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Supporting Information

to

Precise Grafting of Macrocyclics and Dendrons to a Linear Polymer Chain.

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1 Synthesis of Initiators and Linkers

Initiators **1** alkyne (hydroxyl) functional initiator (Scheme S1 and Figure S1), **2** protected alkyne (hydroxyl) functional initiator (Scheme S2 and Figure S2) and **4** dialkyne functional initiator (Scheme S3 and Figure S4), and linker **3** dialkyne hydroxyl linker (Scheme S3 and Figure S3) and **5** methyl 3,5-bis (propargyloxyl) benzoate (Scheme S4 and Figure S5) were synthesized according to the literature procedures reported by our group¹⁻².

Scheme S1: Synthetic route for the preparation of alkyne initiator (1).



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

Scheme S2: Synthetic route for the preparation of protected alkyne initiator (2).



Reactants and conditions: (i) EtMgBr, THF, reflux at 76 °C, (ii) PBr₃, pyridine, ether $0 \sim 25$ °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: Synthetic route for the preparation of di_alkyne linker (3) and di_alkyne initiator (4).



Reactants and conditions: (i) THF, NaH, propargyl bromide, -78 °C, 16 h; ii) THF, 2-bromoisobutyryl bromide, 0 °C - RT, 16 h.

Scheme S4: Synthetic route for the preparation of di_alkyne linker (5).



Reactants and conditions: (i) Acetone, K₂CO₃, RT, 48 h;

2 Synthesis of Polymers and Polymer Topologies

2.1 Synthesis of PSTY₂₈-Br (6), by ATRP

Styrene (11.2 g, 1.0×10^{-1} mol), PMDETA (0.24 mL, 1.1×10^{-3} mol), CuBr₂/PMDETA (6.1×10⁻² g, 2.5×10^{-4} mol) and initiator (0.3 g, 1.5×10^{-3} mol) were added to a 25 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 30 min to remove oxygen. Cu(I)Br (0.16 g, 1.1×10^{-3} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 3 h, an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtered two times. The polymer was dried under high vacuum overnight for 24 h at 25 °C; SEC (M_n = 2820, PDI = 1.10; see SEC

trace in Figure S6) (Scheme S5; Table S1). Final conversion was calculated by gravimetry of 40%; ¹H NMR (Figure S7) and MALDI-ToF (Figure S8).

Scheme S5: Synthetic route for the preparation of alkyne wedge dendron (11)



Conditions: (a) **Azidation**: NaN₃ in DMF at 25 °C, (b) **Click (feed)**: CuBr, PMDETA in toluene by feed at 50 °C, **Click (25 °C)**: CuBr, PMDETA in toluene at 25 °C (one pot).

2.2 Synthesis of PSTY₂₈-N₃ (7) by Azidation with NaN₃

Polymer PSTY₂₈-Br **6** (3.5 g, 1.2×10^{-3} mol) was dissolved in 15 mL of DMF in a 20 mL reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (1.6 g, 2.4×10^{-2} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 2900, PDI = 1.10; Figure S9) (Scheme S5; Table S1), and was further characterized by ¹H NMR (Figure S10) and MALDI-ToF (Figure S11).

2.3 Synthesis of $(\equiv)_2 PSTY_{20}$ -Br (8) by ATRP

Styrene (9.0 g, 8.6×10^{-2} mol), PMDETA (0.27 mL, 1.3×10^{-3} mol), CuBr₂/PMDETA (1.0×10^{-1} g, 2.6×10^{-4} mol) and initiator (0.6 g, 2.5×10^{-3} mol) were added to a 20 mL schlenk tube equipped with a magnetic stirrer and purged with argon for 30 min to remove oxygen. Cu(I)Br (0.18 g, 1.2×10^{-3} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 2 h, an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice

bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtered two times. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 2300$, PDI = 1.09; see SEC trace in Figure S12) (Scheme S5; Table S1). Final conversion was calculated by gravimetry 41%; ¹H NMR (Figure S13) and MALDI-ToF (Figure S14).

2.4 Synthesis of (PSTY₂₈)₂-PSTY₂₀-Br (9) by CuAAC

PSTY₂₈-N₃ 7 (1.2 g, 4.3×10^{-4} mol) and PMDETA (4.5×10^{-2} mL, 2.1×10^{-4} mol) were dissolved in 5 mL of dry toluene in a vial. In a separate vial (=)₂-PSTY₂₀-Br **8** (0.5 g, 2.1×10^{-4} mol) was dissolved in 3.0 mL of dry toluene. Cu(I)Br (3.1×10^{-2} g, 2.1×10^{-4} mol) was taken in a 20 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.25 g, 3.9×10^{-3} mol). After purging all these vessels for 30 min, polymer solution 7 was transferred to the schlenk tube by applying argon pressure using double tip needle, and the schlenk tube was placed in a temperature controlled oil bath at 50 °C. Polymer solution **8** was feed to the schlenk flask using a syringe pump over a period of 60 min (feed rate was set at 20 µL/min). The reaction was stopped after a additional 60 min and diluted with THF, and the copper slats were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum for 24 h at 25 °C; SEC (M_n = 6990, PDI = 1.13; Figure 1A) and Triple Detection SEC (M_n = 8590, PDI = 1.014) (Scheme S5; Table S1). The polymer was further characterized by ¹H NMR (Figure S15) and MALDI-ToF (Figure 2A).

2.5 Synthesis of (PSTY₂₈)₂-PSTY₂₀-N₃ (10) by Azidation with NaN₃

Polymer (PSTY₂₈)₂-PSTY₂₀-Br **10** (1.4 g, 1.7×10^{-4} mol) was dissolved in 8 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (2.3×10⁻¹ g, 3.5×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 7280, PDI = 1.11; Figure S16) and Triple Detection SEC (M_n = 8680, PDI = 1.01) (Scheme S5; Table S1). The polymer was further characterized by ¹H NMR (Figure S17) and MALDI-ToF (Figure 2B).

2.6 Synthesis of $(PSTY_{28})_2$ -PSTY₂₀= (11) by CuAAC

Polymer (PSTY₂₈)₂-PSTY₂₀-N₃ **10** (1.3 g, 1.6×10^{-4} mol) and propargyl ether (3.0×10^{-1} g, 3.2×10^{-3} mol) and PMDETA (3.3×10^{-2} mL, 1.6×10^{-4} mol) were dissolved in 6 mL of dry toluene in a vial. CuBr (2.3×10^{-2} g, 1.6×10^{-4} mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer wrapped with Cu *wire* (0.25 g, 3.9×10^{-3} mol) and both reaction vessels were purged with argon for 20 min. The polymer solution was then transferred to CuBr flask by applying argon pressure using double tip needle. The flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was diluted with THF and passed through alumina column to remove copper salts. Solvent was removed by rotary evaporator and precipitated in excess of MeOH and filtered. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 7510, PDI = 1.10). Polymer was purified by preparative SEC to remove undesired high molecular weight polymers and residual linker. The polymer was dried under high vacuum for 24 h at 25 °C. SEC (M_n = 8640, PDI = 1.009) (Scheme S5; Table 1). The polymer was further characterized by ¹H NMR (Figure S19) and MALDI-ToF (Figure 2C).

2.7 Synthesis of \equiv (HO)-PSTY₂₈-Br (12), (12b) by ATRP

Styrene (12.2 g, 9.0×10^{-2} mol), PMDETA (0.20 mL, 9.7×10^{-4} mol), Cu(II)Br₂/PMDETA (7.7×10^{-2} g, 1.9×10^{-4} mol) and initiator **1** (0.6 g, 1.9×10^{-3} mol) were added to a 10 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 30 min to remove oxygen. Cu(I)Br (0.14 g, 9.7×10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 6 h, an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with DCM (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried *in* high *vacuo* overnight at 25 °C, for **12** (M_n = 3220, PDI = 1.07; see SEC trace in Figure S20). Final conversion was calculated by gravimetry 47%. The polymer was further characterized by ¹H NMR (Figure S21) and MALDI-ToF (Figure S22). Another batch of =(HO)-PSTY₂₅-Br, **12b** (M_n = 3150, PDI = 1.07; SEC Figure S23; ¹H NMR Figure S24 and MALDI-ToF Figure S25) was also synthesized by following similar procedure.

