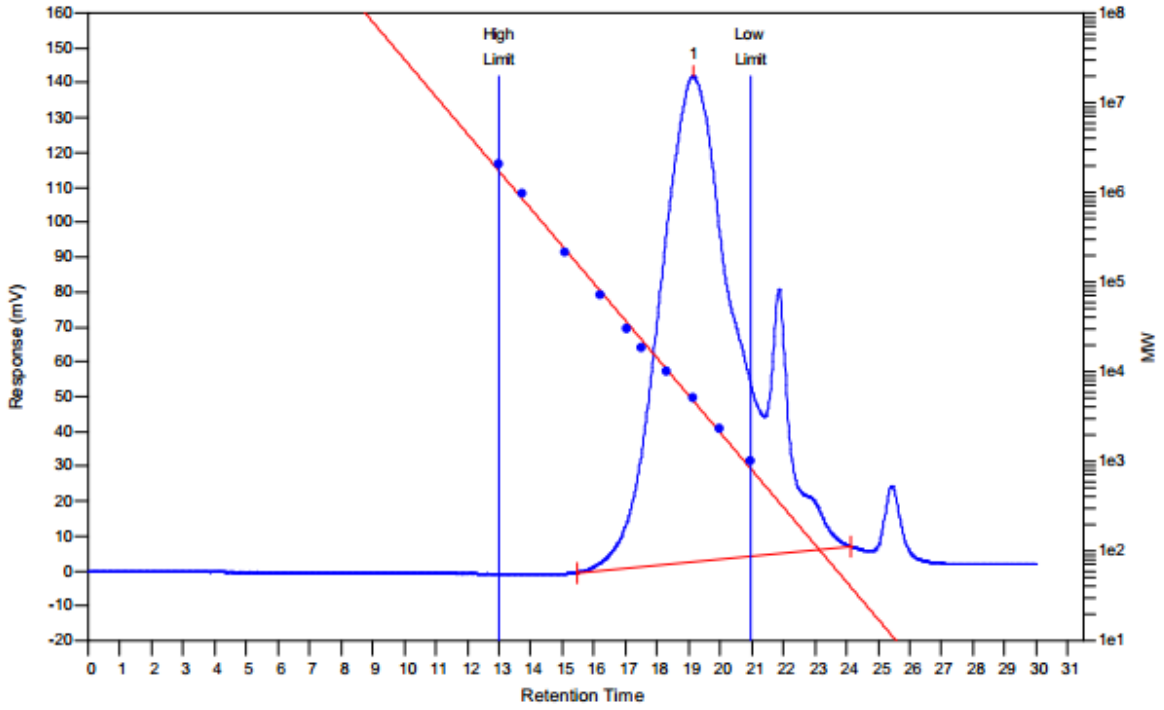


Figure S4: GPC trace of TMeThP-Hex **P8**

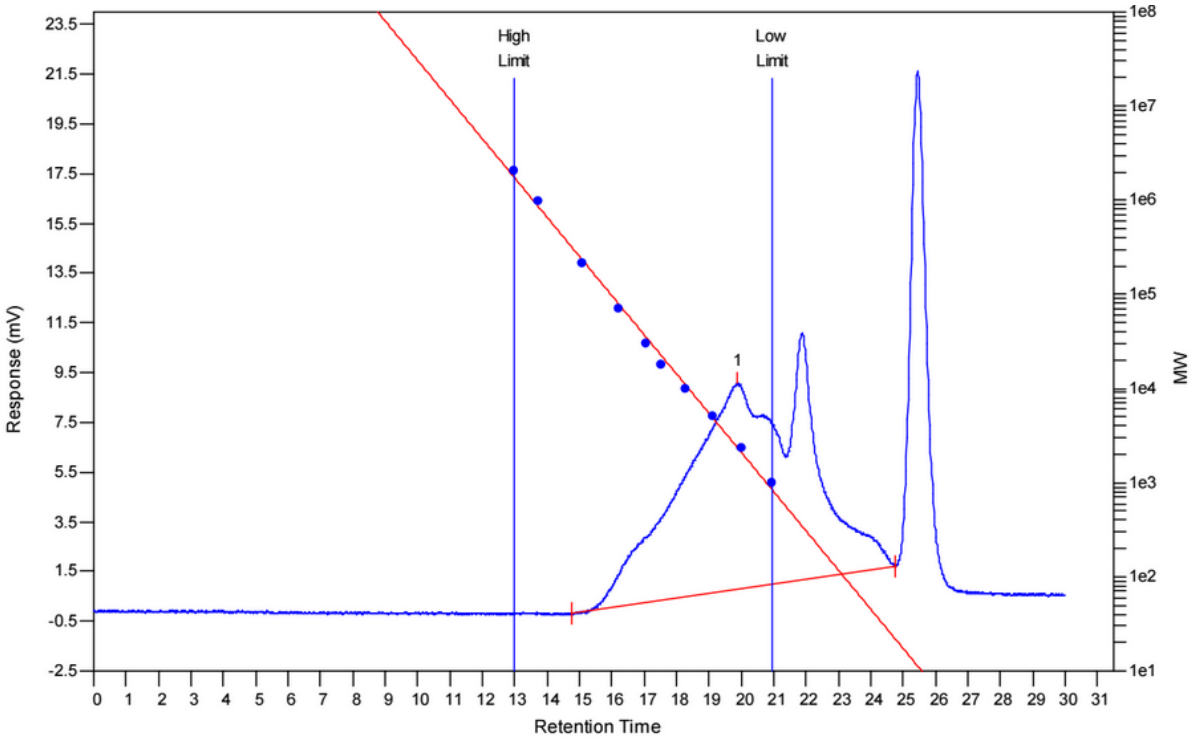


Figure S5: GPC trace of TMeThP-Sty **P9**

Characterisation – AzThP **16**

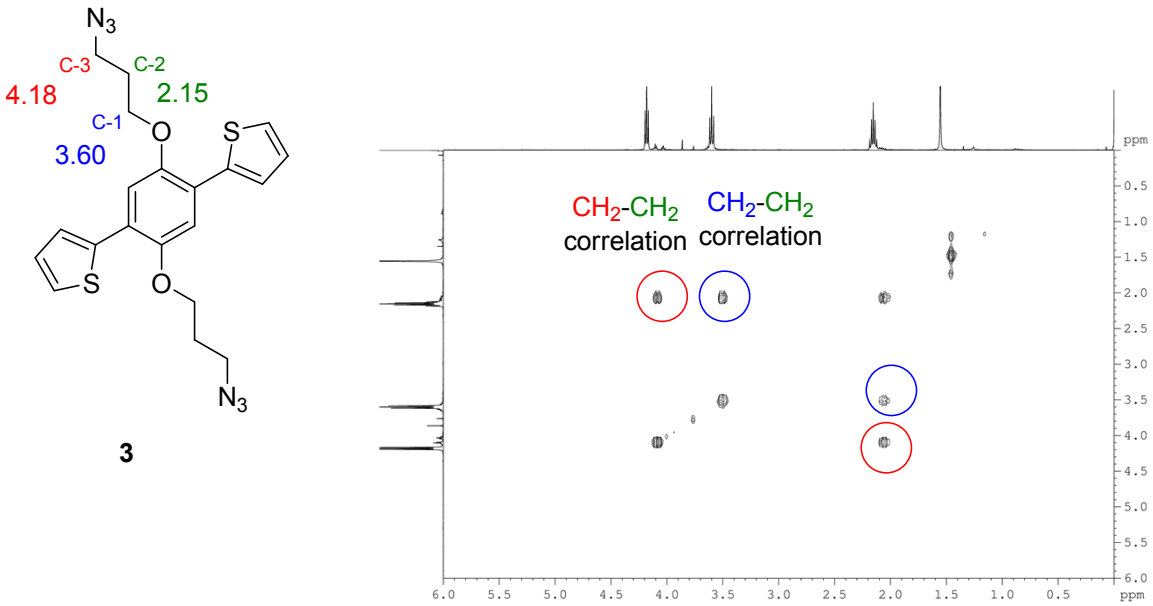


Figure S6: Expansion of COSY spectrum of AzThP **3** highlighting the cross-peaks between H-2 with H-1 and H-3.

Characterisation – TMeThP **P5**

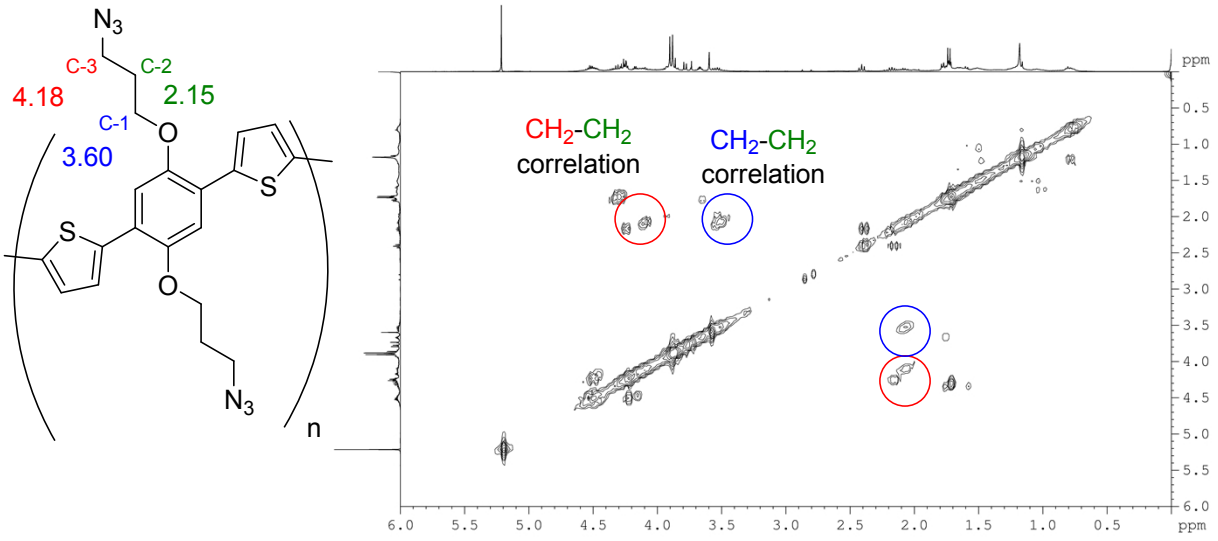


