Corner-opening and corner-capping of mono-substituted T8 POSS: product distribution and isomerization

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Contents

1. Chemicals and Solvents.

Trisilanollsobutyl POSS (Hybrid Plastics), vinyltrimethoxysilane (98%, Aladdin), trichlorovinylsilane (98%, Aladdin), phenyltrimethoxysilane (98%, Aladdin), phenyltrichlorosilane (98%, Aladdin), 35% tetraethylammonium hydroxide (TEAOH, TCI America), triethylamine (TEA, 99.5%, J&K Chemicals), magnesium sulphate ($MgSO_4$, 99.99%, Aladdin), 2M hydrochloric acid (HCl) were used as received. Tetrahydrofuran (THF), methanol (MeOH), petroleum ether, ether, acetone was used as received unless otherwise stated.

2. Instrumentation and Characterization.

Nuclear Magnetic Resonance (NMR). All ^{1}H NMR spectra were acquired in $CDCl_3$ using a Bruker 400 MHz NMR spectrometer. The spectra were referenced to the residual solvent peak in $CDCl_3$ at δ 7.27 ppm. ^{13}C NMR spectra were acquired in $CDCl_3$ using a Bruker 101 MHz NMR spectrometer and referenced to the residual peak in $CDCl_3$ at δ 77.0 ppm. ^{29}Si NMR spectra were acquired in $CDCl_3$ using a Bruker 119 MHz NMR spectrometer and referenced to tetramethylsilane (TMS) at δ 0.00 ppm.

Matrix-Assisted Laser Desorption/ionization Time-of-Flight (MALDI-ToF). MALDI-ToF mass spectroscopy (MS) were acquired on an UltrafleXtreme MALDI-ToF mass spectrometer (Bruker Daltonics) equipped with a 1 kHz smart beam-II laser. Trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Sigma-Aldrich, > 98%) was used as the matrix and prepared in $CHCl_3$ at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in $CHCl_3$ at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the target plate was inserted into the MALDI-ToF mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and maximize the sensitivity.

Reversed-Phase High Performance Liquid Chromatography (RP-HPLC). All RP-HPLC analysis experiments were performed on a chromatographic system consisting of an LC-100 pump (Wufeng Instrument, China) and an E800 evaporative light scattering detector (SANAER Instrument, China). The column was Sepax Bio-C18 (5 μm, 300 Å, 4.6×250 mm) from Sepax Technologies, Inc. THF/H_2O (3/1, v/v) was used as the mobile phase. Solvents were degassed by nitrogen for a minimum of 15 min prior to all HPLC experiments. A flow rate of 0.6 mL/min at a giving a constant pressure of 112 bars was used. The temperature was set at 25 °C, and the injection volume was 20 μL. Once the elution was finished, a blank sample containing mobile phase was injected and flushed through the column to confirm complete elution of the previous injection.

Preparative HPLC. All preparative HPLC experiments were performed on a chromatographic system consisting of an LC-6AD HPLC pump and a RID-10A detector (Shimadzu, Japan). The column selected for separations were Ultimate XB-C18 (5 μm, 120 Å, 21.2×250 mm) from Welch Materials. THF/H_2O (3/1, v/v) was used as the mobile phase. A flow rate of 8 mL/min at a giving a constant pressure of 73 bars was used. The temperature was set at 25 °C, and the injection volume was 3 mL.

3. Synthesis.

T_8 BP-V (1a). To a solution of trisilanollsobutyl POSS (20.0 g, 25.2 mmol) in 30 mL of THF at the room temperature, vinyltrimethoxysilane (3.9 mL, 26.2 mmol) were given. After addition of TEAOH (35% solution in water, 1 mL, 2.4 mmol of base), the mixture was stirred overnight. The resulting cloudy solution was mixed with 300 mL MeOH. After filtering, the residue was purified by silica gel chromatography with PE as eluent to afford a white solid. Yield: 52%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm, δ): 6.08-5.81 (3H, $-C\underline{H}=C\underline{H}_2$), 1.86 (7H, $-CH_2-C\underline{H}-(CH_3)_2$), 0.97 (42H, $-CH_2-CH-(C\underline{H}_3)_2$), 0.61 (14H, $-C\underline{H}_2-CH-(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm, δ):135.8, 129.9, 25.7, 23.9, 22.5. ^{29}Si NMR ($CDCl_3$, 119 MHz, ppm, δ): -67.40, -67.86, -81.53. FT-IR (KBr) υ (cm^{-1}): 3554, 3473, 2963, 2876, 1631, 1464, 1400, 1337, 1233, 1107, 957, 836, 743, 566, 479.