2.8 Synthesis of \equiv (HO)-PSTY₂₅-Br (12c) by ATRP

Styrene (8.11g, 77.86×10⁻³ mol), PMDETA (0.17 mL, 8.1×10⁻⁴ mol), CuBr₂/PMDETA (6.4×10⁻² g, 4.05×10⁻⁴ mol) and initiator (0.5 g, 1.6277×10⁻³ mol) were added to a 100 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 40 min to remove oxygen. Cu(I)Br (0.12 g, 8.1×10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 4 h, an aliquot was taken to check the conversion. The reaction was quenched by cooling to 0 °C in ice bath, exposed to air, and diluted with THF (*ca.* 3 fold to the reaction mixture volume). The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporation and the polymer was recovered by precipitation into large

volume of MeOH (20 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried *in* high *vacuo* overnight at 25 °C, SEC (M_n = 2890, PDI = 1.11; see SEC trace in Figure S26) (Table S1). Final conversion was calculated by gravimetry 53%. The polymer was further characterized by ¹H NMR (Figure S27) and MALDI-ToF (Figure S28).



Scheme S6: Synthetic route for the preparation of cyclic alkyne (17)

Conditions: (a) Azidation: NaN₃ in DMF at 25 °C, (b) Cyclization: CuBr, PMDETA in toluene by feed at 25 °C, (c) Bromination: 2-BPB, TEA in THF; 0 °C- RT. (d) Click (25 °C): CuBr, PMDETA in toluene at 25 °C (one pot).

2.9 Synthesis of \equiv (HO)-PSTY₂₅-N₃ (13) by Azidation with NaN₃

Polymer **12c** (2.9 g, 1.0×10^{-3} mol) was dissolved in 15 mL of DMF in a 20 mL reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (1.6 g, 2.4×10^{-2} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 2880, PDI = 1.11; Figure S29) (Table S1). The polymer was further characterized by ¹H NMR (Figure S30) and MALDI-ToF (Figure S31).

2.10 Synthesis of c-PSTY₂₅-OH (14)

Polymer **13** (2.0 g, 6.667×10⁻⁴ mol) in 80.0 ml of dry toluene and 6.97 mL of PMDETA (33.35×10⁻³ mol) in 80 mL of dry toluene in another flask were purged with argon for 45 min to remove oxygen. 4.78 g of CuBr (33.35×10⁻³ mol) was taken in a 250 mL of dry schlenk flask and maintained under an argon flow in the flask at the same time. A PMDETA solution was transferred to CuBr flask by applying argon pressure using a double tip needle to prepare CuBr/PMDETA complex. After complex formation, the polymer solution was added via syringe pump using a syringe with prefilled argon. The feed rate of argon was set at 1.24 mL/min. After the addition of the polymer solution (after 65 min), the reaction mixture was further stirred for 3 h. At the end of this period (i.e., feed time plus an additional 3 h), toluene was evaporated by air-flow and the copper salts were removed by passage through an activated basic alumina column by adding few drops of glacial acetic acid. The solvent was removed by rotary evaporator and the polymer was recovered by precipitation into MeOH (20 fold excess to polymer solution) and collected by vacuum filtration followed by exhaustive washing with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C. A small fraction of crude product was purified by preparative SEC for characterization. SEC ($M_n = 2140$, PDI = 1.04; Figure S32) (Table S1), Triple Detection SEC ($M_n = 2780$, PDI = 1.016). The polymer was further characterized by ¹H NMR (Figure S33) and MALDI-ToF (Figure S34).

2.11 Synthesis of c-PSTY₂₅-Br (15)

c-PSTY₂₅-OH **14** (1.6 g, 5.867×10^{-4} mol), TEA (1.63 mL, 11.73×10^{-3} mol) and 30.0 ml of dry THF were added under an argon blanket to a dry schlenk flask that has been flushed with argon. The reaction was then cooled on ice bath. To this stirred mixture, a solution of 2-bromopropionyl bromide (1.23 mL, 11.73×10^{-3} mol) in 10 mL of dry THF was added drop wise under argon via an air-tight syringe over 10 min. After stirring the reaction mixture for 48 h at room temperature, the crude polymer solution was added in 300 mL of acetone and filtered to remove salt precipitate. Solvent was removed by rotavap and precipitated into MeOH, filtered and washed three times with MeOH. A fraction of crude product was purified by preparative SEC for characterization. The polymer was dried for 24 h in high vacuum oven at 25 °C. SEC (M_n = 2350, PDI = 1.04; see SEC trace in Figure S35) (Table S1). The polymer was further characterized by ¹H NMR (Figure S36) and MALDI-ToF (Figure S37).

2.12 Synthesis of c-PSTY₂₅-N₃ (16)

Polymer c-PSTY₂₅-Br **15** (1.5 g, 0.5×10^{-3} mol) was dissolved in 15 mL of DMF in a 20 mL reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (1.6 g, 2.4×10^{-2} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 2250, PDI = 1.04; Figure S38) (Table S1) and Triple Detection SEC (M_n = 2930, PDI = 1.02). The polymer was further characterized by ¹H NMR (Figure S39) and MALDI-ToF (Figure S40).

2.13 Synthesis of c-PSTY₂₅= (17)

Polymer c-PSTY₂₅-N₃ **16** (0.4 g, 0.133×10⁻³ mol), PMDETA (27.87×10⁻³ mL, 0.133×10⁻³ mol) and methyl 3,5-bis (propargyloxyl) benzoate **5** (0.49 g, 1.99×10⁻³ mol) were dissolved in 3.0 mL toluene. CuBr (19.0×10⁻³ g, 1.33×10⁻⁴ mol) was added to a 10 mL schlenk flask equipped with magnetic stirrer and both of the reaction vessels were purged with argon for 20 min. The polymer solution was then transferred to CuBr flask by applying argon pressure using double tip needle. The reaction mixture was purged with argon for a further 2 min and the flask was placed in a temperature controlled oil bath at 25 °C for 1.5 h. The reaction was then diluted with THF (*ca.* 3 fold to the reaction mixture volume), and passed through activated basic alumina to remove the copper salts. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into a large amount of MeOH (20 fold excess to polymer solution) and filtration. The polymer was purified by preparative SEC to remove excess linker as well as high MW impurities. After precipitation and filtration, the polymer was dried *in vacuo* for 24 h at 25 °C. SEC (M_n=2440, PDI=1.04; see SEC trace in Figure S41) (Table 1) and Triple Detection SEC (M_n=3170, PDI=1.02). The polymer was further characterized by ¹H NMR (Figure S42) and MALDI-ToF (Figure S43).

2.14 Synthesis of TIPS-≡(HO)-PSTY₂₈-Br (18), (18b)

Styrene (8 g, 6.3×10^{-2} mol), PMDETA (1.3×10^{-1} mL, 6.4×10^{-4} mol), Cu(II)Br₂/PMDETA (5.1×10^{-2} g, 1.29×10^{-4} mol) and initiator **2** (0.6 g, 1.2×10^{-3} mol) were added to a 20 mL schlenk flask equipped with a magnetic stirrer and purged with argon for 30 min to remove oxygen. Cu(I)Br (9.2×10^{-2} g, 6.4×10^{-4} mol) was then carefully added to the solution under an argon blanket. The reaction mixture was further degassed for 5 min and then placed into a temperature controlled oil bath at 80 °C. After 11 h an aliquot was taken to check the conversion. The reaction was quenched by cooling the reaction mixture to 0 °C, exposure to air, and dilution with THF. The copper salts were removed by passage through an activated basic alumina column. The solution was concentrated by rotary evaporator and the polymer was recovered by precipitation into large volume of MeOH (20 fold excess to polymer solution) and vacuum filtration two times. The polymer was dried under high vacuum for 24 hr overnight at 25 °C. SEC ($M_n = 3450$, PDI = 1.06; see SEC trace in Figure S44) (Table S1). Final conversion was calculated by gravimetry (48%); ¹H NMR (Figure S45) and MALDI-ToF (Figure S46). Another batch of TIPS=(HO)-PSTY₂₈-Br, **18b** ($M_n = 3410$, PDI = 1.08; SEC Figure S47) (Table S1); ¹H NMR Figure S48; MALDI-ToF Figure S49) was also synthesized by following similar procedure.

