Supporting Information

Symmetry-Guided, Divergent Assembly of Regio-isomeric Molecular Janus Particles

Di Han,[a,†] Yu Shao,[b,c†] Yang-Dan Tao,[a] Ge Han,[a] Dai-Lin Zhou,[a] Shuguang Yang,[c]

Wen-Bin Zhang,[b,] Qiang Fu,[a,*]*

a. College of Polymer Science & Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

b. Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry & Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Center for Soft Matter Science and Engineering, Peking University, Beijing 100871, China

c. Center for Advanced Low-Dimension Materials, State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, P. R. China

E-mail: wenbin@pku.edu.cn (W.-B. Z.); qiangfu@scu.edu.cn (Q. F.)

† These authors contribute equally to this work.

Experimental section

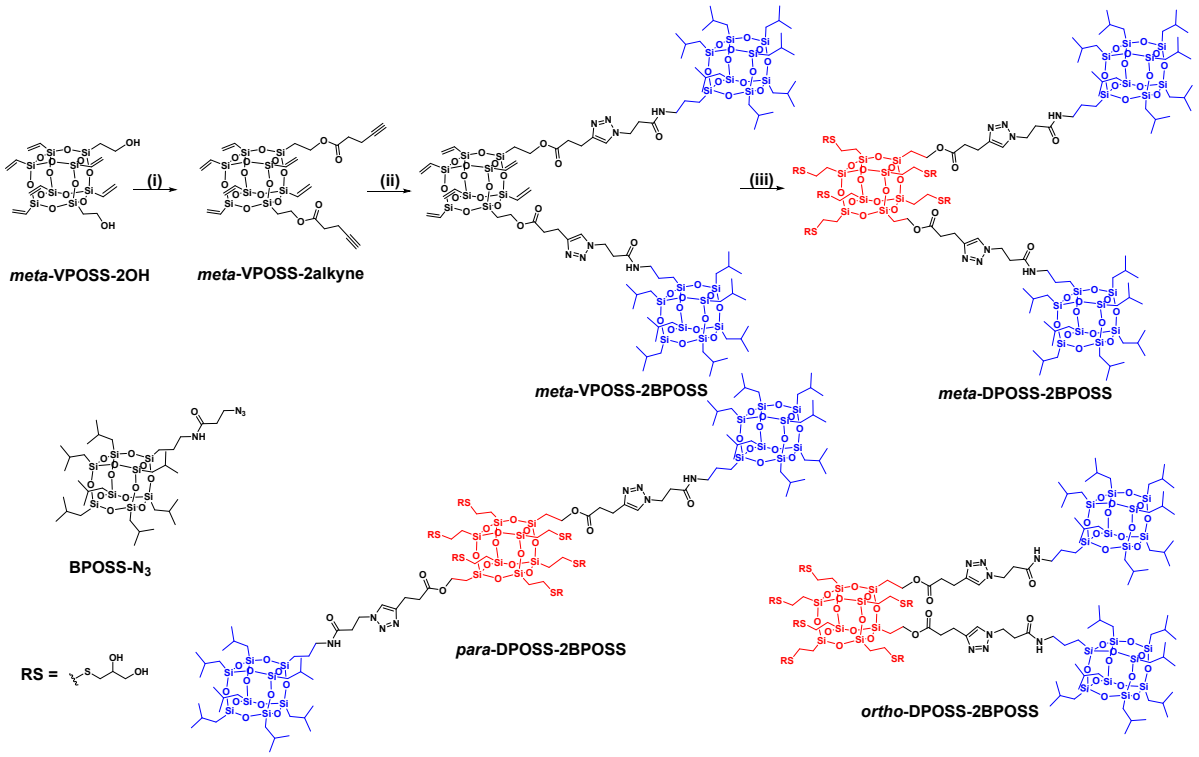
Chemical and solvents. The following chemicals were used as received: octavinyl-POSS (T_8V_8, 98%, Beijing HWRK Chemical Co., LTD), triflic acid (TfOH, J&K Chemicals, 95%), BPOSS-NH_2 (Hybrid Plastics, AM0265), 4-pentynoic acid (J&K Chemicals, 95%), 4-dimethylaminopyridine (DMAP, 98%, J&K Chemicals), N, N'-diisopropyl carbodiimide (DIPC, J&K Chemicals, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, J&K Chemical, 98%), 1-thioglycerol (J&K Chemicals, 95%), 3-bromopropionic acid (J&K Chemicals, 98%), Sodium azide (NaN_3, Alfa Aesar, 99%), 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959, J&K Chemicals, 98%), *N, N, N′,N″,N″*-pentamethyl diethylenetriamine (PMDETA, J&K Chemicals, 98%), cuprous bromide (CuBr, J&K Chemicals, 98%) was purified by washing with acetic acid for three times, washed with methanol, and dried in vacuum. Sodium chloride (NaCl), sodium sulfate (Na_2SO_4), Celite, petroleum ether (PE, b.p. 60-90 ℃), dichloromethane (DCM), acetone, ethyl acetate (EA), methanol (MeOH), and tetrahydrofuran (THF) were purchased from Chengdu Kelong Chemical Co., Ltd. All the solvents were used after distillation or dried through a solvent purification system (SPS-5, Etelux, Beijing, China). VPOSS-2OH,[S1] VPOSS-2Alkyne[S2] *para*-, *meta*-, *ortho*-isomers were synthesized according to previous report.

Instrumentation and Characterizations. The UV lamp used in this work is LUYOR-3109 (3W*9, λ = 365 nm, USA). All the ^1H, ^{13}C and ^{29}Si NMR spectra were performed in $CDCl_3$ by using a Bruker 400 MHz NMR spectrometer at room temperature. Thermogravimetric analysis (TGA) was performed on a thermo-analyzer instrument (TA Instruments Inc., USA) with a scan rate of 10 ℃ min^{-1} under nitrogen atmosphere. The differential scanning calorimetry (DSC) was carried out by using a TA Instruments under nitrogen atmosphere with a heating rate of 10 ℃ min^{-1} to acquire their crystallization

temperature and melting point. Size exclusion chromatography (SEC) results were performed on a Viscoteck SEC 270maxTM (Malvern, U.K.). The polymer samples were dissolved in THF (2 mg/mL) while THF also acted as eluent (flow rate: 0.50 mL/min). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a MALDI TOF/TOF 5800 mass spectrometer (AB Sciex, USA). A positive reflection mode was used with trans-2-[3-(4-tert-butylphenyl)-2-methyl-2- propenylidene]malononitrile (DCTB, TCI, >99%) as the matrix and was dissolved in $CHCl_3$ (20 mg mL^{-1}). Sodium trifluoromethanesulfonate (NaTFA, J&K Chemicals, 98%,) was dissolved in MeOH/$CHCl_3$ (v/v = 1/3) at a concentration of 10 mg mL^{-1} and served as the cationizing agent solution. The samples were typically dissolved in $CHCl_3$ with the concentration of 5 mg mL^{-1}. To prepare the measured samples, 0.5 μL of matrix and the cationizing agent solution mixture was deposited on the wells of a 384-well ground-steel plate and allowed the spots to dry, then depositing 0.5 μL of each sample on top of the spot of dry matrix, finally deposition of another 0.5 μL of matrix and the cationizing agent solution mixture on top of the dry sample. Small-Angle X-ray Scattering (SAXS) experiments were recorded at beamline BL16B1 of the Shanghai Synchrotron Radiation Facility (SSRF). The working voltage of X-ray was 10 kV with the wavelength of 0.124 nm. Some of the X-ray diffraction data were also recorded on the Genesha SAXS Lab instrument with the wavelength of 1.54 Å. Silver behenate (with the *d*-spacing of 58.38 Å) was used for the calibration of sample to detector distance. Bright field transmission electron microscope (TEM) images of the thin-slice samples were recorded on a Tecnai F20 TEM with an accelerating voltage of 200 kV on a digital CCD camera.

