

Supporting Information

to

Complex Polymer Topologies Built from Tailored Multifunctional Cyclic Polymers.

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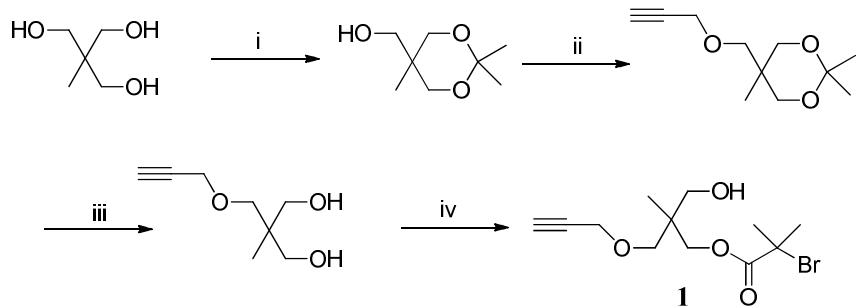
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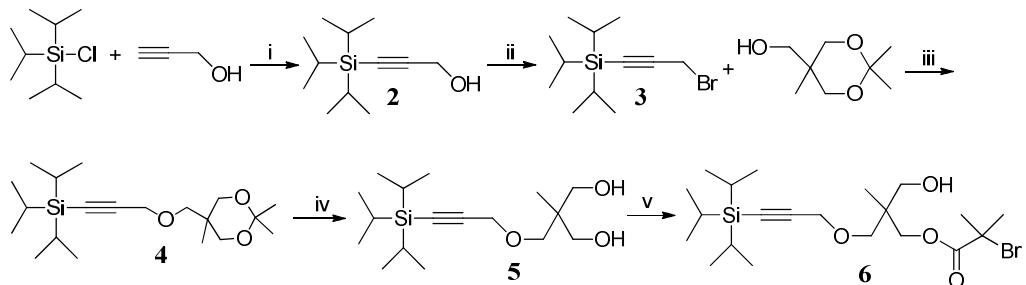
1 Characterization of initiators

Scheme S1: Synthesis of alkyne (hydroxyl) functional initiator (**1**)



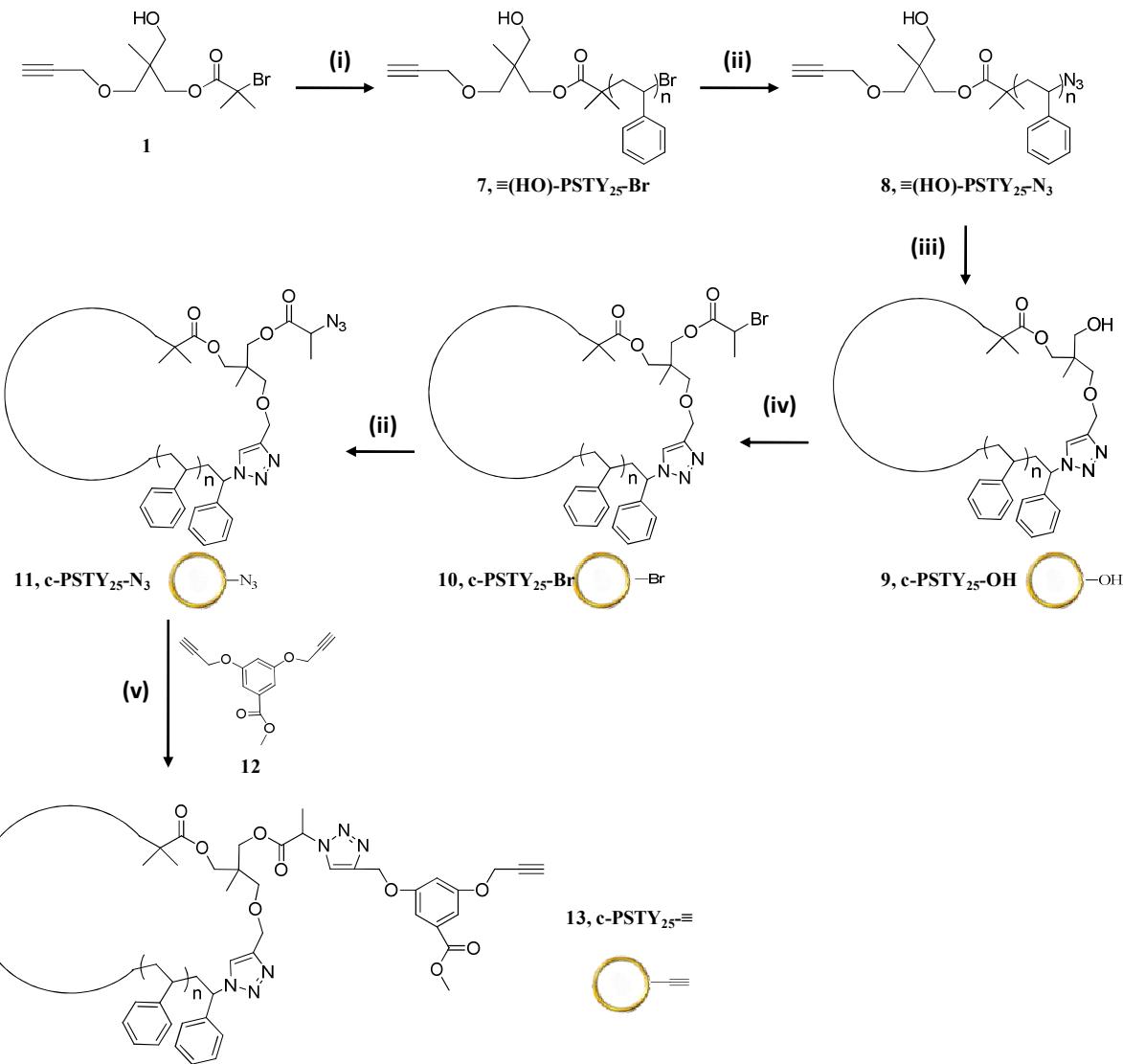
Reactants and conditions: i) Acetone, p-TsOH, RT, 16h; ii) THF, NaH, propargyl bromide, -78 °C, 16 h; iii) DOWEX, Methanol, R.T. 16 h; iv) THF, 2-bromoisobutyryl bromide, 0 °C - RT, 16 h.

Scheme S2: Synthesis of protected alkyne (hydroxyl) functional initiator (**6**)



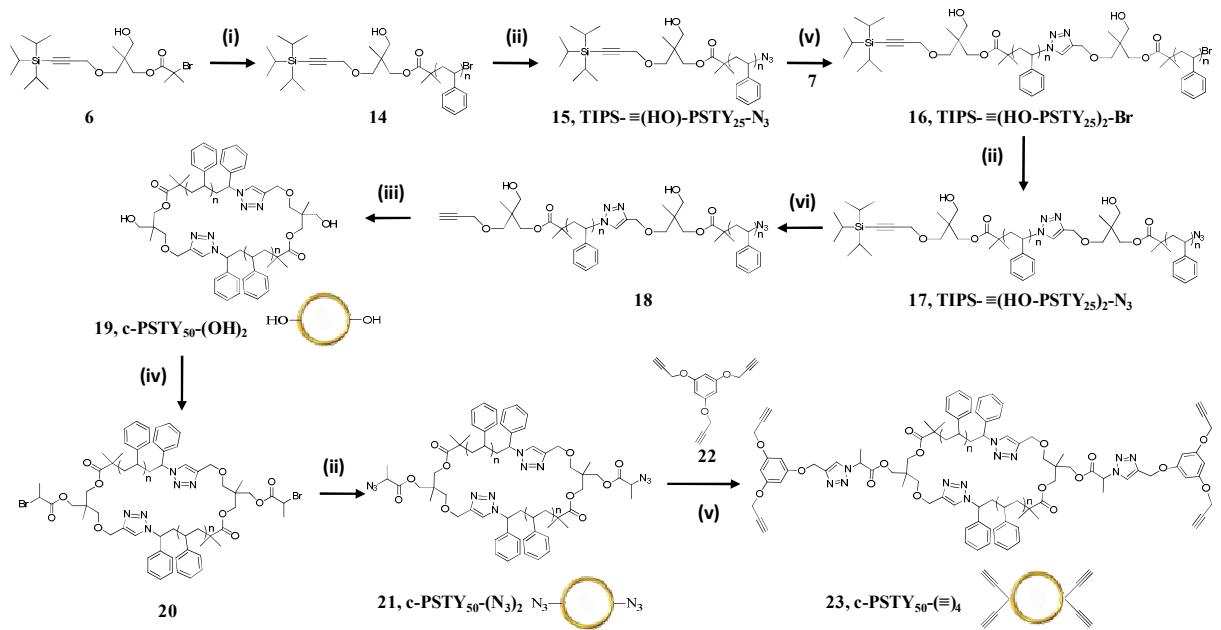
Reactants and conditions: (i) EtMgBr, THF, reflux at 76 °C, (ii) PBr₃, pyridine, ether 0 ~ 25 °C (iii) NaH/ THF, -78 °C ~ 25 °C (iv) DOWEX resin in MeOH at 40 °C (v) TEA in THF at 0 °C ~ RT for 24 h.

Scheme S3: Synthesis of monofunctional alkyne cyclics (**9-13**).



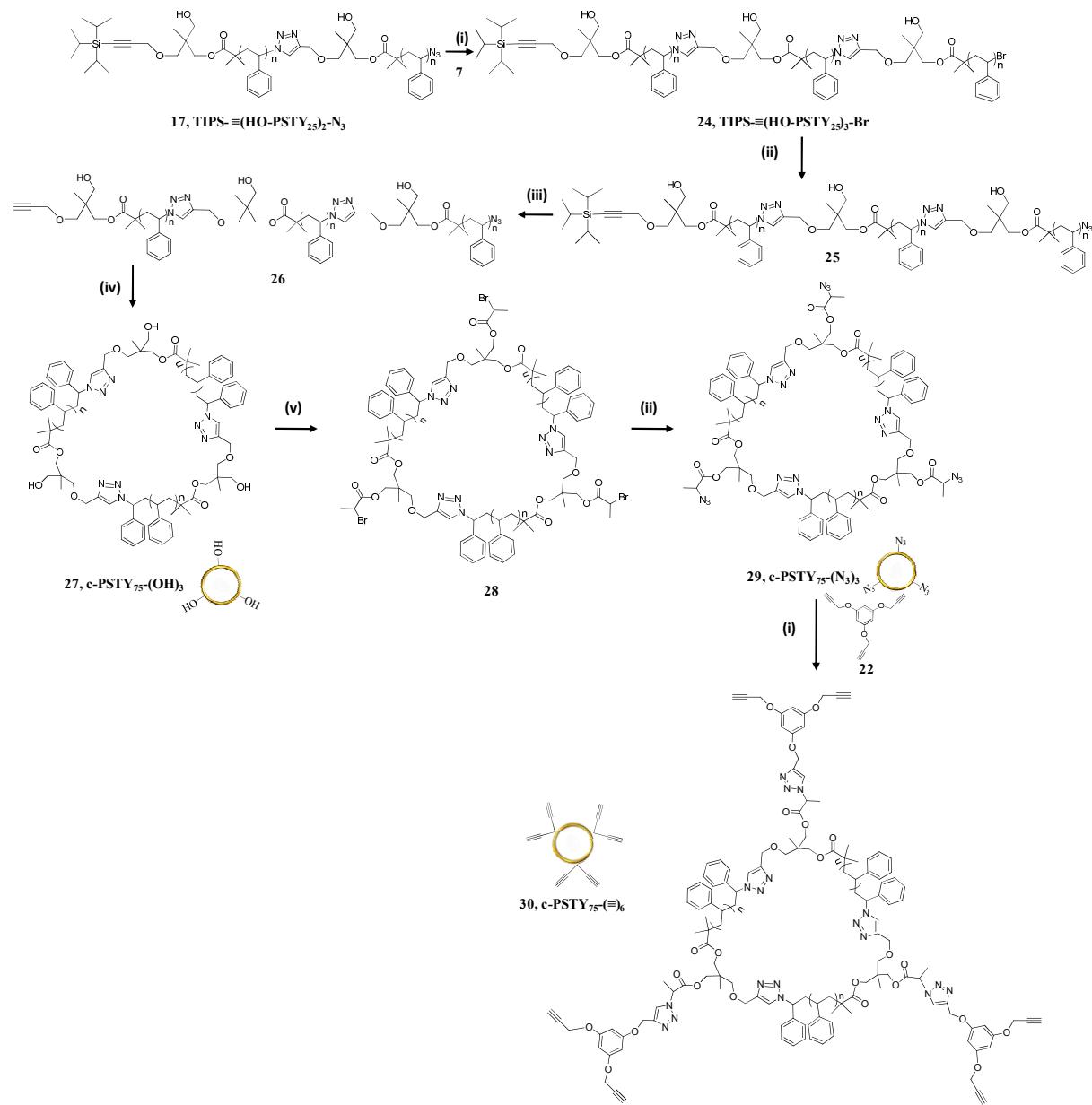
Conditions: (i) **Polymerization:** Styrene, CuBr, PMDETA, CuBr₂/PMDETA in bulk at 80 °C. (ii) **Azidation:** NaN₃ in DMF at 25 °C, (iii) **Cyclization:** CuBr, PMDETA in toluene by feed at 25 °C, (iv) **Bromination:** 2-BPB, TEA in THF; 0 °C- RT, (v) **Click:** CuBr, PMDETA in toluene at 25 °C. (vi) **Deprotection:** TBAF in THF at 25 °C.

Scheme S4: Synthesis of multifunctional cyclics (19-23).



Conditions: (i) **Polymerization:** Styrene, CuBr, PMDETA, CuBr₂/PMDETA in bulk at 80 °C. (ii) **Azidation:** NaN₃ in DMF at 25 °C, (iii) **Cyclization:** CuBr, PMDETA in toluene by feed at 25 °C, (iv) **Bromination:** 2-BPB, TEA in THF; 0 °C- RT, (v) **Click:** CuBr, PMDETA in toluene at 25 °C. (vi) **Deprotection:** TBAF in THF at 25 °C.

Scheme S5: Synthesis of multifunctional cyclics (27-30).



Conditions: (i) 'Click': CuBr, PMDETA in toluene at 25 °C, (ii) Azidation: NaN₃ in DMF at 25 °C, (iii) Deprotection: TBAF in THF at 25 °C, (iv) Cyclization: CuBr, PMDETA in toluene by feed at 25 °C, (v) Bromination: 2-BPB, TEA in THF; 0 °C- RT.

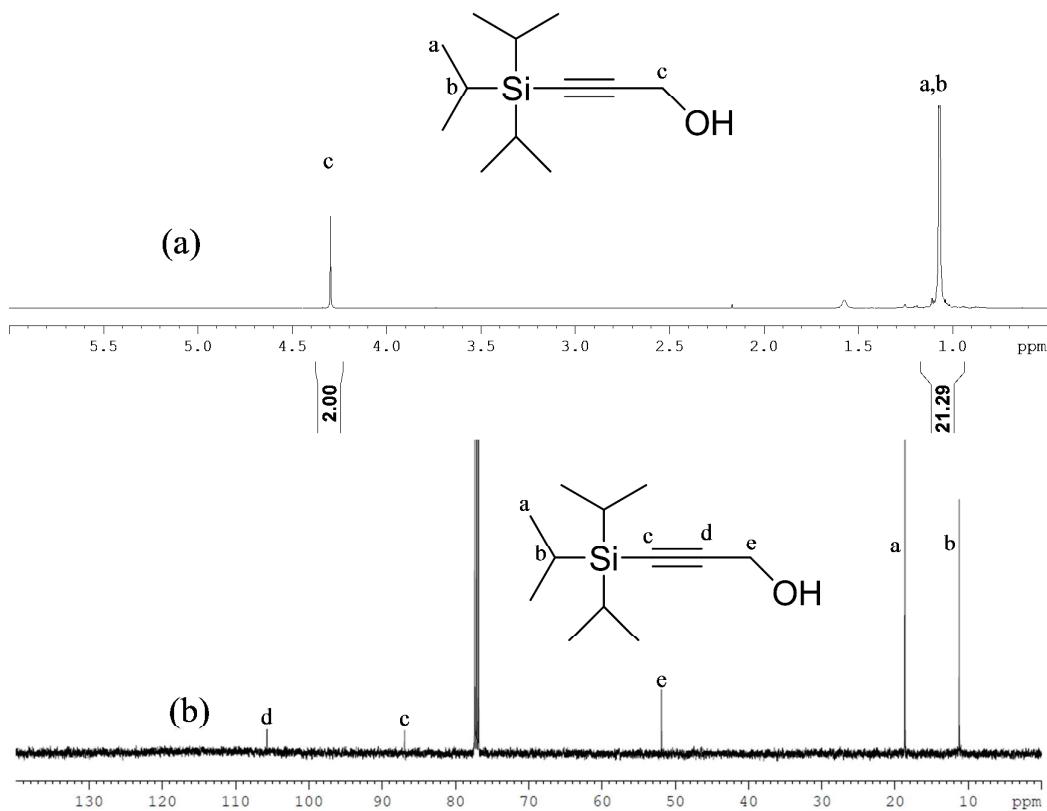


Figure S1: (a) ¹H NMR and (b) ¹³C NMR spectra of (**2**) recorded in CDCl₃ at 298K (500 MHz).