2.15 Synthesis of TIPS-=-(OH)-PSTY₂₈-N₃ (19) by Azidation with NaN₃

Polymer TIPS-=(OH)-PSTY₂₈-Br **18** (1.4 g, 4.0×10^{-4} mol) was dissolved in 10 mL of DMF in a 20 mL reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (5.2×10^{-1} g, 8.1×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 3540, PDI = 1.05; Figure S50) (Table S1). The polymer was further characterized by ¹H NMR (Figure S51) and MALDI-ToF (Figure S52).

2.16 Synthesis of TIPS-=-(OH)-PSTY₂₈-N₃ (19b) by Azidation with NaN₃

Polymer TIPS-=(OH)-PSTY₂₈-Br **18b** (2.9 g, 8.5×10^{-4} mol) was dissolved in 15 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (1.1 g, 1.7×10^{-2} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 3530, PDI = 1.07; Figure S53) (Table S1). The polymer was further characterized by ¹H NMR (Figure S54) and MALDI-ToF (Figure S55).

2.17 Synthesis of TIPS-≡(OH-PSTY₂₈)₂-Br (20) by CuAAC

Polymer TIPS- \equiv (OH)-PSTY₂₈-N₃ **19** (1.1 g, 3.1×10⁻⁴ mol), \equiv (OH)-PSTY₂₈-Br **12** (1.0 g, 3.1×10⁻⁴ mol) and PMDETA (6.4×10⁻² mL, 3.1×10⁻⁴ mol) were dissolved in 10 mL of dry toluene in a 20 mL vial. Cu(I)Br (4.4×10⁻² g, 3.1×10⁻⁴ mol) was taken in a 20 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.25 g, 3.9×10⁻³ mol). Both vessels were purged with argon for 30 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using double tip needle, and the schlenk tube was placed in a temperature controlled oil bath at 25 °C. The reaction was stopped after 1.5 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitated in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 6480, PDI = 1.08; Figure S56) (Table S1). The polymer was further characterized by ¹H NMR (Figure S57) and MALDI-ToF (Figure S58).

2.18 Synthesis of TIPS-≡(OH-PSTY₂₈)₂-Br (20b) by CuAAC

Polymer TIPS-=(OH)-PSTY₂₈-N₃ **19b** (2.8 g, 7.9×10^{-4} mol), =(OH)-PSTY₂₈-Br **12b** (2.49 g, 7.9×10^{-4} mol) and PMDETA (1.6×10^{-1} mL, 7.9×10^{-4} mol) were dissolved in 15 mL of dry toluene in a 20 mL vial. Cu(I)Br (1.13×10^{-1} g, 7.9×10^{-4} mol) was taken in a 25 mL schlenk flask equipped with magnetic stirrer wrapped with Cu *wire* (0.5 g, 7.8×10^{-3} mol). Both vessels were purged with

argon for 30 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using double tip needle, and the schlenk tube was placed in a temperature controlled oil bath at 25 °C. The reaction was stopped after 1.5 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitated in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 6610$, PDI = 1.08; Figure S59) (Table S1). The polymer was further characterized by ¹H NMR (Figure S60) and MALDI-ToF (Figure S61).

2.19 Synthesis of TIPS-≡(OH-PSTY₂₈)₂-N₃ (21) by Azidation with NaN₃

Polymer TIPS-=(OH-PSTY₂₈)₂-Br **20** (1.9 g, 2.7×10^{-4} mol) was dissolved in 15 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (3.5×10^{-1} g, 5.4×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 6980, PDI = 1.08). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 7000, PDI = 1.05; Figure S62) (Table S1). The polymer was further characterized by ¹H NMR (Figure S63) and MALDI-ToF (Figure S64).

2.20 Synthesis of TIPS-≡(OH-PSTY₂₈)₂-N₃ (21b) by Azidation with NaN₃

Polymer TIPS- \equiv (OH-PSTY₂₈)₂-Br **20b** (5.2 g, 7.8×10⁻⁴ mol) was dissolved in 25 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (1.0 g, 1.5×10⁻² mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum

for 24 h at 25 °C; SEC ($M_n = 6660$, PDI = 1.07; Figure S65) (Table S1). The polymer was further characterized by ¹H NMR (Figure S66) and MALDI-ToF (Figure S67).

2.21 Synthesis of TIPS-≡(Br-PSTY₂₈)₂-N₃(22)

TIPS- \equiv (OH-PSTY₂₈)₂-Br **21** (0.2 g, 2.8×10⁻⁵ mmol) and TEA (1.5×10⁻¹ mL, 1.1×10⁻³ mol) were dissolved in 2 ml of dry THF in a 10 mL schlenk tube and purged for 10 min. The reaction mixture was cooled on ice and a solution of 2-bromopropionyl bromide (1.2×10⁻¹ mL, 1.1×10⁻³ mol) in 2 mL of dry THF was transferred drop-wise to the schlenk tube by applying argon pressure using double tip needle. The reaction mixture was further purged for 2 minutes and then stirred for 48 h at room temperature. The polymer was precipitated into MeOH, filtered and washed exhaustively with MeOH. The polymer was dried for 24 h under high vacuum at 25 °C. SEC (M_n = 7170, PDI = 1.07; Figure S68) (Table S1). The polymer was further characterized by ¹H NMR (Figure S69) and MALDI-ToF (Figure S70).

2.22 Synthesis of TIPS-≡(Br-PSTY₂₈)₂-N₃ (22b)

TIPS- \equiv (OH-PSTY₂₈)₂-Br **21b** (2.6 g, 3.9×10^{-4} mmol) and TEA (2.17 mL, 1.5×10^{-2} mol) were dissolved in 20 ml of dry THF in a 50 mL schlenk tube and purged for 15 min. The reaction mixture was cooled on ice and a solution of 2-bromopropionyl bromide (1.67 mL, 1.5×10^{-2} mol) in 5 mL of dry THF was transferred drop-wise to the schlenk tube by applying argon pressure using double tip needle. The reaction mixture was further purged for 2 minutes and then stirred for 48 h at room temperature. The polymer was precipitated into MeOH, filtered and washed exhaustively with MeOH. The polymer was dried for 24 h under high vacuum at 25 °C. SEC (M_n = 6830, PDI = 1.06). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 7080, PDI = 1.04; Figure S71) (Table S1). The polymer was further characterized by ¹H NMR (Figure S72) and MALDI-ToF (Figure S73).

2.23 Synthesis of TIPS-≡(N₃-PSTY₂₈)₂-N₃ (23) by Azidation with NaN₃

TIPS- \equiv (Br-PSTY₂₈)₂-N₃ **22** (0.17 g, 2.3×10⁻⁵ mol), was dissolved in 2.5 mL of DMF in a reaction vessel equipped with magnetic stirrer. To this solution, NaN₃ (9.2×10⁻² g, 1.4×10⁻³ mol) was added and the mixture stirred for 24 h at room temperature. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20 fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C, SEC (M_n = 7180, PDI = 1.05). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 7160, PDI = 1.03; Figure 3A) (Table S1). The polymer was further characterized by ¹H NMR (Figure S74) and MALDI-ToF (Figure S75).

2.24 Synthesis of TIPS-≡(OH-PSTY₂₈)₃-Br (24) by CuAAC

Polymer TIPS- \equiv (OH-PSTY₂₈)₂-N₃ **21** (7.3×10⁻¹ g, 1.0×10⁻⁴ mol) and \equiv (OH)-PSTY₂₈-Br **12** (3.5×10⁻¹ g, 1.0×10⁻⁴ mol) and PMDETA (2.2×10⁻² mL, 1.0×10⁻⁴ mol) were dissolved in 8 mL of dry toluene in a 20 mL vial. Cu(I)Br (1.5×10⁻² g, 1.0×10⁻⁴ mol) was taken in a 20 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.25 g, 3.9×10⁻³ mol). Both vessels were purged with argon for 30 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using double tip needle, and the tube was placed in a temperature controlled oil bath at 25 °C. The reaction was stopped after 1.5 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitated in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 9050, PDI = 1.10; Figure S76) (Table S1). The polymer was further characterized by ¹H NMR (Figure S77) and MALDI-ToF (Figure S78).

2.25 Synthesis of TIPS-≡(OH-PSTY₂₈)₃-N₃ (25) by Azidation with NaN₃

Polymer TIPS-=(OH-PSTY₂₅)₃-Br **24** (9.5×10^{-1} g, 9.2×10^{-5} mol) was dissolved in 10 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (1.2×10^{-1} g, 1.8×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 8610, PDI = 1.16). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 10670, PDI = 1.04; Figure S79) (Table S1). The polymer was further characterized by ¹H NMR (Figure S80) and MALDI-ToF (Figure S81).

