

Supporting information for

**Stereochemically Purified *trans*-Dihydroxy-
Substituted Cage Silsesquioxane-Based Bisurea
Supramolecular Polymer Materials Enable
Metastable-to-Thermodynamic Phase Evolution and
Enhanced Modulus**

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EXPERIMENTAL

Materials. All solvents and chemicals were of reagent-grade and used without further purification. A xylene solution (0.1 M) of Karstedt's catalyst, that is, platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Pt(dvs)), was purchased from Sigma-Aldrich (Tokyo, Japan). 9,19-Di(hydroxy)octaphenyl double-decker silsesquioxane (*mix-DDSQ-2SiOH*) and 9,19-di(hydro)octaphenyl double-decker silsesquioxane (*mix-DDSQ-2SiH*) were obtained from JNC Co.

trans-DDSQ-2SiOH

Recrystallization of **DDSQ-2SiOH** (1.00 g, 0.84 mmol) from THF yielded a white solid *trans*-**DDSQ-2SiOH** (0.21 g, 0.18 mmol, 27%). ²⁹Si-NMR (CDCl₃, 80 MHz) δ -54.0, -78.6, -79.2 ppm.

Bisdimethylsilyl-functionalized *trans*-DDSQ-2SiOH.

Under an N₂ atmosphere, *trans*-**DDSQ-2SiOH** (2.00 g, 1.69 mmol) and pyridine (1.09 mL, 13.49 mmol) were added to a THF solution (16.9 mL), followed by the addition dropwise of chlorodimethylsilane (1.50 mL, 13.49 mmol). This mixture was stirred under reflux at 80 °C for 3 h, and distilled water was then added to quench the reaction. The THF was removed under reduced pressure, and the residue was dissolved in chloroform. The organic layer was then washed three times with distilled water, dried over magnesium sulfate, filtered, and the solvent was removed under reduced pressure to afford a white solid of bisdimethylsilyl-functionalized *trans*-**DDSQ-2SiOH** (1.75 g, 1.34 mmol, 79%). ¹H-NMR (CDCl₃, 400 MHz) δ 7.59–7.18 (m, 40H), 4.74–4.72 (m, 2H), 0.29 (s, 6H), 0.13–0.11 (d, 12H) ppm. ²⁹Si-NMR (CDCl₃, 80 MHz) δ -4.5, -63.4, -79.2, -79.5.

trans-**DDSQ-hexyl-bisurea** (*trans*-1). Toluene solution (12.0 mL) was mixed with bisdimethylsilyl-functionalized *trans*-**DDSQ-2SiOH** (1.25 g, 0.96 mmol) and 1-allyl-3-hexylurea (0.39 g, 2.11 mmol), and then a xylene solution of Pt(dvs) (0.1 M, 38.1 μL) was added under a

nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 28 h. After the reaction, the Pt catalyst was removed using a metal scavenger (SiliaMetS(R) triamine). Volatile components were removed under reduced pressure, and the product was purified by HPLC to yield white solid *trans-1* (1.22 g, 0.73 mmol, 76%). ¹H-NMR (CDCl₃, 400 MHz) δ 7.57-7.17 (m, 40H), 4.20-3.60 (br, 4H), 2.97-2.92 (m, 4H), 2.79–2.75 (m, 4H), 1.36–1.22 (m, 20H), 0.87–0.84 (m, 6H), 0.44–0.40 (m, 4H), 0.28–0.24 (m, 6H), 0.03– -0.03 (m, 12H) ppm. ¹³C-NMR (CDCl₃, 100 MHz) δ 158.3, 134.1, 134.0, 131.8, 130.9, 130.6, 127.9, 127.7, 77.5, 77.2, 76.8, 43.2, 40.4, 31.6, 30.3, 26.6, 24.0, 22.6, 15.1, 14.1, 0.0, –2.7 ppm. ²⁹Si-NMR (CDCl₃, 80 MHz) δ 10.3, –64.1, –79.3, –79.5 ppm. MALDI-TOF MS (m/z): calculated for [M + Na]⁺:1691.4162; found: 1691.4158.