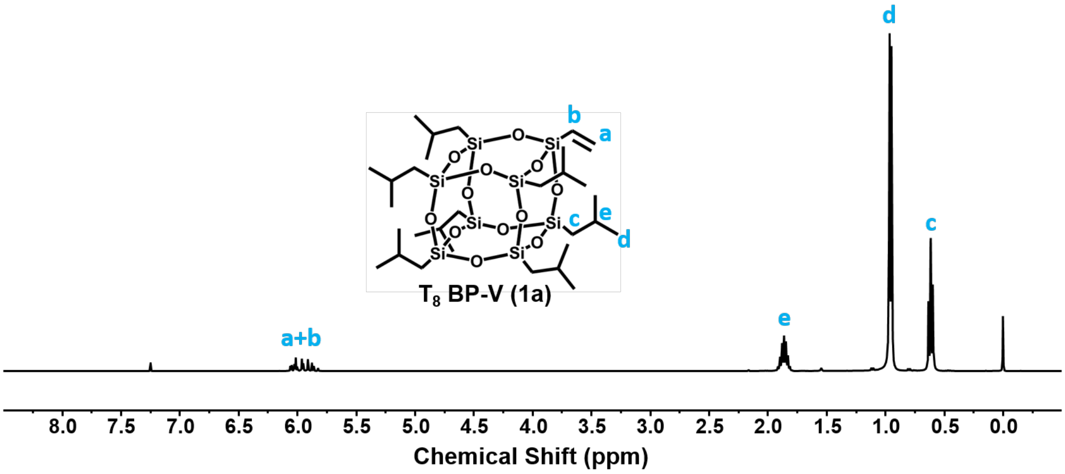

Fig. S1 ^{1}H NMR spectra of **T_8 BP-V (1a)**

T_7 BP-V. 1a (4 g, 4.74 mmol) was dissolved in 80 ml of anhydrous THF in a 100 mL round-bottomed flask. TEAOH (35% solution in water, 2 ml, 4.84 mmol of base) was added dropwise *via* a syringe with severely stirring at room temperature for 6 h. The reaction solution was neutralized with few mL of 2M HCl. After removing the solvent by a rotary evaporator, the crude product was re-dissolved in anhydrous ether. The solution was dried over $MgSO_4$, filtered, and concentrated. The resultant solid was purified by MeOH extraction to provide a viscous solid. Yield: 91%. ^{13}C NMR ($CDCl_3$, 101 MHz, ppm, δ):135.6, 130.7, 25.8, 23.9, 23.2, 22.8, 22.5. ^{29}Si NMR ($CDCl_3$, 119 MHz, ppm, δ): -58.84, -67.45, -67.98, -68.65. FT-IR (KBr) υ (cm^{-1}): 3552, 3473, 3224, 2956, 2873, 1614, 1462, 1398, 1334, 1230, 1114, 896, 828, 744, 601, 476.

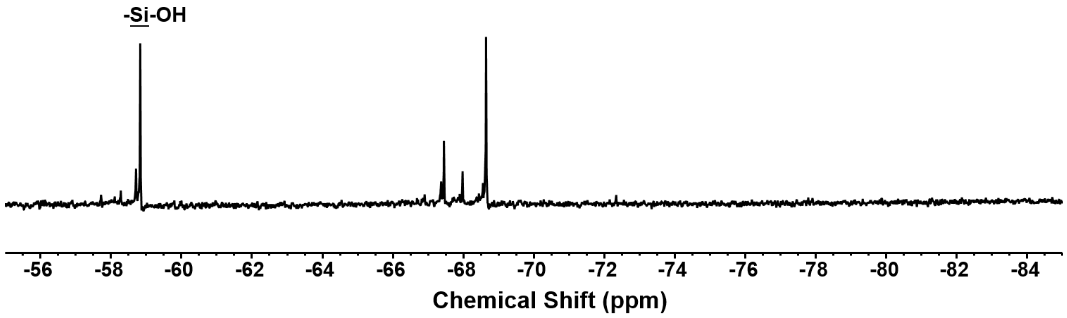

Fig. S2 ^{29}Si NMR spectra of **T$_7$ BP-V**

T$_8$ BP-2V (2). T$_7$ BP-V (1 g, 1.31 mmol), TEA (1.33 g, 13.10 mmol) and anhydrous THF (10 mL) were charged into a round-bottomed flask at room temperature under N$_2$ atmosphere. The reaction mixture was cooled to 0 ℃ in an ice bath. Trichlorovinylsilane (0.25 g, 1.58 mmol) was added to the flask by dropping funnel at the rate of a drop per two second. The mixture was magnetically stirred at 0 ˚C for 1 h and at room temperature for 3 h. After removing the solvent by a rotary evaporator, the crude product was purified by silica gel chromatography with PE as eluent to afford a white solid. The white solid was further separated by preparative HPLC with THF/H$_2$O (3/1, v/v) as the mobile phase. Two fractions **1a** and **2** were separated with the yield of 15.2 % and 2.8 %, respectively. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm, δ): 6.10-5.82 (6H, $-C\underline{H}=C\underline{H}_2$), 1.87 (6H, $-CH_2-C\underline{H}-(CH_3)_2$), 0.95 (36H, $-CH_2-CH-(C\underline{H}_3)_2$), 0.62 (12H, $-C\underline{H}_2-CH-(CH_3)_2$). ^{13}C NMR (CDCl$_3$, 101 MHz, ppm, δ):136.1, 135.9, 129.8, 129.7, 25.7, 23.9, 22.4. ^{29}Si NMR (CDCl$_3$, 119 MHz, ppm, δ): -66.91, -67.38, -67.84, -81.10, -81.53. FT-IR (KBr) υ (cm^{-1}): 3550, 3479, 2961, 2837, 1612, 1462, 1405, 1333, 1233, 1107, 958, 832, 738, 568, 474.