2.26 Synthesis of TIPS-≡(Br-PSTY₂₈)₃-N₃ (26)

TIPS- \equiv (OH-PSTY₂₈)₃-N₃ **25** (0.19×10⁻¹ g, 1.8×10⁻⁵ mmol), TEA (1.5×10⁻¹ mL, 1.0×10⁻³ mol) were dissolved in 2 ml of dry THF in a 10 mL schlenk tube and purged for 10 min. The reaction mixture was cooled on ice and a solution of 2-bromopropionyl bromide (1.1×10⁻¹ mL, 1.0×10⁻³ mol) in 2 mL of dry THF was transferred drop-wise to the schlenk tube by applying argon pressure using double tip needle. The reaction mixture was further purged for 2 minutes and then stirred for 48 h at room temperature. The polymer was precipitated into MeOH, filtered and washed exhaustively with MeOH. The polymer was dried for 24 h under high vacuum at 25 °C. SEC (M_n = 9090, PDI = 1.12; Figure S82) (Table S1). The polymer was further characterized by ¹H NMR (Figure S83) and MALDI-ToF (Figure S84).

2.27 Synthesis of TIPS- \equiv (N₃-PSTY₂₈)₃-N₃ (27)

TIPS-=(Br-PSTY₂₈)₃-N₃ **26** (1.6×10^{-1} g, 1.4×10^{-5} mol), was dissolved in 3 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (8.6×10^{-2} g, 1.3×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water MeOH. The polymer was dried under high vacuum for

24 h at 25 °C; SEC ($M_n = 8970$, PDI= 1.16). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 10830$, PDI = 1.03; Figure 3B) (Table S1). The polymer was further characterized by ¹H NMR (Figure S85) and MALDI-ToF (Figure S86).

2.28 Synthesis of TIPS-=(HO-PSTY₂₈)₃-HO-(PSTY₂₈-OH)₃-=-TIPS (28) by CuAAC Polymer TIPS- \equiv (OH-PSTY₂₈)₃-N₃ 25 (2.8×10^{-1}) g, 2.6×10⁻⁵ mol), 2,2bis(propargyloxymethyl)propan-1-ol (2.5×10⁻³ g, 1.3×10⁻⁵ mol) and PMDETA (1.0×10⁻² mL, 5.2×10⁻⁵ mol) were dissolved in 3 mL of dry toluene in a 7 mL vial. Cu(I)Br (7.5×10⁻³ g, 5.2×10⁻⁵ mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu wire (0.1 g, 1.5×10^{-3} mol). Both vessels were purged with argon for 20 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using double tip needle, and the tube was placed in a temperature controlled oil bath at 25 °C. The reaction was stopped after 1.5 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitated in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 15450$, PDI = 1.20; S87) (Table S1). The polymer was further characterized by ¹H NMR (Figure S88) and MALDI-ToF (Figure S89).

2.29 Synthesis of TIPS-≡(Br-PSTY₂₈)₃-Br-(PSTY₂₈-Br)₃-≡-TIPS (29)

TIPS-=(HO-PSTY₂₈)₃-HO-(PSTY₂₈-OH)₃-=-TIPS **28** (2.4×10^{-1} g, 1.1×10^{-5} mmol), TEA (2.2×10^{-1} mL, 1.6×10^{-3} mol) were dissolved in 2 ml of dry THF in a 10 mL schlenk tube and purged for 10 min. The reaction mixture was cooled on ice and a solution of 2-bromopropionyl bromide (1.7×10^{-1} mL, 4.2×10^{-3} mol) in 2 mL of dry THF was transferred drop-wise to the schlenk tube by applying argon pressure using double tip needle. The reaction mixture was further purged for 2 minutes and then stirred for 48 h at room temperature. The polymer was precipitated into MeOH, filtered and washed exhaustively with MeOH. The polymer was dried for 24 h under high vacuum at 25 °C. SEC (M_n = 17000, PDI =

1.12; see SEC trace in Figure S90) (Table S1). The polymer was further characterized by ¹H NMR (Figure S91) and MALDI-ToF (Figure S92).

2.30 Synthesis of TIPS-= $(N_3$ -PSTY₂₈)₃-N₃-(PSTY₂₈-N₃)₃-=-TIPS (30) by Azidation with NaN₃

TIPS-=(Br-PSTY₂₈)₃-Br-(PSTY₂₈-Br)₃-=-TIPS **29** (2.0×10^{-1} g, 9.4×10^{-6} mol), was dissolved in 2.5 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (1.2×10^{-1} g, 1.9×10^{-3} mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 16810, PDI = 1.12). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 21720, PDI = 1.04; Figure 3C) (Table S1). The polymer was further characterized by ¹H NMR (Figure S93) and MALDI-ToF (Figure S94).

2.31 Synthesis of tri-cyclic architecture (31) by CuAAC

Polymer TIPS- \equiv (N₃-PSTY₂₈)₂-N₃ **23** (3.1×10⁻² g, 4.3×10⁻⁶ mol), polymer c-PSTY₂₅- \equiv **17** (4.2×10⁻² g, 1.7×10⁻⁵ mol) and PMDETA (2.7×10⁻³ mL, 1.2×10⁻⁵ mol) were dissolved in 0.8 mL of dry toluene in a 4 mL vial. Cu(I)Br (1.8×10⁻³ g, 1.2×10⁻⁵ mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.1 g, 1.5×10⁻³ mol). Both vessels were purged with argon for 15 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 13620, PDI = 1.13). The polymer was

purified by preparative SEC to remove undesired high molecular weight polymer and residual reactant polymers. The polymer was reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n = 12620$, PDI = 1.04; Figure 4A), Triple detection ($M_n = 16990$, PDI = 1.01) (Table 1) and ¹H NMR (Figure S95).

2.32 Synthesis of tri-dendron architecture (32) by CuAAC

Polymer TIPS-= $(N_3$ -PSTY₂₈)₂-N₃ **23** (1.6×10⁻² g, 2.2×10⁻⁶ mol), polymer (PSTY₂₈)₂-PSTY₂₀-= **11** (7.0×10⁻² g, 8.9×10⁻⁶ mol) and PMDETA (1.3×10⁻³ mL, 6.7×10⁻⁶ mol) were dissolved in 0.8 mL of dry toluene in a 4 mL vial. Cu(I)Br (9.6×10⁻⁴ g, 6.7×10⁻⁶ mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu wire (0.1 g, 1.5×10^{-3} mol). Both vessels were purged with argon for 15 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 22670$, PDI = 1.26). The polymer was purified by preparative SEC to remove undesired high molecular weight polymer and residual reactant polymers. The polymer was reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n = 27850$, PDI = 1.07; Figure 4B), Triple detection (M_n = 33400, PDI = 1.01) (Table 1) and ¹H NMR (Figure S96).

2.33 Synthesis of tetra-cyclic architecture (33) by CuAAC

Polymer TIPS-≡(N₃-PSTY₂₈)₃-N₃ 27 (3.2×10⁻² g, 2.9×10⁻⁶ mol), polymer c-PSTY₂₅-≡ 17 (3.6×10⁻² g, 1.4×10⁻⁵ mol) and PMDETA (2.4×10⁻³ mL, 1.1×10⁻⁵ mol) were dissolved in 0.8 mL of dry toluene in a 4 mL vial. Cu(I)Br (1.6×10-3 g, 1.1×10-5 mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu wire (0.1 g, 1.5×10⁻³ mol). Both vessels were purged with argon for 15 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 22150$, PDI = 1.18). The polymer was purified by preparative SEC to remove undesired high molecular weight polymer and residual reactant polymers. The polymer was reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n = 18980$, PDI = 1.05; Figure 4C), Triple detection ($M_n = 25240$, PDI = 1.02) (Table 1) and ¹H NMR (Figure S97).