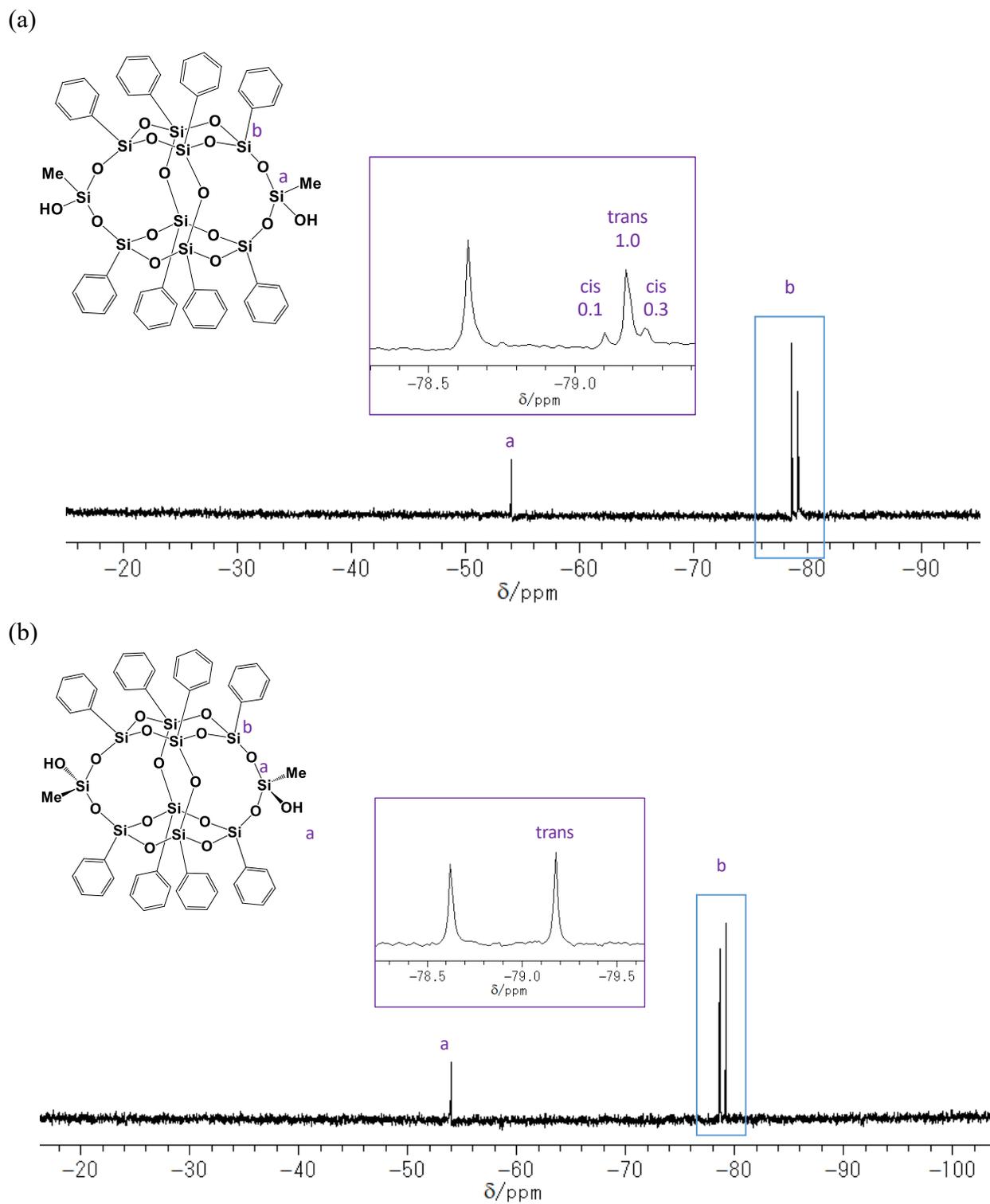
mix-DDSQ-hexyl-bisurea (mix-2).