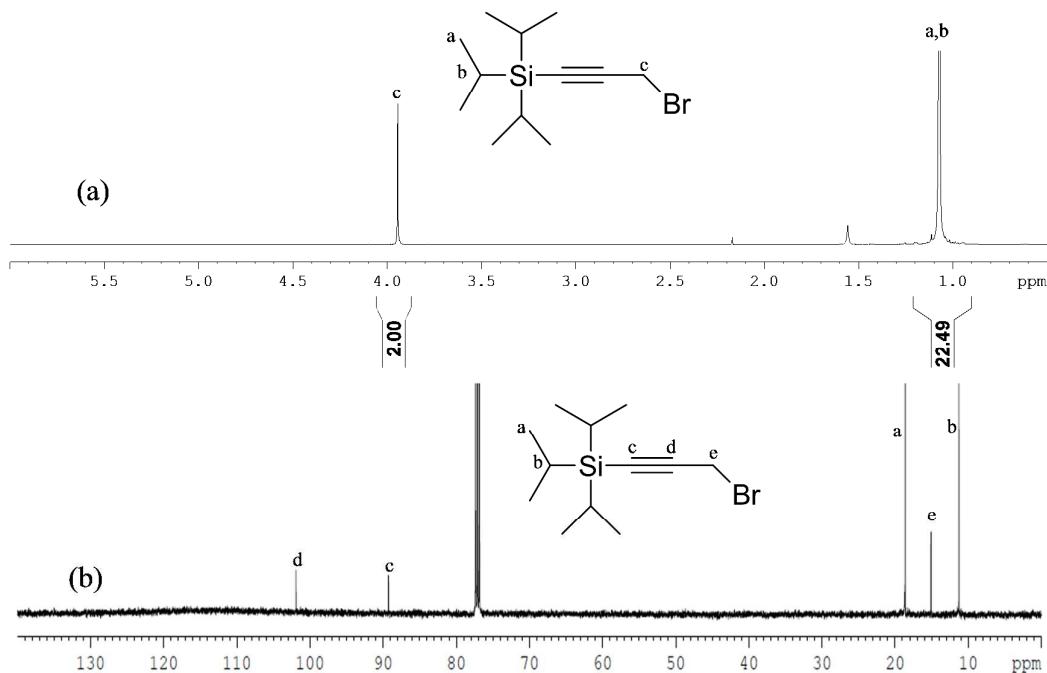


Figure S2: (a) ¹H NMR and (b) ¹³C NMR spectra of (**3**) recorded in CDCl₃ at 298K (500 MHz).

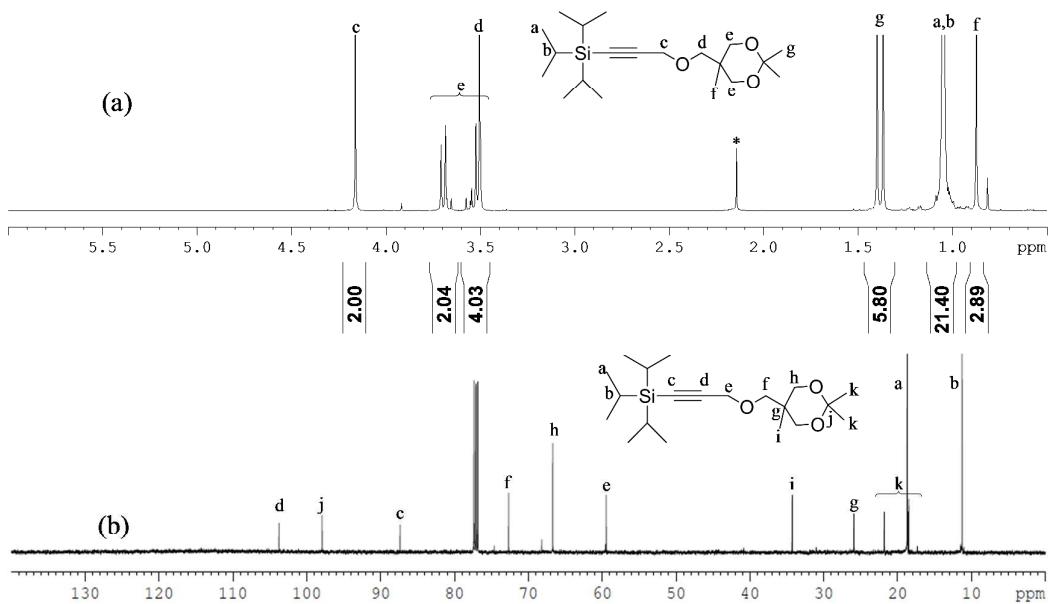


Figure S3: (a) ^1H NMR and (b) ^{13}C NMR spectra of (4) recorded in CDCl_3 at 298K (500 MHz), * acetone peak.

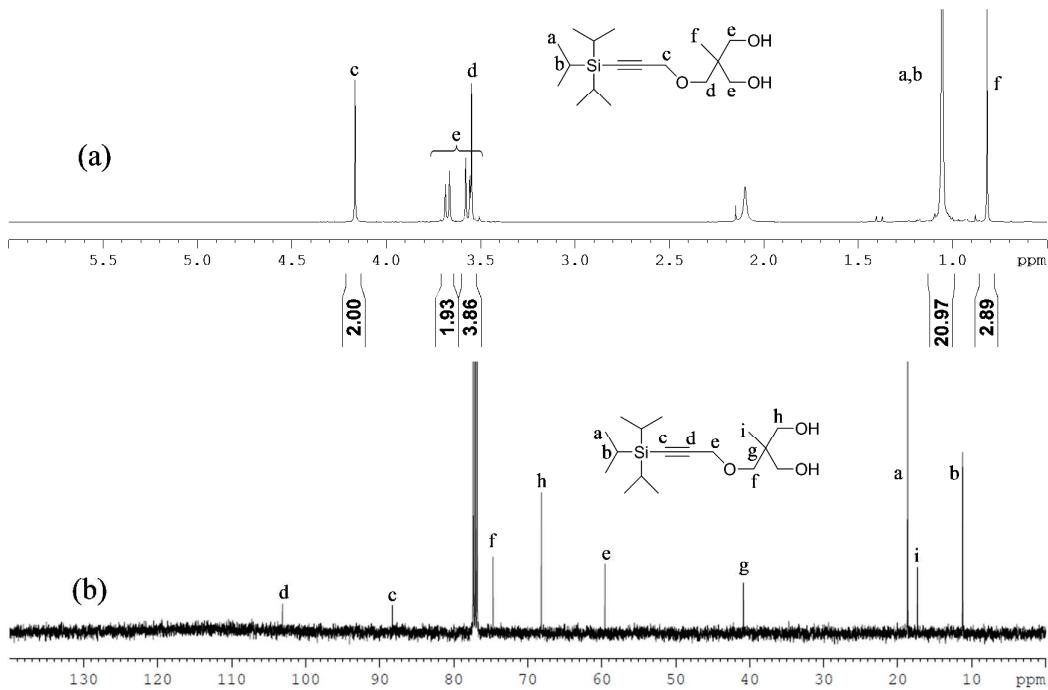


Figure S4: (a) ^1H NMR and (b) ^{13}C NMR spectra of (5) recorded in CDCl_3 at 298K (500 MHz).

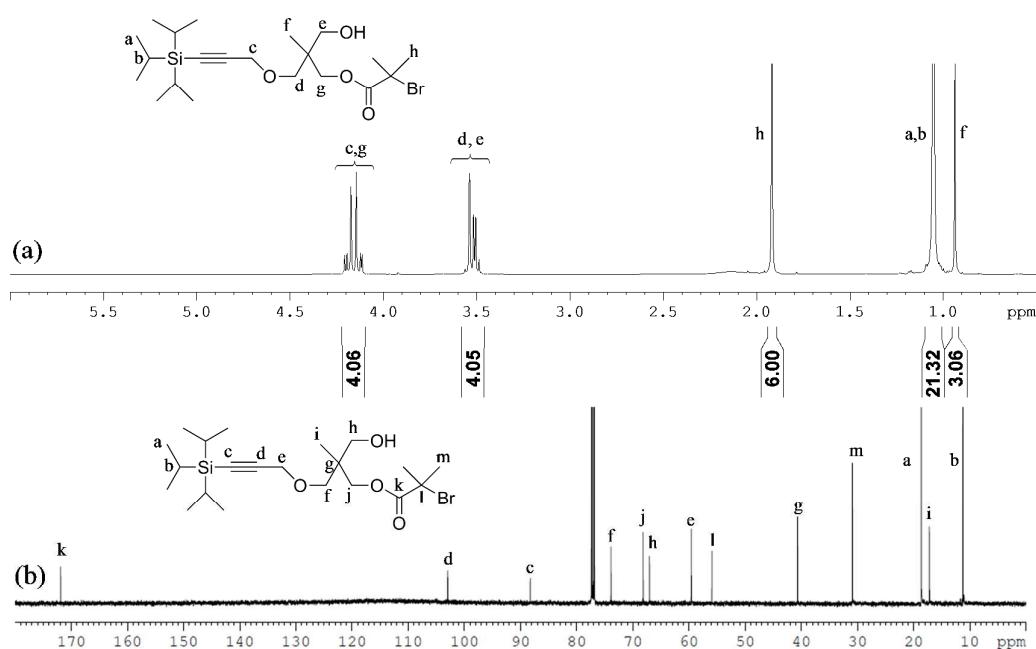


Figure S5: (a) ^1H NMR and (b) ^{13}C NMR spectra of (6) recorded in CDCl_3 at 298K (500 MHz).

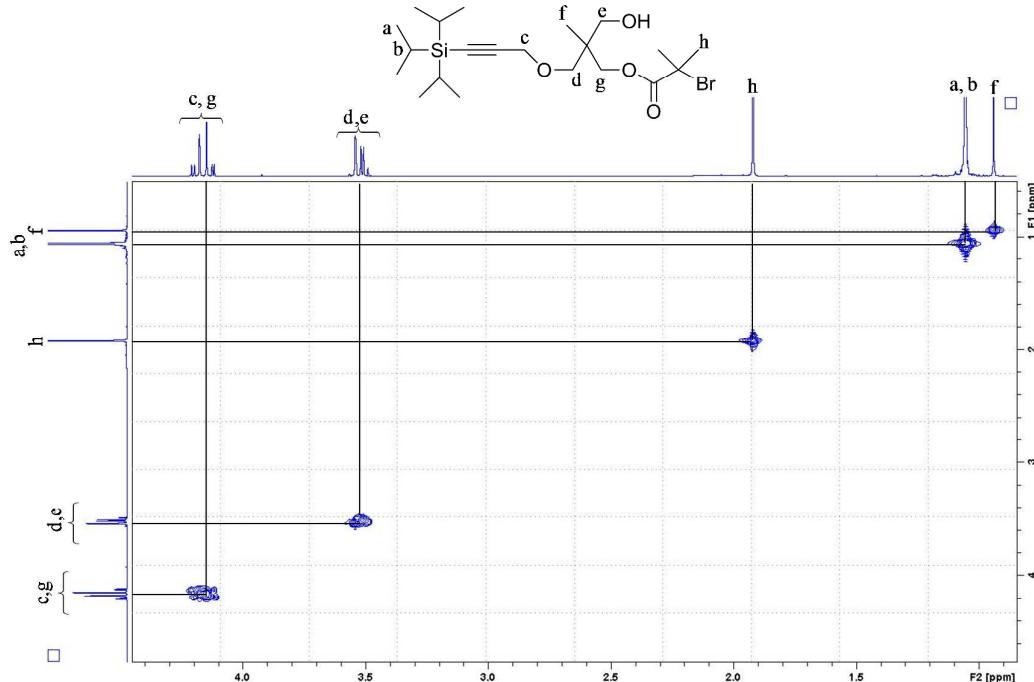


Figure S6: 2D COSY NMR spectrum of (6) recorded in CDCl_3 at 298K (500 MHz).

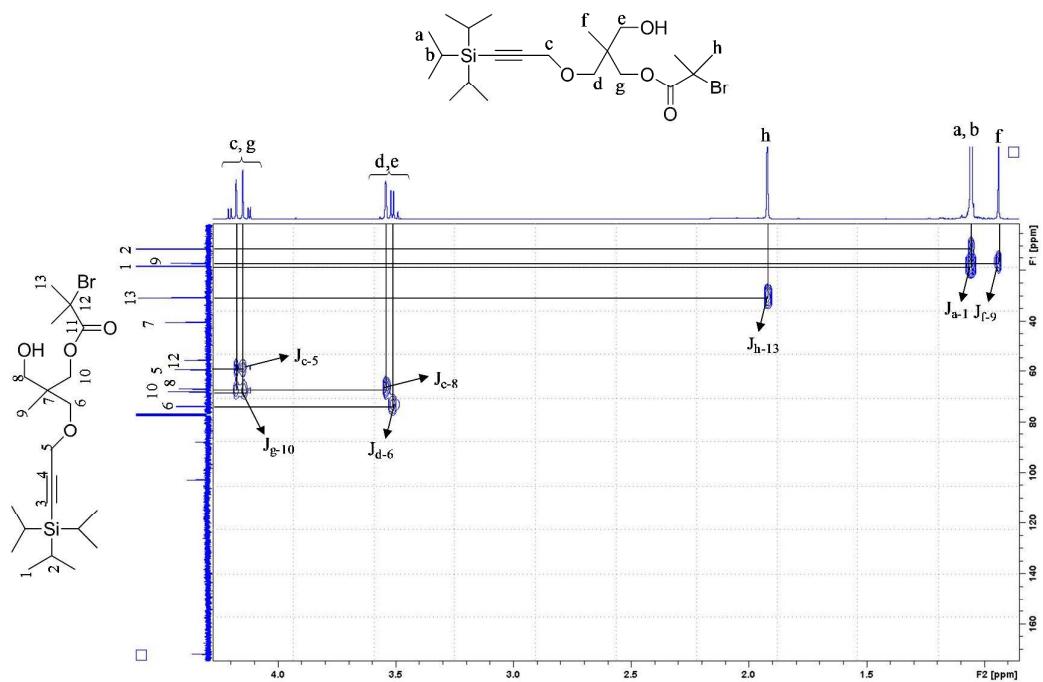


Figure S7: 2D HSQC NMR spectrum of (**6**) recorded in CDCl_3 at 298K (500 MHz).

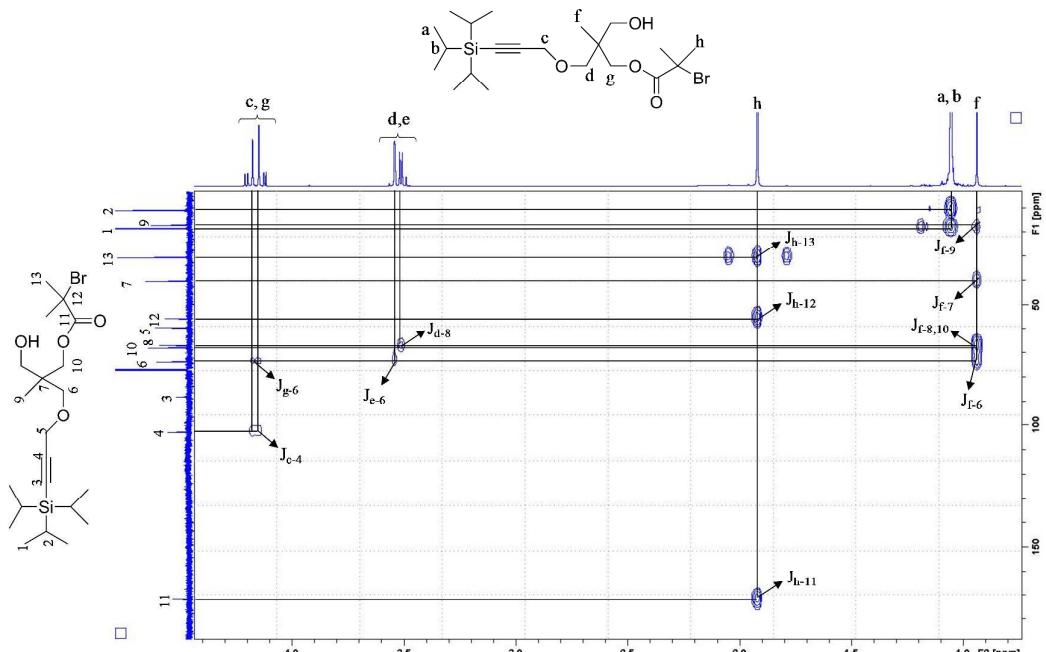


Figure S8: 2D HMBC NMR spectrum of (**6**) recorded in CDCl_3 at 298K (500 MHz).

2 Characterization of $\equiv(\text{OH})\text{-PSTY}_{25}\text{-Br}$ (7)

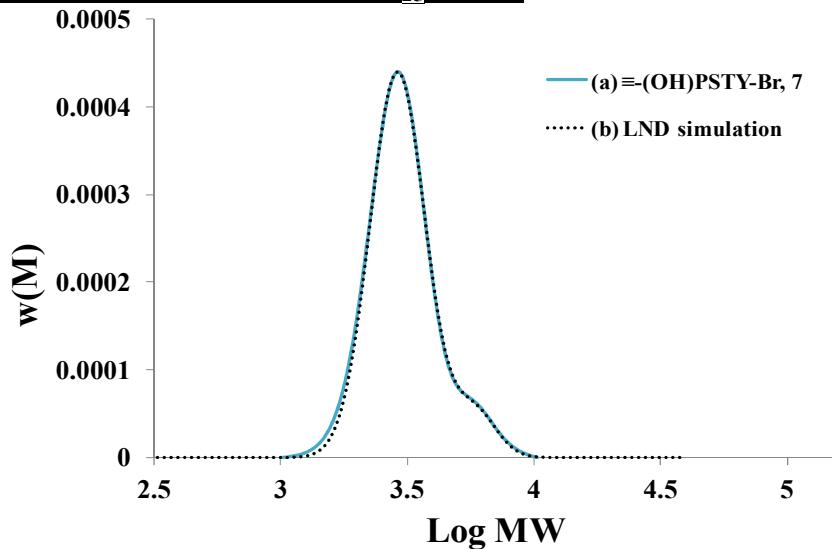


Figure S9: SEC-RI trace of $\equiv(\text{OH})\text{-PSTY}_{25}\text{-Br}$ (7) based on PSTY calibration curve.