2.34 Synthesis of tetra-dendron architecture (34) by CuAAC

Polymer TIPS- \equiv (N₃-PSTY₂₈)₃-N₃ **27** (1.8×10⁻² g, 1.6×10⁻⁶ mol), polymer (PSTY₂₈)₂-PSTY₂₀- \equiv **11** (6.5×10⁻² g, 8.3×10⁻⁶ mol) and PMDETA (1.3×10⁻³ mL, 6.6×10⁻⁶ mol) were dissolved in 0.8 mL of dry toluene in a 4 mL vial. Cu(I)Br (9.5×10⁻⁴ g, 6.6×10⁻⁶ mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.1 g, 1.5×10⁻³ mol). Both vessels were purged with argon for 15 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was

removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 25320$, PDI = 1.49). The polymer was purified by preparative SEC to remove undesired high molecular weight polymer and residual reactant polymers. The polymer was reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n = 37570$, PDI = 1.08; Figure 4D), Triple detection ($M_n = 45240$, PDI = 1.01) (Table 1) and ¹H NMR (Figure S98).

2.35 Synthesis of hepta-cyclic architecture (35) by CuAAC

Polymer TIPS-≡(N₃-PSTY₂₈)₃-N₃-(PSTY₂₈-N₃)₃-≡-TIPS **30** (4.2×10⁻² g, 1.9×10⁻⁶ mol), polymer c-PSTY₂₅= 17 (3.7×10⁻² g, 1.5×10⁻⁵ mol) and PMDETA (2.8×10⁻³ mL, 1.3×10⁻⁵ mol) were dissolved in 0.8 mL of dry toluene in a 4 mL vial. Cu(I)Br (1.9×10⁻³ g, 1.3×10⁻⁵ mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu wire (0.1 g, 1.5×10^{-3} mol). Both vessels were purged with argon for 15 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 36630$, PDI = 1.17). The polymer was purified by preparative SEC to remove undesired high molecular weight polymer and residual reactant polymers. The polymer was reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n =$ 33610, PDI = 1.06; Figure 4E), Triple detection ($M_n = 42940$, PDI = 1.01) (Table 1) and ¹H NMR (Figure S99).

2.36 Synthesis of hepta-dendron architecture (36) by CuAAC

Polymer TIPS-= $(N_3$ -PSTY₂₈)₃-N₃-(PSTY₂₈-N₃)₃-=-TIPS **30** (2.1×10⁻² g, 9.6×10⁻⁷ mol), polymer (PSTY₂₈)₂-PSTY₂₀-≡ **11** (6.0×10⁻² g, 7.7×10⁻⁶ mol) and PMDETA (1.4×10⁻³ mL, 6.7×10⁻⁶ mol) were dissolved in 0.8 mL of dry toluene in a 4 mL vial. Cu(I)Br (9.7×10⁻⁴ g, 9.9×10⁻⁶ mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu wire (0.1 g, 1.5×10^{-10} ³ mol). Both vessels were purged with argon for 15 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 38830$, PDI = 1.21). The polymer was purified by preparative SEC to remove undesired high molecular weight polymer and residual reactant polymers. The polymer was reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n =$ 70950, PDI = 1.12; Figure 4E), Triple detection ($M_n = 83100$, PDI = 1.01) (Table 1) and ¹H NMR (Figure S100).

2.37 Synthesis of TIPS-=(HO-PSTY₂₈)₂-= (37) by CuAAC

Polymer TIPS- \equiv (OH-PSTY₂₈)₂-N₃ **21b** (2.5 g, 3.7×10^{-4} mol) and propargyl ether (7.0×10^{-1} g, 7.5×10^{-3} mol) and PMDETA (7.8×10^{-2} mL, 3.7×10^{-4} mol) were dissolved in 10 mL of dry toluene in a 20 mL vial. Cu(I)Br (5.3×10^{-2} g, 3.7×10^{-4} mol) was taken in a 20 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.25 g, 3.9×10^{-3} mol). Both vessels were purged with argon for 30 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 25 °C. The reaction was stopped after 1.5 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by

rotary evaporator and the polymer recovered by precipitated in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 6700$, PDI = 1.08). The polymer was purified by preparative SEC and recovered by precipitation. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n = 6820$, PDI = 1.07; Figure S101) (Table S1). The polymer was further characterized by ¹H NMR (Figure S102) and MALDI-ToF (Figure S103).

2.38 Synthesis of TIPS-≡(Br-PSTY₂₈)₂-(HO-PSTY₂₈)₂-≡-TIPS (38) by CuAAC

Polymer TIPS-=(Br-PSTY₂₈)₂-N₃ **22b** (1.6 g, 2.3×10^{-4} mol), TIPS-=(HO-PSTY₂₈)₂-= **37** (1.6 g, 2.3×10^{-4} mol) and PMDETA (4.9×10^{-2} mL, 2.3×10^{-4} mol) were dissolved in 10 mL of dry toluene in a 20 mL vial. Cu(I)Br (3.3×10^{-2} g, 2.3×10^{-4} mol) was taken in a 20 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.25 g, 3.9×10^{-3} mol). Both vessels were purged with argon for 30 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 25 °C. The reaction was stopped after 1.5 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitated in 20-fold excess of MeOH, collected by vacuum for 24 h at 25 °C; SEC (M_n = 12770, PDI = 1.18; Figure S104) (Table S1). The polymer was further characterized by ¹H NMR (Figure S105) and MALDI-ToF (Figure 5A).

2.39 Synthesis of TIPS-= $(N_3$ -PSTY₂₈)₂-(HO-PSTY₂₈)₂-=-TIPS (39) by Azidation with NaN₃ TIPS-=(Br-PSTY₂₈)₂-(HO-PSTY₂₈)₂-=-TIPS 38 (3.1 g, 2.2×10⁻⁴ mol), was dissolved in 20 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (5.7×10⁻¹ g, 8.9×10⁻³ mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 12630$, PDI = 1.13). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 13320$, PDI = 1.05; Figure S106) (Table S1). The polymer was further characterized by ¹H NMR (Figure S107) and MALDI-ToF (Figure 5B).

2.40 Synthesis of TIPS-=(Dendron-PSTY₂₈)₂-(HO-PSTY₂₈)₂-=-TIPS (40) by CuAAC

Polymer TIPS-= $(N_3$ -PSTY₂₈)₂-(HO-PSTY₂₈)₂-=-TIPS **39** (1.4×10^{-1} g, 6.4×10^{-6} mol), polymer (PSTY₂₈)₂-PSTY₂₀-= **11** (1.5×10^{-1} g, 1.9×10^{-5} mol) and PMDETA (2.6×10^{-3} mL, 1.2×10^{-5} mol) were dissolved in 3 mL of dry toluene in a 7 mL vial. Cu(I)Br (1.8×10^{-3} g, 2.6×10^{-3} mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.25 g, 3.9×10^{-3} mol). Both vessels were purged with argon for 30 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC ($M_n = 21320$, PDI = 1.29; Figure S108) (Table S1), ¹H NMR (Figure S109).

2.41 Synthesis of TIPS-=(Dendron-PSTY₂₈)₂-(Br-PSTY₂₈)₂-=-TIPS (41)

TIPS-=(Dendron-PSTY₂₈)₂-(HO-PSTY₂₈)₂-=-TIPS **40** (2.3×10^{-1} g, 8.1×10^{-6} mmol), TEA (4.5×10^{-2} mL, 3.2×10^{-4} mol) were dissolved in 2 ml of dry THF in a 10 mL schlenk tube and purged for 10 min. The reaction mixture was cooled on ice and a solution of 2-bromopropionyl bromide (3.5×10^{-2} mL, 4.2×10^{-3} mol) in 2 mL of dry THF was transferred drop-wise to the schlenk tube by applying argon pressure using double tip needle. The reaction mixture was further purged for 2 minutes and then stirred for 48 h at room temperature. The polymer was precipitated into MeOH, filtered and washed exhaustively

with MeOH. The polymer was dried for 24 h under high vacuum at 25 °C. SEC ($M_n = 22880$, PDI = 1.23; Figure S110) (Table S1), ¹H NMR (Figure S111).

2.42 Synthesis of TIPS-≡(Dendron-PSTY₂₈)₂-(N₃-PSTY₂₈)₂-≡-TIPS by Azidation with NaN₃ (42)

TIPS- \equiv (Dendron-PSTY₂₈)₂-(Br-PSTY₂₈)₂- \equiv -TIPS **41** (1.9×10⁻¹ g, 6.7×10⁻⁶ mol), was dissolved in 2.5 mL of DMF in a reaction vessel equipped with a magnetic stirrer. To this solution NaN₃ (2.6×10⁻² g, 4.0×10⁻⁴ mol) was added and the mixture stirred for 24 h at 25 °C. The polymer solution was directly precipitated into MeOH/H₂O (95/5, v/v) (20-fold excess to polymer solution) from DMF, recovered by vacuum filtration and washed exhaustively with water and MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 21580, PDI = 1.26). The polymer was further purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 21580, PDI = 1.26). The polymer was firther purified by preparative SEC, and reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 21690, PDI = 1.08; Figure 6A), Triple detection (M_n = 31950, PDI = 1.01) (Table 1), ¹H NMR (Figure S114).

