Electronic Supplementary Information (ESI)

for

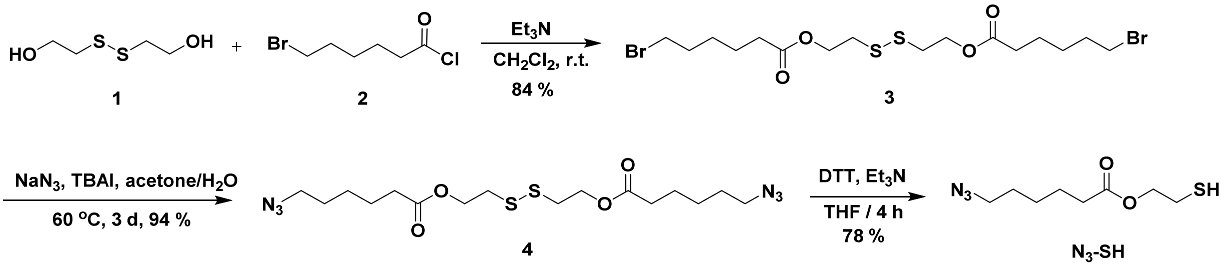
Mixed [2:6] Hetero-Arm Star Polymers Based on Janus POSS with Precisely Defined Arm Distribution

Yu Shao,[a] *Hang Yin,*[a] *Xiao-Man Wang,*[a] *Shuai-Yuan Han,*[a] *Xuesheng Yan,*[b] *Jun Xu,*[b] *Jinlin He,*[*,b]
Peihong Ni,[b] *and Wen-Bin Zhang*[*,a]

[a.] Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Polymer Chemistry & Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China. E-mail: wenbin@pku.edu.cn

[b.] College of Chemistry, Chemical Engineering and Materials Science, State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Soochow University, Suzhou 215123, P. R. China. E-mail: jlhe@suda.edu.cn

Synthetic Procedures

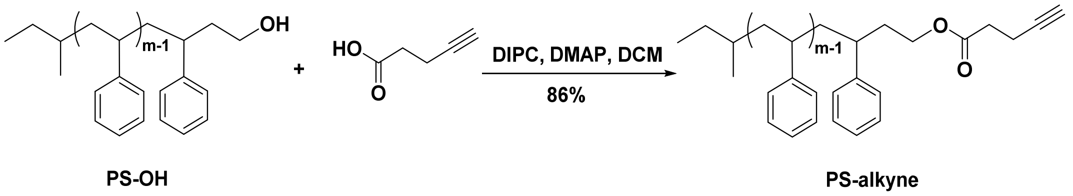


Scheme S1. Synthesis of the “click adaptor”, N_3-SH.

Dibromide ***3***. Bis(hydroxyethyl)disulfide (8.38 g, 54.0 mmol) and 6-bromohexanoyl chloride (25 g, 130 mmol) were dissolved in CH_2Cl_2 (400 mL) at 0 °C, and then the solution of Et_3N in CH_2Cl_2 was added to the mixture. The solution was stirred for 30 min in the cold and for 2 days at room temperature. CH_2Cl_2 (500 mL) was added to dilute the mixture and the diluted solution was washed with 1 M HCl, 1 M $NaHCO_3$, and brine, respectively. The organic layer was dried over Na_2SO_4 and then the filtrate was concentrated under vacuum. The crude product was purified by column chromatography on silica gel using a CH_2Cl_2:hexane (v/v = 7/3) mixture as eluent. The product was obtained as green oil (23.02 g, 84 %). The characterizations are identical to previous reports.[1]

Diazide ***4***. Dibromide **3** (27 g, 32.1 mmol) and NaN_3 (6.28 g, 96.4 mmol) were dissolved in DMF, TBAI (2.37 g, 6.42 mmol) was added and the mixture was kept at 50 °C for 60 h. The mixture was then extracted with CH_2Cl_2, the organic layer was washed with brine, and dried with Na_2SO_4. The solvent was removed under vacuum to get yellow oil which was further purified by column chromatography on silica gel using CH_2Cl_2:hexane (v/v = 7/3) as eluent. The product was obtained as a yellow oil (13.00 g). Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 4.34 (t, J =6.5 Hz, 4H), 3.28 (t, J=6.8 Hz, 4H), 2.93 (t, J=6.5 Hz, 4H), 2.35 (t, J=7.4 Hz, 4H), 1.75-1.55 (m, 8H), 1.50-1.24 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): 173.16, 62.08, 51.18, 37.23, 33.89, 28.51, 26.18, 24.35.

N_3-SH. Diazide **4** (187 mg, 0.432 mmol), DTT (80 mg, 0.519 mmol), and Et_3N (218 mg, 2.16 mmol) were completely dissolved in 20 mL THF. The solution was stirred at room temperature for 4 h under argon. THF was then evaporated under vacuum. The residue was purified by flash column chromatography on silica gel with hexanes:EA (v/v = 10/1) as eluent to afford the target product (220 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 4.20 (t, *J* =6.6 Hz, 2H), 3.28 (t, *J*=6.8 Hz, 2H), 2.78-2.72 (dt, *J*=8.4, 6.6 Hz, 2H), 2.35 (t, *J*=7.4 Hz, 2H), 1.71-1.60 (m, 4H), 1.52-1.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): 173.12, 65.61, 51.22, 33.92, 28.55, 26.23, 24.42, 23.32.



Scheme S2. Synthesis of PS-alkyne by Steglich esterification.

PS-alkyne. To a 250 mL round-bottom glass flask equipped with a magnetic stir bar was added PS-OH (1.5 g, M_n = 1.6 kDa, 1 mmol), 4-pentynoic acid (147 mg 1.5 mmol), DMAP (184 mg, 0.3 mmol) and 100 mL dry DCM. After complete dissolution, DIPC (1.9 mL, 1.5 mmol) was added drop-wise through an addition funnel in ice water bath. Then the mixture was left to stir at room temperature overnight, after which it was precipitated into cold methanol three times, filtered and dried in vacuum for 24 hours to give a white powder (1.4 g). Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.36-6.36 (br, 71H), 4.01-3.67 (br, 2H), 2.48-2.35 (br, 2H), 2.12-1.32 (br, 42H), 0.78-0.63 (m 6H).^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): 171.46, 145.32, 128.01, 127.61, 125.62, 82.48, 68.93, 62.89, 43.83, 40.32, 33.17, 31.48, 14.23, 11.05. SEC: M_n

= 1.8 kDa, PDI = 1.06. MS (MALDI-TOF, Da, Figure S10): Calcd. mass for 13-mer [M·Na$^+$] ($C_{115}H_{122}O_2Na$): 1557.9; Found: 1557.8.

Ring-opening Polymerization of ε-CL. A Schlenk flask equipped with a magnetic stirrer was connected to a high vacuum line and flame-dried three times. After cooling down to room temperature, the flask was transferred into glove box, then $T_8V_6(OH)_2$ (30 mg, 0.045 mmol), ε-CL (0.96g, 9.0 mmol), 5 mL of anhydrous toluene, and $Sn(Oct)_2$ (1.0 M in toluene, 0.045 mL, 0.045mmol) were added. The flask was then placed into an oil bath of 65 °C. After 5 hours, the flask was cooled in ice-water. The mixture was then precipitated into cold methanol three times. The resulting white solids were collected after filtration and dried at 25 °C under vacuum overnight to give 0.44 g of $T_8V_6PCL_2$ as a white powder.

p-$T_8V_6PCL_2$. Yield: 40%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, *δ*): 6.15-5.86 (m, 18H, -C*H*=C*H*$_2$), 4.21 (t, *J*=8.4, 4H, -CH_2O-), 4.07(t, *J*=6.8, 100H), 3.66 (br, 4H, -CH_2OH), 2.31 (t, *J*=7.6, 104H), 1.62 (m, 218H), 1.38 (m, 104H), 1.20 (t, *J*=8.4, 4H, -$SiCH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, *δ*): 173.17, 136.68, 128.15, 63.80, 63.78, 62.04, 60.16, 33.80, 33.78, 32.04, 28.04, 25.22, 25.06, 24.43, 24.26. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm, *δ*): -68.76, -80.30. FT-IR (KBr) ν (cm^{-1}): 2945, 2866, 1726 (very strong), 1631, 1472, 1420, 1369, 1296, 1243, 1191, 1108, 1045,962, 732.