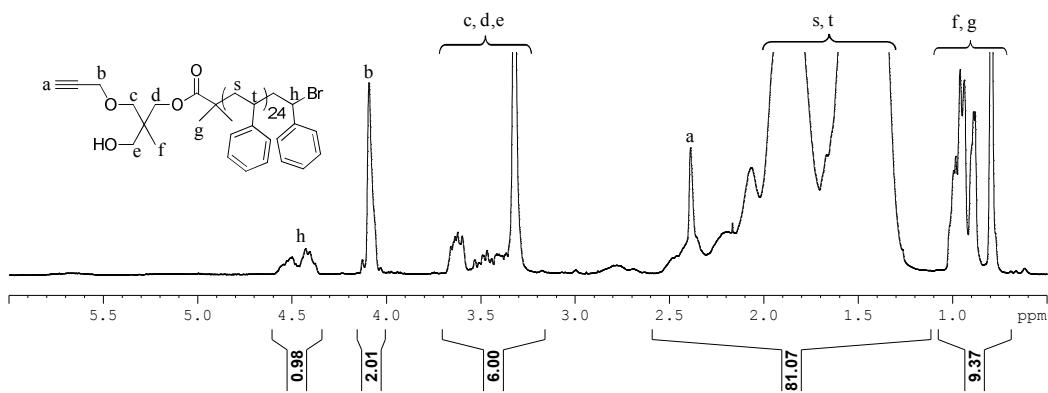


Figure S10. ^1H 1D DOSY NMR spectrum of $\equiv(\text{OH})\text{-PSTY}_{25}\text{-Br}$ (7) recorded in CDCl_3 at 298K (500 MHz).

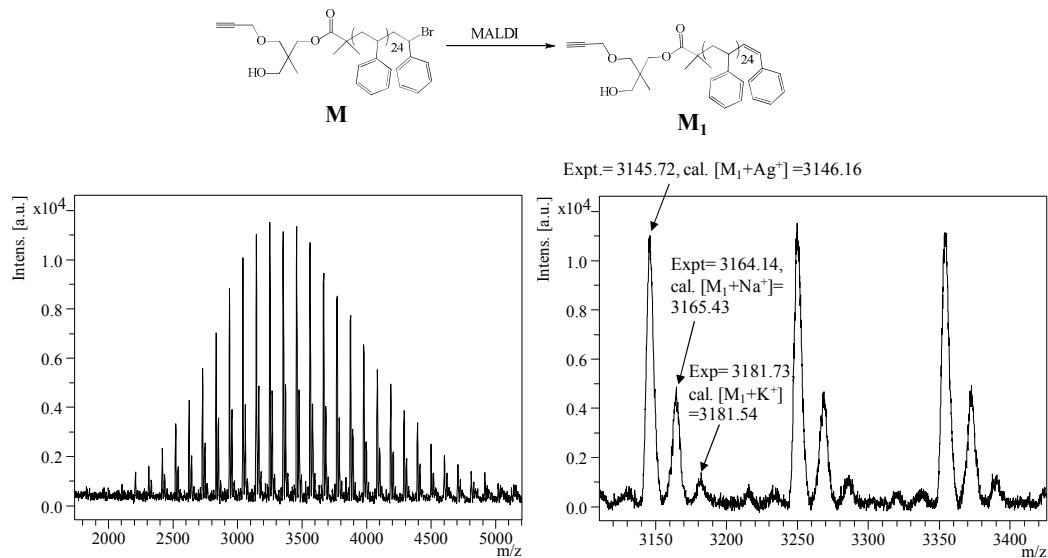


Figure S11: The full and expanded MALDI-ToF mass spectra of \equiv (HO)-PSTY₂₅-Br (**7**) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

3 Characterization of $\equiv(\text{OH})\text{-PSTY}_{25}\text{-N}_3$ (8)

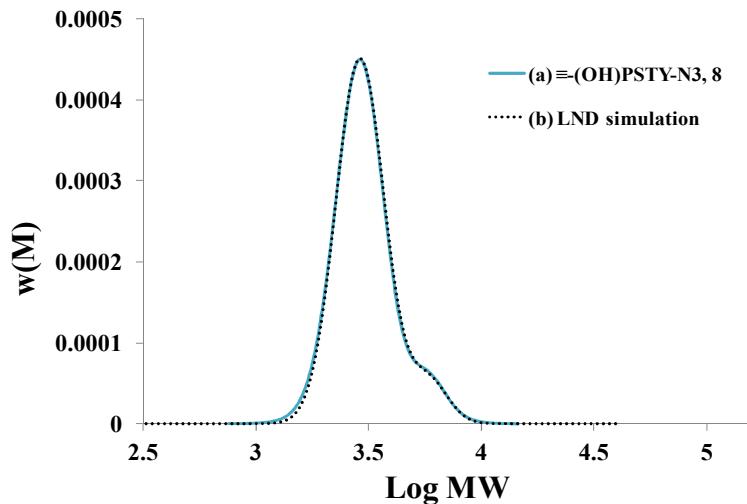


Figure S12: SEC RI trace of $\equiv(\text{OH})\text{-PSTY}_{25}\text{-N}_3$ (8) based on PSTY calibration curve.

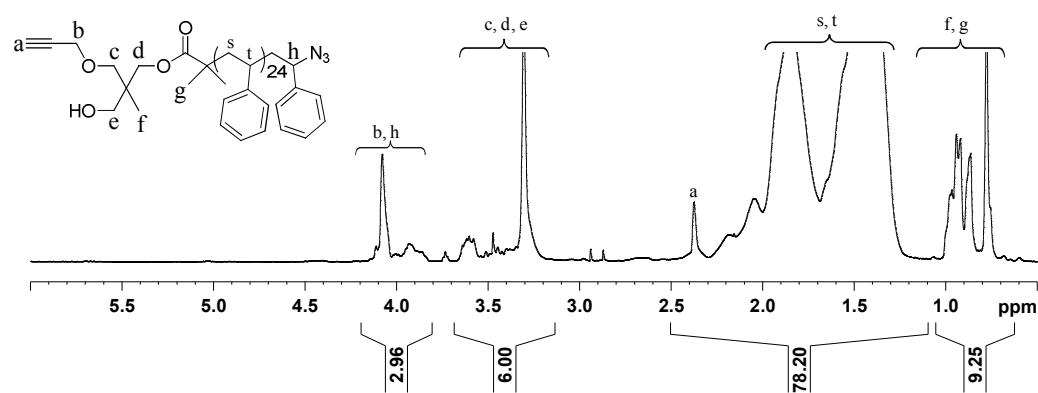


Figure S13: ^1H 1D DOSY NMR spectrum of $\equiv(\text{OH})\text{-PSTY}_{25}\text{-N}_3$ (8) recorded in CDCl_3 at 298K (500 MHz).

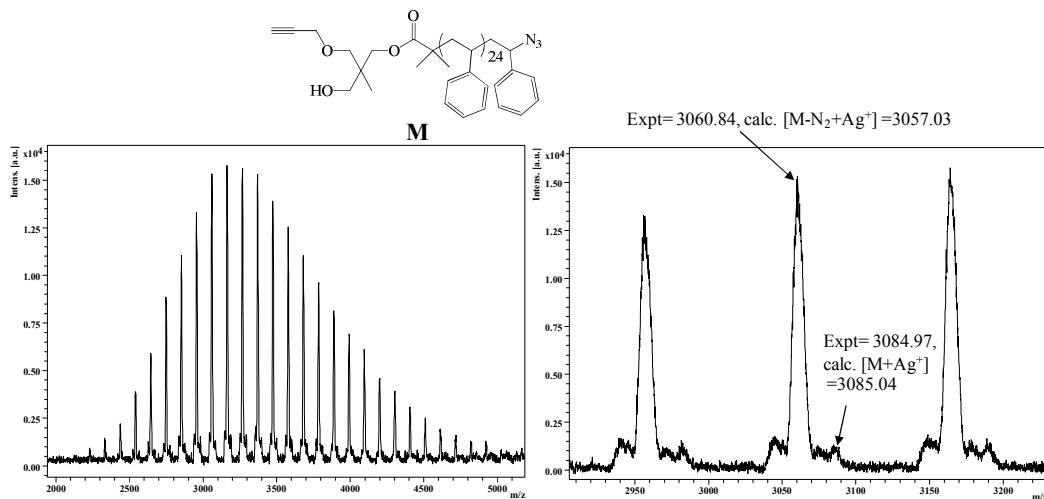


Figure S14: The full and expanded MALDI-ToF mass spectra of \equiv (HO)-PSTY₂₅-N₃ (**8**) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

4 Characterization of c-PSTY₂₅-OH (9)

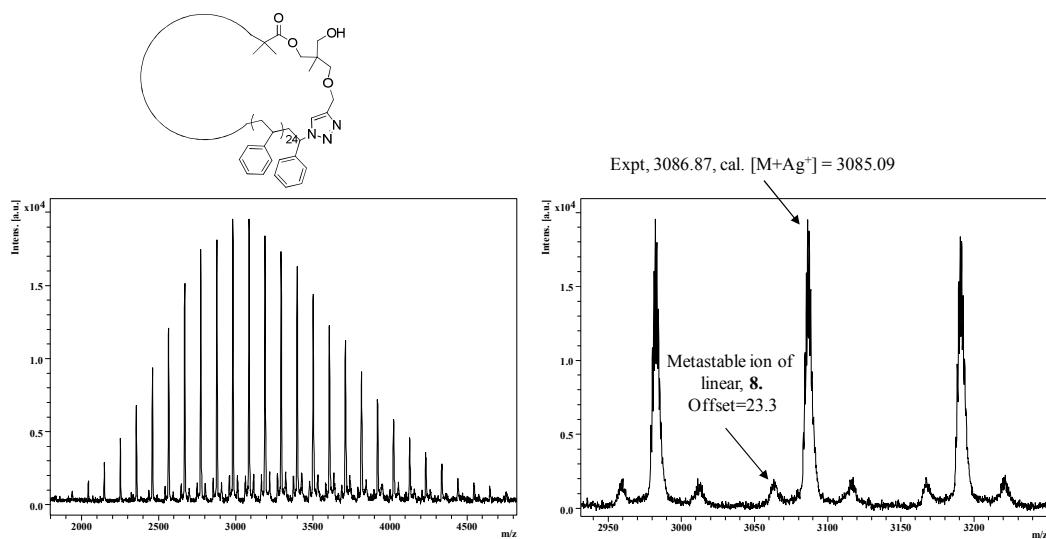


Figure S15: The full and expanded MALDI-ToF mass spectra of c-PSTY₂₅-OH (**9**, purified by preparative SEC) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

5 Characterization of c-PSTY₂₅-Br (10)

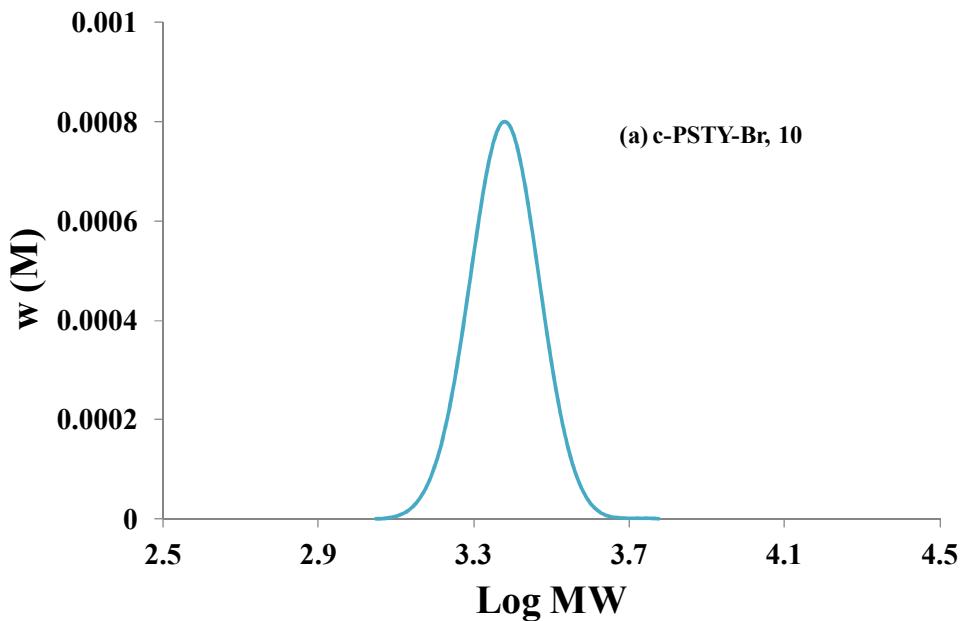


Figure S16: SEC RI trace of c-PSTY₂₅-Br (10) based on PSTY calibration curve.

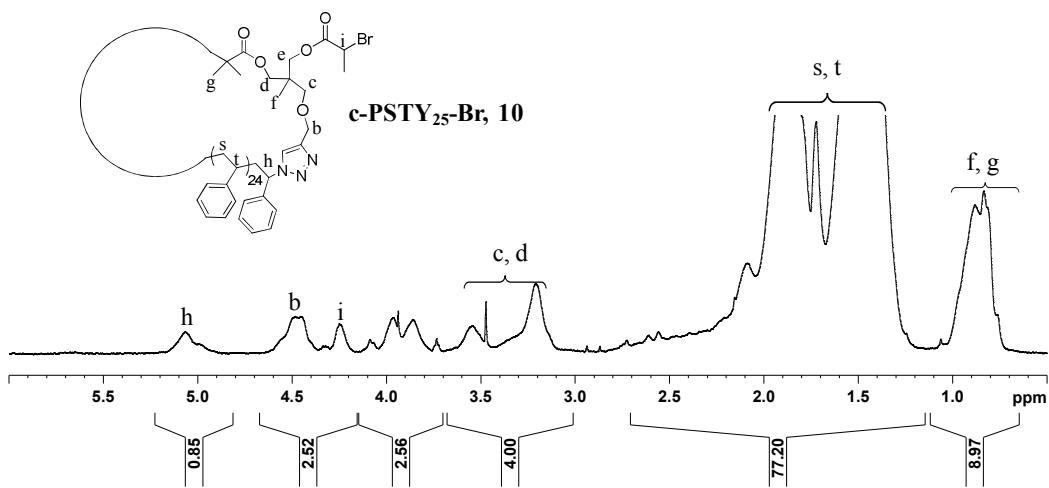


Figure S17: ¹H 1D DOSY NMR spectrum of c-PSTY₂₅-Br (10) recorded in CDCl₃ at 298K (500 MHz).

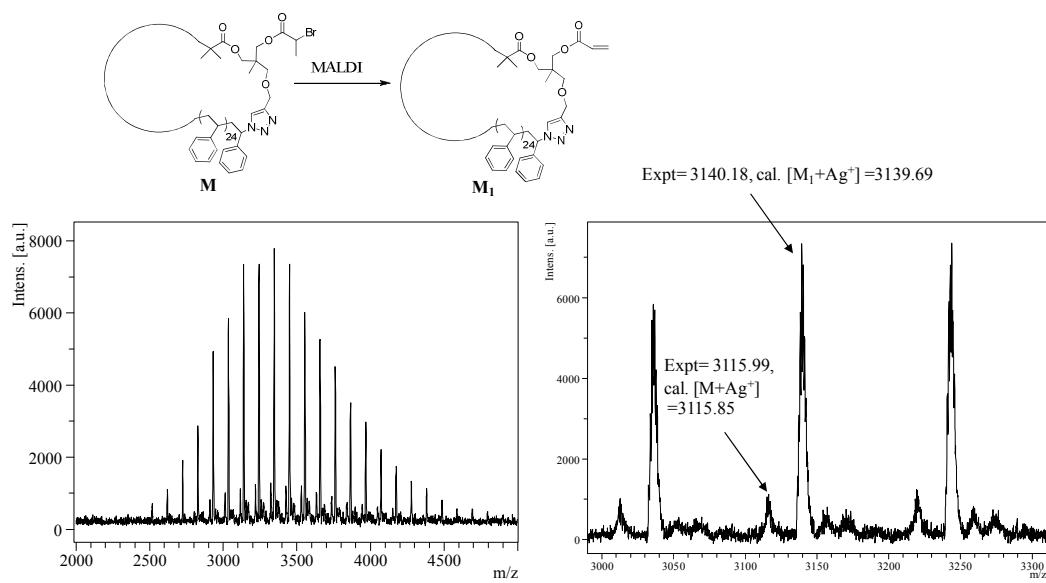


Figure S18: The full and expanded MALDI-ToF mass spectra of c-PSTY₂₅-Br (**10**) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

6 Characterization of c-PSTY₂₅-N₃ (**11**)

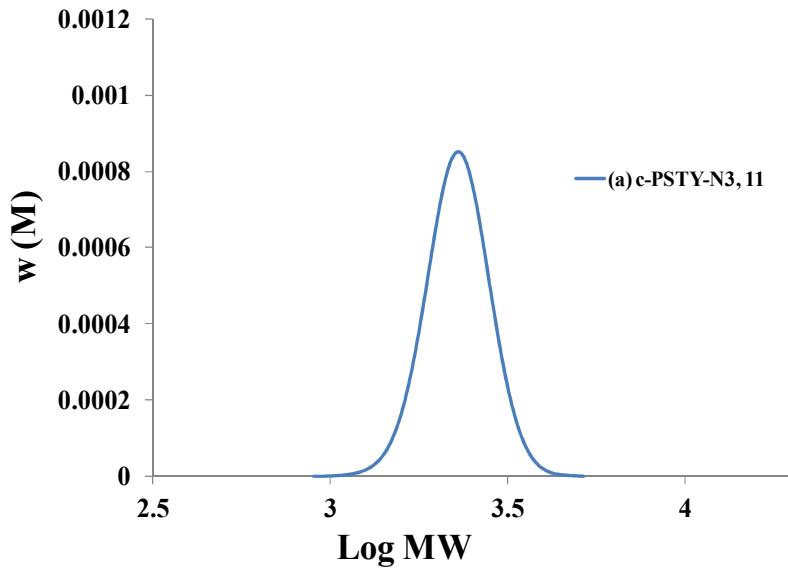


Figure S19: SEC RI trace of c-PSTY₂₅-N₃ (**11**) based on PSTY calibration curve.