2.43 Synthesis of TIPS-=(Dendron-PSTY₂₈)₂-(Cyclic-PSTY₂₈)₂-=-TIPS (43) by CuAAC

Polymer TIPS- \equiv (Dendron-PSTY₂₈)₂-(N₃-PSTY₂₈)₂- \equiv -TIPS **42** (7.0×10⁻² g, 2.4×10⁻⁶ mol), polymer c-PSTY₂₅- \equiv **17** (1.7×10⁻² g, 7.2×10⁻⁶ mol) and PMDETA (1.0×10⁻³ mL, 4.8×10⁻⁶ mol) were dissolved in 0.8 mL of dry toluene in a 4 mL vial. Cu(I)Br (6.9×10⁻⁴ g, 4.8×10⁻⁶ mol) was taken in a 10 mL schlenk tube equipped with magnetic stirrer wrapped with Cu *wire* (0.1 g, 1.5×10⁻³ mol). Both vessels were purged with argon for 15 min. The polymer solution was then transferred to the schlenk tube by applying argon pressure using a double tip needle, and the tube was placed in a temperature controlled oil bath at 50 °C. The reaction was stopped after 1 h and diluted with THF, and the copper salts were removed by passage through an activated basic alumina column. The solvent was removed by rotary evaporator and the polymer recovered by precipitation in 20-fold excess of MeOH, collected by vacuum filtration and washed exhaustively with MeOH. The polymer was dried under high vacuum for 24 h at 25 °C; SEC (M_n = 31440, PDI = 1.16). The polymer was purified by preparative SEC to remove undesired high molecular weight polymer and

residual reactant polymers. The polymer was reprecipitated in 10x volume MeOH, and recovered by vacuum filtration. The polymer was dried under high vacuum for 24 h at 25 °C. SEC ($M_n =$ 31170, PDI = 1.08; Figure 6B), Triple detection ($M_n =$ 38520, PDI = 1.01) and ¹H NMR (Figure S115) (Table 1).

Polymer	RI detection ^a			Purity by LND	Coupling efficiency (%) ^b LND	Mn by NMR	Triple detection ^c			(Mn, _{RI} /Mn, _{TD}) ^e
	Mn	Мр	PDI		. ,		Mn	Мр	PDI ^d	
6	2820	2950	1.10			3110				
7	2900	3050	1.10			3110				
8	2300	2410	1.09			2430				
9	6990	7850	1.13	88	90	8750	8590	8690	1.014	
10	7280	8000	1.11	88		8760	8680	8750	1.01	
11_crude	7510	8140	1.10	88						
11_prep	7860	8080	1.03	98		8850	8640	8980	1.009	0.89
12	3220	3290	1.07			3250				
12b	3150	3250	1.09			3250				
12c	2890	2900	1.11			3120				
13	2880	2900	1.11			2980				
14_crude	2550	2200	1.57	84						
14_prep	2140	2180	1.04	99		2980	2780	2860	1.016	
15	2350	2400	1.04			3110				
16	2250	2300	1.04			3180	2930	3090	1.018	
17	2440	2470	1.04			3520	3170	3320	1.021	0.77
18	3450	3570	1.06			3460				
18b	3410	3550	1.08			3460				
19	3540	3630	1.05			3470				
19b	3530	3660	1.07			3470				
20	6480	6950	1.08	93	93	7030				
20b	6610	6860	1.08	92	93					
21 crude	6980	6990	1.08	92						
21 prep	7000	7110	1.00	98		7020				
21b crude	6660	6940	1.07	92						
22 -	7170	7210	1.07			7320				
22b crude	6830	7090	1.07	92						
22b prep	7080	7220	1.00	99.5		7220				
23 crude	7180	7210	1.01	95						
23 prep	7160	7270	1.03	99		7350				
24	9050	10260	1.05		87	10460				
25 crude	8610	10200	1.10	84						
25 prep	10670	10770	1.10	98						
26	9090	10750	1.04	86		10910				
27 crude	8970	10730	1.12	85						
27 prep	10830	10980	1.03	98		10930				
28	15450	20620	1.05	75	75	21100				
29	17000	21180	1.12	77		22180				
30 crude	16810	21150	1.12	75						
30 prep	21720	21130	1.12	98		22170				
37 crude	6700	6900	1.04	92						
37 prep	6820	7020	1.00	99.5		6880				
38 crude	12770	13000	1.07	85		16690				
39 crude	12770	13050	1.10	80		10070				
39 pren	12030	13750	1.15	97		15600				
40 crude	21320	28240	1.05	81	92	32160				
41 crude	21320	28170	1.27	81	/2	32670				
	22000	201/0	1.43	÷1		22070				

Table S1: Purity, Coupling efficiency, Molecular Weight Data (RI and Triple Detection) and change in

 Hydrodynamic Volume for all starting building blocks and products

^aThe molecular weight distribution from SEC (RI detector) was based on a PSTY calibration curve. ^bCuAAC coupling efficiency was determined from the RI SEC traces, and calculated as follows: purity (LND)/max. purity by theory ×100. ^cThe molecular weight distribution determined from DMAc Triple Detection SEC with 0.03 wt % of LiCl as eluent. ^dPDI values from triple detection underestimate the true PDI values since light scattering is less sensitive to the low molecular weight part of the distribution. ^e(Mn,_{RI}/Mn,_{TD}).

3 Characterization of initiators and linkers



Figure S1: (a) ¹H NMR (400 MHz) and (b) ¹³C NMR (100 MHz) of 1, recorded in CDCl₃ at 298K



Figure S2: (a) ¹H NMR (400 MHz) and (b) ¹³C NMR (100 MHz) of 2 recorded in CDCl₃ at 298K



Figure S3: (a) ¹H NMR (400 MHz) and (b) ¹³C NMR (100 MHz) of 3, recorded in CDCl₃ at 298K



Figure S4: (a) ¹H NMR (400 MHz) and (b) ¹³C NMR (100 MHz) of 4, recorded in CDCl₃ at 298K



Figure S5: (a) 1 H NMR (400 MHz) and (b) 13 C NMR (100 MHz) of 5, recorded in CDCl₃ at 298K

4 Characterization of PSTY₂₈-Br (6)







Figure S7: ¹H 1D DOSY NMR spectrum of PSTY₂₈-Br (6) recorded in CDCl₃ at 298K (500 MHz).



Figure S8: Full and expanded MALDI-ToF mass spectra of $PSTY_{28}$ -Br (6) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

5 Characterization of PSTY₂₈-N₃ (7)



Figure S9: SEC-RI trace of $PSTY_{28}-N_3$ (7) based on PSTY calibration curve.



Figure S10: ¹H 1D DOSY NMR spectrum of $PSTY_{28}-N_3$ (7) recorded in CDCl₃ at 298K (500 MHz).



Figure S11: Full and expanded MALDI-ToF mass spectra of $PSTY_{28}-N_3$ (7) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

6 Characterization of $(\equiv)_2 PSTY_{20}$ -Br (8)



Figure S12: SEC-RI trace of $(\equiv)_2$ PSTY₂₀-Br (8) based on PSTY calibration curve.



Figure S13: ¹H 1D DOSY NMR spectrum of $(\equiv)_2$ PSTY₂₀-Br (8) recorded in CDCl₃ at 298K (500 MHz).



0.75

0.50

0.25

0.00 -



Figure S14: Full and expanded MALDI-ToF mass spectra of $(\equiv)_2$ PSTY₂₀-Br (8) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.
7 Characterization of (PSTY₂₈)₂-PSTY₂₀-Br (9)



Figure S15: ¹H 1D DOSY NMR spectrum of (PSTY₂₈)₂-PSTY₂₀-Br (9) recorded in CDCl₃ at 298K (500 MHz).

8 Characterization of (PSTY₂₈)₂-PSTY₂₀-N₃ (10)



Figure S16: SEC-RI trace of (PSTY₂₈)₂-PSTY₂₀-N₃ (10) based on PSTY calibration curve.