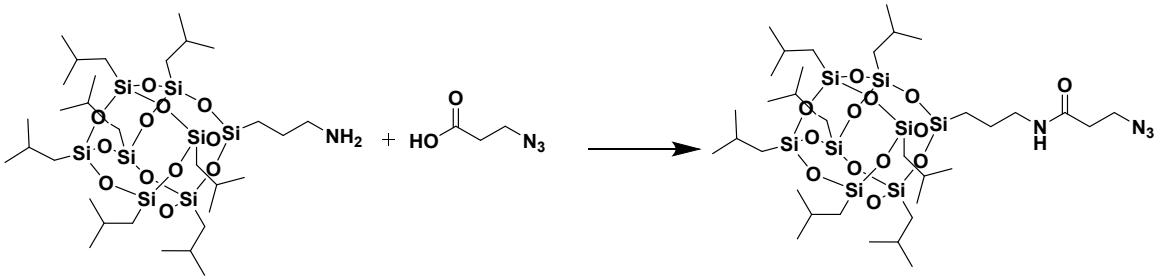
Synthetic procedures.

Scheme S1. Synthetic Route of Regio-isomeric DPOSS-2BPOSS Giant Molecules [a]



[a] Reagent and conditions: (i) 4-pentynoic acid, DIPC, DMAP, DCM, 24h, 70%; (ii) BPOSS-N_3, CuBr, PMDETA, THF, 12 h, 80%; (iii) 1-thioglycerol, Irgacure 2959, UV (365 nm), 15 min, THF, 75%.

Scheme S2. Synthesis of BPOSS-N_3 [a]



[a] Reagents and conditions: DIPC, DMAP, rt, 24h, 81%.

Synthesis of BPOSS-N_3. In a round bottom flask (100 mL) with a magnetic stirring bar, BPOSS-NH_2 (5 g, 0.57 mmol, 1 equiv), 3-azidopropanoic acid (80 mg, 0.69 mmol, 1.2 equiv) and DMAP (14 mg, 0.12 mmol, 0.12 equiv) were fully dissolved in 15 mL dried DCM. The mixture was cooled to 0 ℃ by using ice bath for 5 min, and then DIPC (109 mg, 0.86 mmol, 1.5 equiv) was added dropwise. After 30 min, the mixture was warmed up to room temperature and stirred for 24 h. After that, the mixture was filtered by Celite and the filtrate was concentrated. The residual was purified by using flash column chromatography on silica gel with DCM as eluent to afford 4.5 g product as a white powder. Yield: 81%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 5.64 (br, 1H, -CH_2N<u>H</u>CO-), 3.63 (t, 2H, -C<u>H_2</u>NHCO-), 3.28 (dd, 2H, -NHCOC<u>H_2</u>-), 2.41 (t, 2H, -C<u>H_2</u>N_3), 1.85 (m, 7H, -CH_2C<u>H</u>(CH_3)$_2$), 1.61 (m, 2H, -C<u>H_2</u>CH_2NH-), 0.96 (d, 42H, -CH_2CH(C<u>H_3</u>)$_2$), 0.61 (dd, 16H, SiC<u>H_2</u>CH_2-, SiC<u>H_2</u>CH-). ^{13}C NMR ($CDCl_3$, 100M, Hz, ppm): δ = 169.60, 47.49, 41.93, 35.99, 25.71, 25.69, 23.91, 23.86, 22.96, 22.48, 22.44, 9.45. MALDI-TOF MS: calcd. monoisotopic mass for $[M{\cdot}Na]^+$ ($C_{34}H_{74}N_4NaO_{13}Si_8$) = 993.3 Da. Found: m/z = 993.28 Da.

VPOSS-2BPOSS. Typically, in a glove box, VPOSS-2alkyne (70 mg, 0.08 mmol, 1 equiv), BPOSS-N_3 (233 mg, 0.24 mmol, 3 equiv), CuBr (1 mg) were added into a vial (10 mL) with a magnetic stirring bar and dissolved in 5 mL anhydrous THF. After complete dissolution, one drop PMDETA was added via pipette. The solution mixture was left in the glove box at room temperature overnight. After that, the solution mixture was concentrated and the crude product purified by flash column chromatography on the silica gel. DCM was used to recover BPOSS-N_3 and THF was used to flash the aim product out of the column. After removing the solvent, the aim product was obtained as a white powder.

para-VPOSS-2BPOSS. Yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.41 (s, 2H), 6.17-5.83

(m, 18H), 5.52 (t, 2H), 4.63 (t, 4H), 4.23 (m, 4H), 3,21 (dd, 4H), 3.00 (t, 4H), 2.79 (t, 4H), 2.68 (t,4H), 1.94-1.77 (m,14H), 1.56 (m, 4H), 0.96 (m, 88H) 0.59 (m, 32H). ^{13}C NMR ($CDCl_3$, 100M, Hz, ppm): δ = 172.55, 169.02, 146.18, 137.26, 137.14, 128.45, 128.38, 122.31, 60.70, 42.01, 36.53, 33.61, 25.70, 25.68, 23.89, 23.85, 22.89, 22.48, 22.44, 20.89, 9.45. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm): δ = -67.63, -67.86, -67.98, -69.00, -80.37. MALDI-TOF MS: calcd. monoisotopic mass for $[M{\cdot}Na]^+$ ($C_{94}H_{184}N_8NaO_{42}Si_{24}$) = 2791.7 Da. Found: m/z = 2792.1 Da.

meta-VPOSS-2BPOSS. Yield: 79%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.41 (s, 2H), 6.18-5.83 (m, 18H), 5.59 (t, 2H), 4.63 (t, 4H), 4.22 (m, 4H), 3,21 (dd, 4H), 3.00 (t, 4H), 2.79 (t, 4H), 2.69 (t,4H), 1.86 (m,14H), 1.56 (m, 4H), 0.95 (m, 88H) 0.59 (m, 32H). ^{13}C NMR ($CDCl_3$, 100M, Hz, ppm): δ = 172.53, 169.00, 137.32, 137.21, 128.43, 128.36, 122.32, 60.75, 42.00, 36.55, 33.65, 25.70, 25.68, 23.89, 23.85, 22.88, 22.48, 22.44, 20.89, 9.43. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm): δ = -67.63, -67.87, -67.98, -68.99, -80.24, -80.36, -80.50. MALDI-TOF MS: calcd. monoisotopic mass for $[M{\cdot}Na]^+$ ($C_{94}H_{184}N_8NaO_{42}Si_{24}$) = 2791.7 Da. Found: m/z = 2791.9 Da.

ortho-VPOSS-2BPOSS. Yield: 86%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.43 (s, 2H), 6.18-5.83 (m, 18H), 5.73 (t, 2H), 4.63 (t, 4H), 4.23 (m, 4H), 3,22 (dd, 4H), 3.00 (t, 4H), 2.79 (t, 4H), 2.69 (t,4H), 1.84 (m,14H), 1.56 (m, 4H),0.96 (dd, 88H) 0.59 (m, 32H). ^{13}C NMR ($CDCl_3$, 100M, Hz, ppm): δ = 172.55, 169.02, 146.18, 137.26, 137.14, 128.45, 128.38, 122.31, 60.70, 42.01, 36.53, 33.61, 25.70, 25.68, 23.89, 23.85, 22.89, 22.48, 22.44, 20.89, 14.13, 13.11, 9.45. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm): δ = -67.63, -67.87, -67.96, -69.09, -80.23, -80.37. MALDI-TOF MS: calcd. monoisotopic mass for $[M{\cdot}Na]^+$ ($C_{94}H_{184}N_8NaO_{42}Si_{24}$) = 2791.7 Da. Found: m/z = 2792.3 Da.