Figure S7: Expansion of COSY spectrum of TMeThP **P5**, highlighting the presence of cross- between H-2 with H-1 and H-3 are still present in spectrum after polymerisation

Characterisation of TMeThP-Hex **P8**

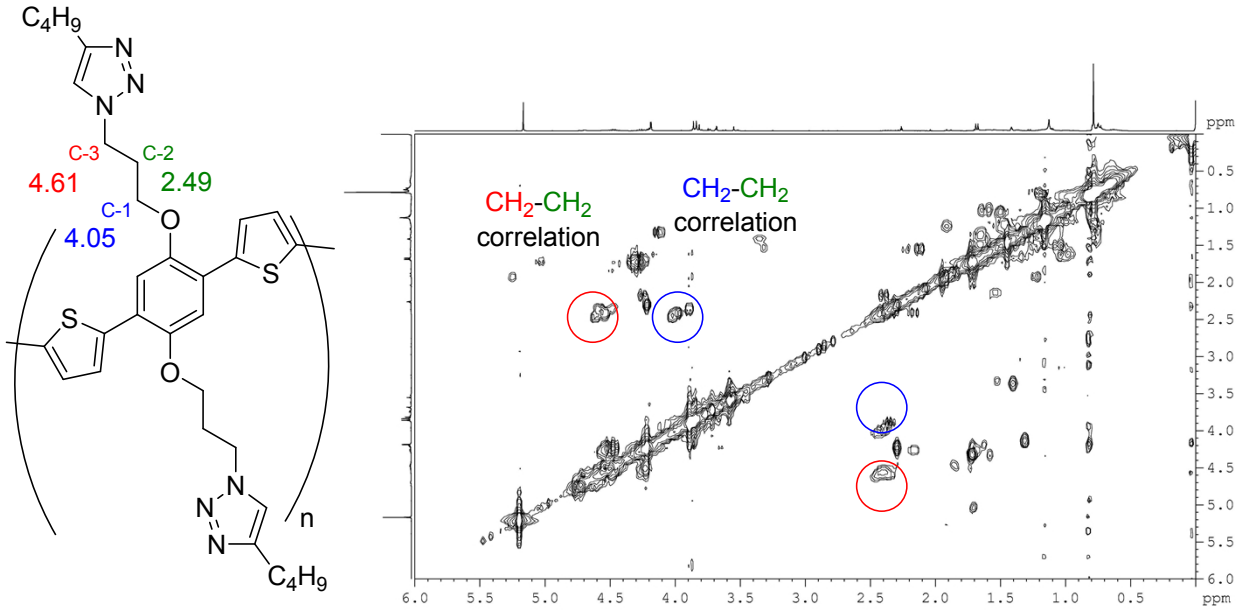


Figure S8: Expansion of COSY spectrum of TMeThP-Hex **P8**, highlighting the shift of the position of cross-peaks after conversion of azide to triazole through 'click' reaction.