m-$T_8V_6PCL_2$. Yield: 46%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, *δ*): 6.14-5.85 (m, 18H, -C*H*=C*H*$_2$), 4.22 (t, *J*=8.4, 4H, -CH_2O-), 4.07 (t, *J*=6.8, 138H), 3.66 (t, *J*=6.8, 4H, -CH_2OH), 2.31 (t, *J*=7.6, 138H), 1.66 (m, 286H), 1.39 (m, 134H), 1.19 (t, *J*=8.0, 4H, -$SiCH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, *δ*): 173.20, 136.89, 128.19, 63.83, 62.11, 60.16, 33.82, 32.07, 28.07, 25.25, 25.09, 24.46, 24.29. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm, *δ*): -68.76, -80.16, -80.29, -80.44. FT-IR (KBr) ν (cm^{-1}):

2944, 2866, 1728 (very strong), 1631, 1470, 1418, 1367, 1295, 1242, 1187, 1109, 1046, 962, 732.

o-$T_8V_6PCL_2$. Yield: 45 %. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, *δ*): 6.15-5.86 (m, 18H, -C*H*=C*H*$_2$), 4.21 (t, *J*=8.4, 4H, -CH_2O-), 4.07 (t, *J*=6.8, 128H), 3.66 (t, *J*=6.8, 4H, -CH_2OH), 2.31 (t, *J*=7.6, 130H), 1.66 (m, 270H), 1.39 (m, 128H) 1.19 (t, *J*=8.4, 4H, -$SiCH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, *δ*): 173.49, 128.39, 62.57, 60.42, 58.39, 34.09, 32.30, 28.32, 25.50, 24.54, 18.39. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm, *δ*): -68.87, -80.13, -80.28. FT-IR (KBr) v (cm^{-1}): 2947, 2866, 1727 (very strong), 1635, 1470, 1418, 1367, 1295, 1242, 1187, 1109, 1046, 962, 732.

Thiol-ene Functionalization. In an open vial, $T_8V_6PCL_2$ (100 mg, 11.8 µmol, 1 eq.), 5-azidopentyl 3-mercaptopropanoate (23 mg, 0.106 mmol, 9 eq., 1.5 eq. per vinyl), and DMPA (0.5 mg, 2.3 µmol) were mixed and dissolved in 1.0 mL of $CHCl_3$. After irradiation with UV 365 nm for 15 min, the mixture was purified by repeated precipitations in cold methanol to give $T_8A_6PCL_2$ as a white powder.

p-$T_8A_6PCL_2$. 192 mg, Yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, *δ*):4.22 (t, *J*=7.2, 16H, -CH_2O-), 4.06 (t, *J*=6.8, 100H), 3.65 (t, *J*=6.8, 4H, -CH_2OH), 3.29 (t, *J*=6.8, 12H, -CH_2N_3), 2.76 (t, *J*=6.8, 12H), 2.66 (*J*=8.4, 12H), 2.31 (t, *J*=7.6, 104H), 1.65 (m, 218H), 1.38 (m, 104H) 1.16 (t, *J*=6.8, 4H, -$SiCH_2$-), 1.04 (t, *J*=8.4, 12H, -$SiCH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, *δ*): 173.17, 63.68, 62.23, 60.11, 50.44, 33.80, 31.78, 28.04, 25.62, 25.16, 24.33, 24.16. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm, *δ*): -68.87, -69.18. FT-IR (KBr) v (cm^{-1}): 2944, 2865, 2096, 1727 (very strong), 1634, 1470, 1420, 1367, 1296, 1244, 1188, 1107, 1045, 1027, 962, 731.

m-$T_8A_6PCL_2$. 192 mg, Yield: 84%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm, *δ*):4.22 (t, *J*=6.8, 16H, -CH_2O-), 4.06 (t, *J*=6.8, 138H), 3.65 (t, *J*=6.4, 4H, -CH_2OH), 3.29 (t, *J*=6.8, 12H, -CH_2N_3), 2.77 (t, *J*=6.8, 12H), 2.66 (t, *J*=8.0, 12H), 2.31 (t, *J*=7.6, 138H), 1.65 (m, 286H), 1.38 (m, 134H) 1.19 (br,4H, -$SiCH_2$-), 1.05 (br, 12H, -$SiCH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): 173.10, 63.70, 62.11, 60.16, 50.79, 33.73, 31.96, 27.95, 25.82, 25.14, 24.36, 24.29. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm, δ): -68.84, -69.16. FT-IR (KBr) v (cm^{-1}): 2946, 2866, 2098, 1726 (very strong), 1623, 1470, 1420, 1367, 1295, 1243, 1188, 1107, 1046, 962, 732.

o-$T_8A_6PCL_2$. Yield: 80%. ^1H NMR (400 MHz, $CDCl_3$, ppm, δ):4.11 (t, *J*=6.8, 16H, -CH_2O-), 3.95 (t, *J*=6.4, 128H), 3.51 (t, *J*=4.8, 4H, -CH_2OH), 3.17 (t, *J*=6.4, 12H, -CH_2N_3), 2.65 (t, *J*=6.8, 12H), 2.55 (t, *J*=8.0, 12H), 2.19 (t, *J*=6.8, 130H), 1.53 (m, 270H), 1.27 (m, 128H), 1.04 (t, *J*=8.4, 4H, -$SiCH_2$-), 0.94 (t, *J*=7.6, 12H, -$SiCH_2$-). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, δ): 173.49, 64.08, 51.06, 34.05, 30.14, 26.07, 25.46, 25.38, 24.51, 24.43. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm, δ): -68.82, -69.13. FT-IR (KBr) v (cm^{-1}): 2947, 2866, 2098, 1729 (very strong), 1631, 1470, 1418, 1367, 1295, 1243, 1189, 1107, 1046, 962, 732.

"Clicking" Polystyrene toward Mixed-arm Stars. To a mixture of the $T_8A_6PCL_2$ and PS-alkyne (2 eq. per azide) in degassed toluene was added one drop of PMDETA and then CuBr in the glove box. The colorless clear solution was then stirred at 25 °C for 24 h. The reaction mixture was concentrated, applied to the top of a short column of silica gel. The column was eluted with toluene first to recollect the excess starting material PS-alkyne. It was then further elute with THF to get the desired product in solution. Then the solution was concentrated and precipitated in cold methanol three times and dried in vacuum at 60 °C to give a white powder.

p-$T_8PS_6PCL_2$. Yield: 65%. ^1H NMR (400 MHz, $CDCl_3$, ppm, δ): 7.44-6.32 (m, 400H), 4.52-4.19 (br, 28H), 4.08 (t, *J*=6.4, 100H), 3.90-3.61 (br, 16H), 2.89 (br, 12H), 2.73 (br, 12H), 2.65 (br, 12H), 2.50 (br, 12H), 2.33 (t, *J*=7.2, 104H), 1.88 and 1.46 (br, 240H), 1.66 (br, 218H), 1.41 (br, 130H), 1.07(br, 12H), 0.91 (br, 12H), 0.81-0.54 (br, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, *δ*): 173.52, 128.02, 127.68, 125.66, 64.13, 40.42, 34.11, 29.68, 28.43, 25.52, 24.57. FT-IR (KBr) v (cm^{-1}): 3026, 2926, 2855, 1735 (very strong), 1601, 1493, 1450, 1357, 1236,1163, 1105, 1027, 760, 701.