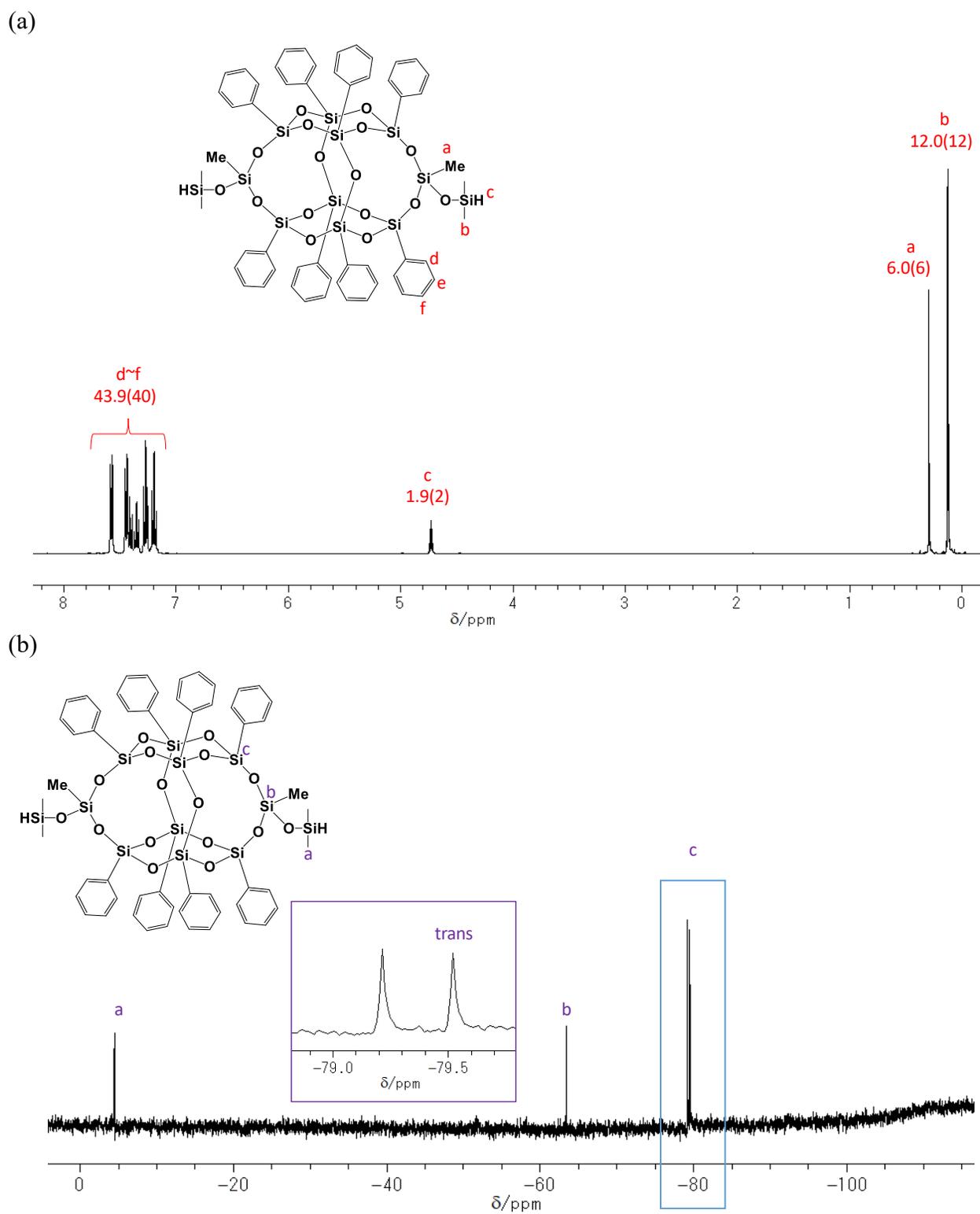
Toluene solution (12.0 mL) was mixed with **DDSQ-2SiH** (1.25 g, 0.96 mmol) and 1-allyl-3-hexylurea (0.39 g, 2.11 mmol), and then a xylene solution of Pt(dvs) (0.1 M, 38.1 μL) was added under a nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 18 h. After the reaction, the Pt catalyst was removed using a metal scavenger (SiliaMetS(R) triamine). Volatile components were removed under reduced pressure, and the product was purified by HPLC to yield white solid *mix-2* (1.11 g, 0.73 mmol, 67%). ¹H-NMR (CDCl₃, 400 MHz) δ 7.52-7.18 (m, 40H), 3.82-3.59 (br, 4H), 3.06-2.98 (m, 4H), 2.97-2.88 (m, 4H), 1.62-1.15 (m, 20H), 0.89-0.82 (m, 6H), 0.75-0.67 (m, 4H), 0.32-0.26 (m, 6H) ppm. ¹³C-NMR (CDCl₃, 100 MHz) δ 158.1, 134.1, 134.0, 131.8, 131.0, 131.0, 130.8, 128.0, 127.9, 127.8, 127.7, 77.4, 77.1, 76.8, 42.8, 40.4, 31.6, 30.2, 26.6, 23.6, 22.6, 14.1, 13.9, –0.8 ppm. ²⁹Si-NMR (CDCl₃, 80 MHz) δ –17.4, –78.6, –79.5, –79.6, –79.8 ppm. MALDI-TOF MS (m/z): calculated for [M + Na]⁺: 1543.3786; found: 1543.3790.