DPOSS-2BPOSS. In a vial (5 mL) with a magnetic stirring bar, VPOSS-2BPOSS (150 mg, 0.05 mmol, 1 equiv), 1-thioglycerol (65 mg, 0.60 mmol, 12 equiv), and the photo initiator Irgacure 2959 (2

mg) were fully dissolved in 3 mL THF. The mixture was reacted under irradiation by using UV light (365 nm) for 15 min. The solution mixture was purified by repeated precipitation into the mixture of cold water/methanol (v/v = 1:1) for three times, centrifuged and dried in vacuum to afford a white powder.

para-DPOSS-2BPOSS. Yield: 70%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.53 (s, 2H), 5.99 (t, 2H), 4.64 (t, 4H), 4.24 (m, 4H), 3.94-3.50 (m, 18H), 3,19 (dd, 4H), 3.00 (t, 4H), 2.80 (t, 4H), 2.65 (m,28H), 1.85 (m,14H), 1.56 (m, 4H), 0.96 (m, 100H) 0.59 (m, 32H). ^{13}C NMR ($CDCl_3$, 100M, Hz, ppm): δ = 172.96, 169.36, 145.93, 125.53, 122.86, 71.12, 65.43, 60.97, 46.18, 42.15, 36.41, 35.29, 34.24, 33.64, 30.38, 29.70, 26.65, 25.71, 23.89, 23.85, 22.84, 22.49, 22.45, 20.79, 12.83, 9.50. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm): δ = -67.64, -67.87, -68.00, -68.78, -69.18.

meta-DPOSS-2BPOSS. Yield: 75%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.53 (s, 2H), 6.01 (t, 2H), 4.64 (t, 4H), 4.21 (m, 4H), 3.95-3.50 (m, 18H), 3,19 (dd, 4H), 3.00 (t, 4H), 2.79 (t, 4H), 2.65 (m,28H), 1.85 (m,14H), 1.56 (m, 4H), 0.96 (m, 100H) 0.59 (m, 32H). ^{13}C NMR ($CDCl_3$, 100M, Hz, ppm): δ = 172.96, 169.36, 145.93, 125.53, 122.86, 71.12, 65.43, 60.7, 46.12, 42.11, 36.43, 35.27, 34.23, 33.61, 31.44, 30.33, 29.70, 26.67, 25.79, 23.89, 23.85, 22.86, 22.48, 22.44, 20.82, 12.82, 9.49. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm): δ = -67.63, -67.86, -68.00, -68.72, -68.75, -68.79, -69.26.

ortho-DPOSS-2BPOSS. Yield: 79%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 7.52 (s, 2H), 6.01 (t, 2H), 4.64 (t, 4H), 4.21 (m, 4H), 3.94-3.50 (m, 18H), 3,20 (dd, 4H), 3.00 (t, 4H), 2.80 (t, 4H), 2.65 (m,28H), 1.85 (m,14H), 1.56 (m, 4H), 0.96 (m, 100H) 0.58 (m, 32H). ^{13}C NMR ($CDCl_3$, 100M, Hz, ppm): δ = 172.75, 169.25, 145.97, 125.53, 122.78, 71.11, 65.44, 60.90, 46.13, 42.13, 36.44, 35.28, 34.24, 33.63, 30.33, 29.70, 26.72, 25.70, 23.89, 23.85, 22.84, 22.48, 22.44, 20.78, 12.80, 9.49. ^{29}Si NMR (99 MHz, $CDCl_3$, ppm): δ = -67.64, -67.87, -67.98, -68.71, -68.77, -69.28.

Equations and Calculations.

The volume fraction of BPOSS (V_f^{BPOSS}) is calculated by Eq. (S1):

$$V_f^{BPOSS} = \frac{2 \times M_{BPOSS}/\rho_{BPOSS}}{2 \times M_{BPOSS}/\rho_{BPOSS} + M_{DPOSS}/\rho_{DPOSS}} \quad \text{Eq. (S1)}$$

The volume fraction of DPOSS (V_f^{DPOSS}) is calculated by Eq. (S2):

$$V_f^{DPOSS} = \frac{M_{DPOSS}/\rho_{DPOSS}}{2 \times M_{BPOSS}/\rho_{BPOSS} + M_{DPOSS}/\rho_{DPOSS}} \quad \text{Eq. (S2)}$$

where M_{DPOSS} = 1748 g/mol, M_{BPOSS} = 816 g/mol. The density values are 1.13 g/cm^3 for BPOSS, 1.43 g/cm^3 for DPOSS.[S3] Amido bonds in the linkers will have non-negligible hydrogen bonding interactions with DPOSS head, so the linkers are classified into the DPOSS domain in the calculation Therefore, the calculated values for DPOSS-2BPOSS are in the following:

$$V_f^{BPOSS} = 0.54$$

$$V_f^{DPOSS} = 0.46$$

Calculation of the spacing *d*. The value of d is calculated from q_1, the first peak in the SAXS by Eq. (S4):

$$d = 2\pi/q_1 \quad \text{Eq. (S3)}$$

The characteristic dimension (a) is calculated from d accordingly following Eqs.

$$a = d \text{ for LAM} \quad \text{Eq. (S4)}$$

$$a = \sqrt{6} d_{211} \text{ for DG} \quad \text{Eq. (S5)}$$

Calculation of the average interfacial area per molecule (A_0).

For LAM phase,

$$A_0 = \frac{2M_{BPOSS}}{d\rho_{BPOSS}N_A V_f^{BPOSS}} \quad \text{Eq. (S6)}$$

where N_A is the Avogadro constant.

For DG phase,

$$A_0 = \frac{xM_{BPOSS}}{a\rho_{BPOSS}N_A V_f^{BPOSS}} \quad \text{Eq. (S7)}$$

where a is the cubic unit cell length ($a = \sqrt{6}d_{211}$), x is the specific surface area to bulk volume ratio of the double-gyroid structure as a function of the volume fraction of the gyroid network, and the x value can be obtained from literature[S4] and the value used in this work is 4.5.