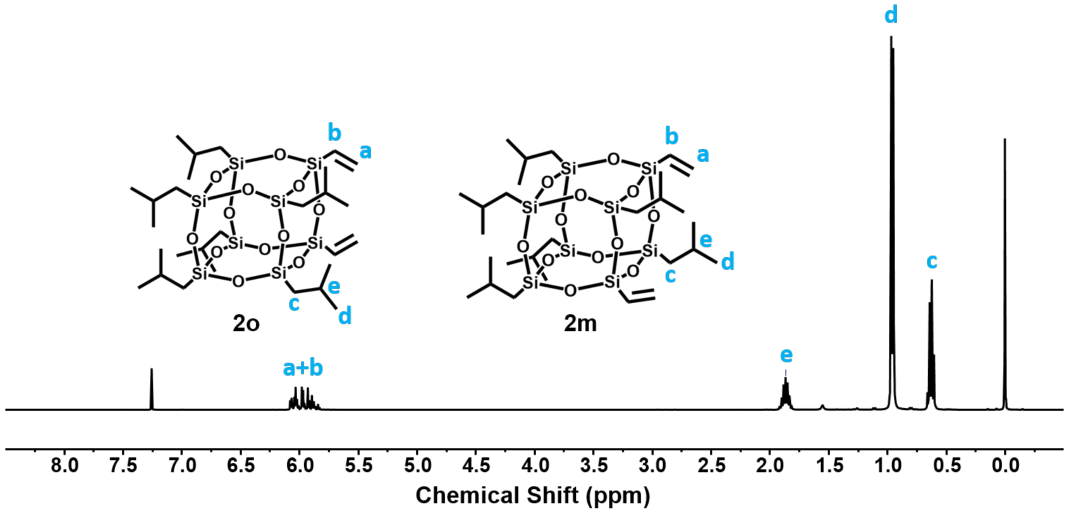

Fig. S3 ^{1}H NMR spectra of **T$_8$ BP-2V (2)**

T$_8$ BP-Ph (1b). To a solution of trisilanolIsobutyl POSS (20.0 g, 25.2 mmol) in 30 mL of THF at the room temperature, phenyltrimethoxysilane (4.9 mL, 26.2 mmol) were given. After addition of TEAOH (35% solution in water, 1 mL, 2.4 mmol of base) was stirred overnight. The resulting cloudy solution was mixed with 300 mL MeOH. After filtering, the residue was purified by silica gel chromatography with PE as eluent to afford a white solid. Yield: 43%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm, δ): 7.68-7.33 (5H, Ph), 1.87 (7H, $-CH_2-C\underline{H}-(CH_3)_2$), 0.97 (42H, $-CH_2-CH-(C\underline{H}_3)_2$), 0.63 (14H, $-C\underline{H}_2-CH-(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm, δ):134.0, 131.8, 130.2, 127.6, 25.7, 23.9, 22.5. ^{29}Si NMR ($CDCl_3$, 119 MHz, ppm, δ): -67.19, -67.81, -80.51. FT-IR (KBr) υ (cm^{-1}): 3546, 3478, 2956, 2870, 1621, 1464, 1392, 1334, 1235, 1105, 833, 740, 693, 568, 478.

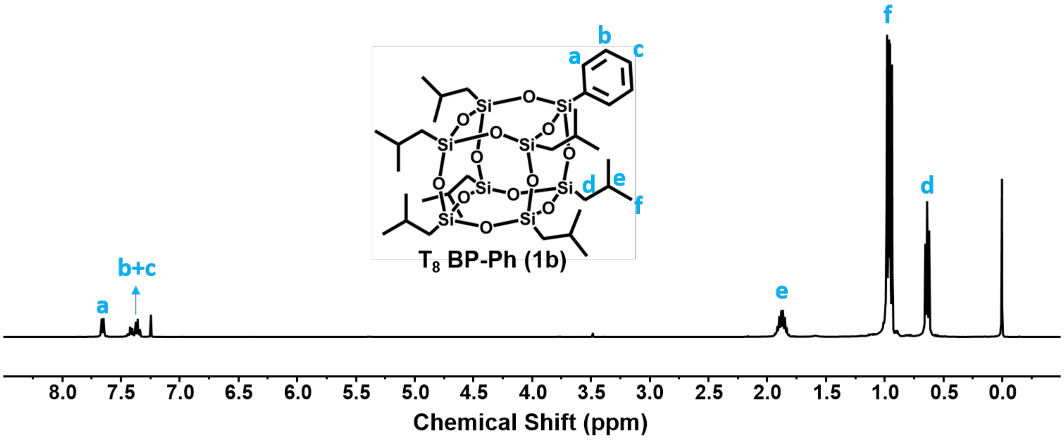

Fig. S4 ^{1}H NMR spectra of **T_8 BP-Ph (1b)**

T_7 BP-Ph. 1b (4 g, 4.48 mmol) was dissolved in 80 ml of anhydrous THF in a 100 mL round-bottomed flask. TEAOH (35% solution in water, 1.90 ml, 4.57 mmol of base) was added dropwise *via* a syringe with severely stirring at room temperature for 6 h. The reaction solution was neutralized with few mL of 2M HCl. After removing the solvent by a rotary evaporator, the crude product was re-dissolved in anhydrous ether. The solution was dried over $MgSO_4$, filtered, and concentrated. The resultant solid was purified by MeOH extraction to provide a viscous solid. Yield: 88%. ^{13}C NMR ($CDCl_3$, 101 MHz, ppm, δ):134.0, 130.1, 127.6, 25.7, 23.9, 23.2, 22.8, 22.5. ^{29}Si NMR ($CDCl_3$, 119 MHz, ppm, δ): -58.76, -67.44, -67.75, -68.61. FT-IR (KBr) υ (cm^{-1}): 3550, 3471, 3139, 2954, 2875, 1625, 1468, 1395, 1232, 1108, 889, 832, 731, 601, 484.