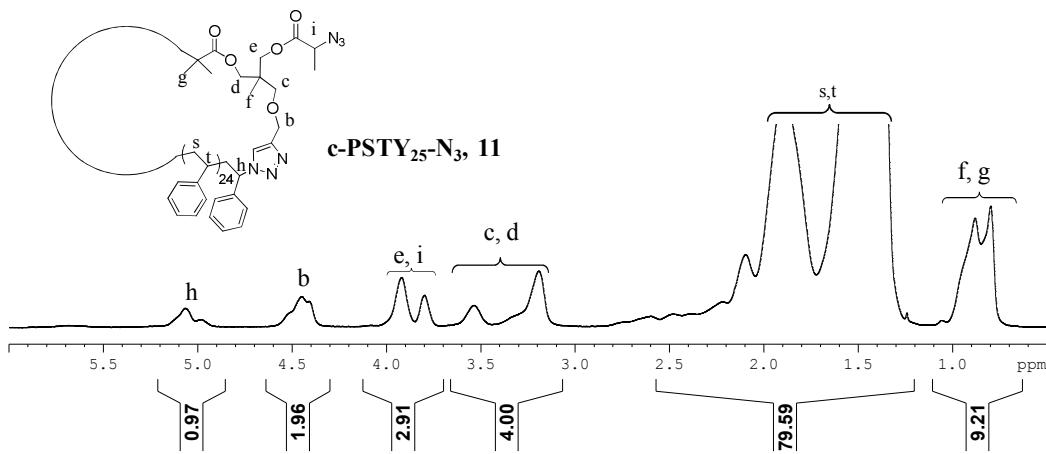


Figure S20: ¹H 1D DOSY NMR spectrum of c-PSTY₂₅-N₃ (**11**) recorded in CDCl₃ at 298K (500 MHz).

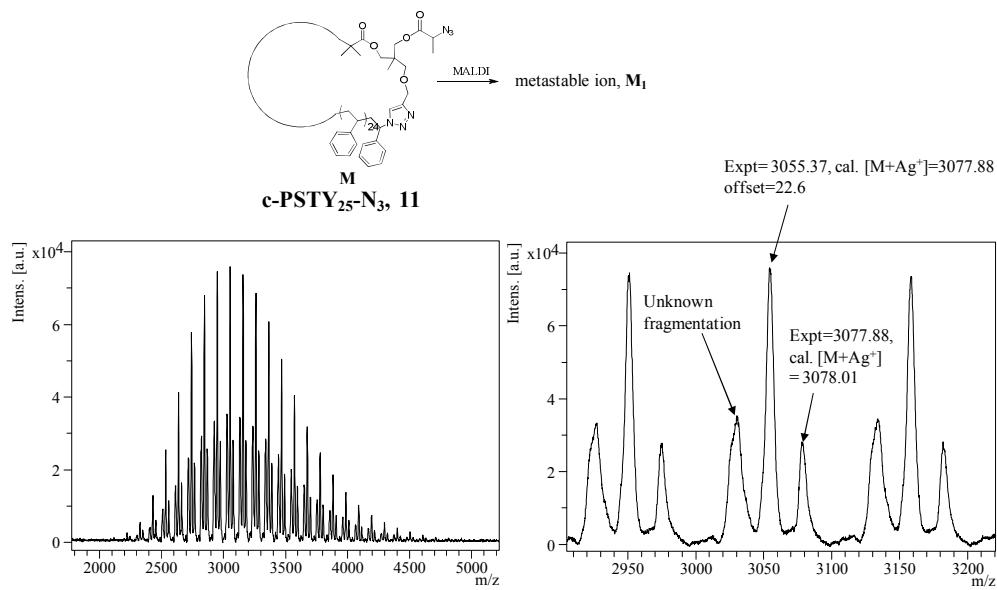


Figure S21: The full and expanded MALDI-ToF mass spectra of c-PSTY-N₃ (**11**) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

7 Characterization of c-PSTY_{25-≡} (13)

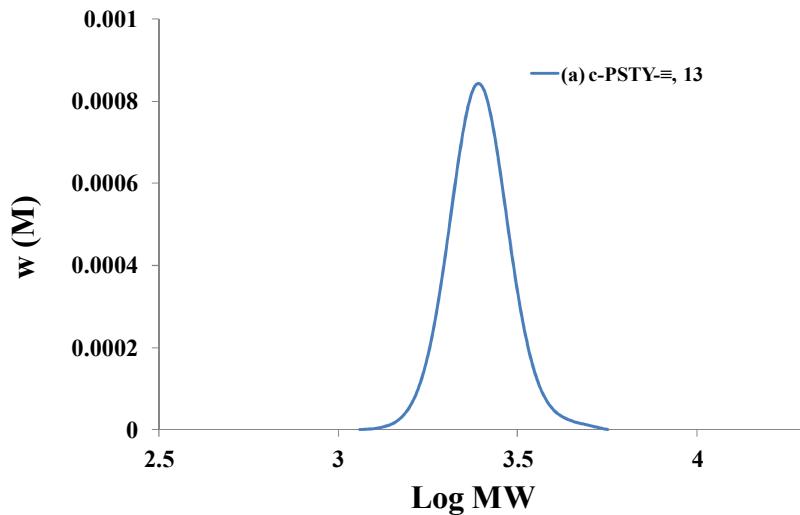


Figure S22: SEC RI trace of c-PSTY_{25-≡} (13, purified by preparative SEC) based on PSTY calibration curve.

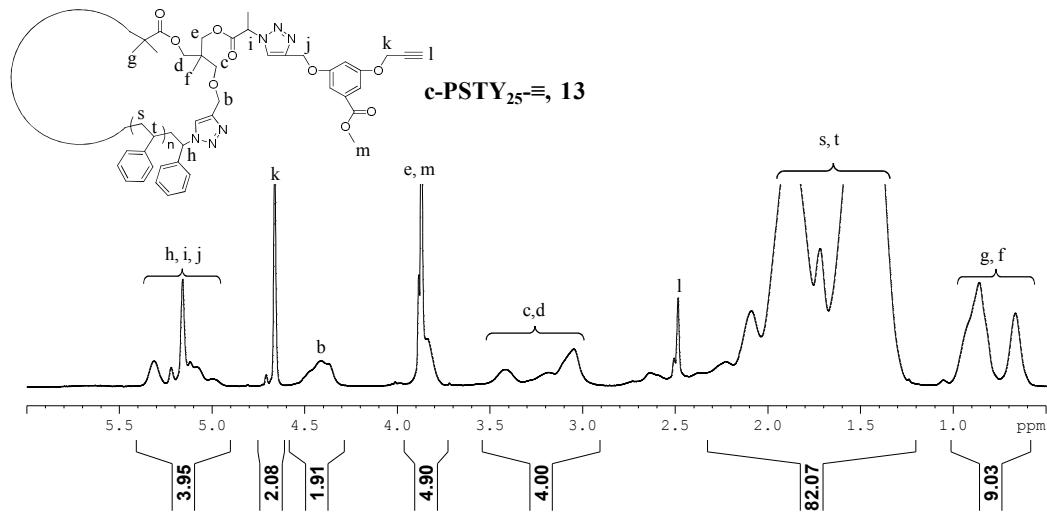
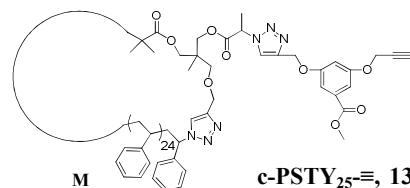


Figure S23. ¹H 1D DOSY NMR spectrum of c-PSTY_{25-≡} (13, purified by preparative SEC) recorded in CDCl₃ at 298K (500 MHz).



c-PSTY_{25-≡}, 13

Expt=3530.29, cal. [M+Ag⁺]=3530.51

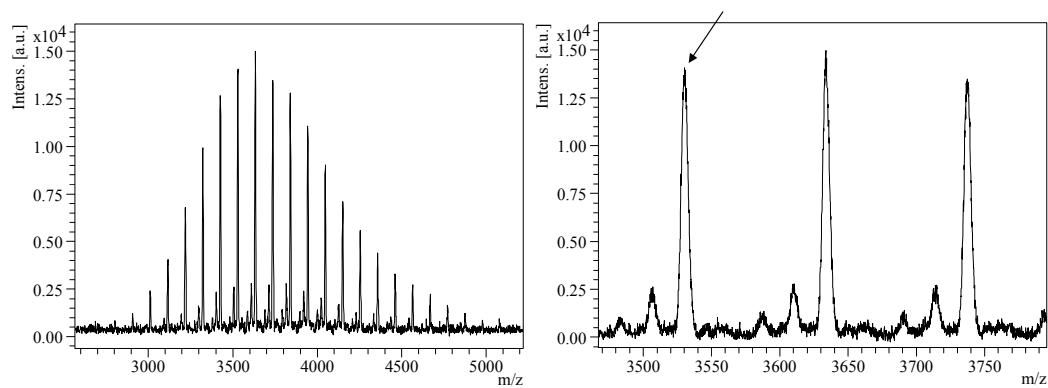


Figure S24: The full and expanded MALDI-ToF mass spectra of c-PSTY_{25-≡} (**13**, purified by preparative SEC) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

8 Characterization of TIPS-≡(HO)-PSTY₂₅-Br (14)

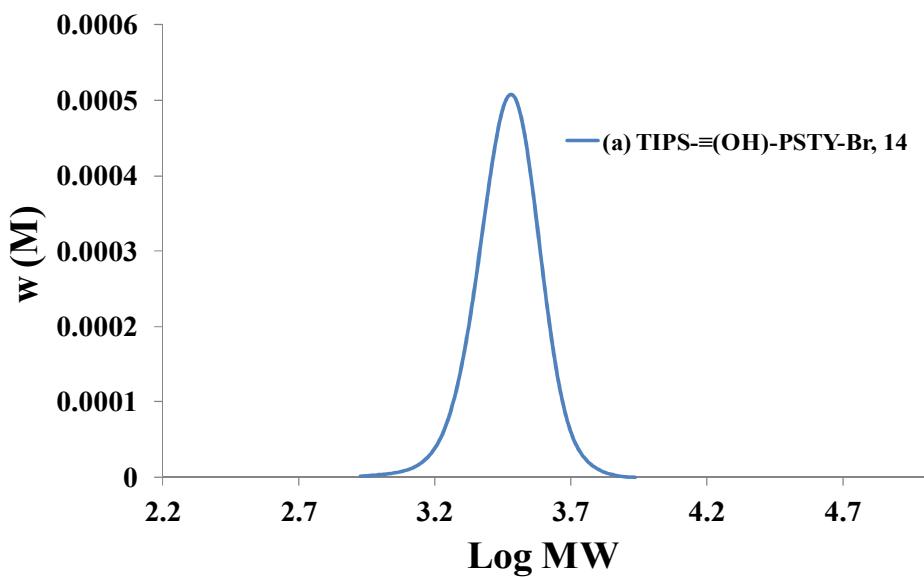


Figure S25: SEC RI trace of TIPS-≡(HO)-PSTY₂₅-Br (14) based on PSTY calibration curve.

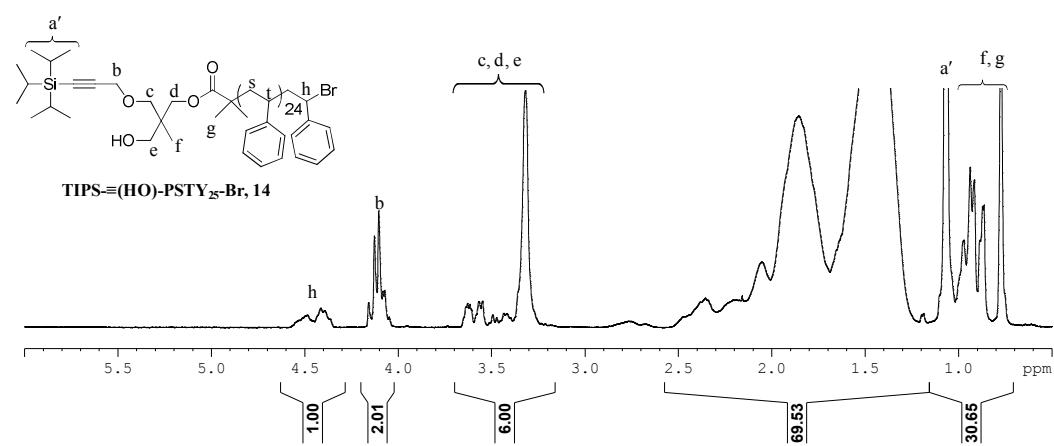


Figure S26: ¹H 1D DOSY NMR spectrum of TIPS-≡(HO)-PSTY₂₅-Br (14) recorded in CDCl₃ at 298K (500 MHz).

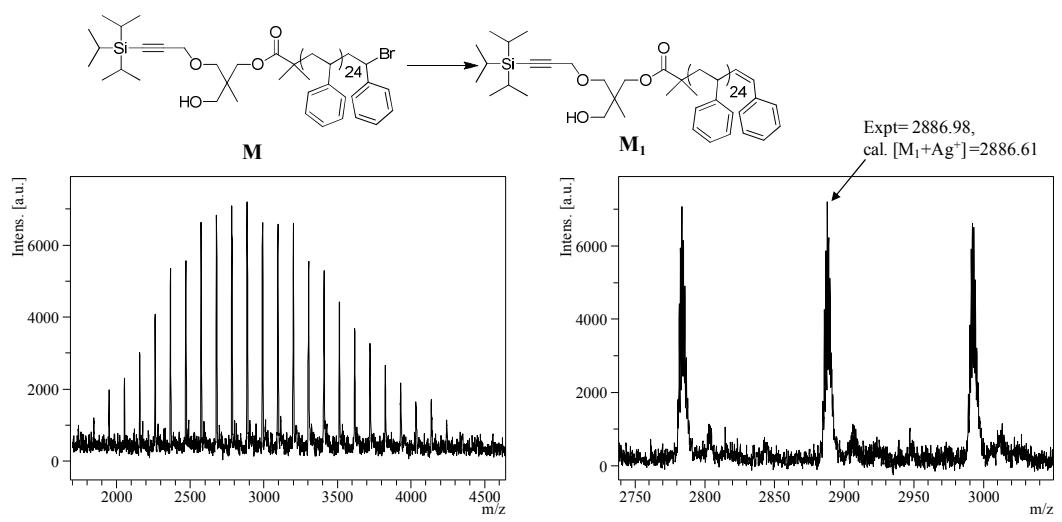


Figure S27: The full and expanded MALDI-ToF mass spectra of TIPS-≡(HO)-PSTY₂₅-Br (**14**) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

9 Characterization of TIPS-≡(HO)-PSTY₂₅-N₃ (**15**)

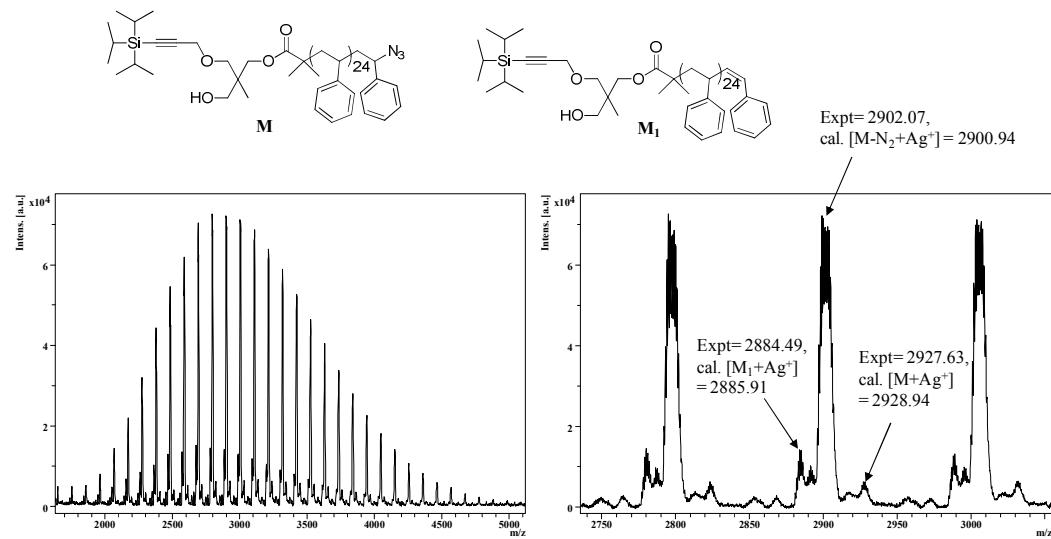


Figure S28: The full and expanded MALDI-ToF mass spectra of TIPS-≡(HO)-PSTY₂₅-N₃ (**15**) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

10 Characterization of TIPS- \equiv (HO-PSTY₂₅)₂-Br (**16**)

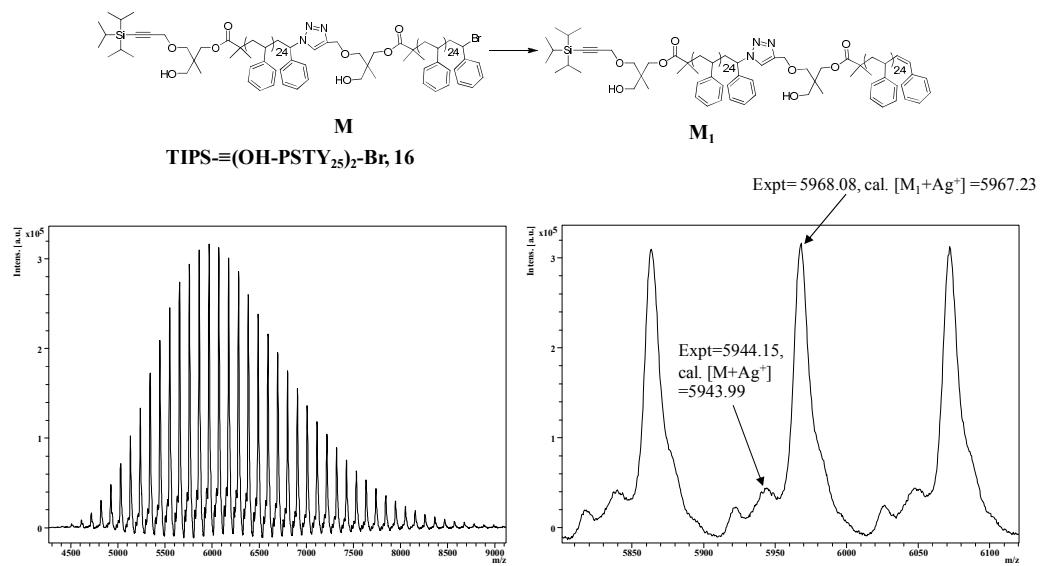


Figure S29: The full and expanded MALDI-ToF mass spectra of TIPS- \equiv (HO-PSTY₂₅)₂-Br (**16**, crude) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