The thickness of DPOSS domain (D_{DPOSS}) is calculated by Eq. (S8):

$$D_{DPOSS} = d_1 V_f^{DPOSS} \quad \text{Eq. (S8)}$$

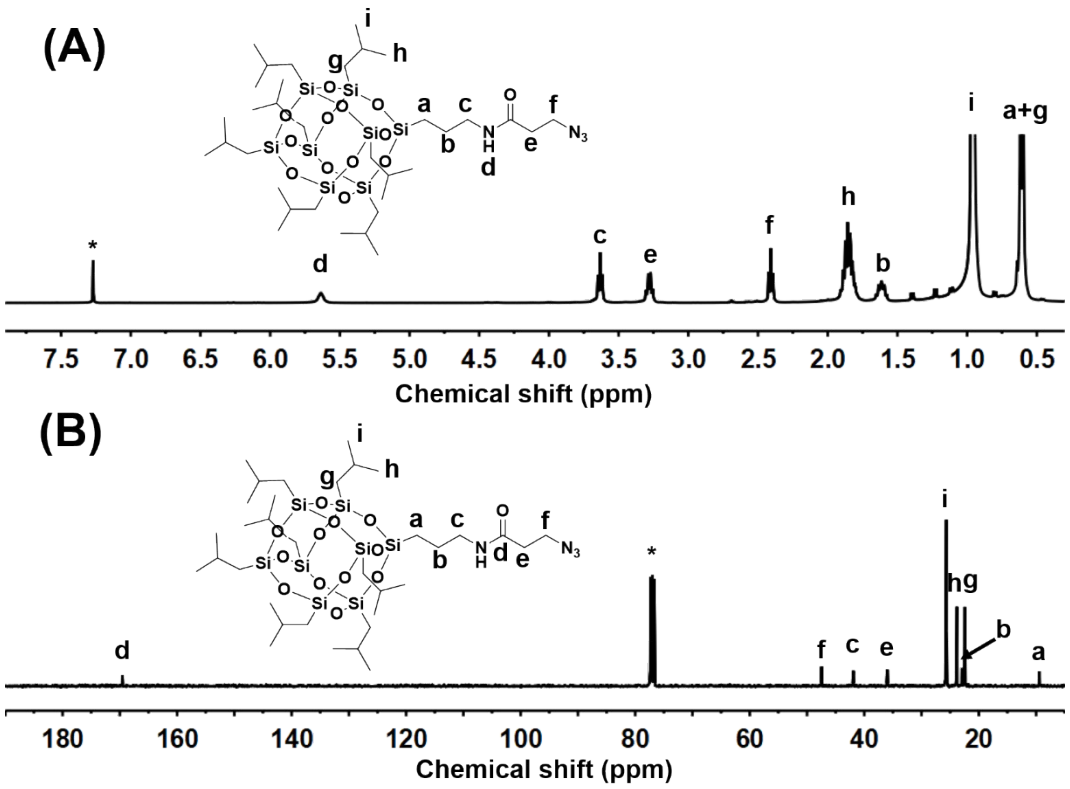


Figure S1. (A) ^{1}H NMR spectrum and (B) ^{13}C NMR of spectrum BPOSS-N_3.

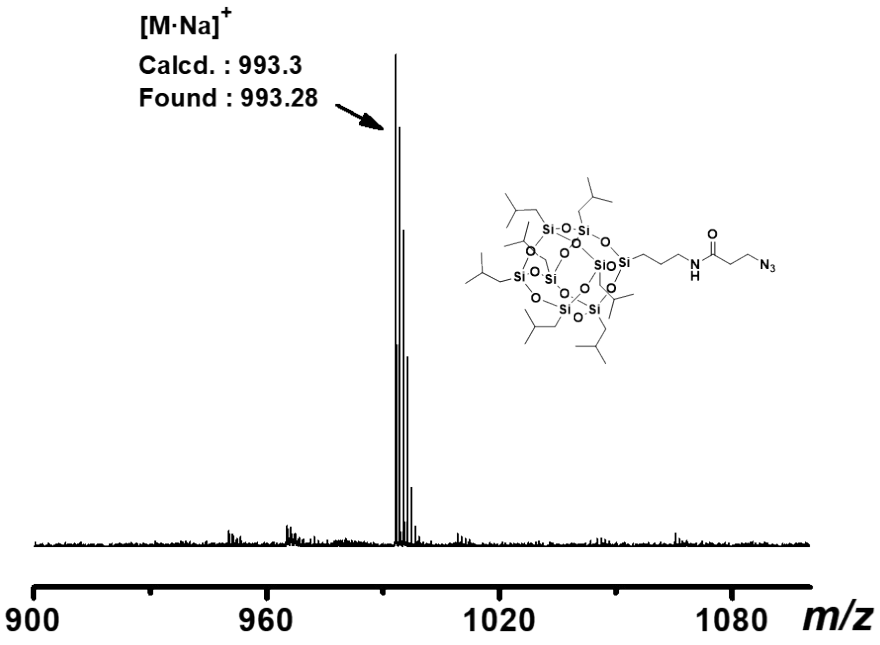


Figure S2. MALDI-TOF MS spectrum of BPOSS-N_3.

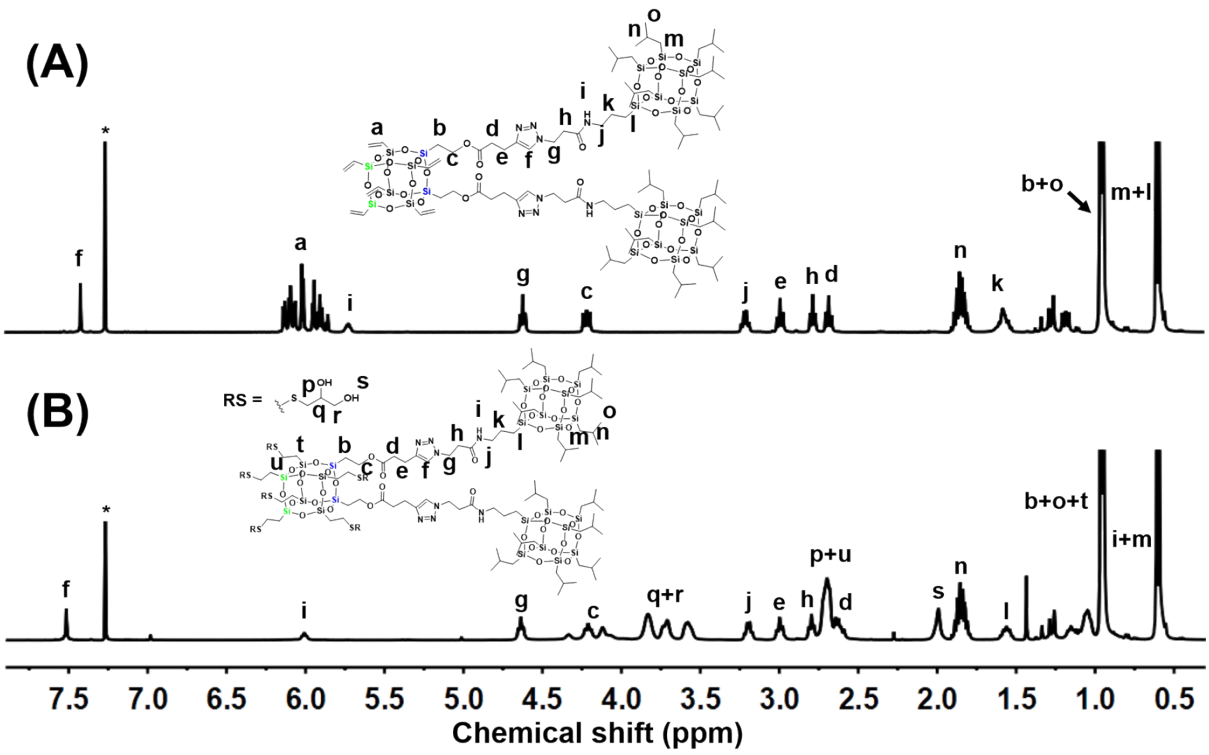


Figure S3. ^{1}H NMR spectra of (A) *ortho*-VPOSS-2BPOSS, (B) *ortho*-DPOSS-2BPOSS, and the corresponding assignments are shown inside. Asterisks denoted signals from $CDCl_3$.

