Supporting information for

para-Bisvinylhexaisobutyl-Substituted T₈ Caged Monomer: Synthesis and Hydrosilylation Polymerization

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Experimental

Materials

All solvents and chemicals used here were obtained as reagent-grade quality and used without further purification. All the reactions were performed under a nitrogen atmosphere. Heptaisobutyl-vinyl-T8-silsesquioxane (1) was obtained form Hybrid Plastics Co.

Measurement

¹H-(400 MHz), ¹³C-(100 MHz), and ²⁹Si-(80 MHz) NMR spectra were recorded on a BRUKER PDX-300. Samples were analyzed in CDCl₃ using Me₄Si as an internal standard. High-resolution mass spectra were obtained on a JEOL JMS700 spectrometer. Fourier transform infrared (FTIR) spectra were obtained on a JASCO FT/IR-4100 spectrometer using KBr pellets. UV-vis spectra were recorded on a JASCO spectrophotometer V-670 KKN. Thermogravimetric analysis (TGA) was measured on a TA Instruments Hi-Res Modulated TGA 2950 thermogravimetric analyzer. Differential scanning calorimetry (DSC) was recorded on a TA Instruments 2920 Modulated DSC. Gel permeation chromatography (GPC) was performed using a TOSOH LC-8320 GPC instrument (TOSOH, Tokyo, Japan) with series connection of TSKgel G3000HHR 4000HHR, 3000HHR, and 2000HHR columns using CHCl₃ as an eluent. Powder X-ray diffractometry (XRD) studies were performed on a Rigaku Smartlab X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2 θ/θ mode at room temperature. The 2 θ scan data were collected at 0.01° intervals and the scan speed was 5° (2 θ /min.

Synthesis

Partially condensed trisilanol vinyl hexaisobutyl-T₈ cage (2)

Heptaisobutyl-vinyl-T8-silsesquioxane (1) (1.00 g, 1.19 mmol), 35% tetraethylammonium hydroxide (TEAOH) (0.5 ml, 1.21 mmol), THF

(20 ml) were charged into a round-bottomed flask under air atmosphere and magnetically stirred at room temperature for 6 h. The reaction solution was neutralized with few ml of 2N HCl and filtered by suction filtration. The solution was dried over MgSO₄, filtered, and concentrated. The resultant solid was purified by methanol extraction to provide a colorless solid in 89% yield. ¹H-NMR (CDCl₃): 0.60 (m, CH₂-Si,12H) 0.96 (d,-CH₃,36H) 1.85 (m,-CH₂CH(CH₃)₂,6H) 6.0 (m, CH=CH₂, 3H) ²⁹Si-NMR (CDCl₃): δ -58.3 (*Si*-OH) -67.3 (*Si*-CH=CH₂) -68.4 (the remaining *Si* of the POSS

 29 SI-NMR (CDCl₃): δ -58.3 (Si-OH) -67.3 (Si-CH=CH₂) -68.4 (the remaining Si of the POSS cage)

¹³C-NMR (CDCl₃): 22.5 (-CH₂CH(CH₃)₂) 23.9 (-CH₂CH(CH₃)₂) 27.7 (-CH₂CH(CH₃)₂) 129.9 (Si-CH=CH₂) 135.8 (Si-CH=CH₂)

FT-IR (KBr): v = 893, 1117, 1333, 1366, 1467, 2954, 3377 cm⁻¹.

Bisvinylhexisobutyl-T₈ cage (3)

2 (0.7792 g, 1.02 mmol), triethylamine (1.43 ml, 10.2 mmol), anhydrous THF (20 ml) were charged into a round-bottomed flask at room temperature under N_2 atmosphere. Trichlorovinylsilane (0.16 ml, 1.23 mmol) in anhydrous THF (5 ml) 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. The reaction solution was dried under vaccum and dissolved in hexane. After the solution was transferred to a separating funnel, the hexane phase was washed with H_2O and dried over MgSO₄, filtered, and concentrated. The resultant solid was purified by fractionation with gel permeation chromatography using CHCl₃ as an eluent to provide a colorless solid in 20% yield.