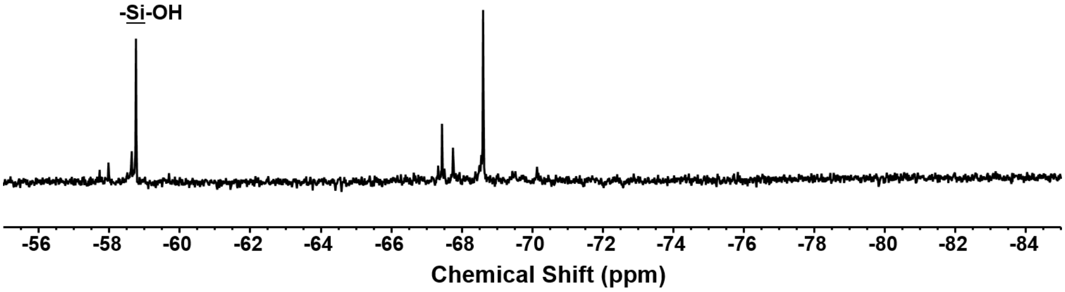

Fig. S5 ^{29}Si NMR spectra of **T_7 BP-Ph**

T_8 BP-2Ph (3). T_7 BP-Ph (1 g, 1.23 mmol), TEA (1.25 g, 12.35 mmol) and anhydrous THF (10 mL) were charged into a round-bottomed flask at room temperature under N_2 atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. Phenyltrimethoxysilane (0.33 g, 1.58 mmol) was added to the flask by dropping funnel at the rate of a drop per two second and magnetically stirred at 0 ˚C for 1 h and room temperature for

3 h. After removing the solvent by a rotary evaporator, the crude product was purified by silica gel chromatography with PE as eluent to afford a white solid. The white solid was further separated by preparative HPLC with THF/H_2O (3/1, v/v) as the mobile phase. Two fractions **1b** and **3** were separated with the yields of 12.6 % and 2.4 %, respectively. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm, δ): 7.70-7.31 (10H, Ph), 1.88 (6H, $-CH_2-C\underline{H}-(CH_3)_2$), 0.96 (36H, $-CH_2-CH-(C\underline{H}_3)_2$), 0.66 (12H, $-C\underline{H}_2-CH-(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm, δ):134.0, 131.8, 131.7, 130.2, 127.6, 25.7, 23.9, 22.5. ^{29}Si NMR ($CDCl_3$, 119 MHz, ppm, δ): -66.50, -67.12, -67.75, -79.87, -80.45. FT-IR (KBr) υ (cm^{-1}): 3557, 3480, 2957, 2872, 1607, 1459, 1388, 1325, 1233, 1099, 830, 732, 697, 576, 484.