Characterisation of TMeThP-HexSty **P10**

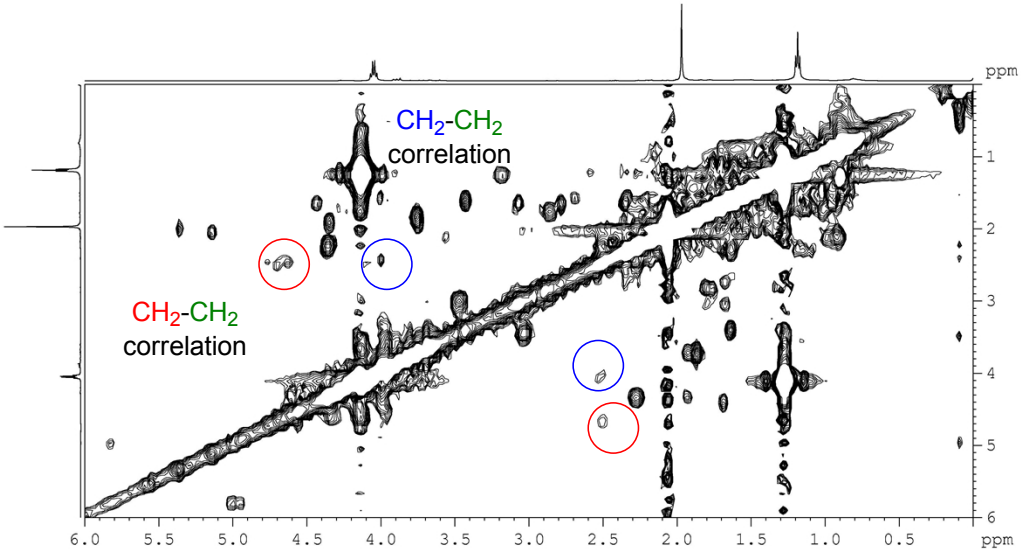


Figure S9: Expansion of COSY spectrum of TMeThP-HexSty **P14**, highlighting the presence of cross-peaks at positions consistent with triazole formation.

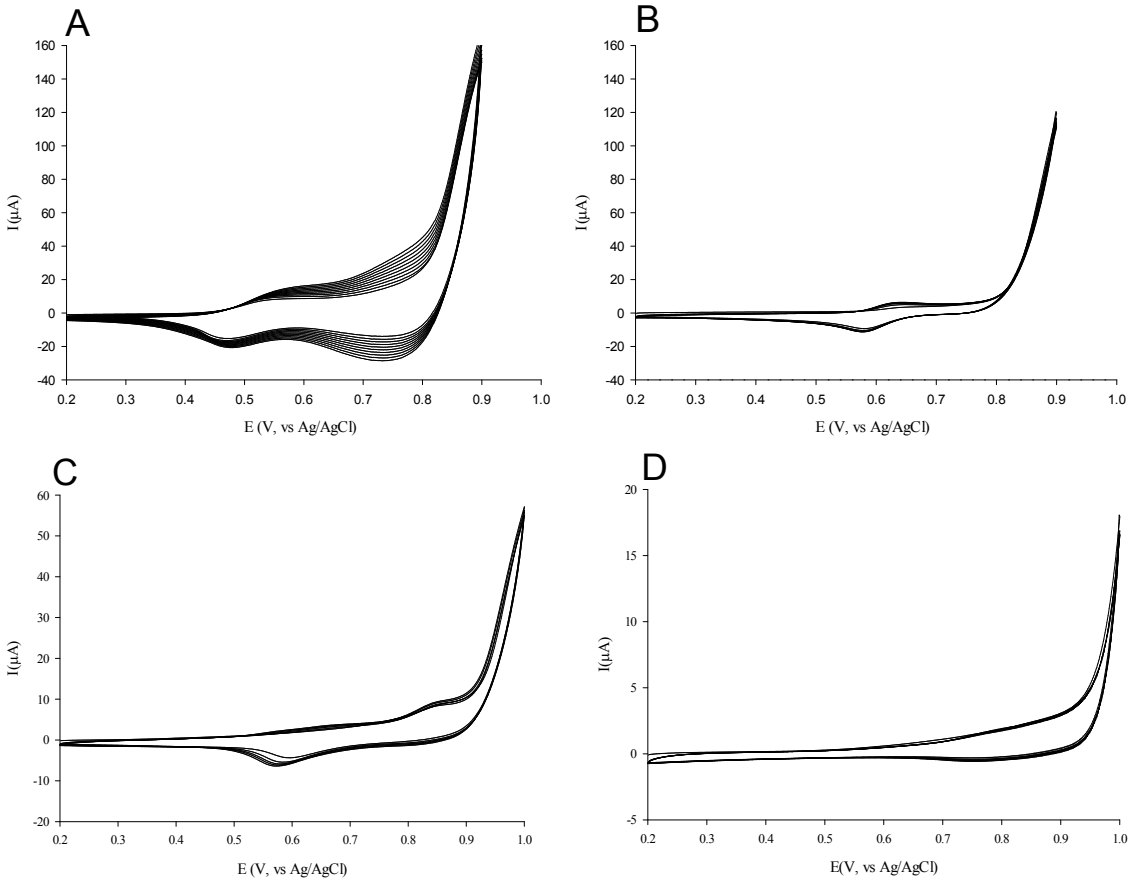


Figure S10: Electropolymerisation CV of 0.02 M monomer solutions in 0.1 M LiClO4 in H_2O/MeCN (4:1) at 100 mV s^{-1} for: A: MeThP **2**, B: TGThP **1**, C: AzThP **3**, D: BIThP **4**

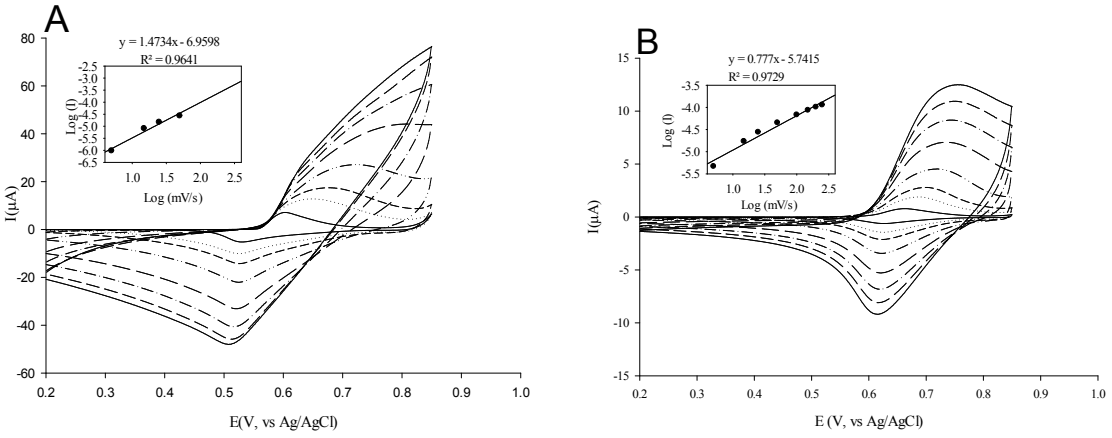


Figure S11: Cyclic voltammogrammes of terpolymers **A**: TMeThP **P5 B**: TGThP **P6**; at scan rates between 5 mVs^{-1} to 250 mVs^{-1} in monomer-free solution 0.1 M $LiClO_4$ in 4:1 (H_2O:MeCN) ; **Inset:** Linear dependence of log of scan rate over log of current at the oxidation peak.