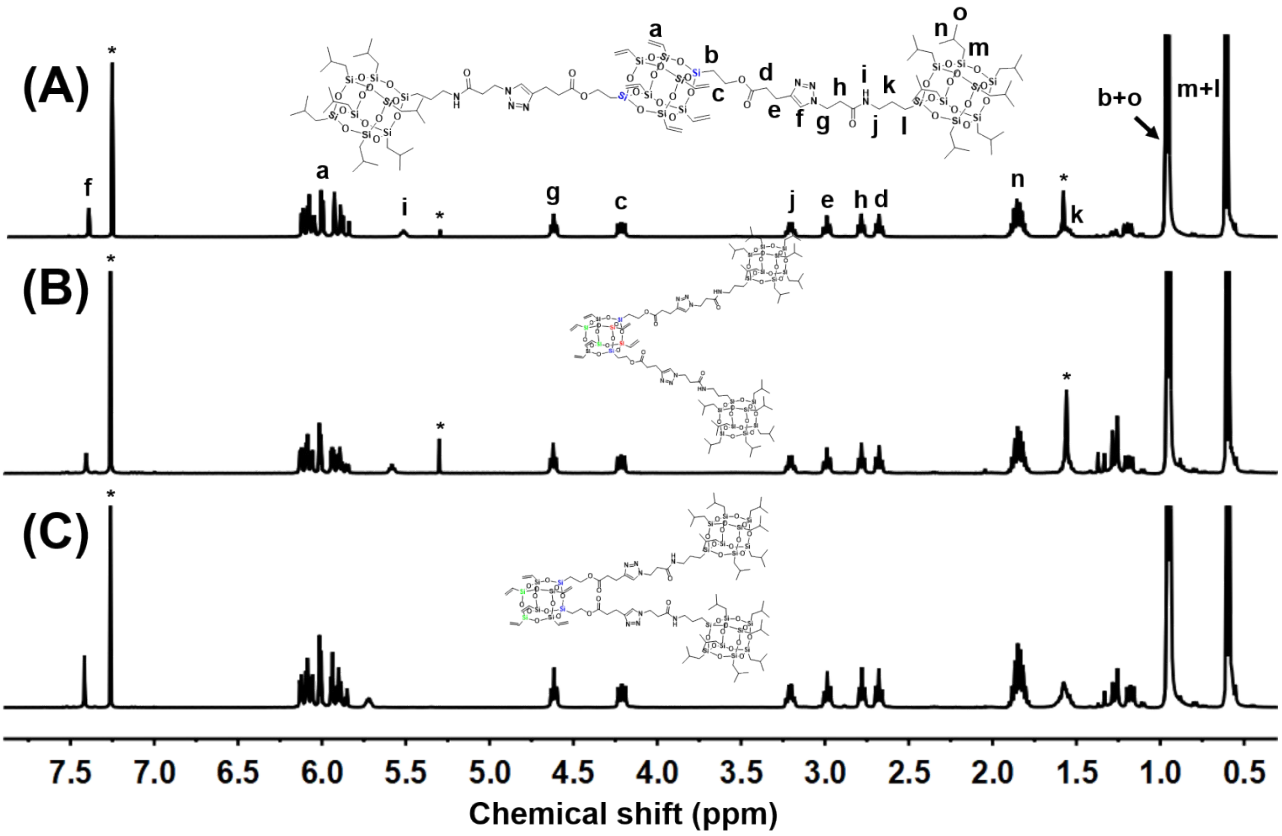


Figure S4. ^{1}H NMR spectra of VPOSS-2BPOSS: (A) *para*-VPOSS-2BPOSS, (B) *meta*-VPOSS-2BPOSS, (C) *ortho*-VPOSS-2BPOSS.

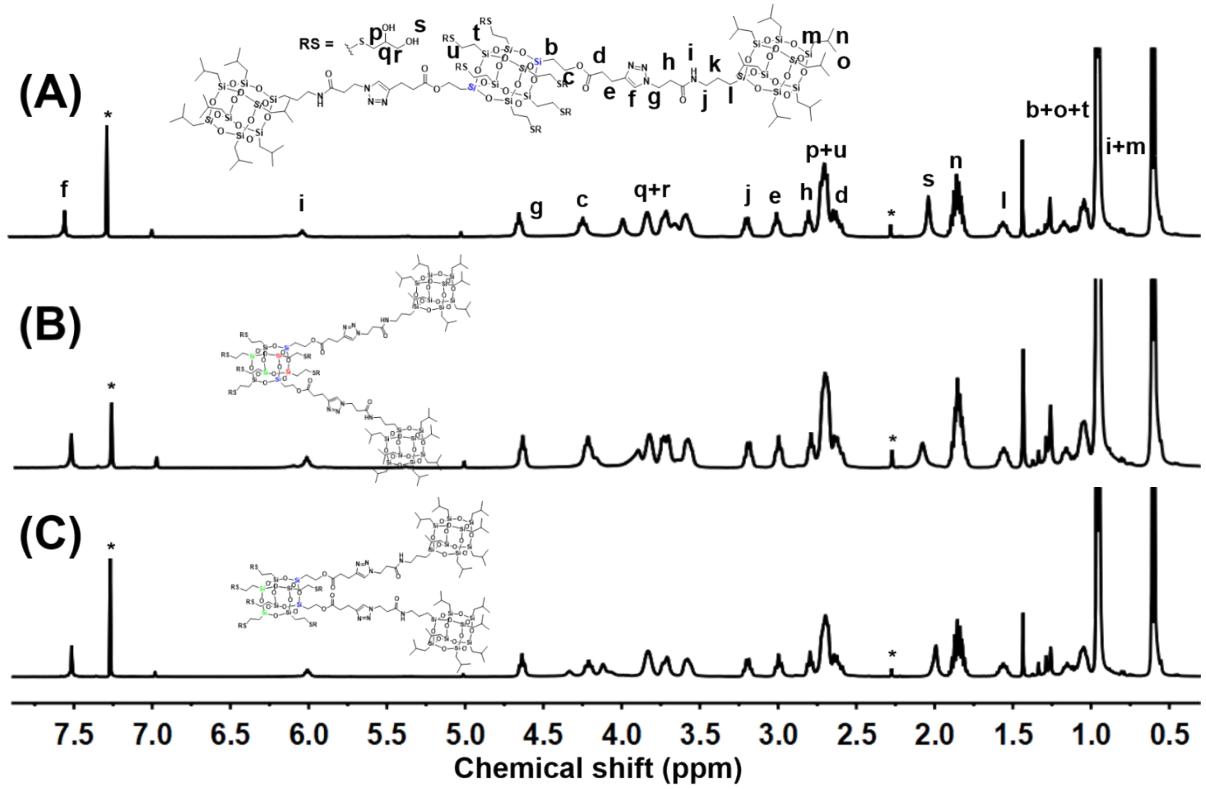


Figure S5. ^{1}H NMR spectra of DPOSS-2BPOSS: (A) *para*-DPOSS-2BPOSS, (B) *meta*-DPOSS-2BPOSS, (C) *ortho*-DPOSS-2BPOSS.