m-T$_8$PS$_6$PCL$_2$. Yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm, *δ*): 7.34-6.29 (m, 402H), 4.34-4.14 (br, 28H),4.06 (t, *J*=6.0, 138H), 3.91-3.60, (br, 16H), 2.88 (br, 12H), 2.73 (br, 12H), 2.65 (br, 12H), 2.50 (br, 12H), 2.30 (t, *J*=7.6, 138H), 1.85 and 1.46 (br, 241H),1.65 (br, 286H, -O*H*), 1.38 (br, 134H), 1.05(br, 12H), 0.88 (br, 12H), 0.80-0.64 (br, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, *δ*): 173.40, 127.94, 127.56, 125.56, 64.03, 40.30, 37.28, 37.00, 34.02, 33.61, 33.33, 32.65, 31.84, 30.05, 29.60, 29.27, 28.89, 28.26, 26.99, 26.61, 25.44, 24.48. FT-IR (KBr) v (cm^{-1}): 3025, 2931, 2862, 1726 (very strong), 1600, 1493, 1453, 1369, 1295, 1244, 1192, 1106, 1046, 760, 700.

o-T$_8$PS$_6$PCL$_2$. Yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$, ppm, *δ*): 7.32-6.32 (br, 401H), 4.51-4.19 (m, 28H),4.08 (t, *J*=6.8, 128H), 3.91-3.62 (br, 16H), 2.89 (br, 12H), 2.75 (br, 12H), 2.67 (br, 12H), 2.50 (br, 12H), 2.32 (t, *J*=7.6, 130H), 1.85 and 1.46 (br, 241H), 1.69 (br, 270H, -O*H*), 1.40 (br, 128H), 1.07 (br, 12H), 0.90 (br, 12H), 0.81-0.64 (br, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm, *δ*): 173.44, 127.84, 127.23, 125.43, 64.11, 40.34, 37.24, 37.03, 34.11, 33.23, 33.34, 32.65, 31.84, 30.05, 29.60, 29.27, 28.89, 28.26, 26.99, 26.61, 25.67, 24.55. FT-IR (KBr) v (cm^{-1}): 3026, 2925, 2852, 1734 (very strong), 1600 1496, 1456, 1359, 1237,1164, 1101, 1043, 760, 701.

For PS-alkyne, the molecular weight calculation was based on the integration ratio in ^1H NMR spectra between the peak of δ 7.36-6.36 ppm ($S_{(\mathrm{Phenyl})}$) and of δ 4.01-3.67 ppm ($S_{(\mathrm{CH_2O})}$) using the following equations where N is the number of repeating units of PS-alkyne, $M_{\mathrm{n,\,PS}}$ is the MW of PS-alkyne, M_{sty} is the MW of the styrene monomer (104 Da) and M_1 is the MW of the rest of the molecule (182 Da):

$$M_{\mathrm{n,\,PS}} = N \times M_{\mathrm{sty}} + M_1$$

$$N = \frac{S_{(Phenyl)}/5}{S_{(CH_2O)}/2}$$

For $T_8V_6PCL_2$, the molecular weight calculation was based on the integration ratio in ^1H NMR spectra between the peak of and δ~2.31 ppm ($S_{(\mathrm{CH_2})}$), which is the methylene group of PCL, and the characteristic peak of the POSS cage (18H) at δ 6.14-5.85 ($S_{(\mathrm{Vinyl})}$) using the following equations where N_1 is the number of repeating units of $\mathrm{T_8V_6PCL_2}$, M_{CL} is the MW of the ε-caprolactone monomer (114 Da) and M_2 is the MW of the initiator $\mathrm{T_8V_6(OH)_2}$ (669 Da):

$$M_{\mathrm{n,\,T_8V_6PCL_2}} = N_1 \times M_{\mathrm{CL}} + M_2$$

$$N_1 = \frac{S_{(CH_2)}/2}{S_{(Vinyl)}/18}$$

For $T_8A_6PCL_2$, the molecular weight calculation was directly calculated from the addition of $M_{\mathrm{n},\ T8V6PCL2}$ and six $\mathrm{N_3}$-SH ligands using the following equations where M_{SH} is the MW of $\mathrm{N_3}$-SH (217 Da):

$$M_{\mathrm{n,\,T_8A_6PCL_2}} = M_{\mathrm{n,\,T_8V_6PCL_2}} + 6 \times M_{\mathrm{SH}}$$

For $T_8PS_6PCL_2$, the molecular weight of PS is calculated based on the integration ratio in ^1H NMR spectra between the peak of δ 7.32-6.32 ppm ($S_{(\mathrm{Phenyl})}$) and the characteristic peak of the PCL (δ ~2.31 ppm, –$\mathrm{CH_2}$–) ($S_{(\mathrm{CH2})}$), respectively, using the following equations where N_2

is the number of repeating units of PS in $T_8PS_6PCL_2$, and M_3 is the MW of the rest of the molecule $T_8A_6(OH)_2$ (2451 Da):

$$M_{n,\,star} = N_1 \times M_{CL} + N_2 \times M_{sty} + M_3$$

$$N_2 = N_1 \times \frac{S_{(Phenyl)} / 5}{S_{(CH_2)} / 2}$$

The average number of PS arms per molecule (n) can be calculated using the following equation.

$$n = \frac{N_2}{N}$$

Table S1. Crystal data and structure refinement for *p*-$T_8V_6OH_2$

Identification code	*p*-$T_8V_6OH_2$
Empirical formula	$C_{16}H_{28}O_{14}Si_8$
Formula weight	669.10
Temperature/K	180.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.6776(5)
b/Å	12.2867(7)
c/Å	14.1117(8)
α/°	88.433(5)
β/°	89.033(4)
γ/°	82.691(4)
Volume/Å^3	1491.65(14)
Z	2
ρ_{calc}g/cm^3	1.490
μ/mm^{-1}	0.421
F(000)	696.0
Crystal size/mm^3	0.1 × 0.1 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.132 to 52.038
Index ranges	$-10 \le h \le 8$, $-15 \le k \le 13$, $-17 \le l \le 11$
Reflections collected	9512
Independent reflections	5853 [R_{int} = 0.0280, R_{sigma} = 0.0585]
Data/restraints/parameters	5853/26/345
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0767, wR_2 = 0.1965
Final R indexes [all data]	R_1 = 0.1114, wR_2 = 0.2366
Largest diff. peak/hole / e Å^{-3}	1.39/-0.78

Table S2. Crystal unit cell parameters for $T_8V_6OH_2$

$T_8V_6(OH)_2$	**a**	**b**	**c**	**α**	**β**	**γ**
p-	8.67	12.28	14.11	88.43	89.03	82.69
m-	13.46	13.45	14.08	90.02	90.14	119.73
o-	12.31	15.87	10.06	90.00	113.91	90.00

Table S3. Summary of ^{29}Si NMR Molecular characterizations of Janus POSS based on mixed [2:6] octakis-adducts

Compound	*Si with B group*			*Si with B group*		
p-$T_8V_6(OH)_2$	-67.98 (2)				-80.37 (6)	
p-$T_8V_6PCL_2$		-68.76 (2)			-80.30 (6)	
p-$T_8A_6PCL_2$		-68.87 (6)	-69.18 (2)			
m-$T_8V_6(OH)_2$	-67.79 (2)			-80.17 (2)	-80.37 (2)	-80.58 (2)
m-$T_8V_6PCL_2$		-68.76 (2)		-80.16 (2)	-80.29 (2)	-80.44 (2)
m-$T_8A_6PCL_2$		-68.48 (6)	-69.16 (2)			
o-$T_8V_6(OH)_2$	-68.02 (2)			-80.16 (2)	-80.38 (4)	
o-$T_8V_6PCL_2$		-68.87 (2)		-80.13 (2)	-80.28 (4)	
o-$T_8A_6PCL_2$		-68.82 (6)	-69.13 (2)			

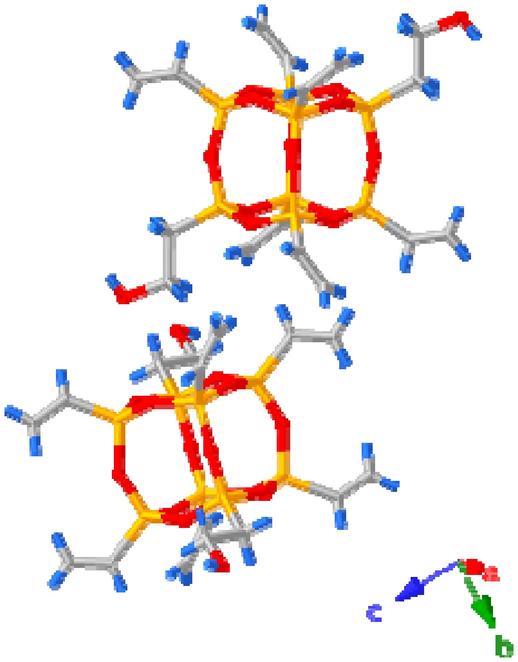


Fig. S1. The structure of *p*-$T_8V_6OH_2$ in the single crystal. Each unit cell contains two molecules.