Figure S17: ¹H 1D DOSY NMR spectrum of $(PSTY_{28})_2$ -PSTY₂₀-N₃ (10) recorded in CDCl₃ at 298K (500 MHz).



9 Characterization of $(PSTY_{28})_2$ -PSTY₂₀= (11)

Figure S18: SEC-RI trace of $(PSTY_{28})_2$ -PSTY₂₀-= (11) crude (a) and purified (b) based on PSTY calibration curve.



Figure S19: ¹H 1D DOSY NMR spectrum of $(PSTY_{28})_2$ -PSTY₂₀-= (11) recorded in CDCl₃ at 298K (500 MHz).

10 Characterization of \equiv (OH)-PSTY₂₈-Br (12)



Figure S20: SEC-RI trace of \equiv (OH)-PSTY₂₈-Br (12) based on PSTY calibration curve.



Figure S21: ¹H 1D DOSY NMR spectrum of \equiv (OH)-PSTY₂₈-Br (12) recorded in CDCl₃ at 298K (500 MHz).



Figure S22: Full and expanded MALDI-ToF mass spectra of \equiv (OH)-PSTY₂₈-Br (12) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

11 Characterization of \equiv (OH)-PSTY₂₈-Br (12b)







Figure S24: ¹H 1D DOSY NMR spectrum of \equiv (OH)-PSTY₂₈-Br (12b) recorded in CDCl₃ at 298K (500 MHz).



Figure S25: Full and expanded MALDI-ToF mass spectra of \equiv (OH)-PSTY₂₈-Br (12b) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

12 Characterization of \equiv (OH)-PSTY₂₅-Br (12c)



Figure S26: SEC-RI trace of \equiv (OH)-PSTY₂₅-Br (12c) based on PSTY calibration curve.



Figure S27: ¹H 1D DOSY NMR spectrum of \equiv (OH)-PSTY₂₅-Br (12c) recorded in CDCl₃ at 298K (500 MHz).



Figure S28: Full and expanded MALDI-ToF mass spectra of \equiv (OH)-PSTY₂₅-Br (12c), acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

13 Characterization of \equiv (OH)-PSTY₂₅-N₃ (13)



Figure S29: SEC-RI trace of \equiv (OH)-PSTY₂₅-N₃ (13) based on PSTY calibration curve.



Figure S30: ¹H 1D DOSY NMR spectrum of \equiv (OH)-PSTY₂₅-N₃ (13) recorded in CDCl₃ at 298K (500 MHz).



Figure S31: Full and expanded MALDI-ToF mass spectra of \equiv (OH)-PSTY₂₅-N₃ (13), acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

14 Characterization of c-PSTY₂₅-OH (14)







Figure S33: ¹H 1D DOSY NMR spectrum of c-PSTY₂₅-OH (14) recorded in CDCl₃ at 298K (500 MHz).



Figure S34: Full and expanded MALDI-ToF mass spectra of c-PSTY₂₅-OH (14), acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

15 Characterization of c-PSTY₂₅-Br (15)







Figure S36: ¹H 1D DOSY NMR spectrum of c-PSTY₂₅-Br (15) recorded in CDCl₃ at 298K (500 MHz).



Figure S37: Full and expanded MALDI-ToF mass spectra of c-PSTY₂₅-Br (15), acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

16 Characterization of c-PSTY₂₅-N₃(16)



Figure S38: SEC-RI trace of c-PSTY₂₅-N₃ (16) based on PSTY calibration curve.



Figure S39: ¹H 1D DOSY NMR spectrum of c-PSTY₂₅-N₃ (16) recorded in CDCl₃ at 298K (500 MHz).



Figure S40: Full and expanded MALDI-ToF mass spectra of c-PSTY₂₅-N₃ (16), acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

17 Characterization of c-PSTY₂₅=(17)







Figure S42: ¹H 1D DOSY NMR spectrum of c-PSTY₂₅- \equiv (17) recorded in CDCl₃ at 298K (500 MHz).



Figure S43: Full and expanded MALDI-ToF mass spectra of c-PSTY₂₅= (17), acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.



Figure S44: SEC trace of TIPS- \equiv -(HO)-PSTY₂₈-Br (18) SEC analysis based on polystyrene calibration curve.



Figure S45: 500 MHz ¹H 1D DOSY NMR spectra in CDCl₃ of TIPS- \equiv -(HO)-PSTY₂₈-Br (18) recorded in CDCl₃ at 298K (500 MHz).



Figure S46: The full and expanded MALDI-ToF mass spectra of TIPS- \equiv -(HO)-PSTY₂₈-Br (18) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

19 Characterization of TIPS-=-(OH)-PSTY₂₈-N₃ (18b)







Figure S48: ¹H 1D DOSY NMR spectrum of TIPS-≡-(HO)-PSTY₂₈-Br (**18b**) recorded in CDCl₃ at 298K (500 MHz).



Figure S49: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv -(HO)-PSTY₂₈-Br (18b) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

20 Characterization of TIPS-≡-(HO)-PSTY₂₈-N₃ (19)



Figure S50: SEC trace of TIPS- \equiv -(HO)-PSTY₂₈-N₃ (19) SEC analysis based on polystyrene calibration curve.



Figure S51: 500 MHz ¹H 1D DOSY NMR spectra in CDCl₃ of TIPS- \equiv -(HO)-PSTY₂₈-N₃ (19) recorded in CDCl₃ at 298K (500 MHz).



Figure S52: The full and expanded MALDI-ToF mass spectra of TIPS- \equiv -(HO)-PSTY₂₈-N₃ (19) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.

21 Characterization of TIPS-=-(OH)-PSTY₂₈-N₃(19b)







Figure S54: ¹H 1D DOSY NMR spectrum of TIPS-≡-(HO)-PSTY₂₈-N₃ (19b) recorded in CDCl₃ at 298K (500 MHz).



Figure S55: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv -(HO)-PSTY₂₈-N₃ (19b) acquired in reflectron mode with Ag salt as cationizing agent and DCTB matrix.



Figure S56: SEC-RI trace of TIPS- \equiv (OH-PSTY₂₈)₂-Br (20) based on PSTY calibration curve.



Figure S57: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (OH-PSTY₂₈)₂-Br (20) recorded in CDCl₃ at 298K (500 MHz).



Figure S58: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (OH-PSTY₂₈)₂-Br (20) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

23 Characterization of TIPS-≡(OH-PSTY₂₈)₂-Br (20b)







Figure S60: ¹H 1D DOSY NMR spectrum of TIPS-≡(OH-PSTY₂₈)₂-Br (**20b**) recorded in CDCl₃ at 298K (500 MHz).



Figure S61: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (OH-PSTY₂₈)₂-Br (20b) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

24 Characterization of TIPS-≡(OH-PSTY₂₈)₂-N₃ (21)



Figure S62: SEC-RI traces of TIPS- \equiv (OH-PSTY₂₈)₂-N₃ (21) crude (a) and purified (b) based on PSTY calibration curve.



Figure S63: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (OH-PSTY₂₈)₂-N₃ (21) recorded in CDCl₃ at 298K (500 MHz).



⁶²⁰⁰ ⁶³⁰⁰ ⁶⁴⁰⁰ _{m/z} ⁶⁰⁰⁰ ⁷⁰⁰⁰ ⁸⁰⁰⁰ _{m/z} **Figure S64:** Full and expanded MALDI-ToF mass spectra of TIPS-≡(OH-PSTY₂₈)₂-N₃ (21) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix..

25 Characterization of TIPS-≡(OH-PSTY₂₈)₂-N₃ (21b)



Figure S65: SEC-RI trace of TIPS-≡(OH-PSTY₂₈)₂-N₃ (21b) based on PSTY calibration curve.



Figure S66: ¹H 1D DOSY NMR spectrum of TIPS-≡(OH-PSTY₂₈)₂-N₃ (**21b**) recorded in CDCl₃ at 298K (500 MHz).



Figure S67: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (OH-PSTY₂₈)₂-N₃ (21b) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

26 Characterization of TIPS-≡(Br-PSTY₂₈)₂-N₃ (22)



Figure S68: SEC-RI trace of TIPS- \equiv (Br-PSTY₂₈)₂-N₃ (22) based on PSTY calibration curve.