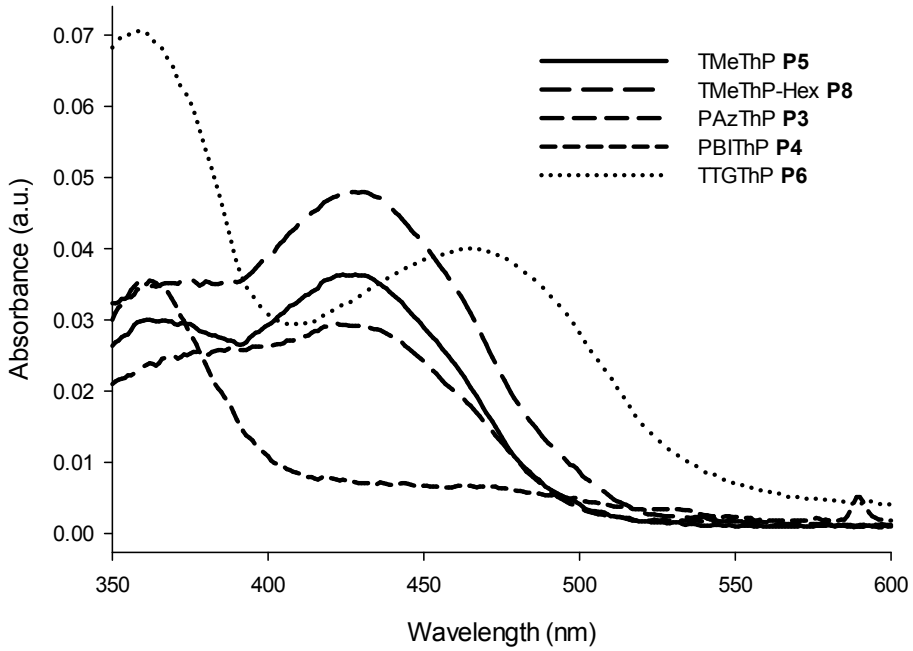


Figure S12: UV visible spectrum

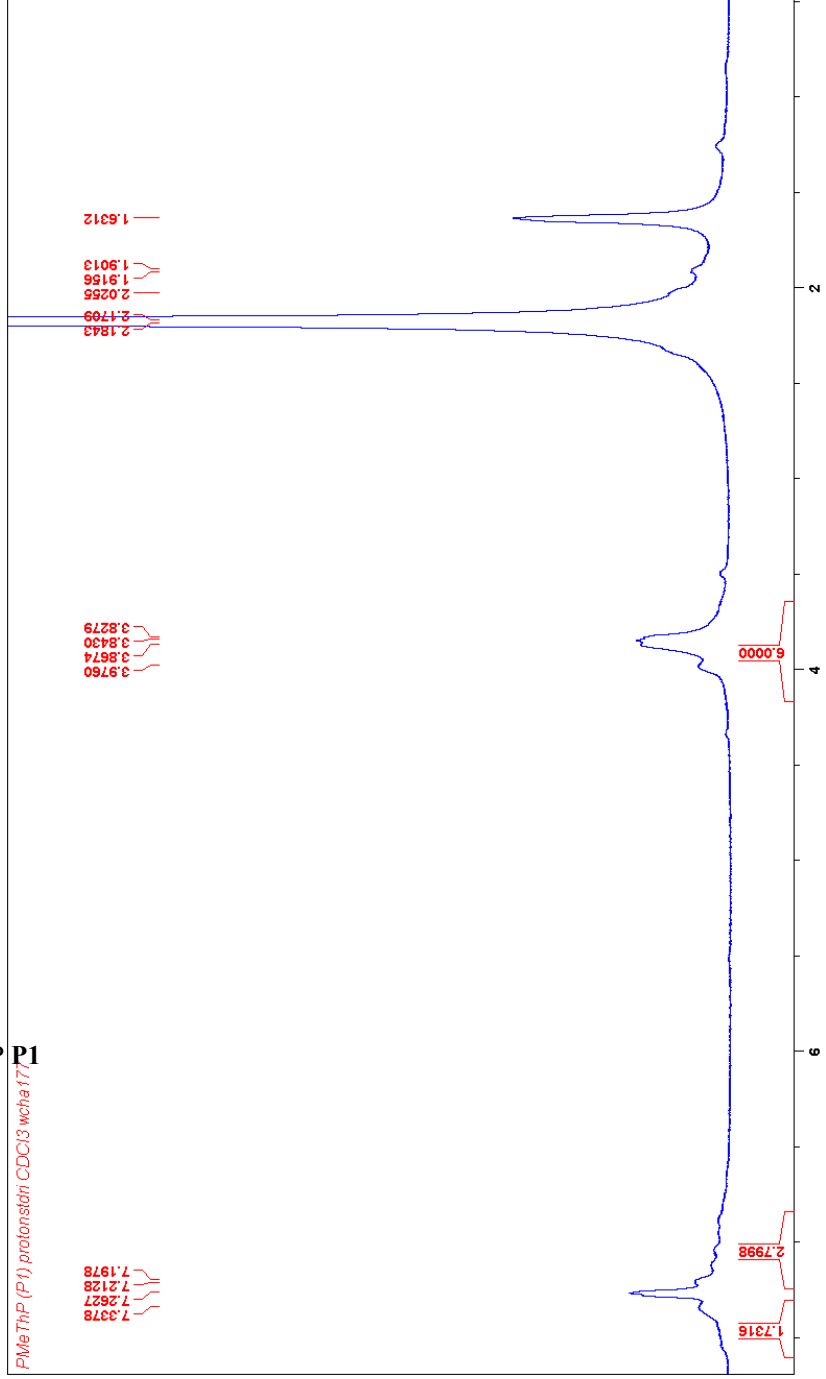


Figure S13: ^{1}H NMR of PMeThP **P1**

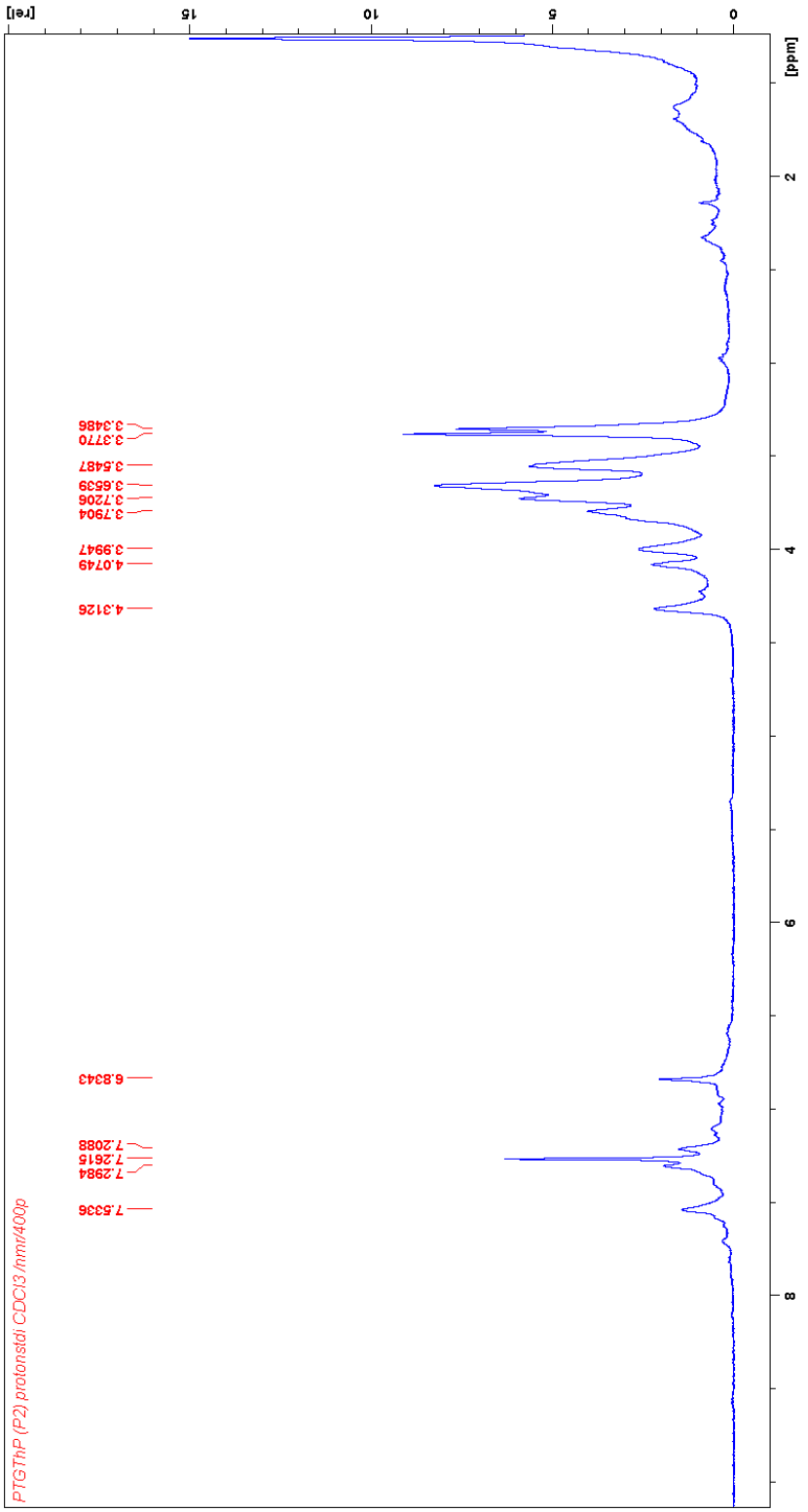


Figure S14: ^{1}H NMR of PTGThP **P2**

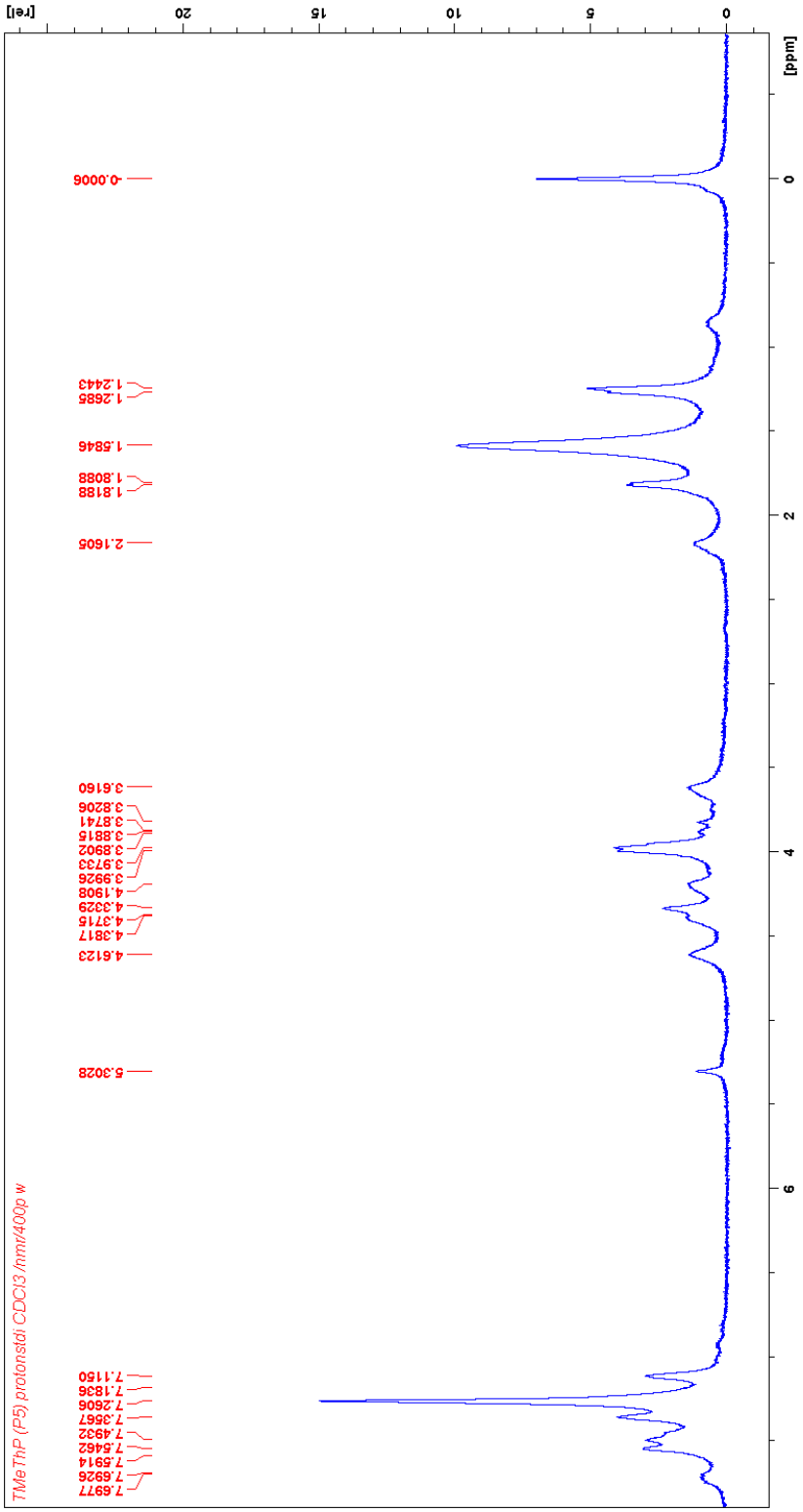


Figure S15: ^{1}H NMR of TMeThP **P5**

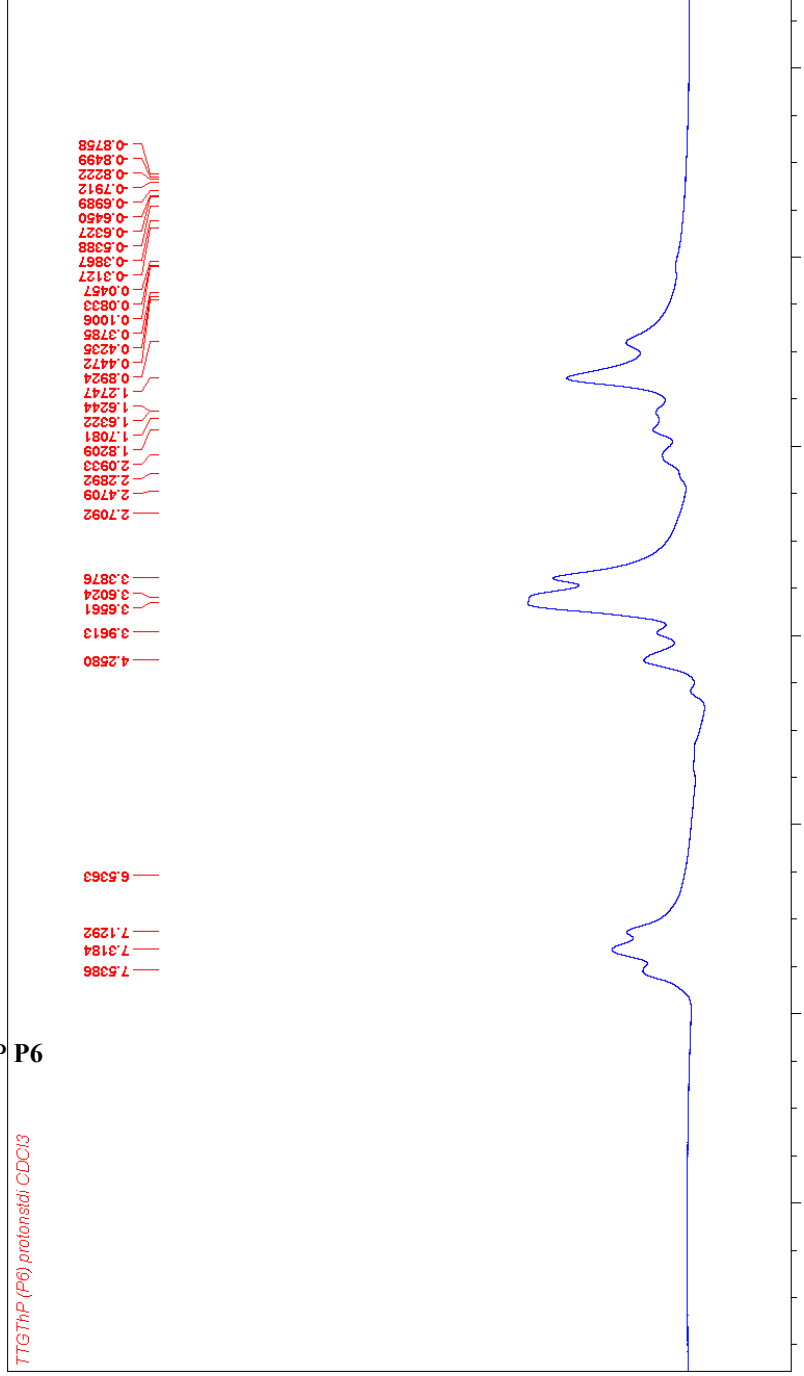