11 Characterization of TIPS-≡(OH-PSTY₂₅)₂-N₃ (**17**, crude)

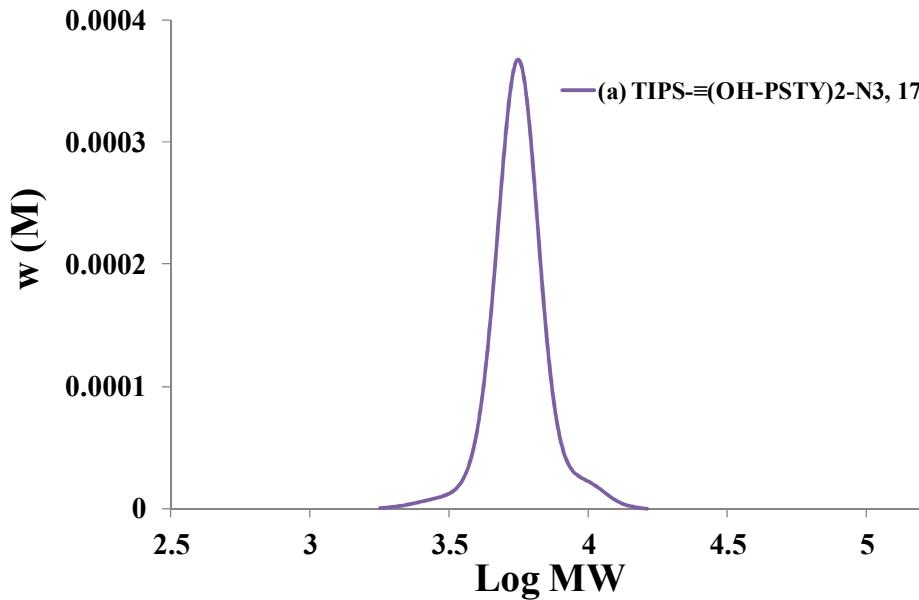


Figure S30: SEC RI trace of TIPS-≡(OH-PSTY₂₅)₂-N₃ (**17**, crude) based on PSTY calibration curve.

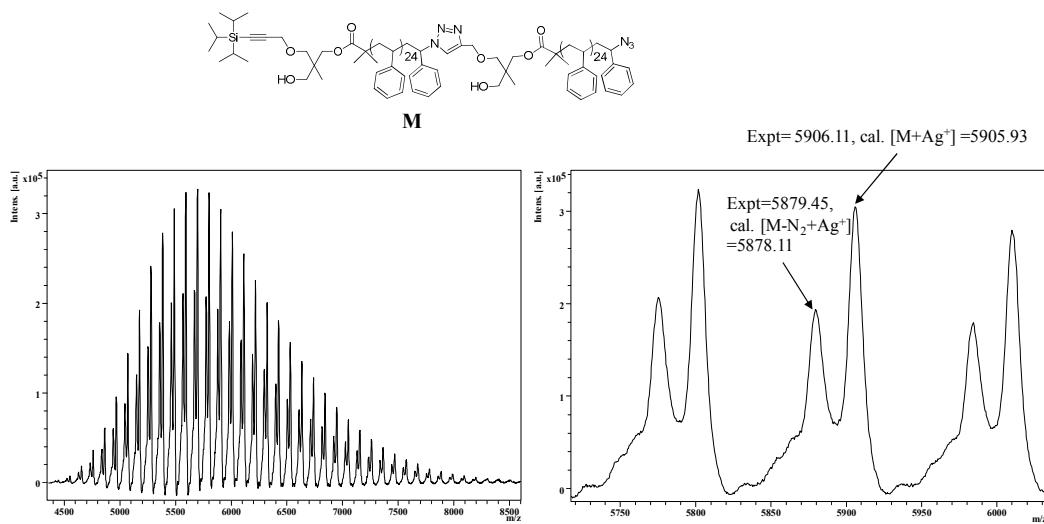


Figure S31: The full and expanded MALDI-ToF mass spectra of TIPS-≡(HO-PSTY₂₅)₂-N₃ (**17**, crude) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

12 Characterization of $\equiv(\text{OH-PSTY}_{25})_2\text{-N}_3$ (**18**)

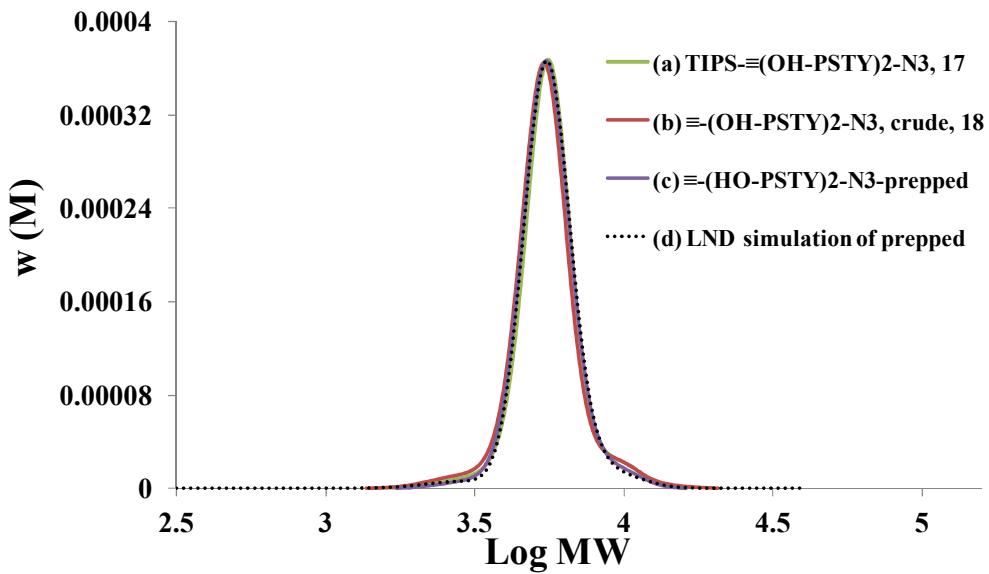


Figure S32: SEC RI traces of (a) TIPS- $\equiv(\text{OH-PSTY}_{25})_2\text{-N}_3$ (**17**), (b) $\equiv(\text{OH-PSTY}_{25})_2\text{-N}_3$ (**18**, crude), (c) $\equiv(\text{OH-PSTY}_{25})_2\text{-N}_3$ (**18**, purified by preparative SEC) based on PSTY calibration curve, and (d) LND simulation of $\equiv(\text{OH-PSTY}_{25})_2\text{-N}_3$ (**18**, purified by preparative SEC).

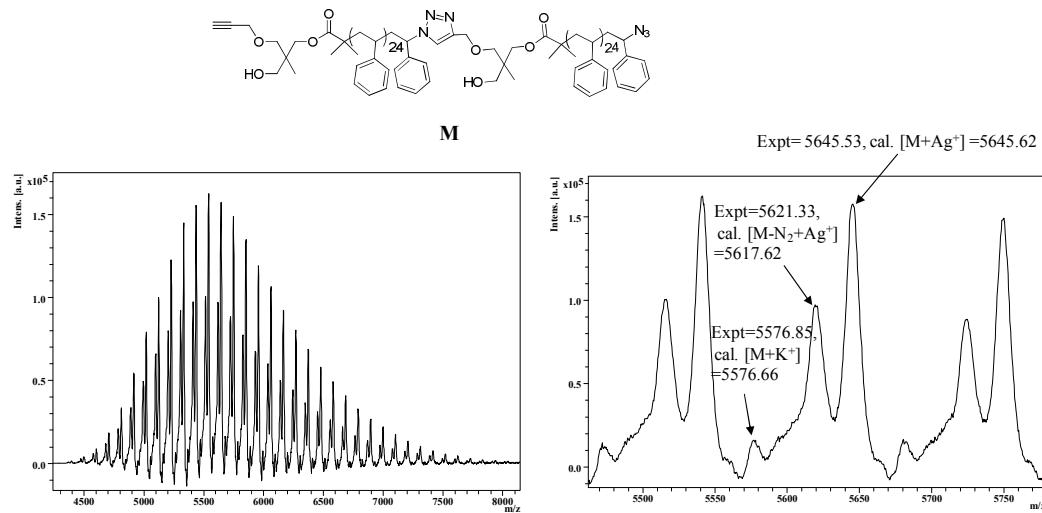


Figure S33: The full and expanded MALDI-ToF mass spectra of $\equiv(\text{HO-PSTY}_{25})_2\text{-N}_3$ (**18**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

13 Characterization of c-PSTY-(OH)₂ (**19**)

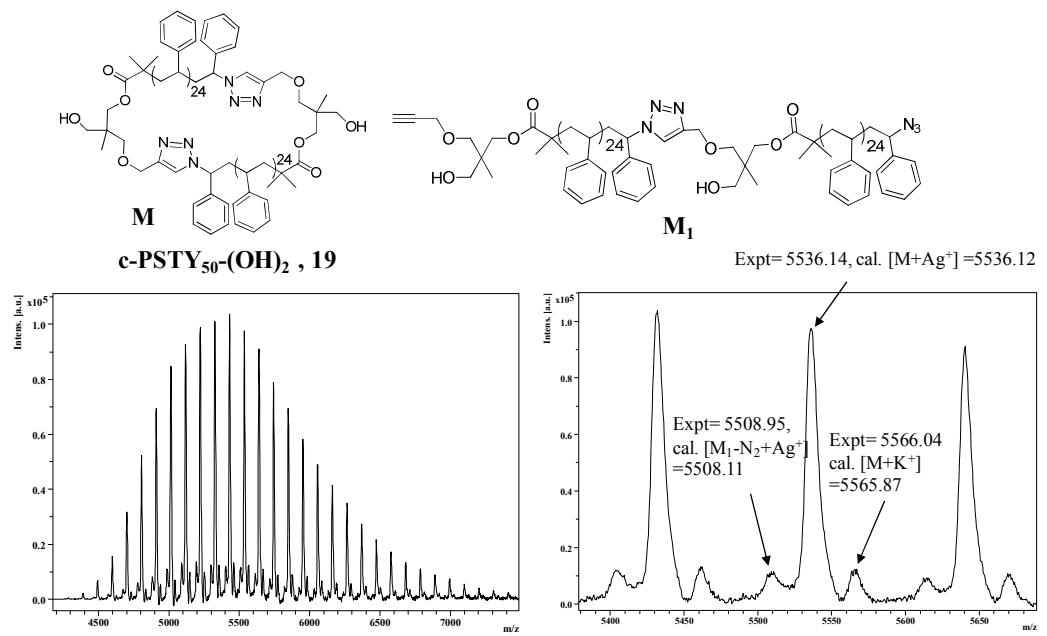


Figure S34: The full and expanded MALDI-ToF mass spectra of c-PSTY-(OH)₂ (**19**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

14 Characterization of c-PSTY₅₀-Br₂ (**20**)

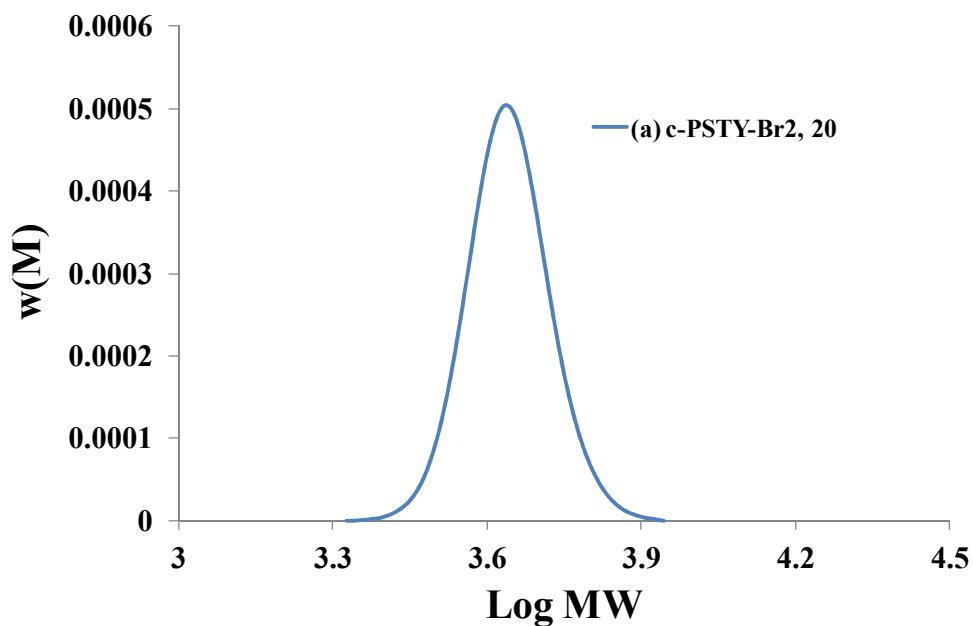


Figure S35: SEC RI trace of c-PSTY₅₀-Br₂ (**20**) based on PSTY calibration curve.

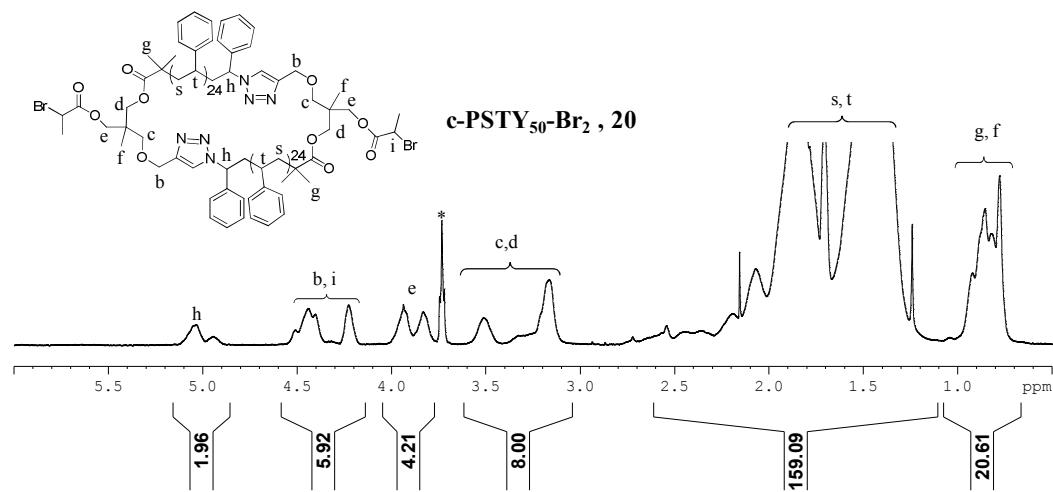
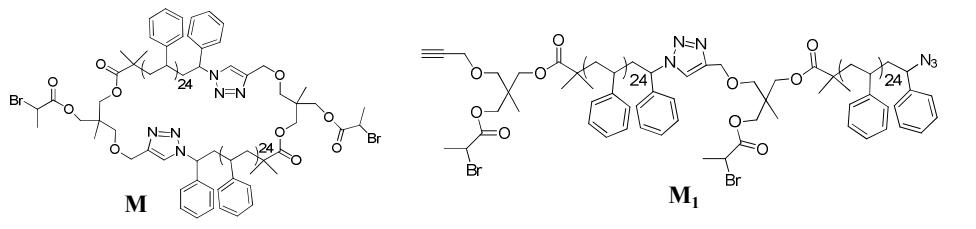


Figure S36: ¹H 1D DOSY NMR spectrum of c-PSTY₅₀-Br₂ (**20**) recorded in CDCl₃ at 298K (500 MHz).



Expt=5914.4 , cal. [M+Ag⁺] =5915.54

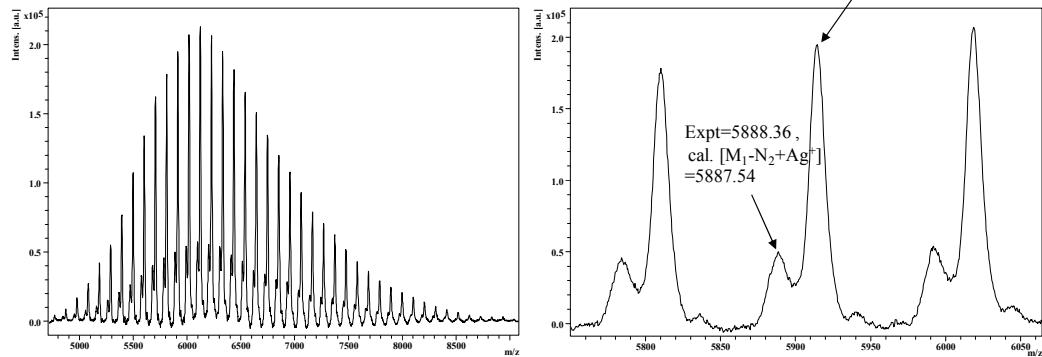


Figure S37: The full and expanded MALDI-ToF mass spectra of c-PSTY₅₀-Br₂ (**20**) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

15 Characterization of c-PSTY-(N₃)₂ (**21**)

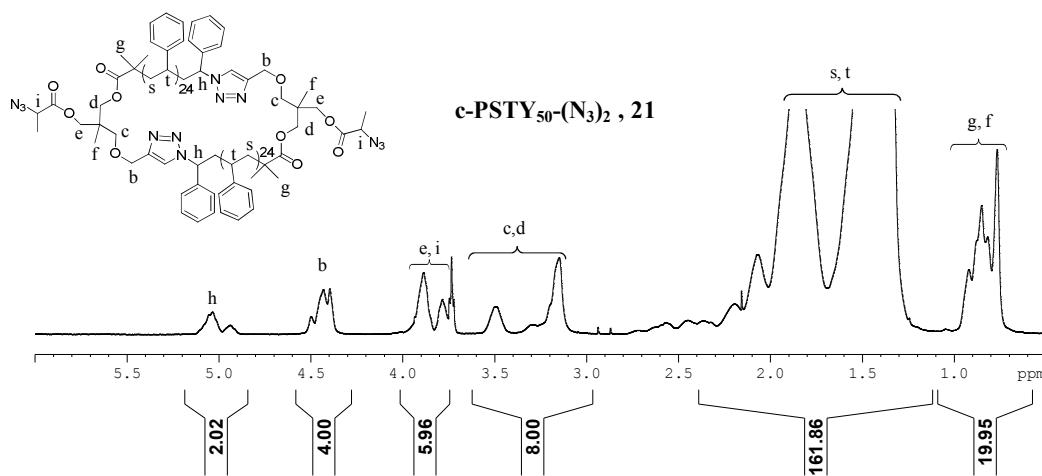


Figure S38: ¹H 1D DOSY NMR spectrum of c-PSTY-(N₃)₂ (**21**) recorded in CDCl₃ at 298K (500 MHz).