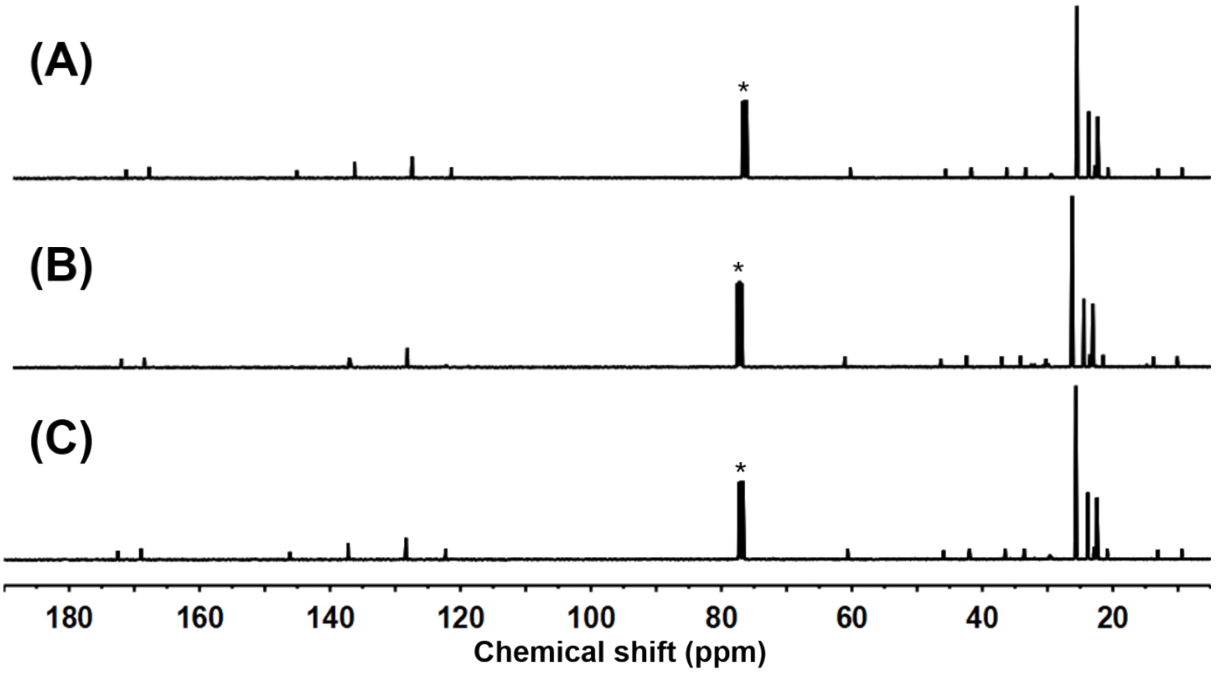


Figure S6. ^{13}C NMR spectra of VPOSS-2BPOSS: (A) *para*-VPOSS-2BPOSS, (B) *meta*-VPOSS-2BPOSS, (C) *ortho*-VPOSS-2BPOSS.

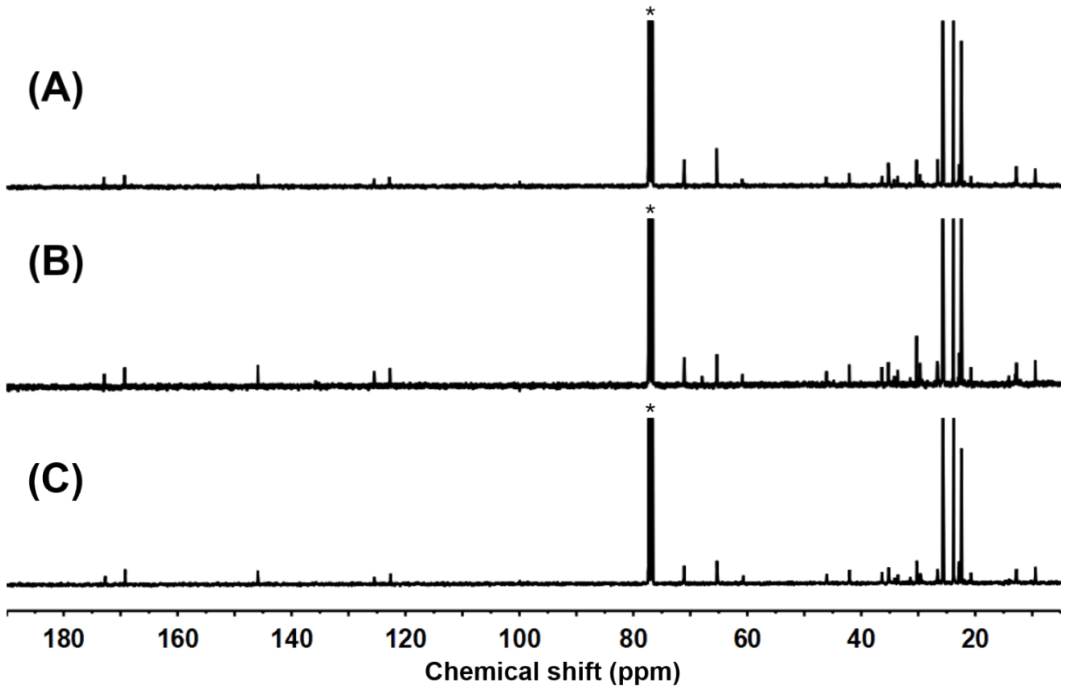


Figure S7. ^{13}C NMR spectra of DPOSS-2BPOSS: (A) *para*-DPOSS-2BPOSS, (B) *meta*-DPOSS-2BPOSS, (C) *ortho*-DPOSS-2BPOSS.

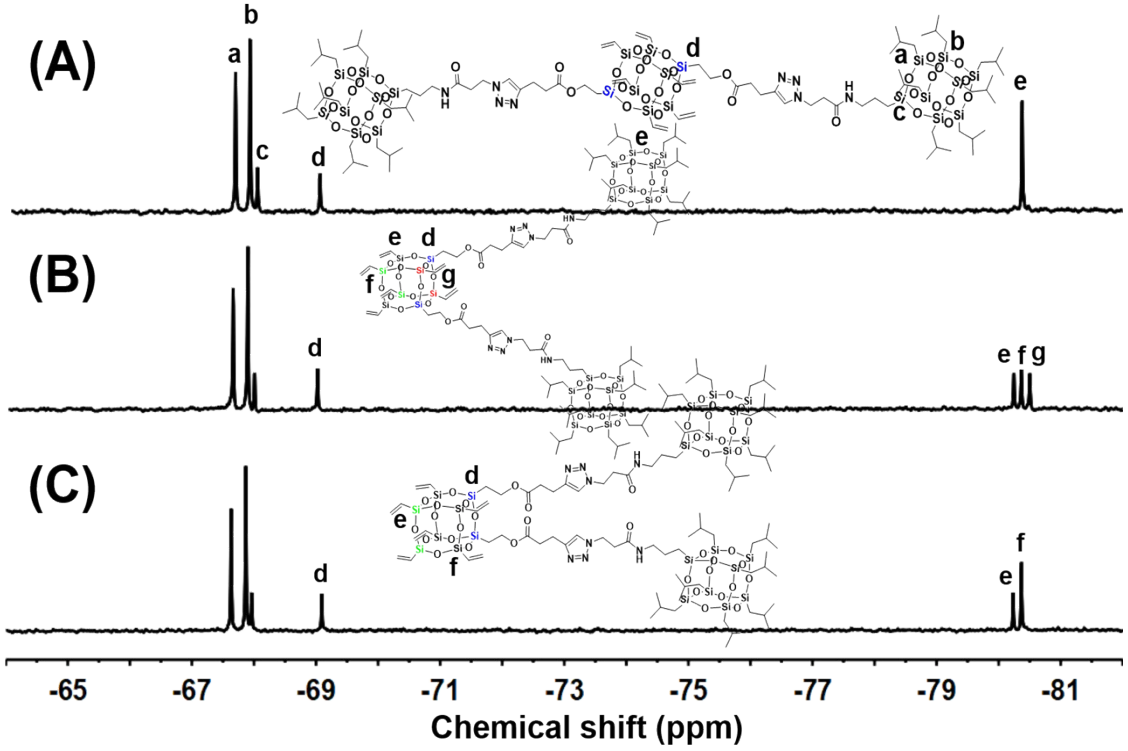


Figure S8. ^{29}Si NMR spectra of the VPOSS-2BPOSS: (A) *para*-VPOSS-2BPOSS, (B) *meta*-VPOSS-2BPOSS, (C) *ortho*-VPOSS-2BPOSS.