Figure S16: ^{1}H NMR of TTGThP **P6**

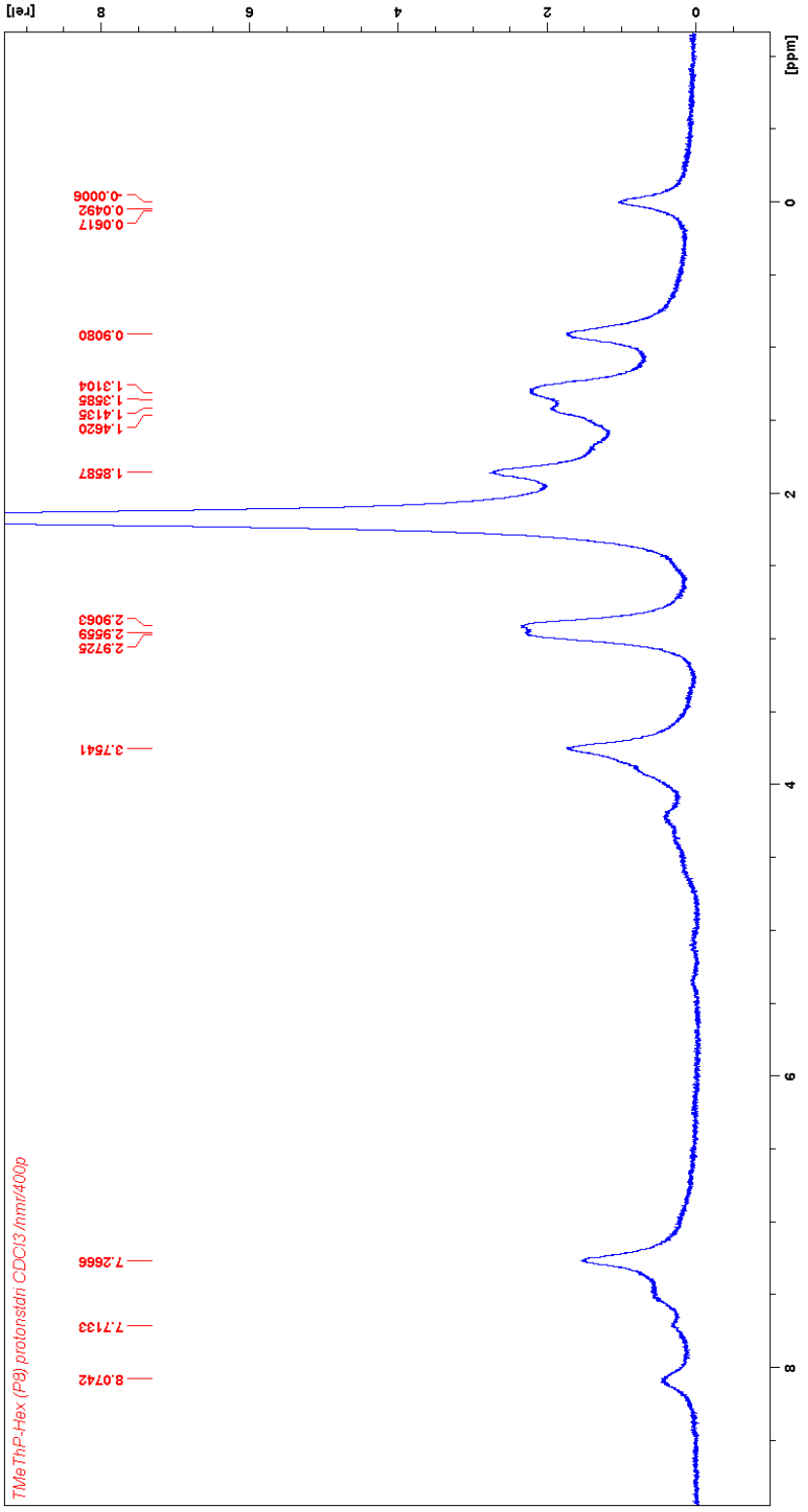


Figure S17: ^{1}H NMR of TMeThP-Hex **P8**

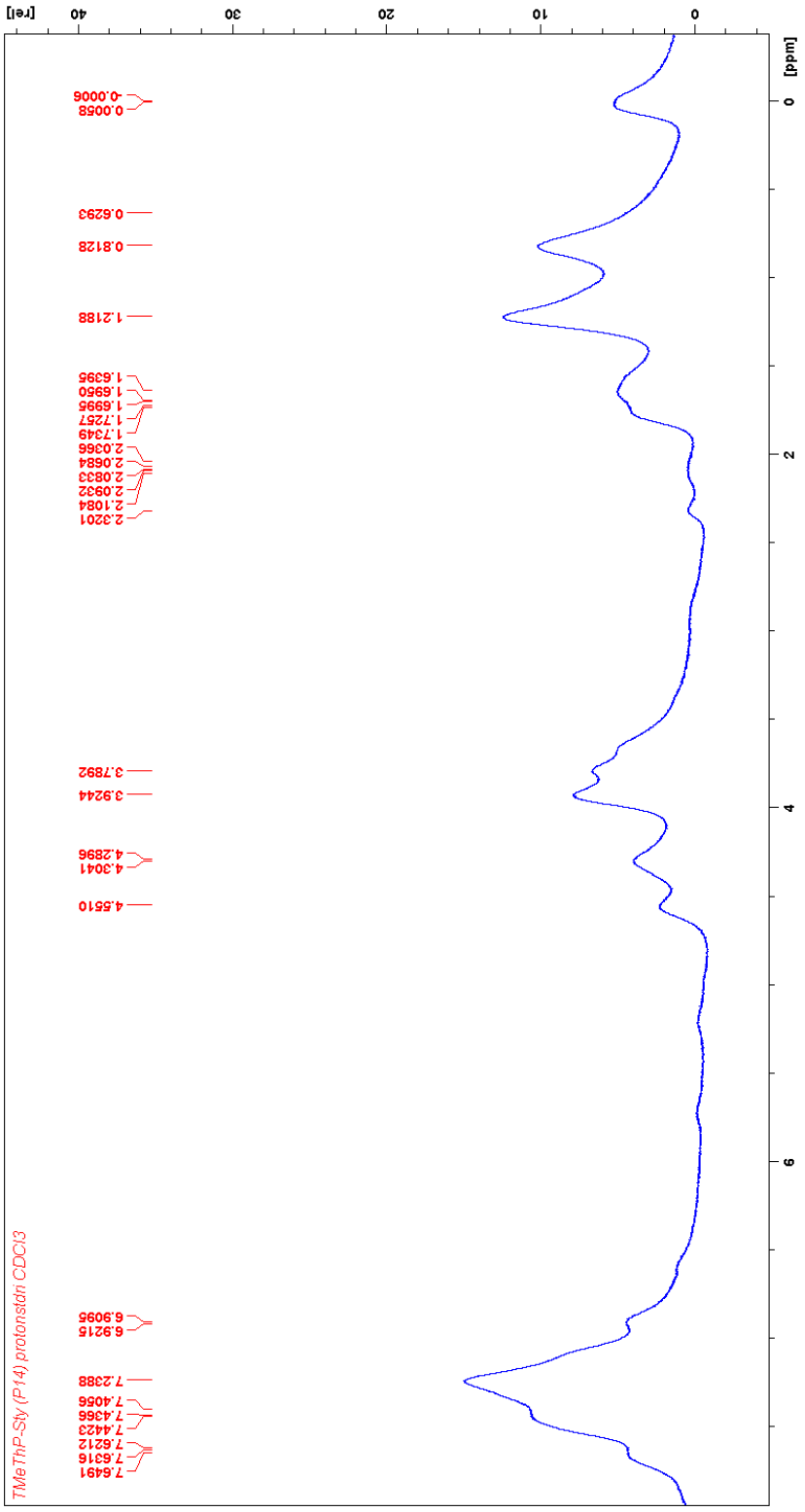


Figure S18: ^{1}H NMR of TMeThP-Sty **P14**

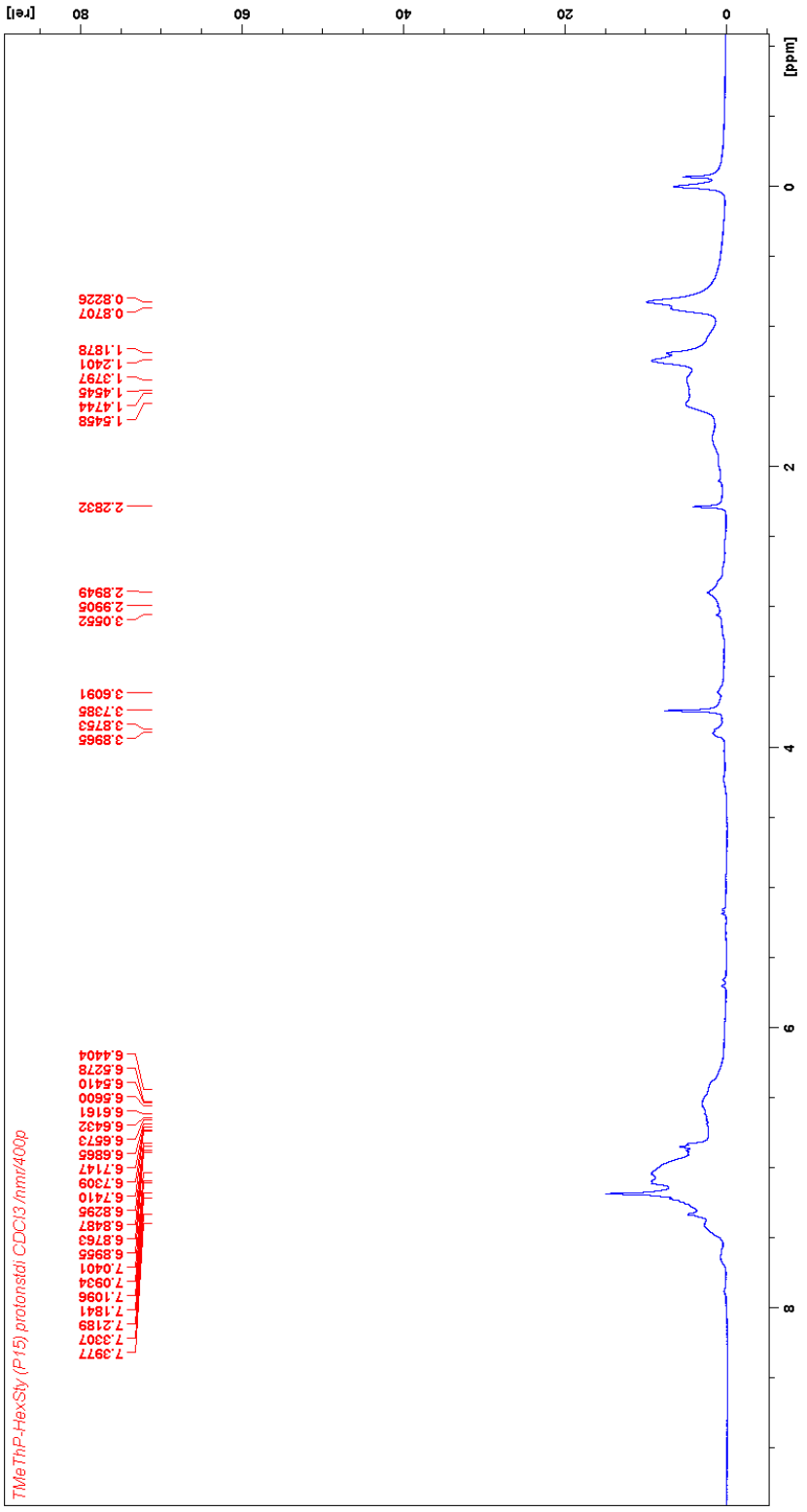
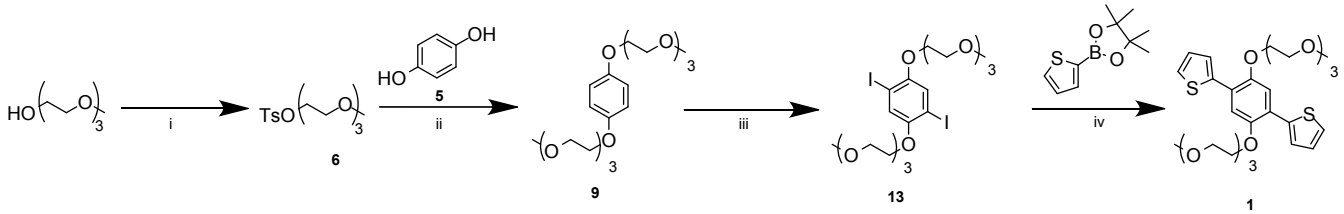
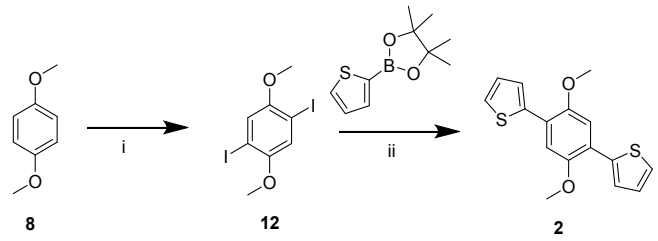


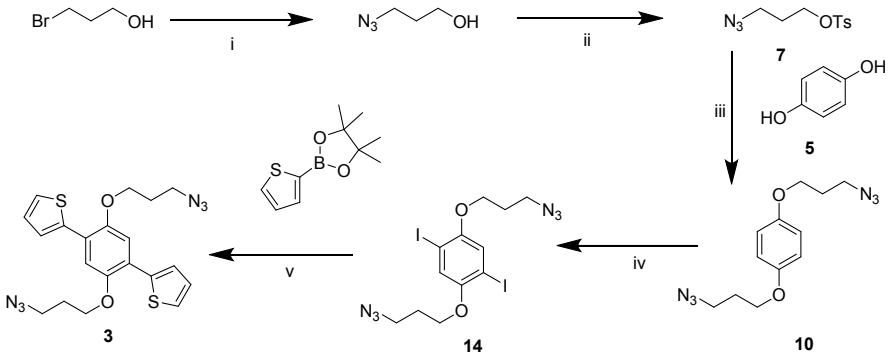