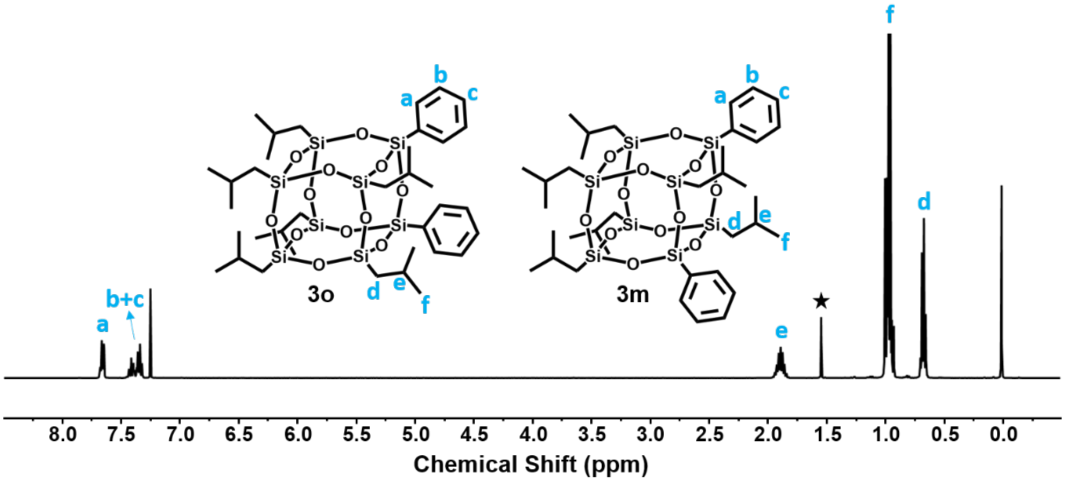

Fig. S6 ^{1}H NMR spectra of **T_8 BP-2Ph (3)**

T_8 BP-V-Ph (4). T_7 BP-V (1 g, 1.31 mmol), TEA (1.33 g, 13.10 mmol) and anhydrous THF (10 mL) were charged into a round-bottomed flask at room temperature under N_2 atmosphere. The reaction mixture was cooled to 0 °C in an ice bath. Phenyltrimethoxysilane (0.33 g, 1.58 mmol) was added to the flask by dropping funnel at the rate of a drop per two second and magnetically stirred at 0 ˚C for 1 h and room temperature for 3 h. After removing the solvent by a rotary evaporator, the crude product was purified by silica gel chromatography with PE as eluent to afford a white solid. The white solid was further separated by preparative HPLC with THF/H_2O (3/1, v/v) as the mobile phase. Two fractions **1b** and **4** were separated with the yields of 13.9% and 2.1 %, respectively. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm, δ): 7.70-7.31 (5H, Ph), 6.10-5.82 (3H, $-C\underline{H}=C\underline{H}_2$), 1.88 (6H, $-CH_2-C\underline{H}-(CH_3)_2$), 0.96 (36H, $-CH_2-CH-(C\underline{H}_3)_2$), 0.64 (12H, $-C\underline{H}_2-CH-(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 101 MHz, ppm, δ):136.2, 136.0, 134.0, 131.7, 131.5, 130.8, 129.8, 129.6, 127.6, 25.71, 23.85, 22.42. ^{29}Si NMR ($CDCl_3$, 119 MHz, ppm, δ): -66.69, -67.15, -67.31, -67.77, -80.01, -80.47, -80.82, -81.44. FT-IR (KBr) υ (cm^{-1}): 3561, 3481, 2959, 2880, 1613, 1465, 1397, 1329, 1232, 1102, 834, 738, 698, 573, 482.

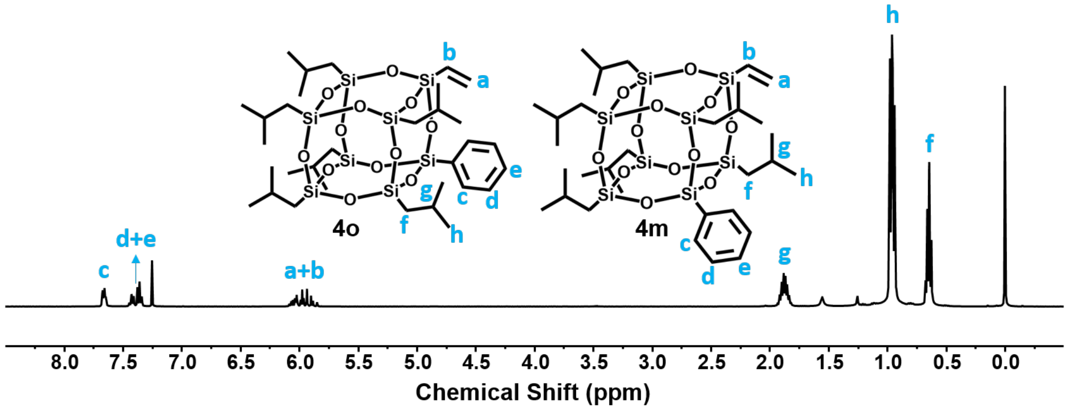

Fig. S7 ^{1}H NMR spectra of **T_8 BP-V-Ph (4)**

4. Calculations

In Table 1 and Table S1, we list the chemical environments of each equivalent Si atoms on **0**, **1a**, **1b**, **2o-p**, **3o-p** and **4o-p**. The shifting factor F_δ is defined by Eq. 1 in the main text. The three coefficients in Eq. 1 is different for Si_V and Si_{Ph}. Based on the experimental ^{29}Si NMR data and peak assignment of **0**, **1a** and **1b**, we can calculate the coefficients for Si_V and Si_{Ph}. We first define the experimental δ of Si_B (-67.90 ppm), Si_V (-81.53 ppm) and Si_{Ph} (-80.51 ppm) of **0**, **1a** and **1b**, respectively, as the reference δ values for Si_B, Si_V and Si_{Ph}, because they share the same chemical environment of Si(BBB)(BBB)B. Then, based on the experimental δ and chemical environments of three groups of Si_B atoms on **1a**, we can list the following equations:

$$\text{For SiB}^3\text{:}\quad 1*a + 3*0 + 3*0 = -67.40 - (-67.90)$$

$$\text{For SiB}^2\text{:}\quad 3*0 + 1*b + 3*0 = -67.86 - (-67.90)$$

$$\text{For SiB}^1\text{:}\quad 3*0 + 3*0 + 1*c = -67.86 - (-67.90)$$

Coefficients a, b, c of F_δ caused by Si_V can be easily obtained:

$$a_V = 0.50 \text{ ppm},\ b_V = 0.04 \text{ ppm},\ c_V = 0.04 \text{ ppm}$$

The shifting factor F_δ caused by Si_V can be written as follows:

$$F_\delta = 0.50*N_{o\text{-V}} + 0.04*N_{m\text{-V}} + 0.04*N_{p\text{-V}} \qquad \text{(Eq. S1)}$$