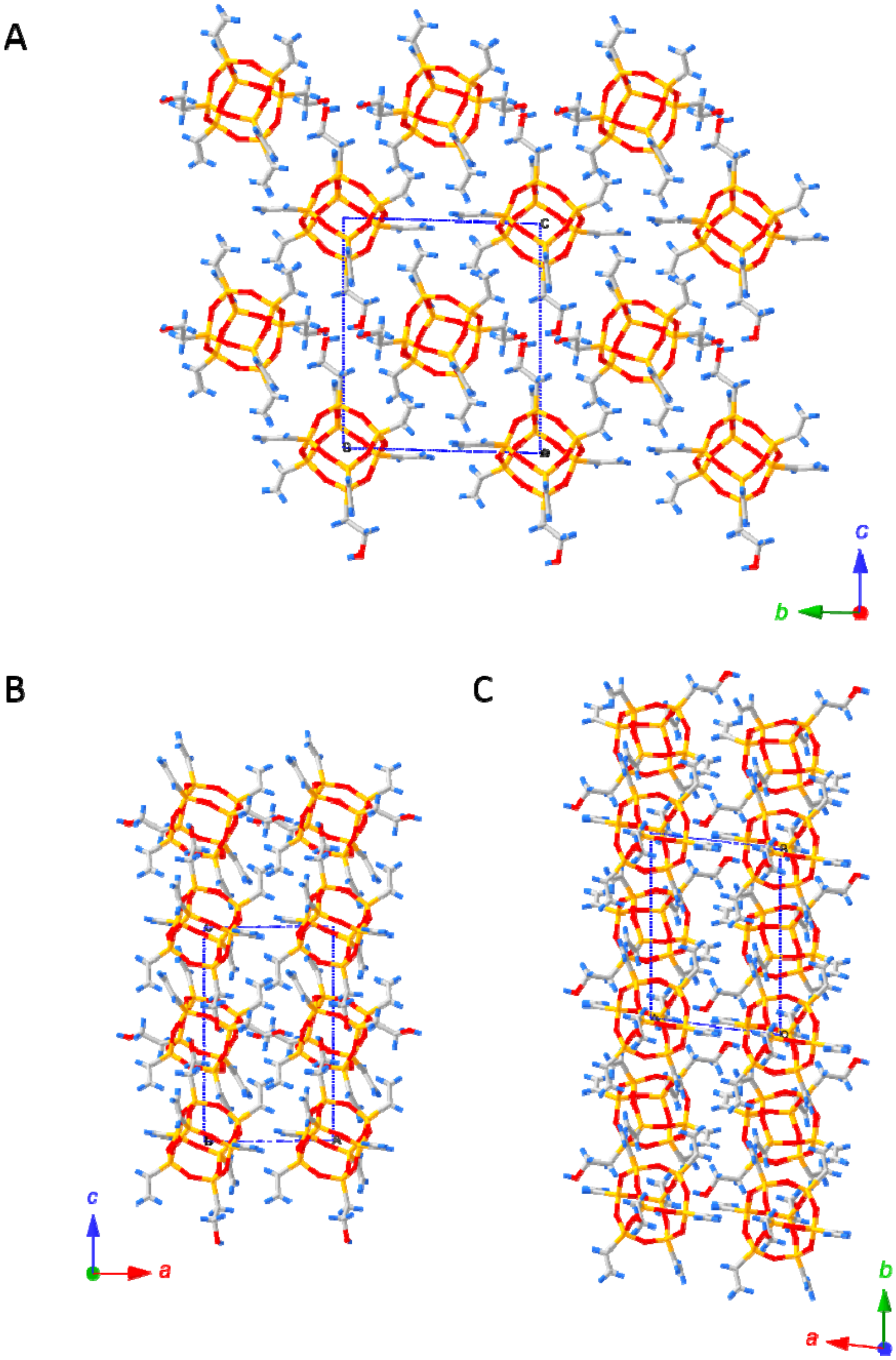


Fig. S2. Molecular packing of *p*-$T_8V_6(OH)_2$ in the single crystal viewed along the *a* axis (A), *b* axis (B), and *c* axis (C).

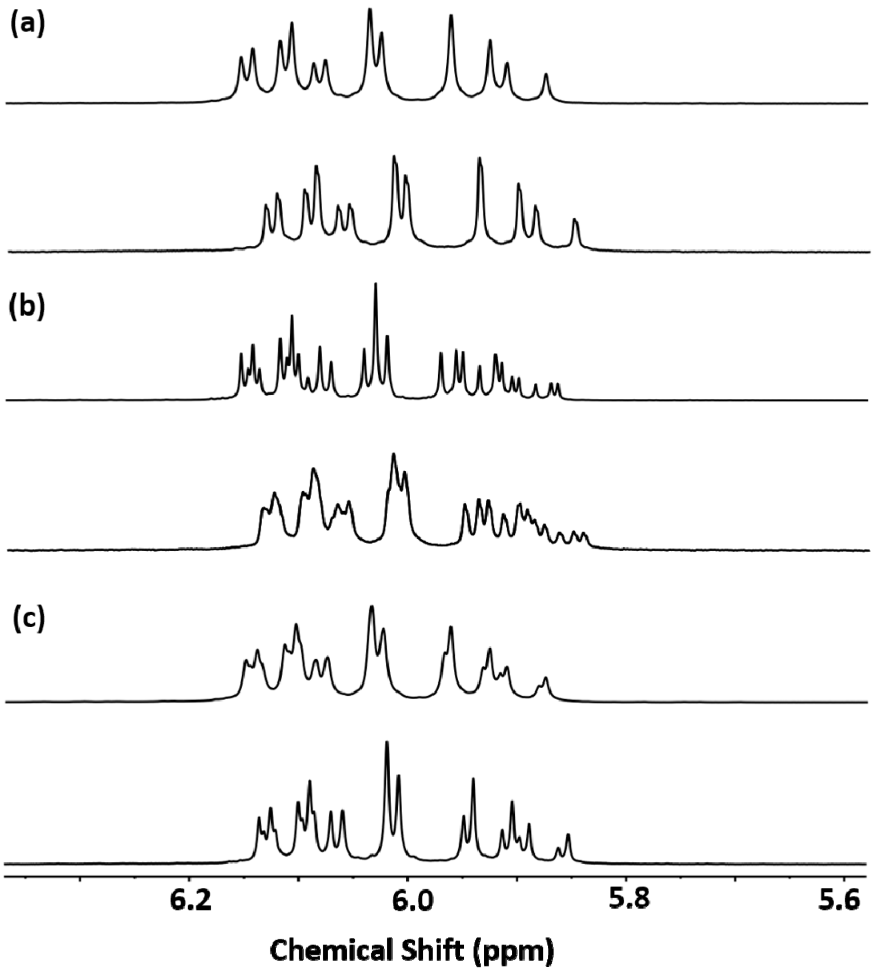


Fig. S3. The ^{1}H NMR spectra of the diadducts of $T_8V_6(OH)_2$ (upper) and $T_8V_6PCL_2$ (lower) for *para*- (a), *meta*- (b), and *ortho*- (c) configurations at the vinyl proton region.