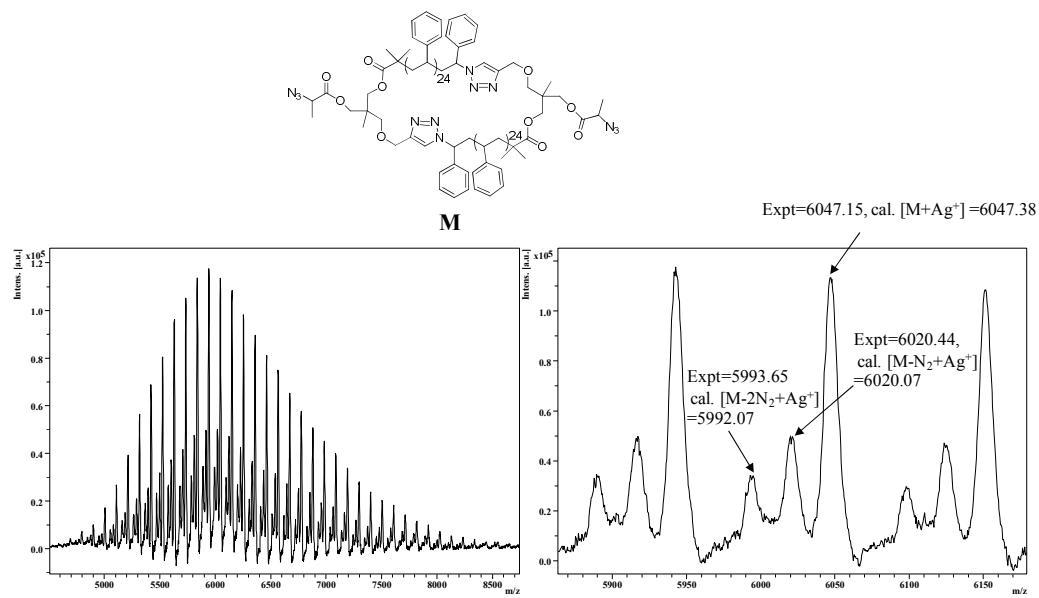


Figure S39: The full and expanded MALDI-ToF mass spectra of c-PSTY₅₀-(N₃)₂ (**21**) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

16 Characterization of c-PSTY-(\equiv)₄ (23)

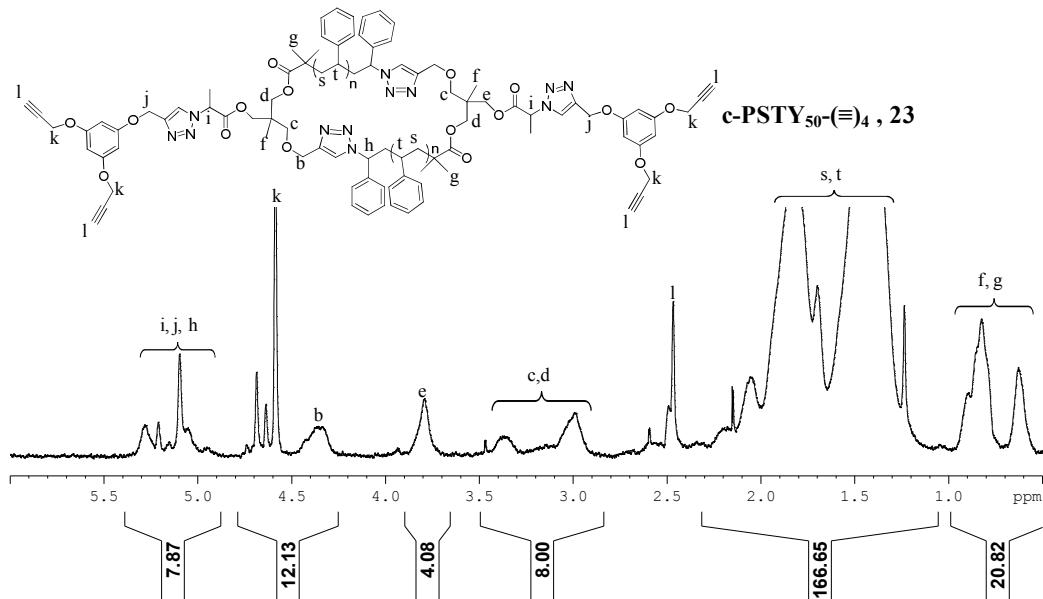


Figure S40: ^1H 1D DOSY NMR spectrum of c-PSTY-(\equiv)₄ (23, purified by preparative SEC) recorded in CDCl_3 at 298K (500 MHz).

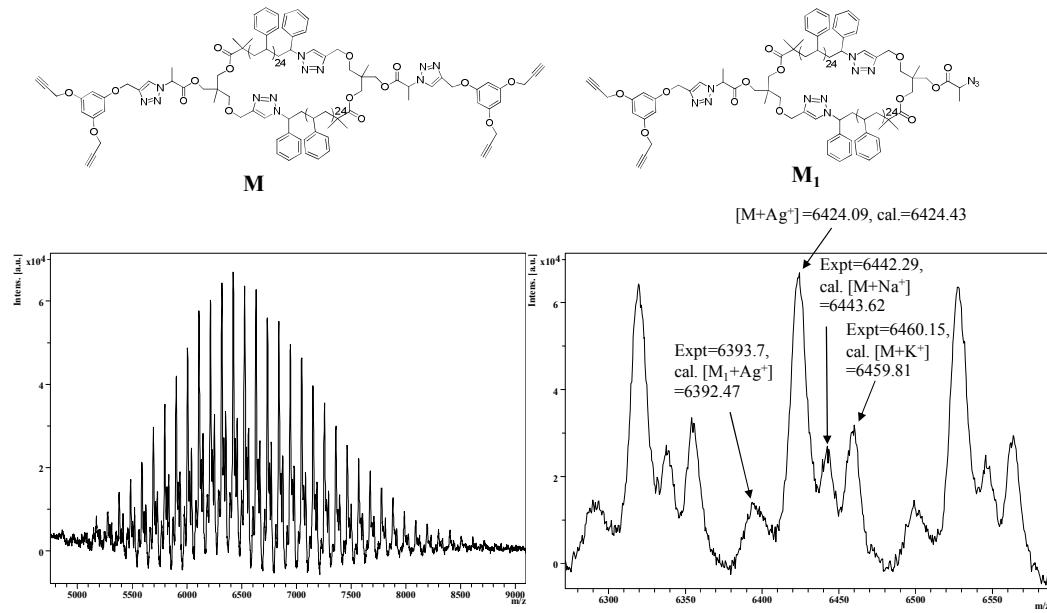


Figure S41: The full and expanded MALDI-ToF mass spectra of c-PSTY₅₀-(\equiv)₄ (23, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

17 Characterization of TIPS- \equiv (OH-PSTY₂₅)₃-Br (24)

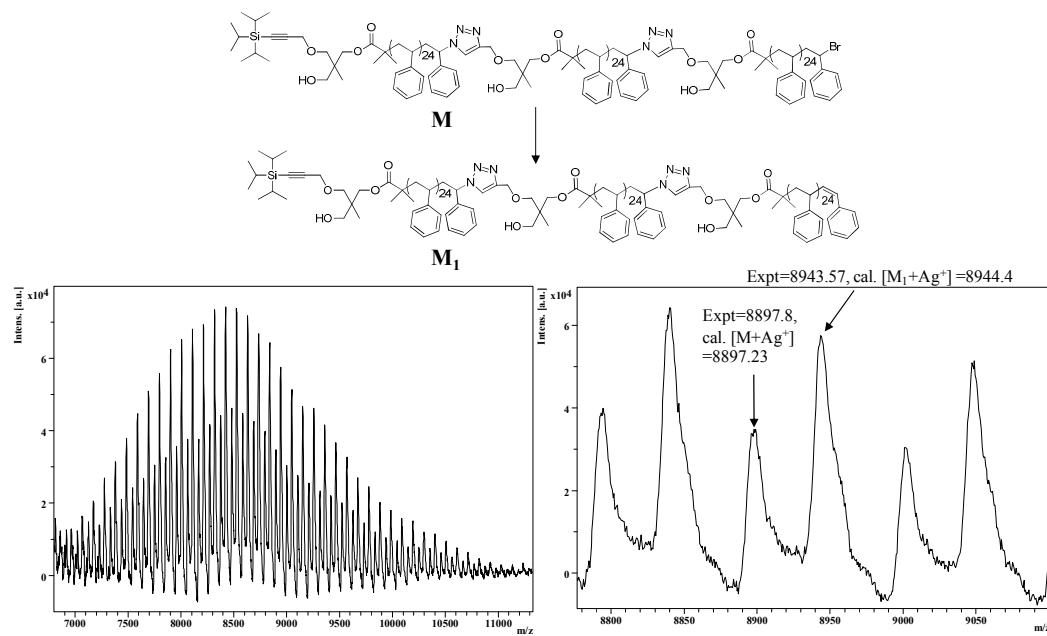


Figure S42: The full and expanded MALDI-ToF mass spectra of TIPS- \equiv (OH-PSTY₂₅)₃-Br (24) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

18 Characterization of TIPS-≡(OH-PSTY₂₅)₃-N₃ (**25**)

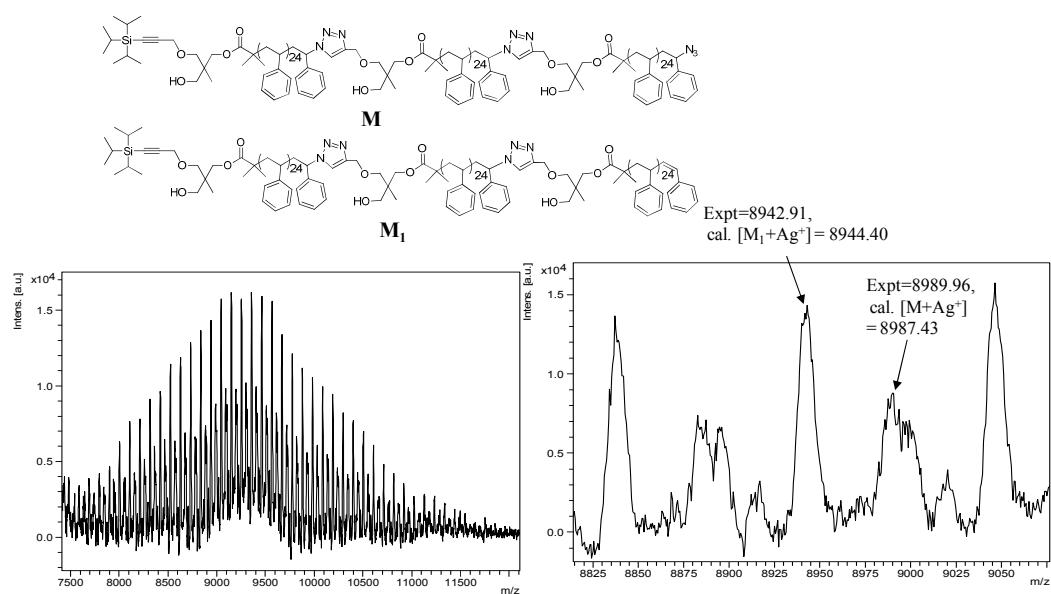


Figure S43: The full and expanded MALDI-ToF mass spectra of TIPS-≡(OH-PSTY₂₅)₃-N₃ (**25**)

acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

19 Characterization of $\equiv(\text{OH-PSTY}_{25})_3\text{-N}_3$ (**26**)

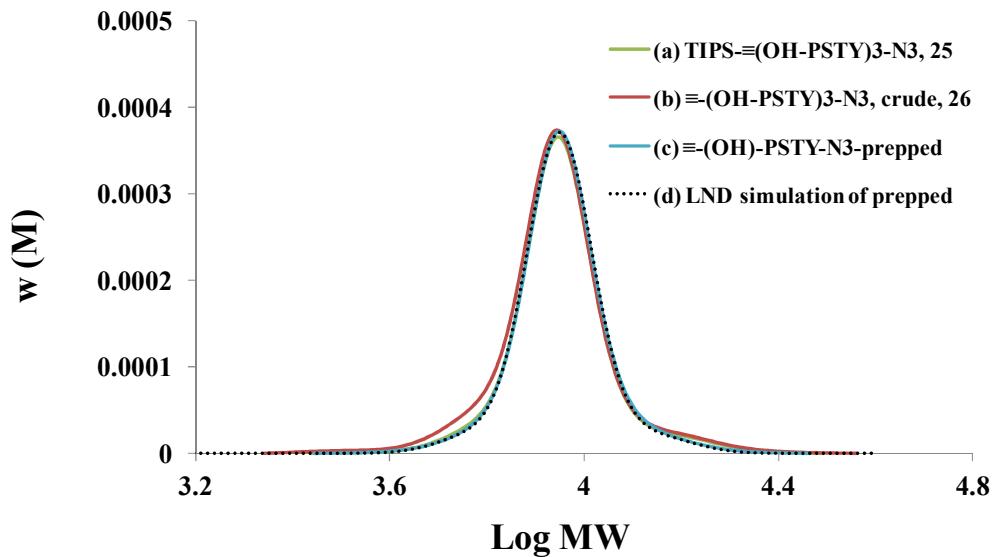


Figure S44: SEC RI traces of (a) TIPS- $\equiv(\text{OH-PSTY}_{25})_3\text{-N}_3$ (**25**), (b) $\equiv(\text{OH-PSTY}_{25})_3\text{-N}_3$ (**26**, crude), (c) $\equiv(\text{OH-PSTY}_{25})_3\text{-N}_3$ (**26**, purified by preparative SEC) based on PSTY calibration curve and (d) LND simulation of $\equiv(\text{OH-PSTY}_{25})_3\text{-N}_3$ (**26**, purified by preparative SEC).

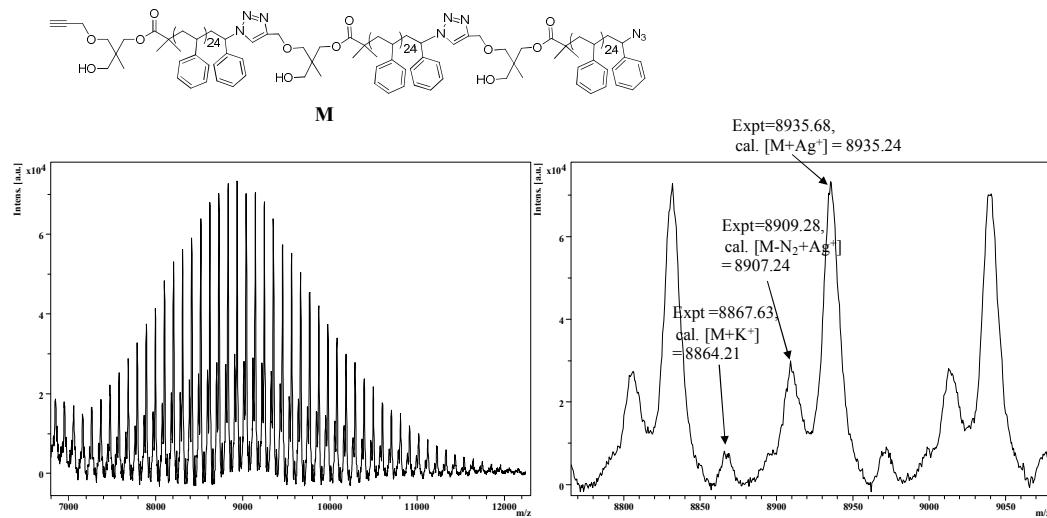


Figure S45: The full and expanded MALDI-ToF mass spectra of $\equiv(\text{OH-PSTY}_{25})_3\text{-N}_3$ (**26**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