In the same way, based on the experimental δ and chemical environments of three groups of Si_B atoms on **1b**, we can list the following equations:

$$\text{For SiB}^3\text{:}\quad 1*a + 3*0 + 3*0 = -67.19 - (-67.90)$$

$$\text{For SiB}^2\text{:}\quad 3*0 + 1*b + 3*0 = -67.81 - (-67.90)$$

$$\text{For SiB}^1\text{:}\quad 3*0 + 3*0 + 1*c = -67.81 - (-67.90)$$

Coefficients a, b, c of F_δ caused by Si_{Ph} can be easily obtained:

$$a_{Ph} = 0.71 \text{ ppm},\ b_{Ph} = 0.09 \text{ ppm},\ c_{Ph} = 0.09 \text{ ppm}$$

The shifting factor F_δ caused by Si_{Ph} can be written as follows:

$$F_\delta = 0.71*N_{o\text{-Ph}} + 0.09*N_{m\text{-Ph}} + 0.09*N_{p\text{-Ph}} \qquad \text{(Eq. S2)}$$

Combining Eq. 2, Eq. S1 and Eq. S2, we can obtain these equations:

$$\delta_{\mathrm{calcd.}}(\mathrm{Si_B}) = -67.90 + (0.50*\mathrm{N}_{o\text{-V}} + 0.04*\mathrm{N}_{m\text{-V}} + 0.04*\mathrm{N}_{p\text{-V}}) + (0.71*\mathrm{N}_{o\text{-Ph}} + 0.09*\mathrm{N}_{m\text{-Ph}} + 0.09*\mathrm{N}_{p\text{-Ph}}) \tag{Eq. S3}$$

$$\delta_{\mathrm{calcd.}}(\mathrm{Si_V}) = -81.53 + (0.50*\mathrm{N}_{o\text{-V}} + 0.04*\mathrm{N}_{m\text{-V}} + 0.04*\mathrm{N}_{p\text{-V}}) + (0.71*\mathrm{N}_{o\text{-Ph}} + 0.09*\mathrm{N}_{m\text{-Ph}} + 0.09*\mathrm{N}_{p\text{-Ph}}) \tag{Eq. S4}$$

$$\delta_{\mathrm{calcd.}}(\mathrm{Si_{Ph}}) = -80.51 + (0.50*\mathrm{N}_{o\text{-V}} + 0.04*\mathrm{N}_{m\text{-V}} + 0.04*\mathrm{N}_{p\text{-V}}) + (0.71*\mathrm{N}_{o\text{-Ph}} + 0.09*\mathrm{N}_{m\text{-Ph}} + 0.09*\mathrm{N}_{p\text{-Ph}}) \tag{Eq. S5}$$

Now, let us perform the calculation by using Eq. S3, Eq. S4 and Eq. S5.

For example **2o**:

$\delta_{\mathrm{calcd.}}(\mathrm{Si_V}) = -81.53 + (0.50*1 + 0.04*0 + 0.04*0) = -81.03$ (ppm)

$\delta_{\mathrm{calcd.}}(\mathrm{Si_B}^1) = -67.90 + (0.50*1 + 0.04*1 + 0.04*0) = -67.36$ (ppm)

$\delta_{\mathrm{calcd.}}(\mathrm{Si_B}^2) = -67.90 + (0.50*0 + 0.04*1 + 0.04*1) = -67.82$ (ppm)

For another example **4o**:

$\delta_{\mathrm{calcd.}}(\mathrm{Si_V}) = -81.53 + (0.50*0 + 0.04*0 + 0.04*0) + (0.71*1+ 0.09*0 + 0.09*0) = -80.82$ (ppm)

$\delta_{\mathrm{calcd.}}(\mathrm{Si_{Ph}}) = -81.51 + (0.50*1 + 0.04*0 + 0.04*0 + (0.71*0 + 0.09*0 + 0.09*0) = -81.01$(ppm)

$\delta_{\mathrm{calcd.}}(\mathrm{Si_B}^1) = -67.90 + (0.50*1 + 0.04*0 + 0.04*0) + (0.71*0 + 0.09*1 + 0.09*0) = -67.31$ (ppm)

$\delta_{\mathrm{calcd.}}(\mathrm{Si_B}^2) = -67.90 + (0.50*0 + 0.04*1 + 0.04*0) + (0.71*1 + 0.09*0 + 0.09*0) = -67.15$ (ppm)

$\delta_{\mathrm{calcd.}}(\mathrm{Si_B}^3) = -67.90 + (0.50*0 + 0.04*0 + 0.04*1) + (0.71*0 + 0.09*1 + 0.09*0) = -67.77$ (ppm)

$\delta_{\mathrm{calcd.}}(\mathrm{Si_B}^4) = -67.90 + (0.50*0 + 0.04*1 + 0.04*0) + (0.71*0 + 0.09*0 + 0.09*1) = -67.77$ (ppm)