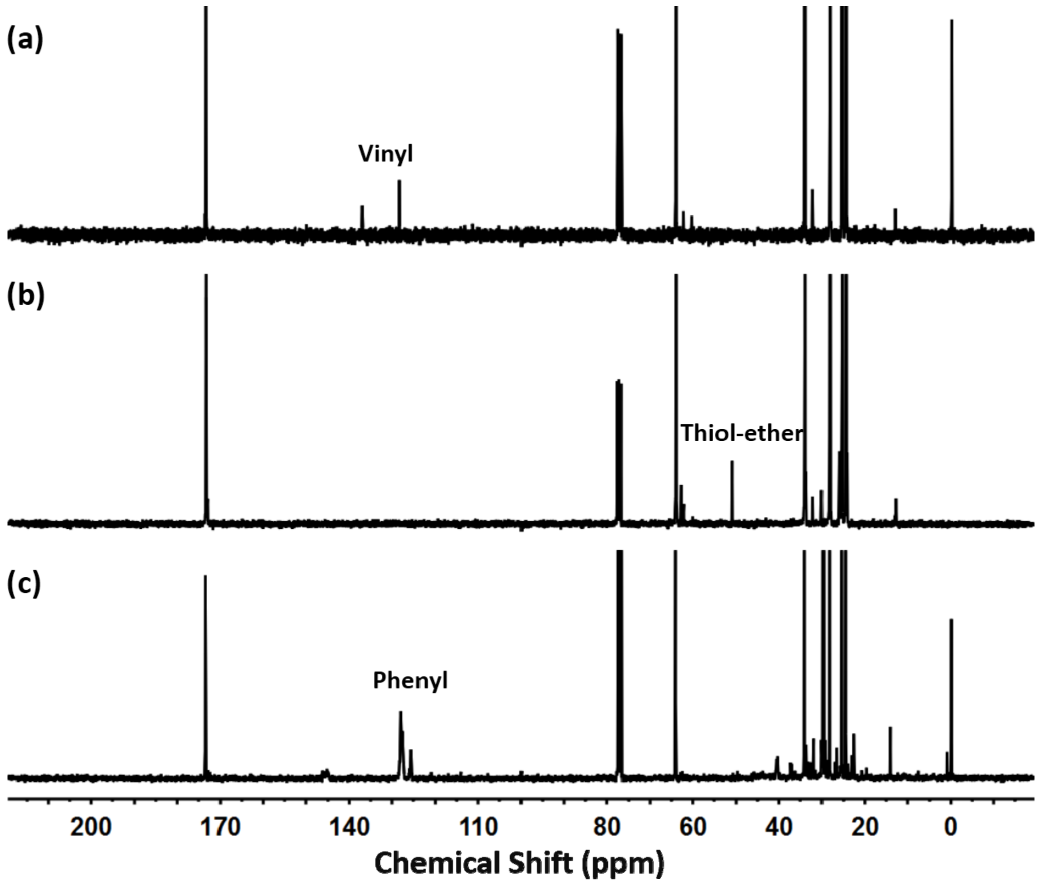


Fig. S4. The ^{13}C NMR spectra of the *p*-$T_8V_6PCL_2$ (a) *p*-$T_8A_6PCL_2$ (b) and *p*-$T_8PS_6PCL_2$ (c)

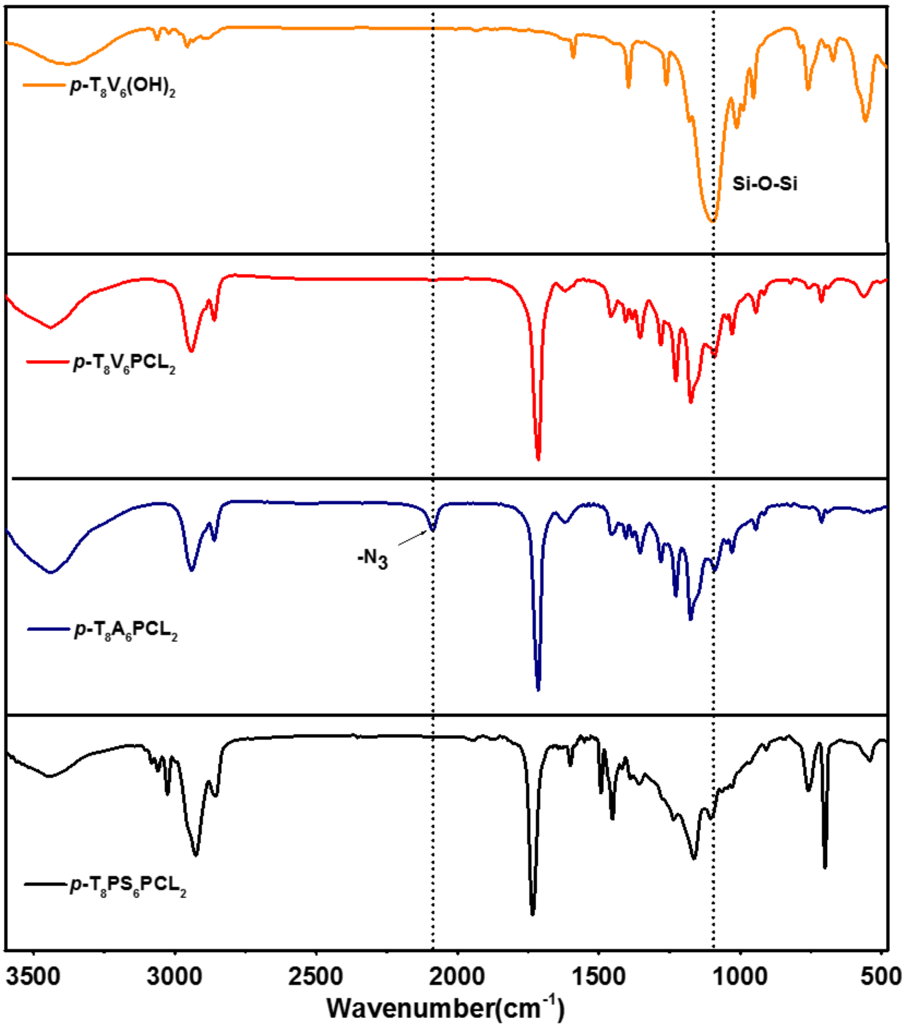


Fig. S5. FT-IR spectra show the progression of reaction.