Figure S19: ^{1}H NMR of TMeThP-HexSty **P15**



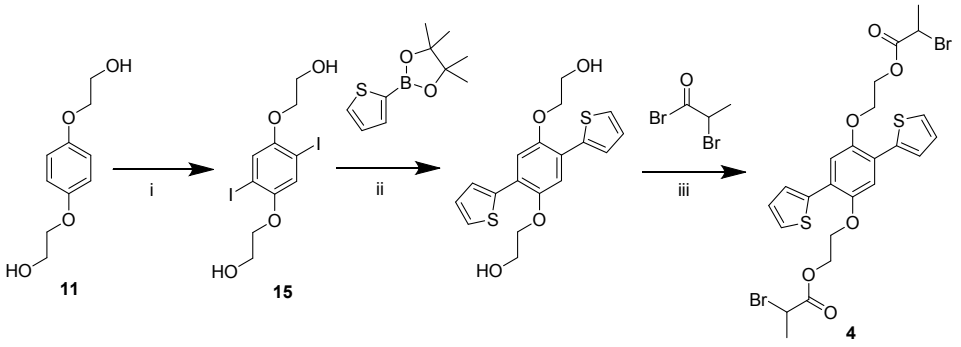
Scheme S1: Synthesis of 2,2'-(2,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,4-phenylene)dithiophene (TGThP) **1**. (i) TsCl, Et_3N, CH_2Cl_2, 0 °C to r.t., 24 h 86% (ii) ^{t}BuOK, EtOH, 70 °C, 24 h, 49% (iii) I_2, $Hg(OAc)_2$, r.t., 6 h, 76% (iv) $Pd(OAc_2)$, SPhos, K_3PO_4, ^{n}butanol, 110 °C, 20 h, 58%.