20 Characterization of c-PSTY₇₅-(OH)₃ (**27**)

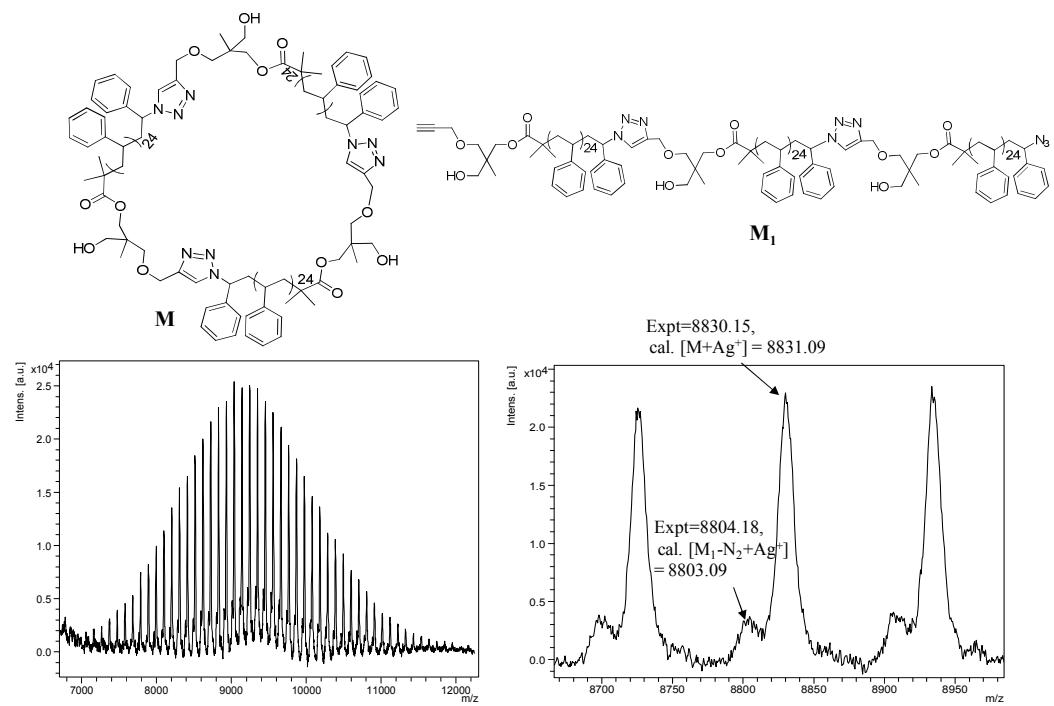


Figure S46: The full and expanded MALDI-ToF mass spectra of c-PSTY₇₅-(OH)₃ (**27**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

21 Characterization of c-PSTY₇₅-Br₃ (**28**)

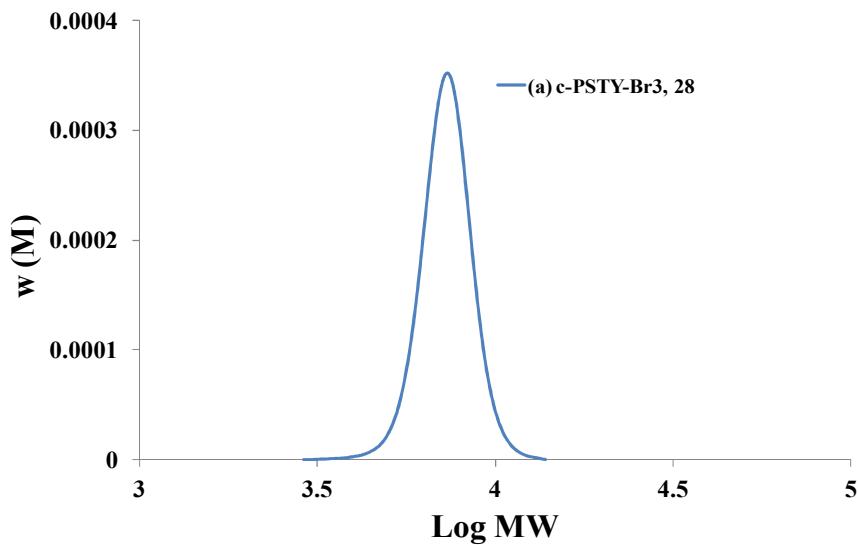


Figure S47: SEC RI trace of c-PSTY₇₅-Br₃ (**28**) based on PSTY calibration curve.

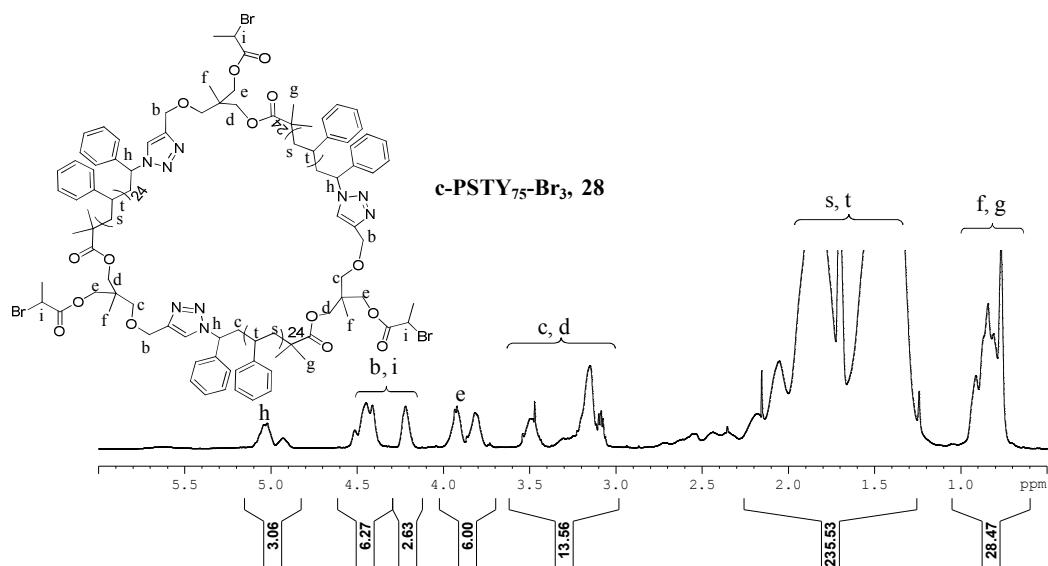


Figure S48: ¹H 1D DOSY NMR spectrum of c-PSTY₇₅-Br₃ (**28**) recorded in CDCl₃ at 298K (500 MHz).

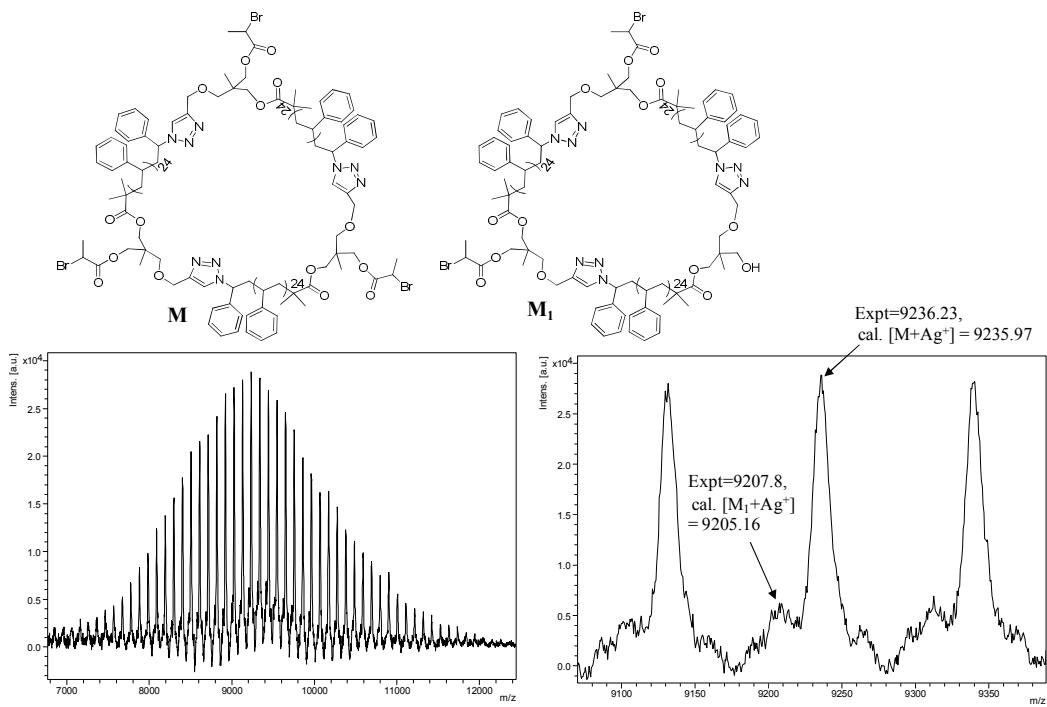


Figure S49: The full and expanded MALDI-ToF mass spectra of c-PSTY₇₅-Br₃ (**28**) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

22 Characterization of c-PSTY₇₅-(N₃)₃ (**29**)

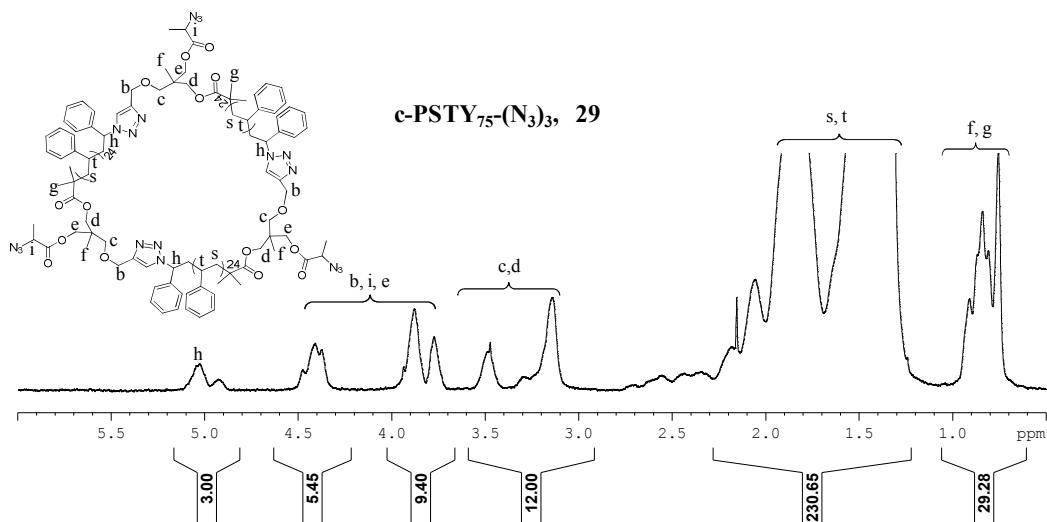


Figure S50: ¹H 1D DOSY NMR spectrum of c-PSTY₇₅-(N₃)₃ (**29**) recorded in CDCl₃ at 298K (500 MHz).

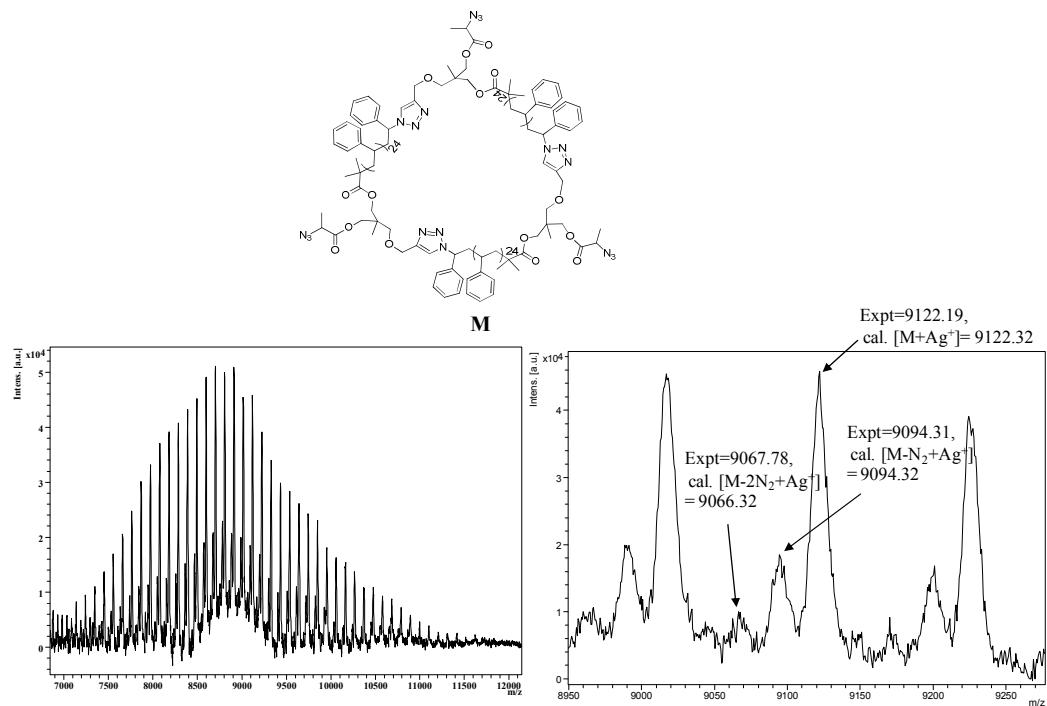


Figure S51: The full and expanded MALDI-ToF mass spectra of c-PSTY₇₅-(N₃)₃ (**29**) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

23 Characterization of c-PSTY_{75-(≡)6} (**30**)

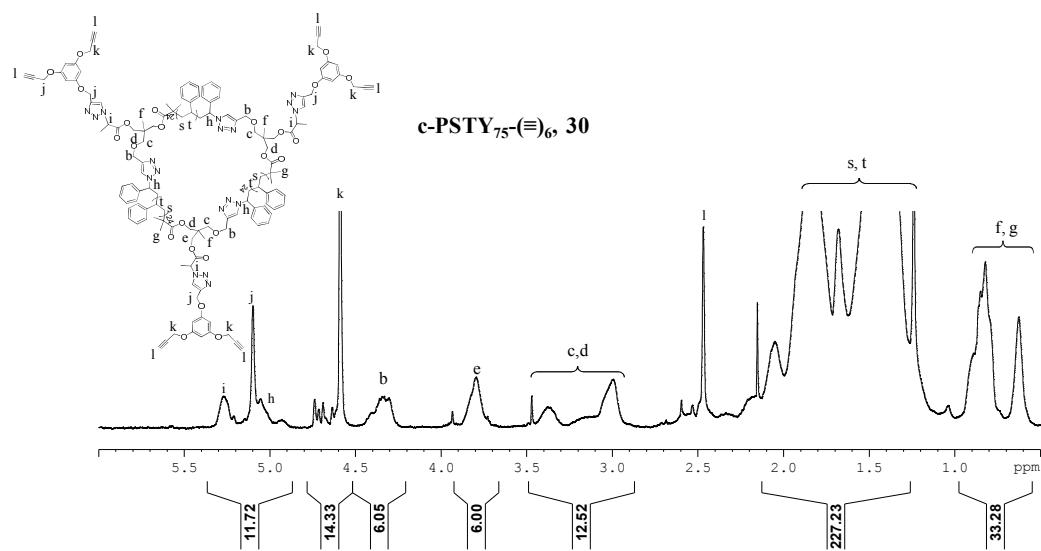


Figure S52: ^1H 1D DOSY NMR spectrum of c-PSTY_{75-(≡)6} (**30**, purified by preparative SEC) recorded in CDCl_3 at 298K (500 MHz).

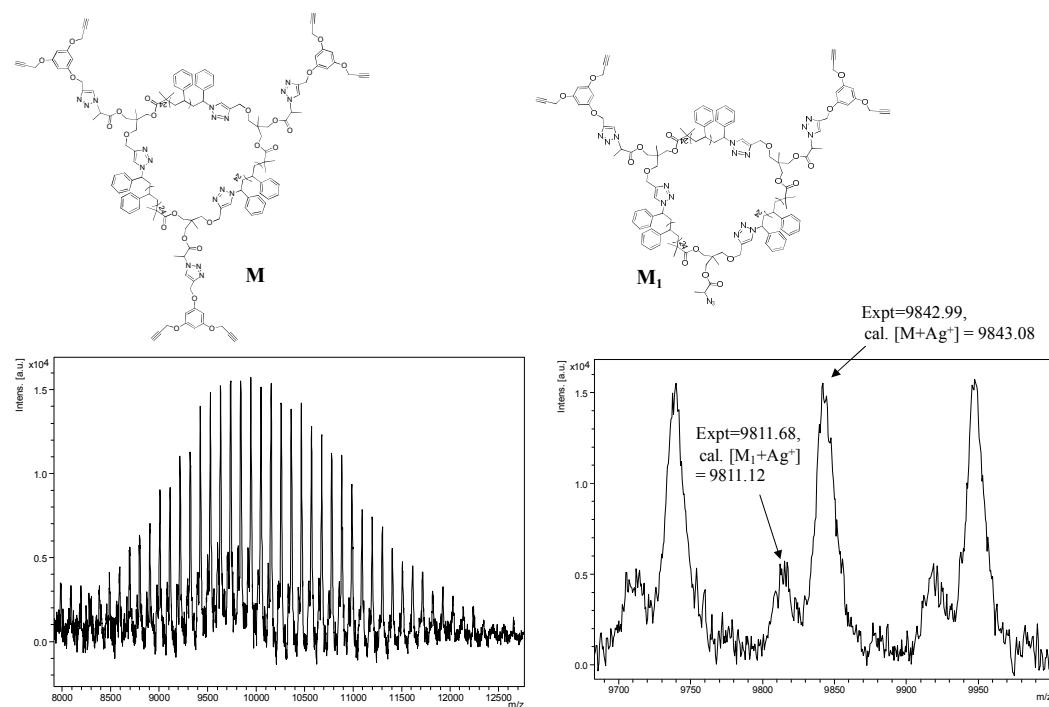


Figure S53: The full and expanded MALDI-ToF mass spectra of c-PSTY_{75-(≡)6} (**30**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

24 Characterization of spiro (c-PSTY)₃ (**31**)

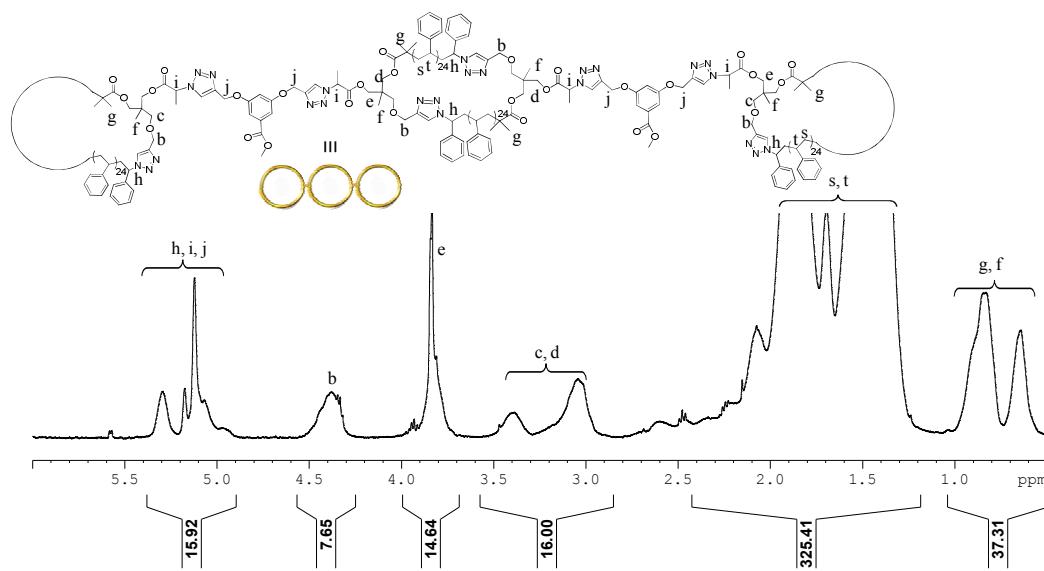


Figure S54: ^1H 1D DOSY NMR spectrum of spiro (c-PSTY)₃ (**31**, purified by preparative SEC)

recorded in CDCl_3 at 298K (500 MHz).