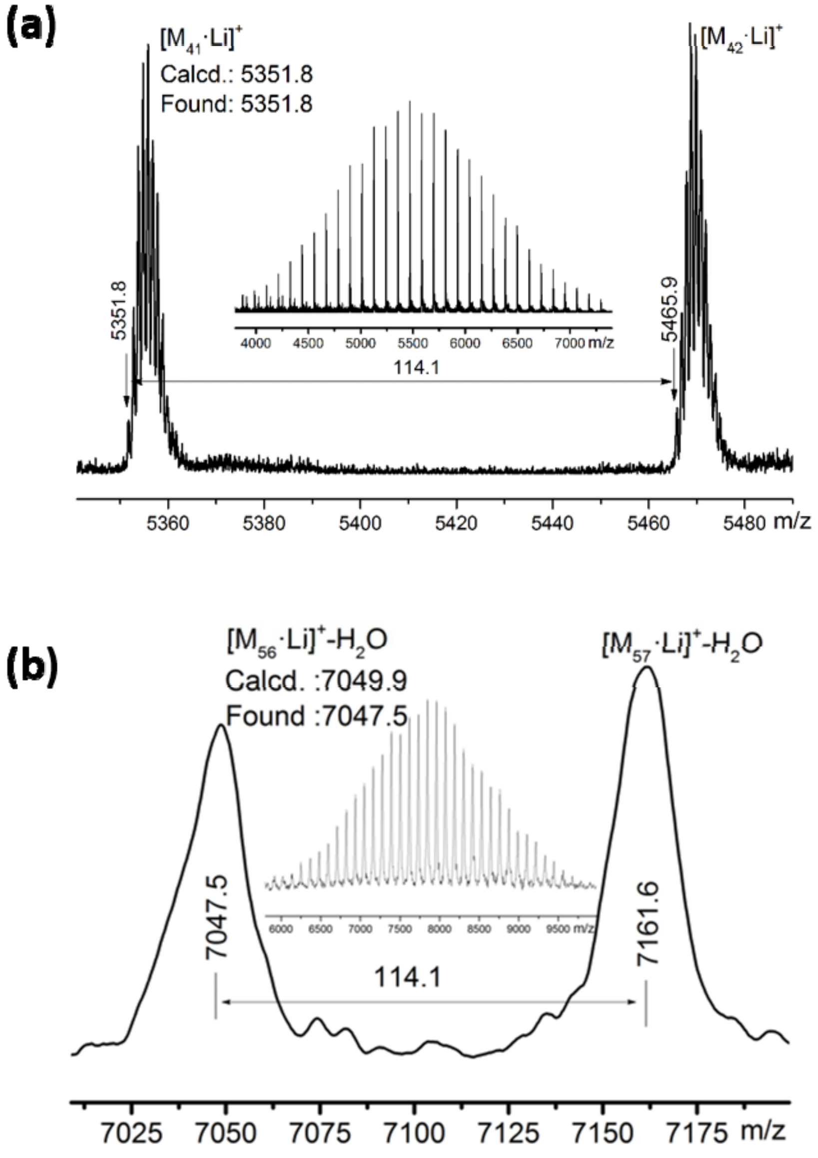


Fig. S6. Exemplary MALDI-TOF mass spectra of $T_8V_6PCL_2$ for (a) a lower MW sample and (b) a higher MW sample, both of which showing only one distribution with MW closely matching that of the calculated ones. It should be noted that for high MW $T_8V_6PCL_2$, there is no monoisotopic resolution.

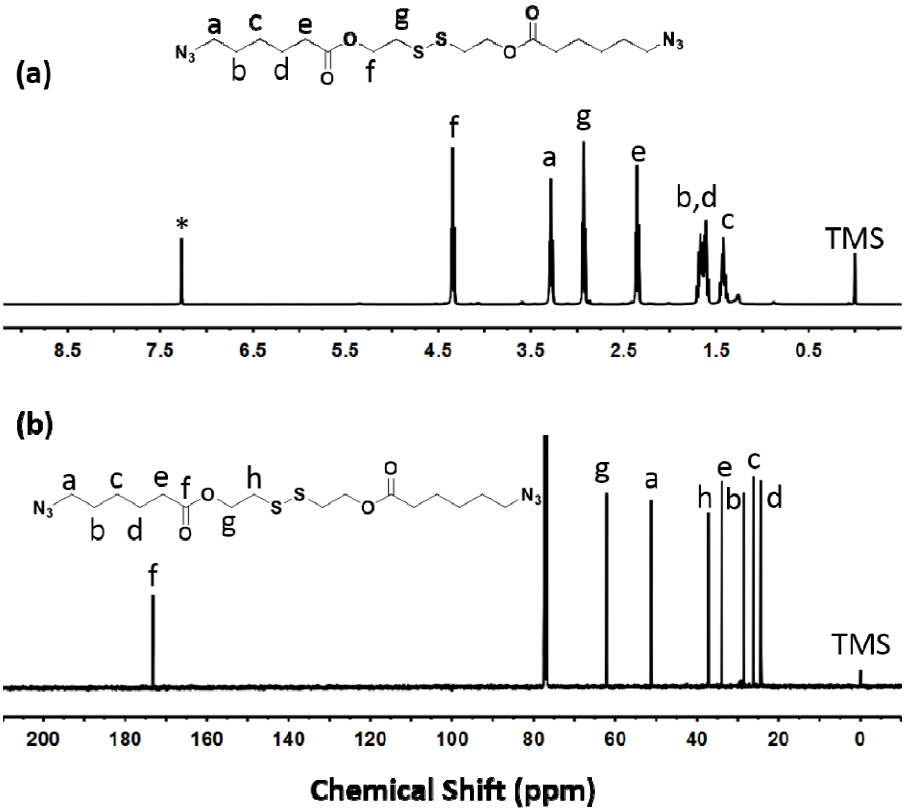


Fig. S7. The ^{1}H NMR (a) and ^{13}C NMR (b) spectra of the diazide **4**.

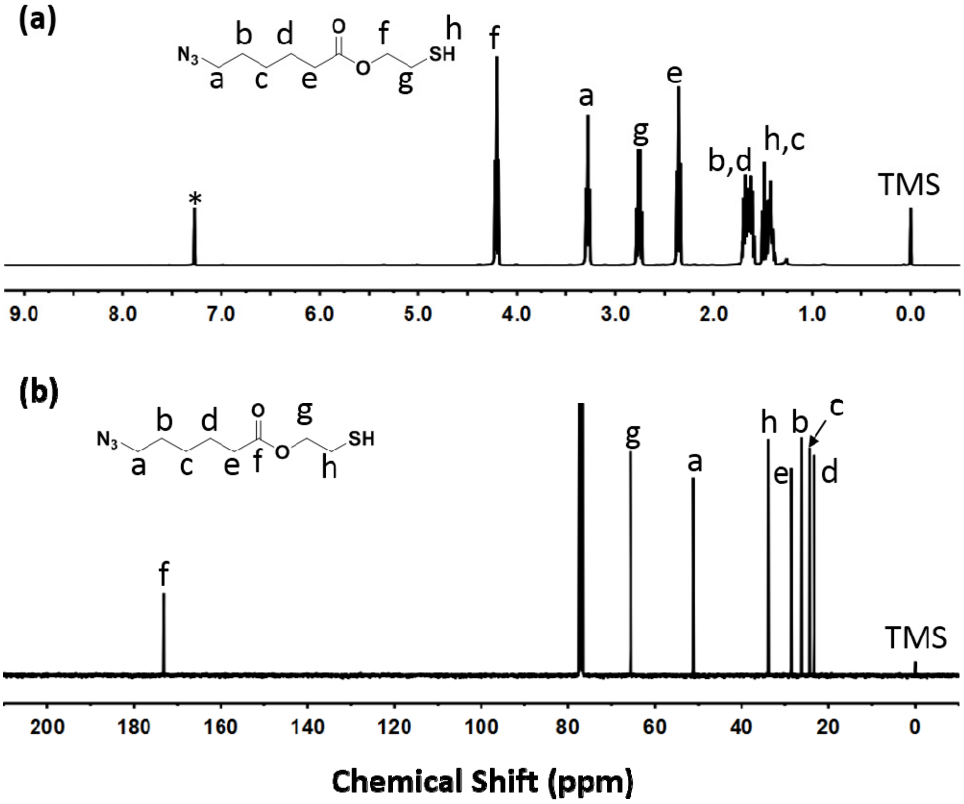


Fig. S8. The ^{1}H NMR (a) and ^{13}C NMR (b) spectra of N_3-SH.

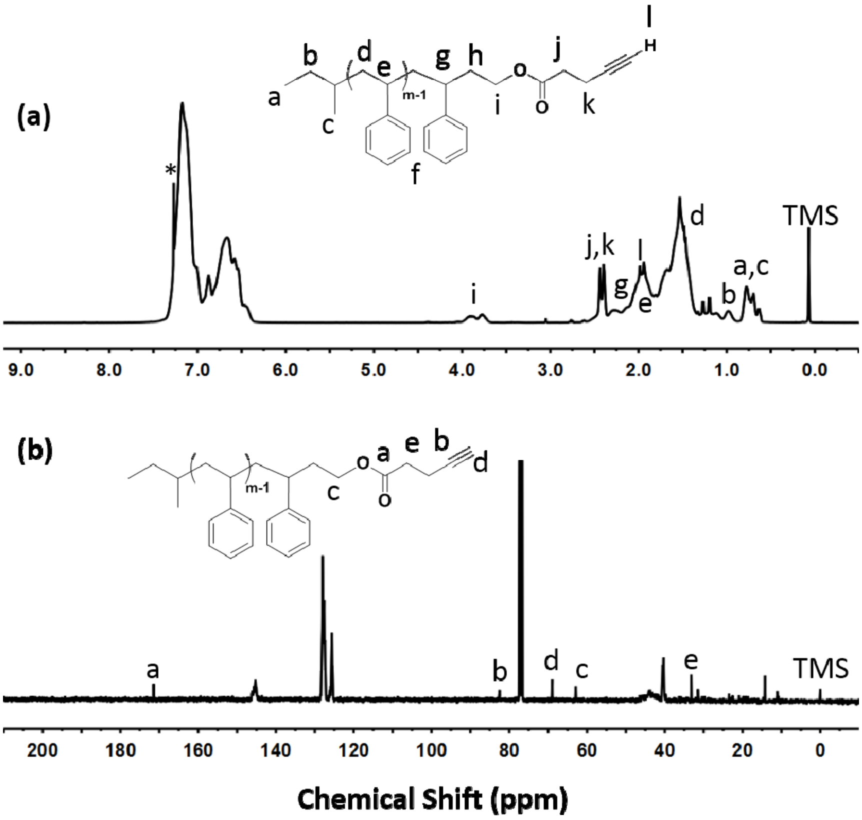


Fig. S9. The ^{1}H NMR (a) and ^{13}C NMR (b) spectra of PS-alkyne.