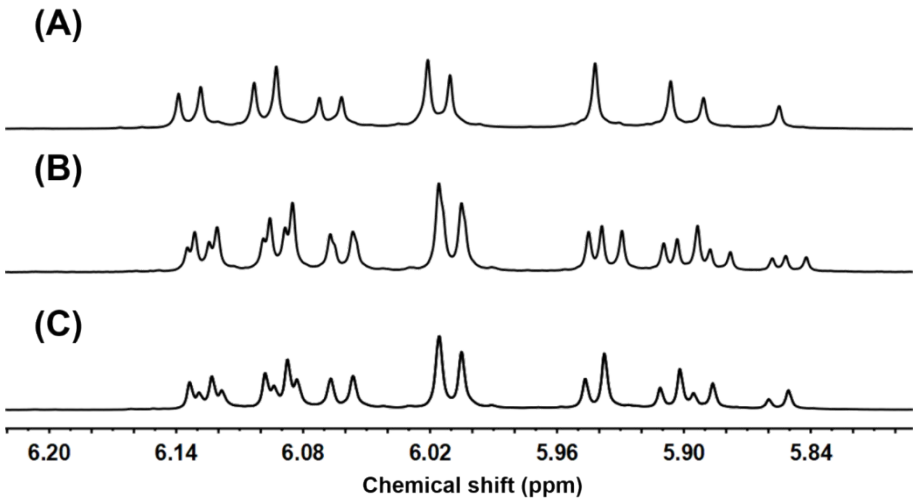


Figure S9. [1]H NMR spectra of the vinyl protons of VPOSS-2BPOSS: (A) *para*-VPOSS-2BPOSS, (B) *meta*-VPOSS-2BPOSS, (C) *ortho*-VPOSS-2BPOSS.

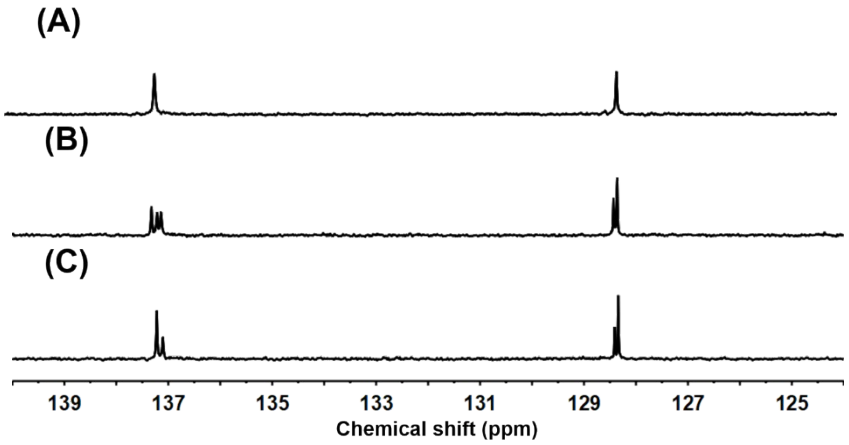


Figure S10. [1]H NMR spectra of the vinyl carbons of VPOSS-2BPOSS: (A) *para*-VPOSS-2BPOSS, (B) *meta*-VPOSS-2BPOSS, (C) *ortho*-VPOSS-2BPOSS.

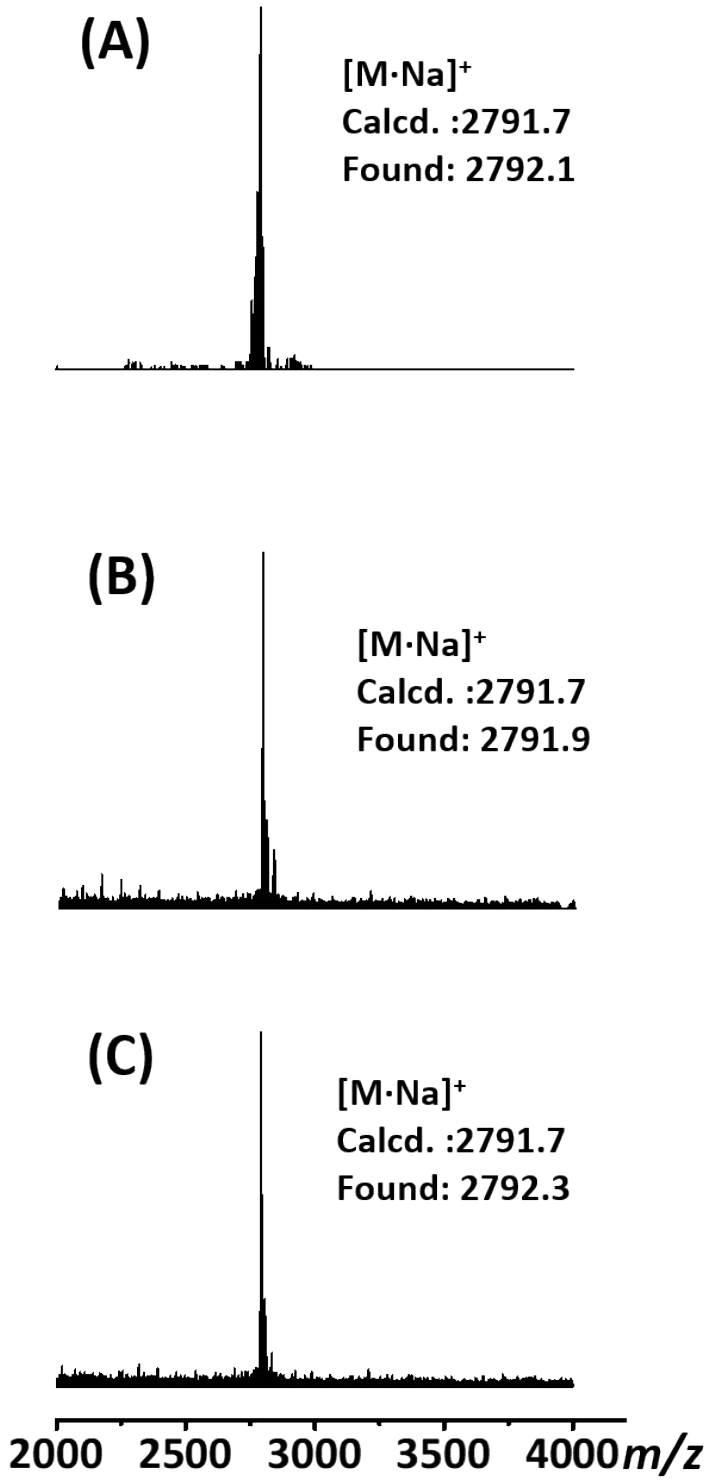


Figure S11. MALDI-TOF MS spectra of the regio-isomers of VPOSS-2BPOSS: (A) *para*-isomer, (B) *meta*-isomer, and (C) *ortho*-isomer.