Figure S69: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Br-PSTY₂₈)₂-N₃ (22) recorded in CDCl₃ at 298K (500 MHz).



Figure S70: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (Br-PSTY₂₈)₂-N₃ (22) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

27 Characterization of TIPS-=(Br-PSTY₂₈)₂-N₃ (22b)



Figure S71: SEC-RI trace of TIPS- \equiv (Br-PSTY₂₈)₂-N₃ (22b) crude (a) and purified (b) based on PSTY calibration curve.



Figure S72: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Br-PSTY₂₈)₂-N₃ (**22b**) recorded in CDCl₃ at 298K (500 MHz).



0 -

m/z m/z **Figure S73:** Full and expanded MALDI-ToF mass spectra TIPS= $(Br-PSTY_{28})_2$ -N₃ (22b) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

28 Characterization of TIPS-≡(N₃-PSTY₂₈)₂-N₃ (23)



Figure S74: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (N₃-PSTY₂₈)₂-N₃ (23) recorded in CDCl₃ at 298K (500 MHz).



Figure S75: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (N₃-PSTY₂₈)₂-N₃ (23) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.



Figure S76: SEC-RI trace of TIPS-≡(HO-PSTY₂₈)₃-Br (24) based on PSTY calibration curve.



Figure S77: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (HO-PSTY₂₈)₃-Br (24) recorded in CDCl₃ at 298K (500 MHz).



Figure S78: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (HO-PSTY₂₈)₃-Br (24) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.



Figure S79: SEC-RI trace of TIPS- \equiv (HO-PSTY₂₈)₃-N₃ (25) crude (a) and purified (b) based on PSTY calibration curve.



Figure S80: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (HO-PSTY₂₈)₃-N₃ (25) recorded in CDCl₃ at 298K (500 MHz).



Figure S81: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (HO-PSTY₂₈)₃-N₃ (25) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.



Figure S82: SEC-RI trace of TIPS-=(Br-PSTY₂₈)₃-N₃ (26) based on PSTY calibration curve.



Figure S83: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Br-PSTY₂₈)₃-N₃ (26) recorded in CDCl₃ at 298K (500 MHz).



Figure S84: Full and expanded MALDI-ToF mass spectra of TIPS= $(Br-PSTY_{28})_3-N_3$ (26) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

32 Characterization of TIPS-≡(N₃-PSTY₂₈)₃-N₃ (27)



Figure S85: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (N₃-PSTY₂₈)₃-N₃ (27) recorded in CDCl₃ at 298K (500 MHz).



Figure S86: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (N₃-PSTY₂₈)₃-N₃ (27) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.



Figure S87: SEC-RI trace of TIPS- \equiv (HO-PSTY₂₈)₃-HO-(PSTY₂₈-OH)₃- \equiv -TIPS (28) based on PSTY calibration curve.



Figure S88: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (HO-PSTY₂₈)₃-HO-(PSTY₂₈-OH)₃- \equiv -TIPS (28) recorded in CDCl₃ at 298K (500 MHz).



Figure S89: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (HO-PSTY₂₈)₃-HO-(PSTY₂₈-OH)₃- \equiv -TIPS (28) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.



Figure S90: SEC-RI trace of TIPS- \equiv (Br-PSTY₂₈)₃-Br-(PSTY₂₈-Br)₃- \equiv -TIPS (29) based on PSTY calibration curve.



Figure S91: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Br-PSTY₂₈)₃-Br-(PSTY₂₈-Br)₃- \equiv -TIPS (29) recorded in CDCl₃ at 298K (500 MHz).



Figure S92: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (Br-PSTY₂₈)₃-Br-(PSTY₂₈-Br)₃- \equiv -TIPS (29) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix.

35 Characterization of TIPS-≡(N₃-PSTY₂₈)₃-N₃-(PSTY₂₈-N₃)₃-≡-TIPS (30)



Figure S93: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (N₃-PSTY₂₈)₃-N₃-(PSTY₂₈-N₃)₃- \equiv -TIPS (30) recorded in CDCl₃ at 298K (500 MHz).



Figure S94: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (N₃-PSTY₂₈)₃-N₃-(PSTY₂₈-N₃)₃- \equiv -TIPS (**30**) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix..

36 Characterization of tri-cyclic architecture (31)



(500 MHz).

37 Characterization of tri_dendron architecture (32)



Figure S96: ¹H 1D DOSY NMR spectrum of tri_dendron architecture (**32**) recorded in CDCl₃ at 298K (500 MHz).

38 Characterization of tetra_cyclic architecture (33)



Figure S97: ¹H 1D DOSY NMR spectrum of tetra_cyclic architecture (**33**) recorded in CDCl₃ at 298K (500 MHz).

39 Characterization of tetra_dendron architecture (34)



Figure S98: ¹H 1D DOSY NMR spectrum of tetra_dendron architecture (**34**) recorded in CDCl₃ at 298K (500 MHz).



Figure S99: ¹H 1D DOSY NMR spectrum of hepta_cyclic architecture (**35**) recorded in CDCl₃ at 298K (500 MHz).

41 Characterization of hepta_dendron architecture (36)



Figure S100: ¹H 1D DOSY NMR spectrum of hepta_dendron architecture (**36**) recorded in CDCl₃ at 298K (500 MHz).

42 Characterization of TIPS-≡(HO-PSTY₂₈)₂-≡ (37)



Figure S101: SEC-RI trace of TIPS- \equiv (HO-PSTY₂₈)₂- \equiv (37) crude (a) and purified (b) based on PSTY calibration curve.



Figure S102: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (HO-PSTY₂₈)₂- \equiv (**37**) recorded in CDCl₃ at 298K (500 MHz).



Figure S103: Full and expanded MALDI-ToF mass spectra of TIPS- \equiv (HO-PSTY₂₈)₂- \equiv (37) acquired in linear mode with Ag salt as cationizing agent and DCTB matrix..


Figure S104: SEC-RI trace of TIPS- \equiv (Br-PSTY₂₈)₂-(HO-PSTY₂₈)₂- \equiv -TIPS (**38**) based on PSTY calibration curve.



Figure S105: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Br-PSTY₂₈)₂-(HO-PSTY₂₈)₂- \equiv -TIPS (38) recorded in CDCl₃ at 298K (500 MHz).





Figure S106: SEC-RI trace of TIPS- \equiv (N₃-PSTY₂₈)₂-(HO-PSTY₂₈)₂- \equiv -TIPS (**39**) crude (a) and purified (b) based on PSTY calibration curve.



recorded in CDCl₃ at 298K (500 MHz).

45 Characterization of TIPS-≡(Dendron-PSTY₂₈)₂-(HO-PSTY₂₈)₂-≡-TIPS (40)



Figure S108: SEC-RI trace of TIPS- \equiv (Dendron-PSTY₂₈)₂-(HO-PSTY₂₈)₂- \equiv -TIPS (40) based on PSTY calibration curve.



Figure S109: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Dendron-PSTY₂₈)₂-(HO-PSTY₂₈)₂- \equiv -TIPS (40) recorded in CDCl₃ at 298K (500 MHz).

46 Characterization of TIPS-≡(Dendron-PSTY₂₈)₂-(Br-PSTY₂₈)₂-≡-TIPS (41)



Figure S110: SEC-RI trace of TIPS- \equiv (Dendron-PSTY₂₈)₂-(Br-PSTY₂₈)₂- \equiv -TIPS (41) based on PSTY calibration curve.



Figure S111: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Dendron-PSTY₂₈)₂-(Br-PSTY₂₈)₂- \equiv -TIPS (41) recorded in CDCl₃ at 298K (500 MHz).

47 Characterization of TIPS-≡(Dendron-PSTY₂₈)₂-(N₃-PSTY₂₈)₂-≡-TIPS (42)



Figure S112: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Dendron-PSTY₂₈)₂-(N₃-PSTY₂₈)₂- \equiv -TIPS (42) recorded in CDCl₃ at 298K (500 MHz).

49 Characterization of TIPS-=(Dendron-PSTY₂₈)₂-(Cyclic-PSTY₂₈)₂-=-TIPS (43)



Figure S113: ¹H 1D DOSY NMR spectrum of TIPS- \equiv (Dendron-PSTY₂₈)₂-(Cyclic-PSTY₂₈)₂- \equiv -TIPS (43) recorded in CDCl₃ at 298K (500 MHz).

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