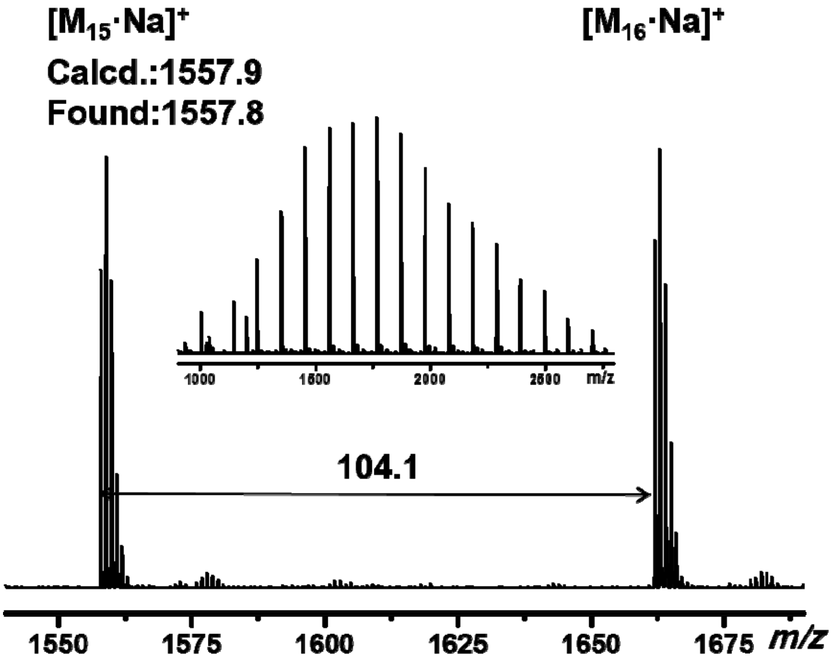


Fig. S10. The MALDI-TOF mass spectrum of PS-alkyne.

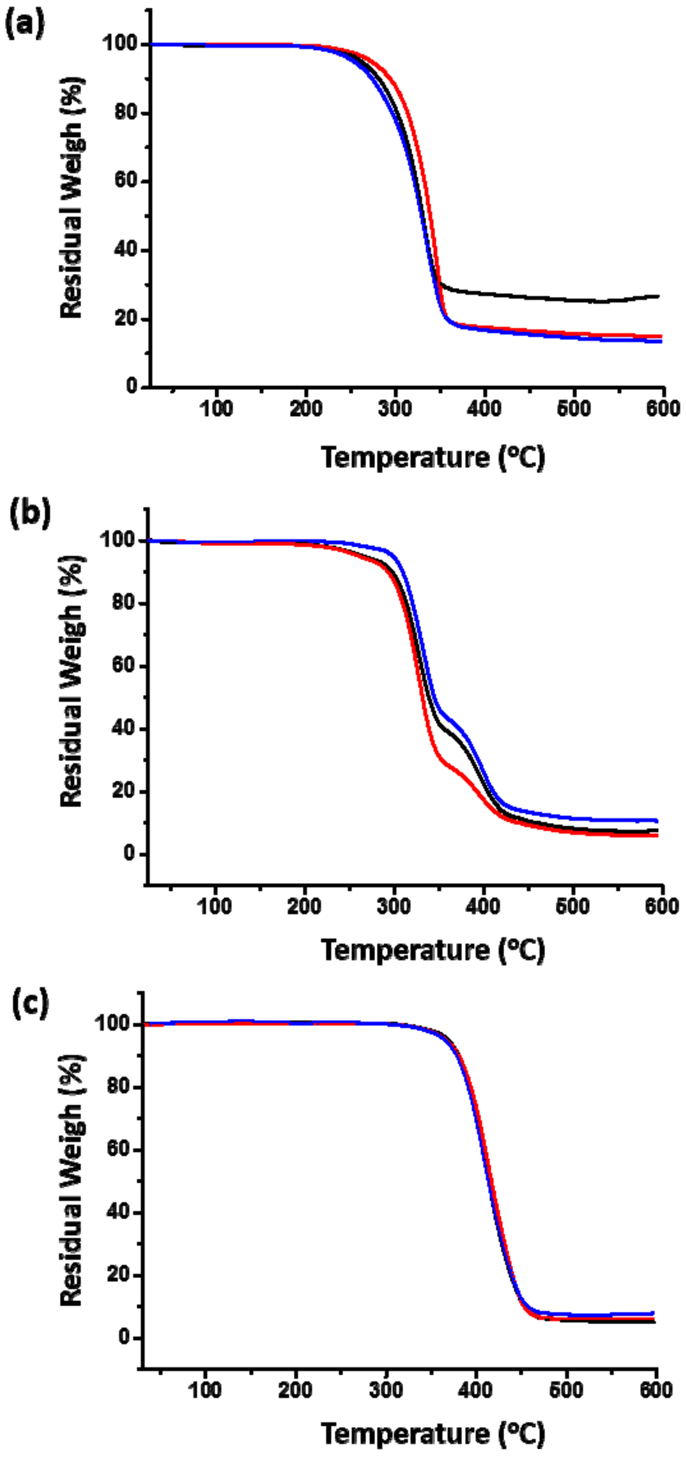


Fig. S11. The TGA profiles of (a) $T_8V_6PCL_2$, (b) $T_8A_6PCL_2$, and (c) $T_8PS_6PCL_2$. The black line is the *para*-adduct, red for *meta*- and blue for *ortho*-adducts.