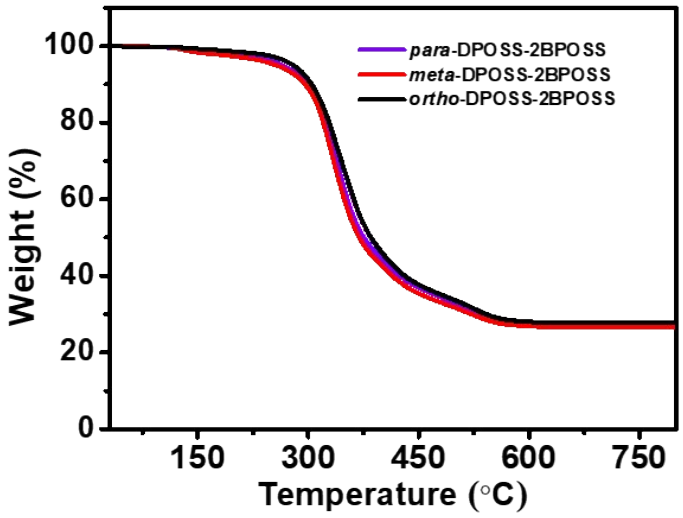


Figure S12. TGA curves of DPOSS-2BPOSS under nitrogen atmosphere with the heating rate of 10 °C/min.

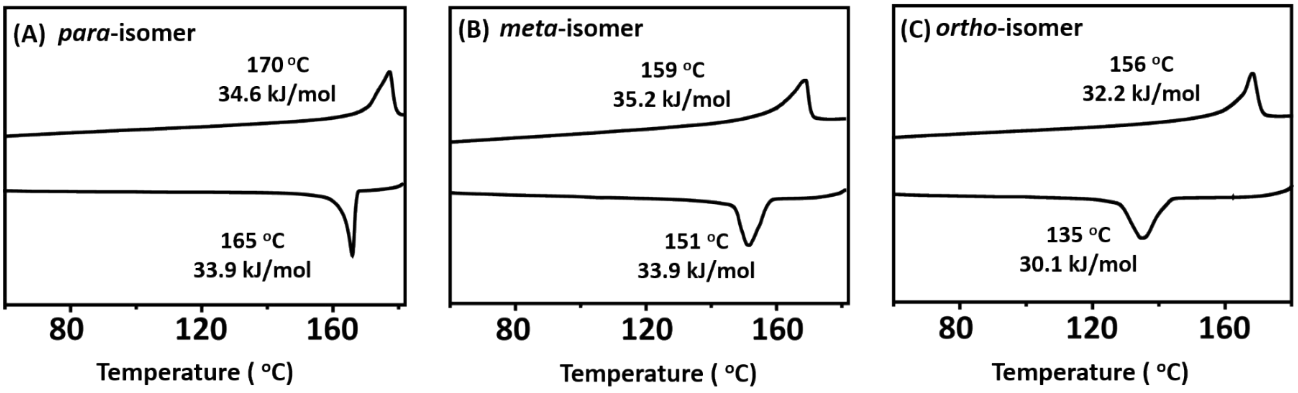


Figure S13. DSC curves of DPOSS-2BPOSS: (A) *para*-isomer, (B) *meta*-isomer, and (C) *ortho*-isomer. The first cooling curves and the second heating curves are shown with the heating and cooling rates of 10 °C min^{-1}. The extrapolated onset temperatures are shown for the corresponding melting, and the peak values are shown for crystallization processes.

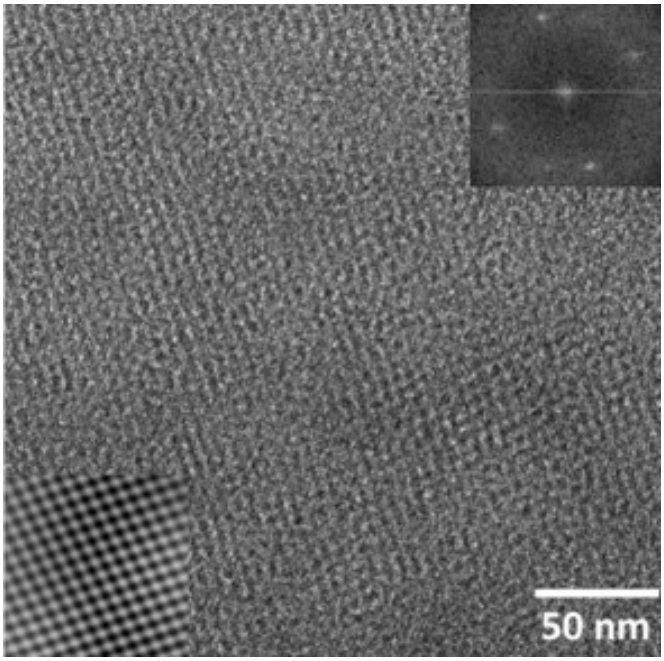


Figure S14. TEM image of *ortho*-isomer along the [100] direction of DG structure, the bottom inset is the local TEM image after Fourier filtering, and the upper inset is the corresponding FFT pattern.

Table S1. SAXS peak assignments for *ortho*-DPOSS-2BPOSS.

Double gyroid, ($Ia\bar{3}d$), a=12.04 nm		
(*hkl*)	q_{calc}†	q_{obs}‡
211	1.278	1.278
220	1.476	1.489
321	1.953	1.965
400	2.087	2.106
420	2.334	2.335
332	2.448	2.458
422	2.557	2.582

†Expected peak positions for assigned space group with given lattice dimensions.

‡Peak positions from SAXS data, obtained by fitting individual peaks with a Gaussian curve.

References

(S1) Wang, X. M.; Guo, Q. Y.; Han, S. Y.; Wang, J. Y.; Han, D.; Fu, Q.; Zhang, W. B., Stochastic/Controlled Symmetry Breaking of the T_8-POSS Cages toward Multifunctional Regioisomeric Nanobuilding Blocks. *Chem. Eur. J.* **2015,** *21* (43), 15246-15255.

(S2) Wang, X.-M.; Shao, Y.; Xu, J.; Jin, X.; Shen, R.-H.; Jin, P.-F.; Shen, D.-W.; Wang, J.; Li, W.; He, J., Precision synthesis and distinct assembly of double-chain giant surfactant Regioisomers. *Macromolecules* **2017,** *50* (10), 3943-3953.

(S3) Feng, X.; Zhang, R.; Li, Y.; Hong, Y.-l.; Guo, D.; Lang, K.; Wu, K.-Y.; Huang, M.; Mao, J.; Wesdemiotis, C.; Nishiyama, Y.; Zhang, W.; Zhang, W.; Miyoshi, T.; Li, T.; Cheng, S. Z. D., Hierarchical Self-Organization of AB_n Dendron-like Molecules into a Supramolecular Lattice Sequence. *ACS Cent. Sci.* **2017,** *3* (8), 860-867.

(S4) Scherer, M. R. J., *Double-Gyroid-Structured Functional Materials: Synthesis and Applications*. Springer Science & Business Media: **2013**.