Scheme S2: Synthesis of 2,2'-(2,5-dimethoxy-1,4-phenylene)dithiophene (MeThP) **2**. (i) I_2, H_5IO_6, MeOH, r.t., 4 h 97% (ii) $Pd(OAc_2)$, SPhos, K_3PO_4, ^{n}butanol, 110 °C, 20 h, 90%.



Scheme S3: Synthesis of 2,2'-(2,5-bis(3-azidopropoxy)-1,4-phenylene)dithiophene (AzThP) **3**, (i) NaN_3, H_2O, 70 °C, 24 h, 89% (ii) TsCl, Et_3N, CH_2Cl_2, 0 °C to r.t., 24 h, 93% (iii) ^{t}BuOK, EtOH, 70 °C, 24 h, 62% (iv) I_2, $Hg(OAc_2)$, r.t., 6 h, 70% (v) $Pd(Ph_3)_4$, K_3PO_4, DMF, 70 °C, 48 h, 32%.



Scheme S4: Synthesis of ((2,5-di(thiophen-2-yl)-1,4-phenylene)bis(oxy))bis(ethane-2,1-diyl) bis(2-bromopropanoate) (BIThP) **4**, (i) ICl, MeOH, reflux, 6 h, 74% (ii) $Pd(Ph_3)_4$, K_3PO_4, DMF, 70 °C, 48 h, 71% (iii) Et_3N, DMAP, CH_2Cl_2, r.t. 24 h, 85%.