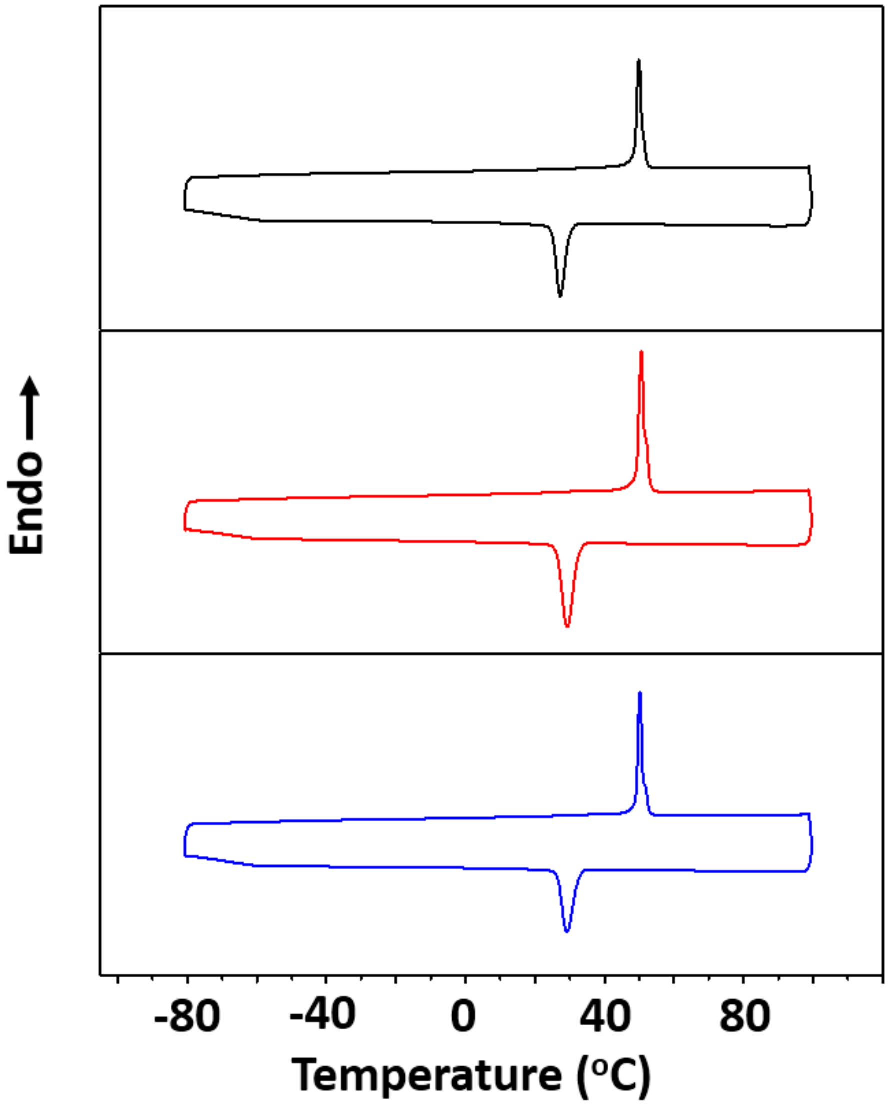


Fig. S12. The DSC profiles of *p*-$T_8V_6PCL_2$ (black line), *m*-$T_8V_6PCL_2$ (red line), and *o*-$T_8V_6PCL_2$ (blue line).

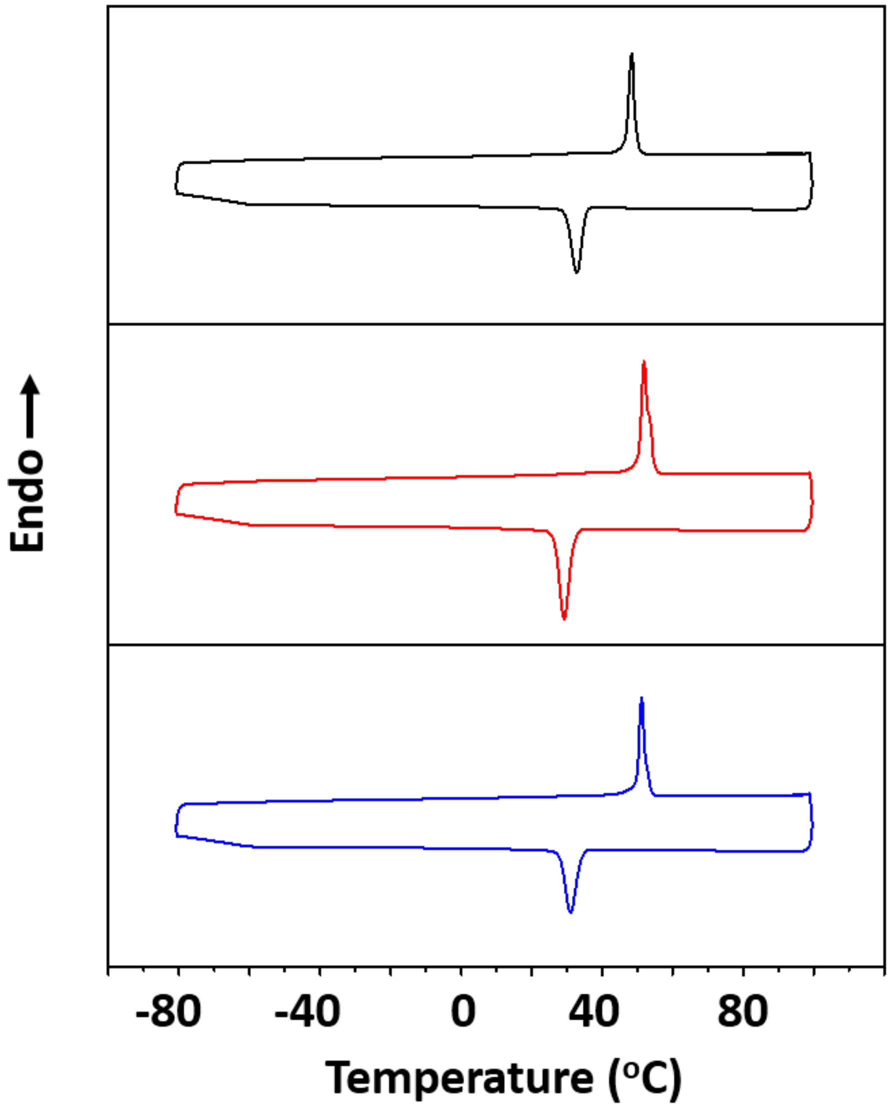


Fig. S13. The DSC profiles of *p*-$T_8A_6PCL_2$ (black line), *m*-$T_8A_6PCL_2$ (red line), and *o*-$T_8A_6PCL_2$ (blue line).

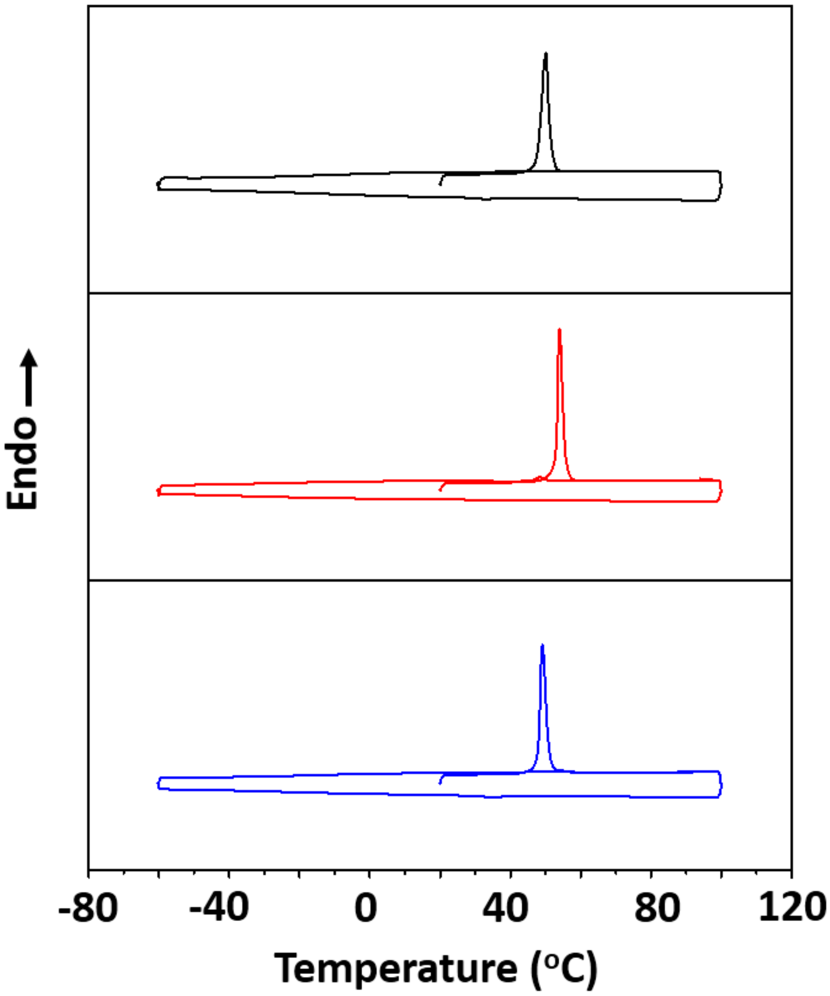


Fig. S14. (a) The DSC profiles of *p*-$T_8PS_6PCL_2$ (black line), *m*-$T_8PS_6PCL_2$ (red line), and *o*-$T_8PS_6PCL_2$ (blue line).

References

[1] R. Wang, F. Yan, D. Qiu, J. S. Jeong, Q. Jin, T. Y. Kim and L. Chen, *Bioconjug. Chem.,* 2012, **23**, 705-713.