Preparation of the cast film: Chloroform solutions with 0.246 g/mL and 0.10 g/mL were prepared for thermal conductivity evaluation and other studies, respectively, cast them onto a PTFE sheet, cover them with a Petri dish, and air dry at 25 °C for 3 days.

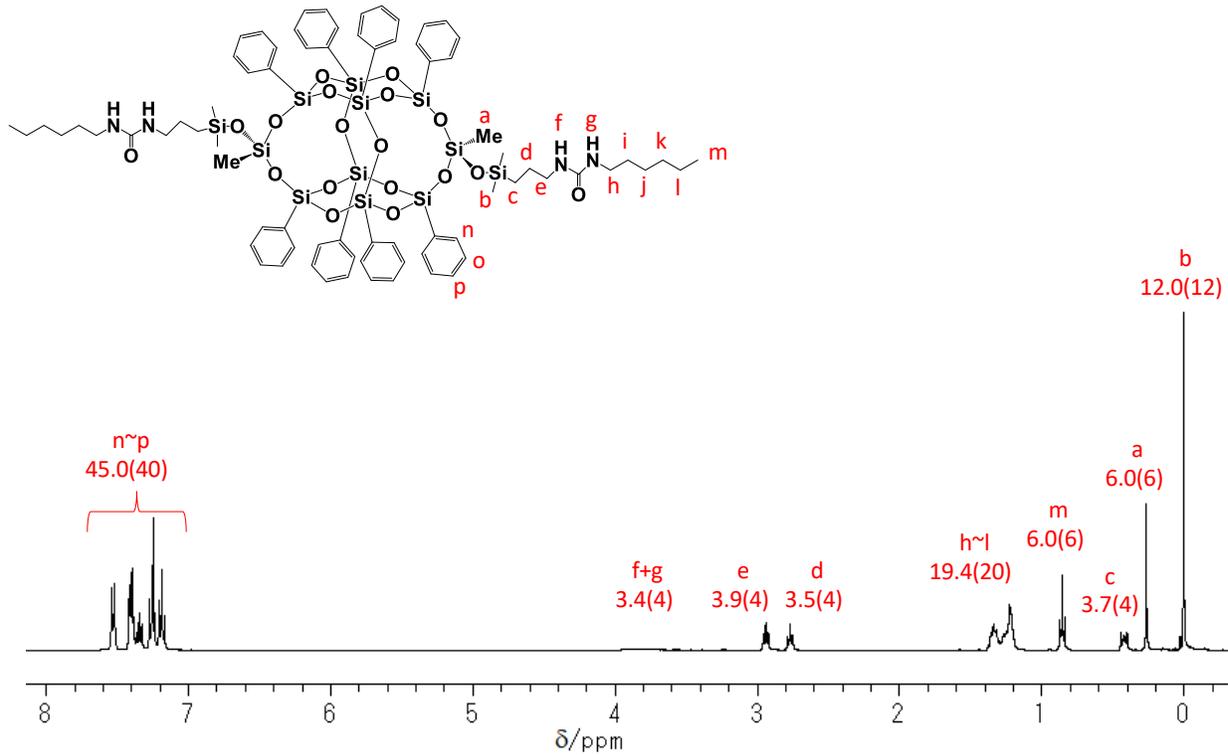
Measurements. ^1H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (80 MHz) nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AVANCE III 400 NMR spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany) in CDCl_3 , with residual CHCl_3 as an internal standard. Precise mass analysis of the compounds was performed using matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) with a Bruker Autoflex II instrument (Bruker Daltonics, Billerica, MA, USA) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile as the matrix (20 mg/mL in CHCl_3) and silver trifluoroacetate cationizing agents (1 mg/mL in THF). Thermal properties were studied using differential scanning calorimetry (DSC) with a DSC-60 Plus instrument (Shimadzu, Kyoto, Japan) under nitrogen and air atmospheres at a heating rate of 10 °C/min. X-ray diffractometry (XRD) experiments were performed on a Rigaku MiniFlex600 X-ray diffractometer ($\lambda = 1.54 \text{ \AA}$) with a D/teX Ultra2 semiconductor detector. The samples were mounted on non-reflective silicon plates. Scanning electron microscopy (SEM) images were obtained using a VE-8800 microscope (KEYENCE, Osaka, Japan). The elastic moduli of the cast films were measured using a Shimadzu DUH-211 instrument. Hardness tests of the deposited coatings were performed in the ‘load–unload mode,’ in which a 1.00 mN load was applied; the indented area was observed and measured using a high-resolution microscope. The crosshead speed of the indenter during the loading was 1.00 mN s⁻¹. The thermal conductivities of the films were calculated by multiplying the corresponding thermal diffusivities α , specific heat capacities (C_p), and densities ρ . The thermal diffusivity in the thickness direction of the film, defined as the ratio of thermal conductivity to specific heat capacity, was measured using the ai-Phase mobile 1u (ai-Phase Co., Ltd., Tokyo, Japan) based on the temperature wave analysis method. Specific heat capacity was determined using a DSC-60 Plus instrument (Shimadzu, Kyoto, Japan). Alumina was used as a reference for C_p determination. The