5. Supplementary Figures and Tables.

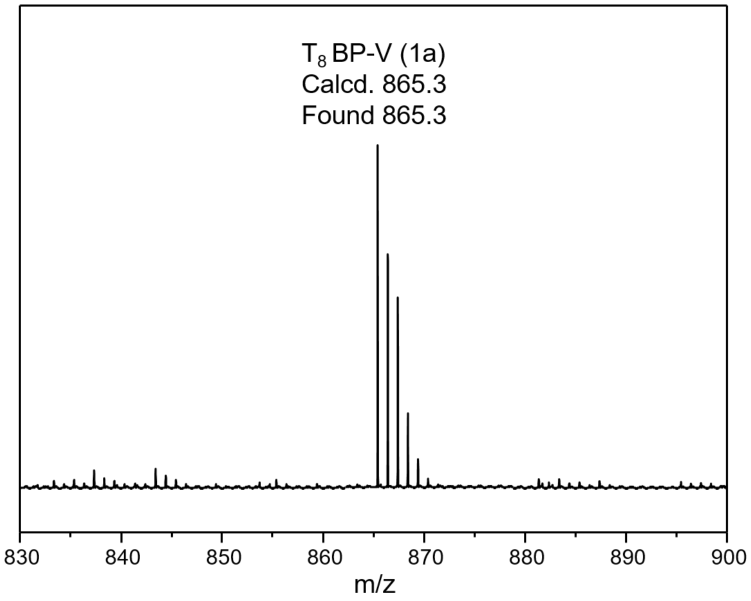

Fig. S8 MALDI-ToF MS spectra of **T_8 BP-V (1a)**

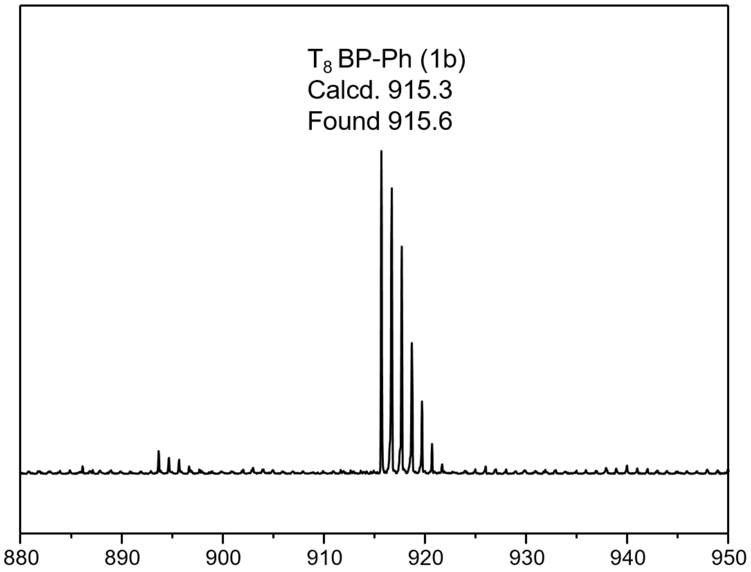

Fig. S9 MALDI-ToF MS spectra of **T_8 BP-Ph (1b)**

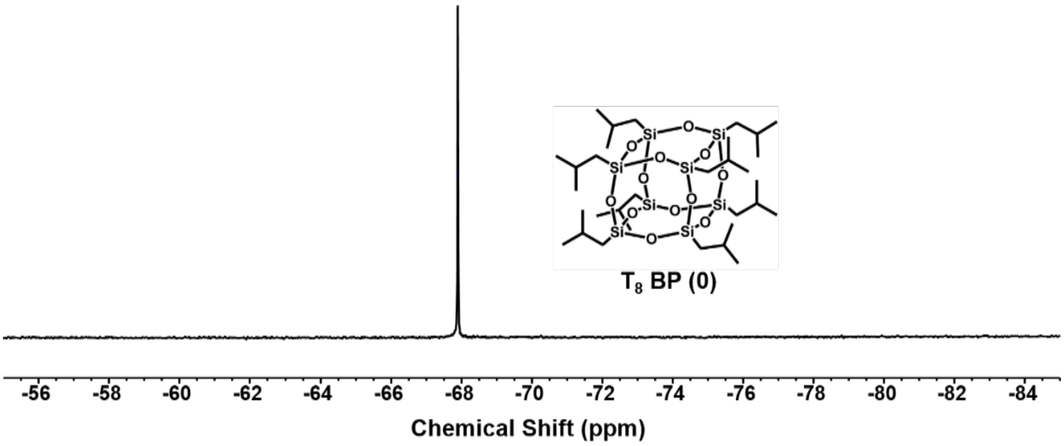

Fig. S10 ^{29}Si NMR spectra of **T_8 BP (0)**

Table S1. Summary of the chemical environment and ^{29}Si NMR chemical shift analysis of **0**, **1**, **2** and **3**.