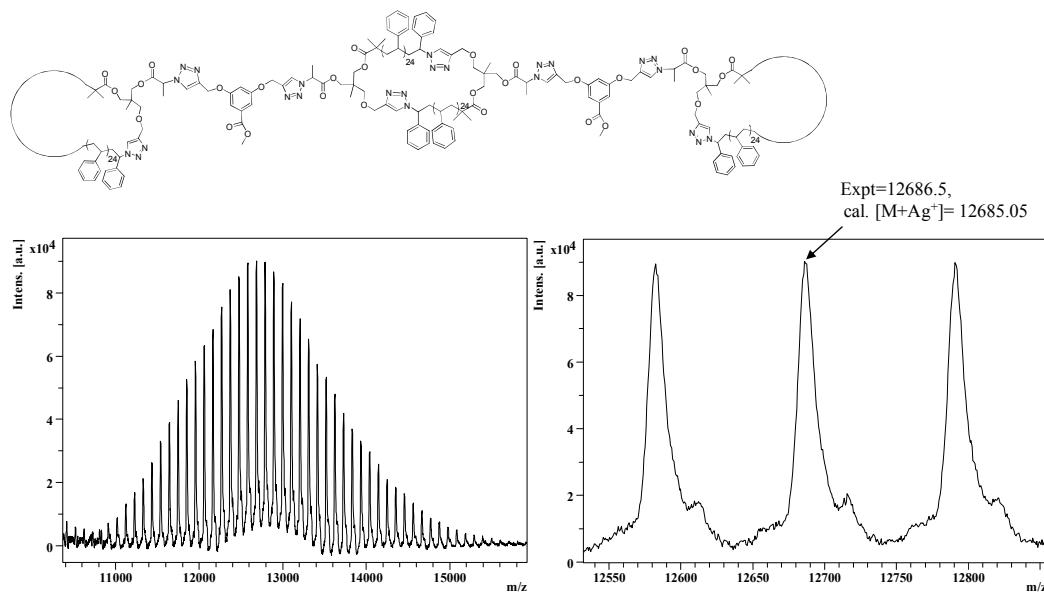


Figure S55: The full and expanded MALDI-ToF mass spectra of spiro (c-PSTY)₃ (**31**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

25 Characterization of G1 (c-PSTY)₅ (**32**)

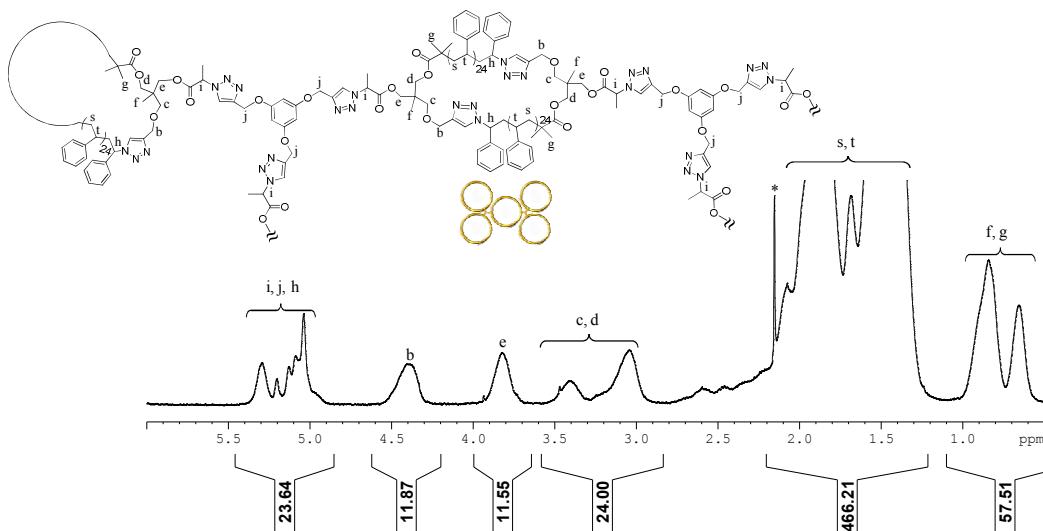


Figure S56: ^1H 1D DOSY NMR spectrum of G1 (c-PSTY)₅ (**32**, purified by preparative SEC) recorded in CDCl_3 at 298K (500 MHz), * acetone peak.

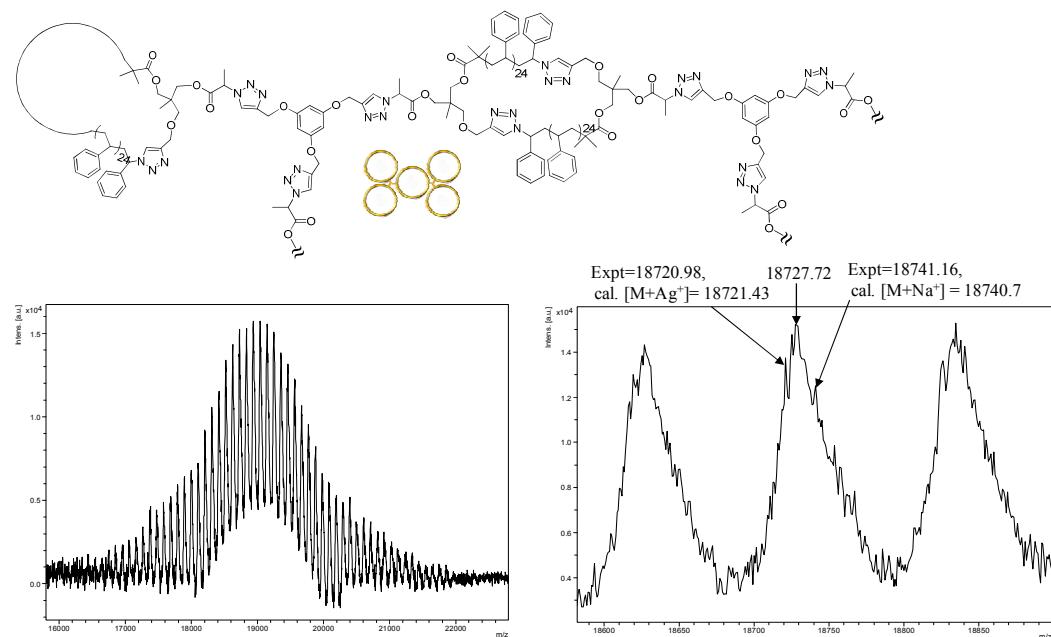


Figure S57: The full and expanded MALDI-ToF mass spectra of G1 (c-PSTY)₅ (**32**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

26 Characterization of G1 (c-PSTY)₄ (33)

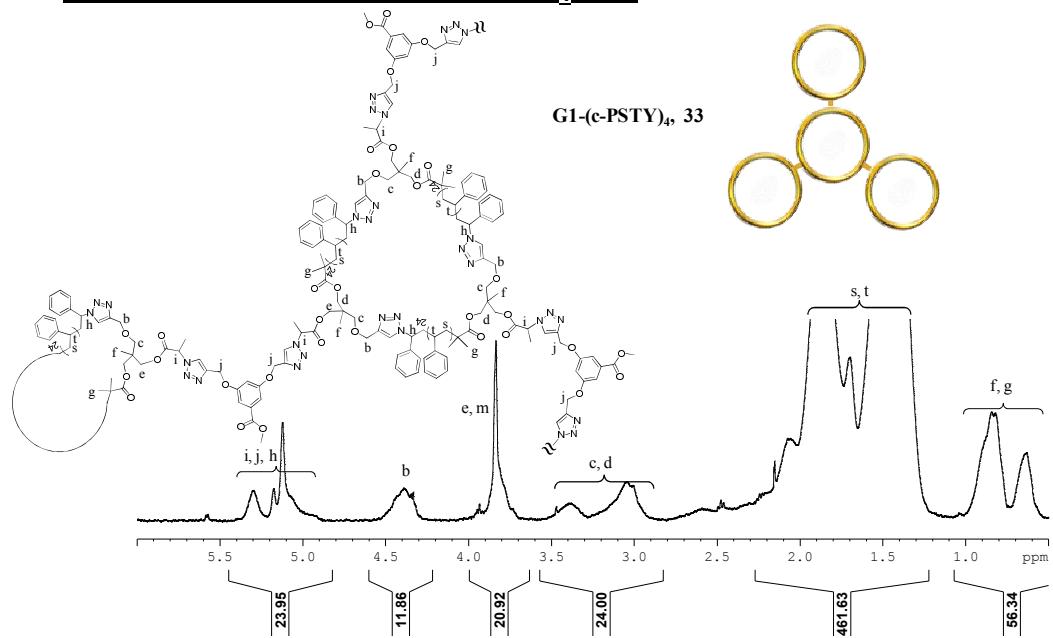


Figure S58: ¹H 1D DOSY NMR spectrum of G1 (c-PSTY)₄ (33, purified by preparative SEC) recorded in CDCl₃ at 298K (500 MHz).

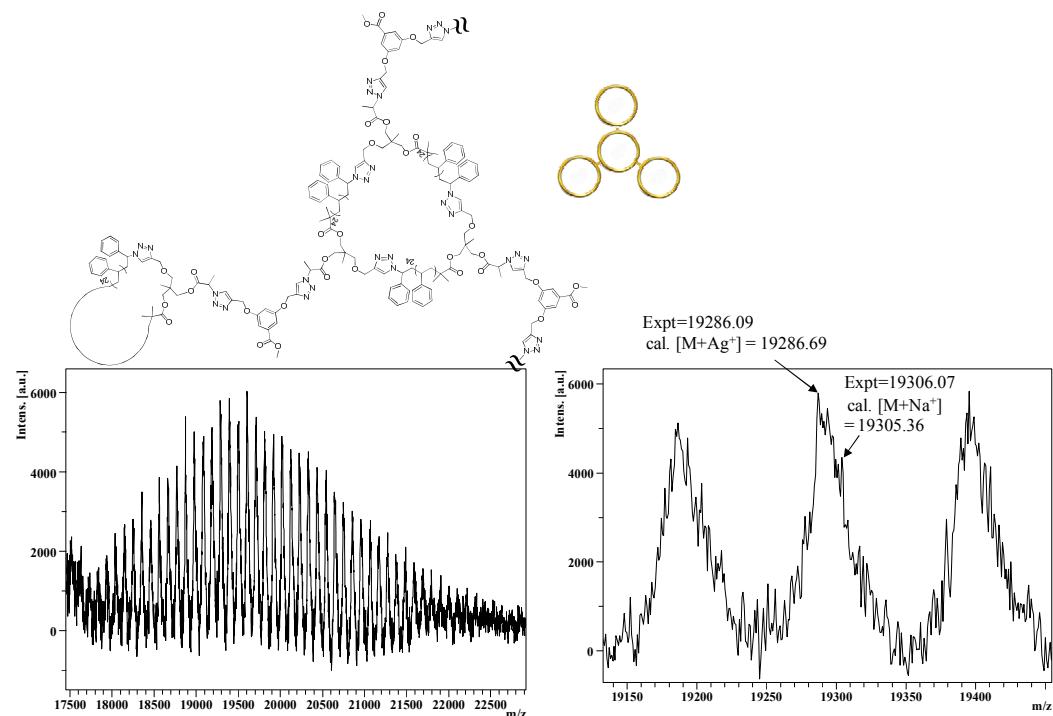


Figure S59: The full and expanded MALDI-ToF mass spectra of G1 (c-PSTY)₄ (33, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

27 Characterization of G1 (c-PSTY)₇ (34)

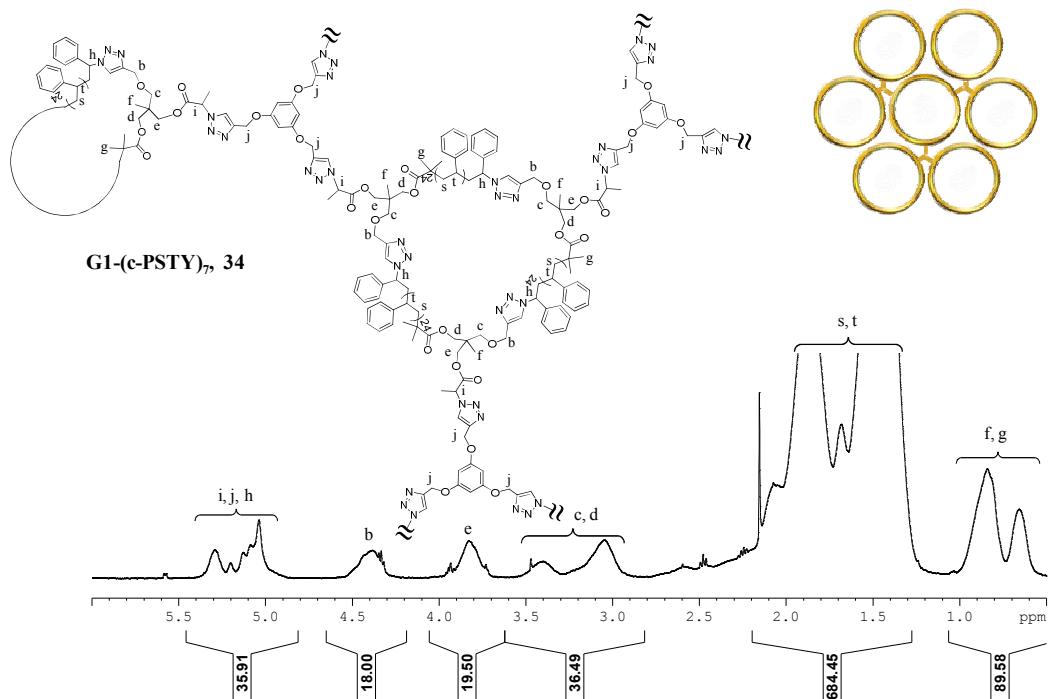


Figure S60: ¹H 1D DOSY NMR spectrum of G1 (c-PSTY)₇ (**34**, purified by preparative SEC) recorded in CDCl₃ at 298K (500 MHz).

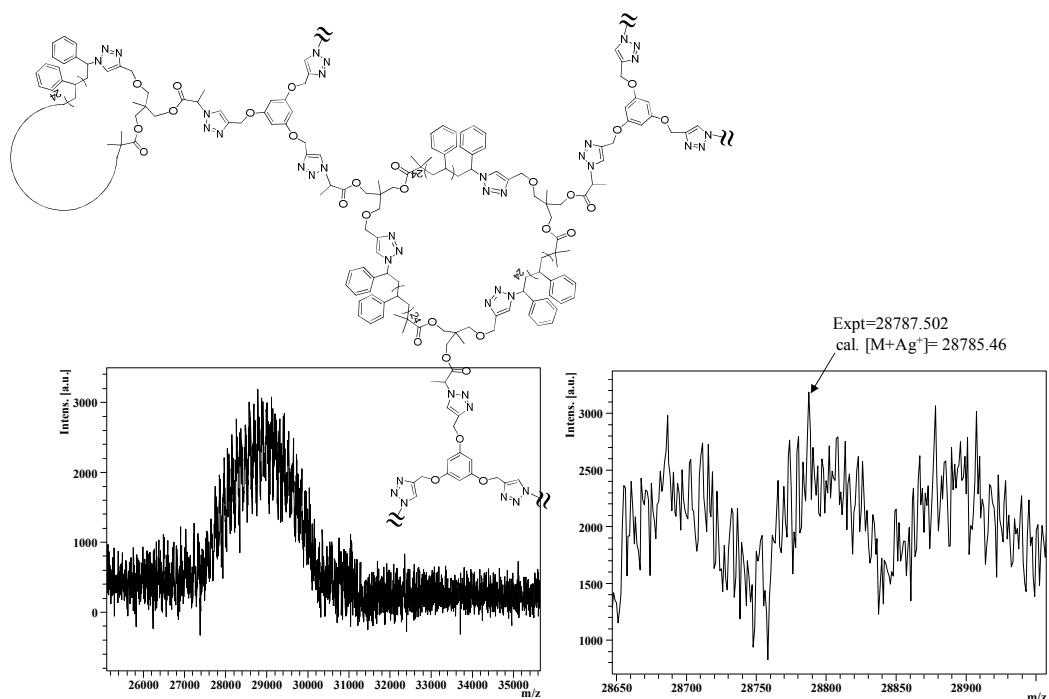


Figure S61: The full and expanded MALDI-ToF mass spectra of G1 (c-PSTY)₇ (**34**, purified by preparative SEC) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.