¹H-NMR (CDCl₃): δ 0.60 (m, CH₂-Si,12H) 0.96 (d,-CH₃,36H) 1.85 (m,-CH₂CH(CH₃)₂,6H) 6.0

(m, C*H*=C*H*₂, 6H)

²⁹Si-NMR (CDCl₃): δ -67.4 (*Si*-CH=CH₂) -67.9 (*Si*-CH₂)
¹³C-NMR (CDCl₃): δ 22.5 (-*C*H₂CH(CH₃)₂) 23.9 (-CH₂CH(CH₃)₂) 27.7 (-CH₂CH(CH₃)₂) 129.9 (Si-CH=CH₂) 135.8 (Si-CH=CH₂)
FT-IR (KBr): v = 1113, 1334, 1367, 1467, 2955, 3450 cm⁻¹.
HR-FAB-MS (m/z): calcd for [M+H]⁺, 813.2317; obs, 813.2313.

Polymerization

A mixture of **3** (0.2410 g, 0.296 mmol), 1,1,3,3,5,5-Hexamethyltrisiloxane (0.075 ml, 0.296 mmol) , Pt(dvs) (0.02 ml) in toluene (2 ml) was stirred at 90 °C for 24 h under N₂ atmosphere. After the solution was transferred to a separating funnel, the toluene phase was washed with ammonia water and dried over MgSO₄, filtered, and concentrated. The resultant solid was dissolved in CHCl₃, and reprecipitated from chloroform solution into methanol to provide a white solid in 25% yield.

¹H-NMR (CDCl₃): δ 1.80 (b, -CH₂C*H*(CH₃)₂, 6H) 0.90 (b, -CH₃, 36H) 0.54 (b, CH₂-Si,4H) 0.00 (b, CH₃-Si and CH₂-Si(CH₃)₂, 20H).

FT-IR (KBr): v = 743, 795, 839, 1120, 1230, 1258, 2956, 3450 cm⁻¹.



Figure S1 (left) ¹H- and (right) ¹³C- NMR spectra of 2 in CDCl₃.



Figure S2 (left) ¹H- and (right) ¹³C- NMR spectra of **3** in CDCl₃.



Figure S3 ²⁹Si NMR spectrum of 2 in CDCl₃. Expanded spectrum of Figure 1a.



Figure S4 ²⁹Si NMR spectrum of 3 in CDCl₃. Expanded spectrum of Figure 1b.



Figure S5 ¹H-NMR spectrum of 4 in CDCl₃.



Figure S6. TGA thermogram of 4 at a heating rate of 10 $^{\circ}$ C/min in N₂ flow.



Figure S7. DSC trace of 4 at a heating rate of 10 $^{\circ}$ C/min in N₂ flow.

DFT Calculation



Table S1 Contribution to the molecular orbital in LUMO+2 from atomic orbital of Si in 1.

	4s of	4p _x of	4s of	4p _x of	4s of	$4p_x$ of	4s of	4p _x of
	7Si	7Si	2Si	2Si	1Si	1Si	4Si	4Si
orbital coefficient	-0.253	0.185	-0.300	0.175	0.256	0.155	0.321	0.163
(orbital coefficient) ²	0.065	0.034	0.090	0.031	0.066	0.024	0.103	0.027
sum of squaring	0.099		0.121		0.090		0.130	
orbital coefficients								

Table S2 Contribution to the molecular orbital in LUMO+3 from atomic orbital of Si in 1

	4s of	$4p_{\rm v}$ of	4p _z of	4s of	$4p_x$ of	$4p_{\rm v}$ of	
	3Si	3Si	3Si	5Si	5Si	5Si	
orbital coefficient	-0.228	0.206	-0.188	-0.254	0.052	0.265	
(orbital coefficient) ²	0.052	0.042	0.035	0.065	0.003	0.070	
sum of squaring	0.124			0.138			
orbital coefficients							