Compound	Si Grouping[a]	Chemical Environment Analysis			F_δ[b]	δ [ppm]	
		ortho-Si	*meta*-Si	*para*-Si		Calcd.[c]	Exptl.[d]
0	$\mathrm{Si_B}$ (8)	3B	3B	B	0	-	-67.90
1a	$\mathrm{Si_V}$ (1)	3B	3B	B	0	-	-81.53
	$\mathrm{Si_B}^1$ (1)	3B	3B	V	0.04	-	-67.86
	$\mathrm{Si_B}^2$ (3)	3B	V, 2B	B	0.04	-	-67.86
	$\mathrm{Si_B}^3$ (3)	V, 2B	3B	B	0.5	-	-67.40
2o	$\mathrm{Si_V}$ (2)	V, 2B	3B	B	0.5	-81.03	-81.10
	$\mathrm{Si_B}^1$ (4)	V, 2B	V, 2B	B	0.54	-67.36	-67.38
	$\mathrm{Si_B}^2$ (2)	3B	V, 2B	V	0.08	-67.82	-67.84
2m	$\mathrm{Si_V}$ (2)	3B	V, 2B	B	0.04	-81.49	-81.52
	$\mathrm{Si_B}^1$ (2)	2V, B	3B	B	1	-66.90	-66.91
	$\mathrm{Si_B}^2$ (2)	V, 2B	3B	V	0.54	-67.36	-67.38
	$\mathrm{Si_B}^3$ (2)	3B	2V, B	B	0.08	-67.82	-67.84
2p	$\mathrm{Si_V}$ (2)	3B	3B	V	0.04	-81.49	-
	$\mathrm{Si_B}$ (6)	V, 2B	V, 2B	B	0.54	-67.36	-
1b	$\mathrm{Si_{Ph}}$ (1)	3B	3B	B	0	-	-80.51
	$\mathrm{Si_B}^1$ (1)	3B	3B	Ph	0.09	-	-67.81
	$\mathrm{Si_B}^2$ (3)	3B	Ph, 2B	B	0.09	-	-67.81
	$\mathrm{Si_B}^3$ (3)	Ph, 2B	3B	B	0.71	-	-67.19
3o	$\mathrm{Si_{Ph}}$ (2)	Ph, 2B	3B	B	0.71	-79.80	-79.87
	$\mathrm{Si_B}^1$ (4)	Ph, 2B	Ph, 2B	B	0.8	-67.10	-67.12
	$\mathrm{Si_B}^2$ (2)	3B	Ph, 2B	Ph	0.18	-67.72	-67.75
3m	$\mathrm{Si_{Ph}}$ (2)	3B	Ph, 2B	B	0.09	-80.42	-80.45
	$\mathrm{Si_B}^1$ (2)	2Ph, B	3B	B	1.42	-66.48	-66.50
	$\mathrm{Si_B}^2$ (2)	Ph, 2B	3B	Ph	0.8	-67.10	-67.12
	$\mathrm{Si_B}^3$ (2)	3B	2Ph, B	B	0.18	-67.72	-67.75
3p	$\mathrm{Si_{Ph}}$ (2)	3B	3B	Ph	0.09	-80.42	-
	$\mathrm{Si_B}$ (6)	Ph, 2B	Ph, 2B	B	0.8	-67.10	-

[a] The subscripts represent the grouping of Si atoms with equivalent chemical environment. The numbers in parentheses are the number of chemically equivalent Si atoms.

[b] Calculated by Eq.1. For $\mathrm{Si_V}$, a=0.5, b=0.04, c=0.04; For $\mathrm{Si_{Ph}}$, a=0.71, b=0.09, c=0.09.

[c] Calculated by Eq. 2. Reference δ values for $\mathrm{Si_B}$, $\mathrm{Si_V}$ and $\mathrm{Si_{Ph}}$ are -67.90 ppm, -81.53 ppm and -80.51 ppm, respectively.

[d] All δ values are referenced to tetramethylsilane (TMS) at δ=0.00 ppm.

Table S2. Summary of the chemical environment and ^{29}Si NMR chemical shift analysis of **4**.

Compound	Si Grouping	Chemical Environment Analysis			F_δ	δ [ppm]	
		ortho-Si	*meta*-Si	*para*-Si		Calcd.	Exptl.
4o	Si_V (1)	Ph, 2B	3B	B	0.71	-80.82	-80.89
	Si_{Ph} (1)	V, 2B	3B	B	0.5	-80.01	-81.10
	Si_B^1 (2)	V, 2B	Ph, 2B	B	0.59	-67.31	-67.34
	Si_B^2 (2)	Ph, 2B	V, 2B	B	0.75	-67.15	-67.18
	Si_B^3 (1)	3B	Ph, 2B	V	0.13	-67.77	-67.80
	Si_B^4 (1)	3B	V, 2B	Ph	0.13	-67.77	-67.80
4m	Si_V (1)	3B	Ph, 2B	B	0.09	-81.44	-81.49
	Si_{Ph} (1)	3B	V, 2B	B	0.04	-80.47	-80.50
	Si_B^1 (2)	V, Ph, B	3B	B	1.21	-66.69	-66.71
	Si_B^2 (1)	Ph, 2B	3B	V	0.75	-67.15	-67.18
	Si_B^3 (1)	V, 2B	3B	Ph	0.59	-67.31	-67.34
	Si_B^4 (2)	3B	V, Ph, B	B	0.13	-67.77	-67.80
4p	Si_V (1)	3B	3B	Ph	0.09	-81.44	-
	Si_{Ph} (1)	3B	3B	V	0.04	-80.47	-
	Si_B^1 (3)	V, 2B	Ph, 2B	B	0.59	-67.31	-
	Si_B^2 (3)	Ph, 2B	V, 2B	B	0.75	-67.15	-