density data were obtained using an AccuPyc II 1340 gas displacement pycnometry system (Micromeritics Instrument Corporation, Norcross, USA). The sample was placed in a 1.0 cm³ chamber. The measurement He pressure was 135 kPa at room temperature.

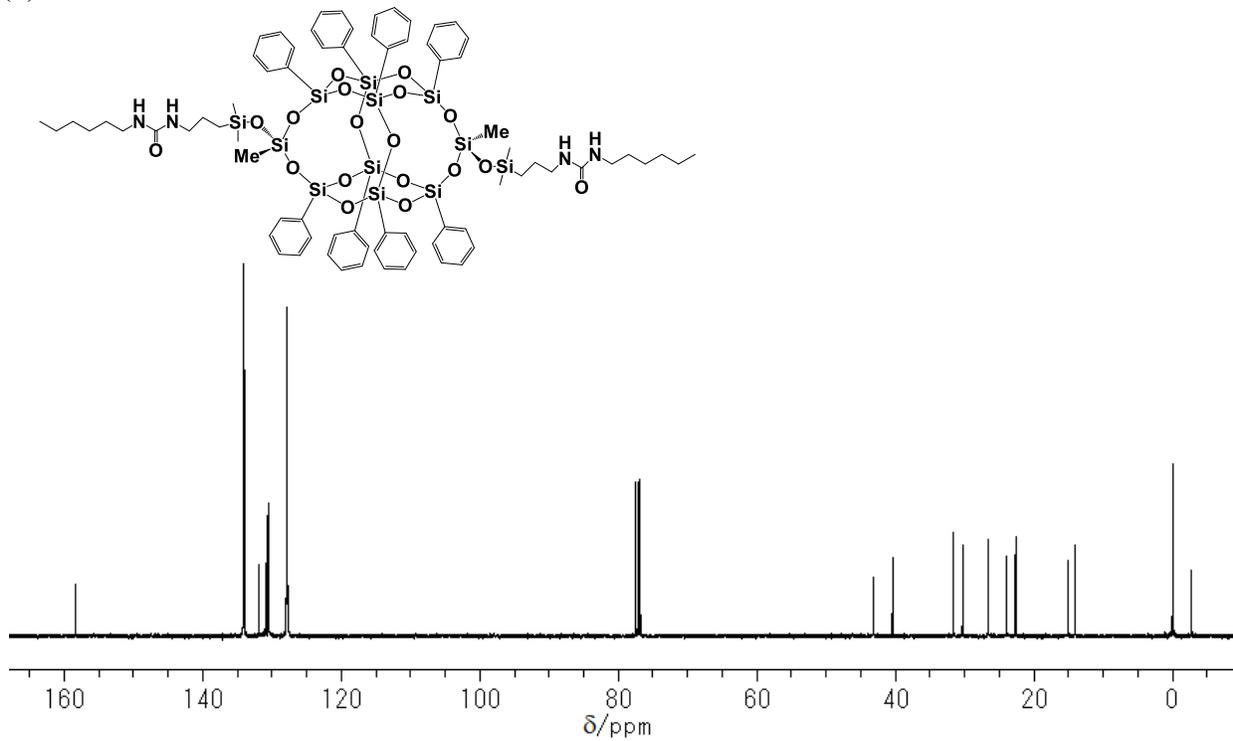




(a)



(b)



(c)

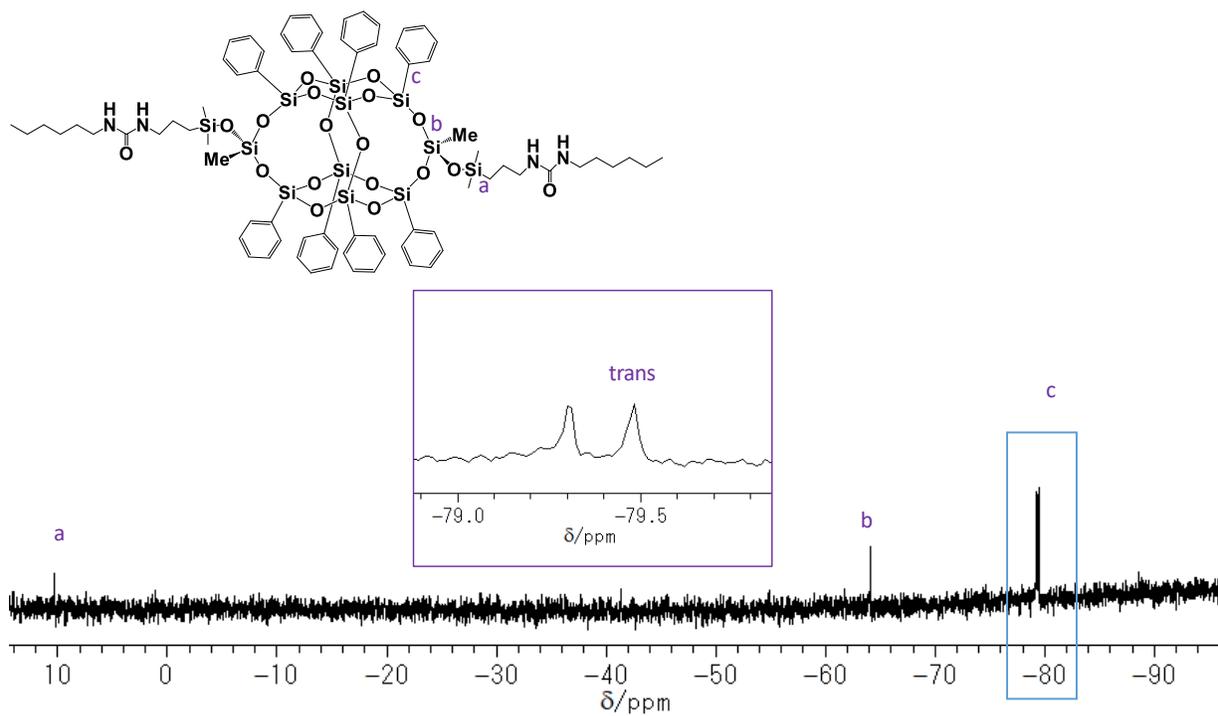


Figure S3 (a) ^1H -, (b) ^{13}C -, and (c) ^{29}Si -NMR spectra of *trans-1* in CDCl_3 .

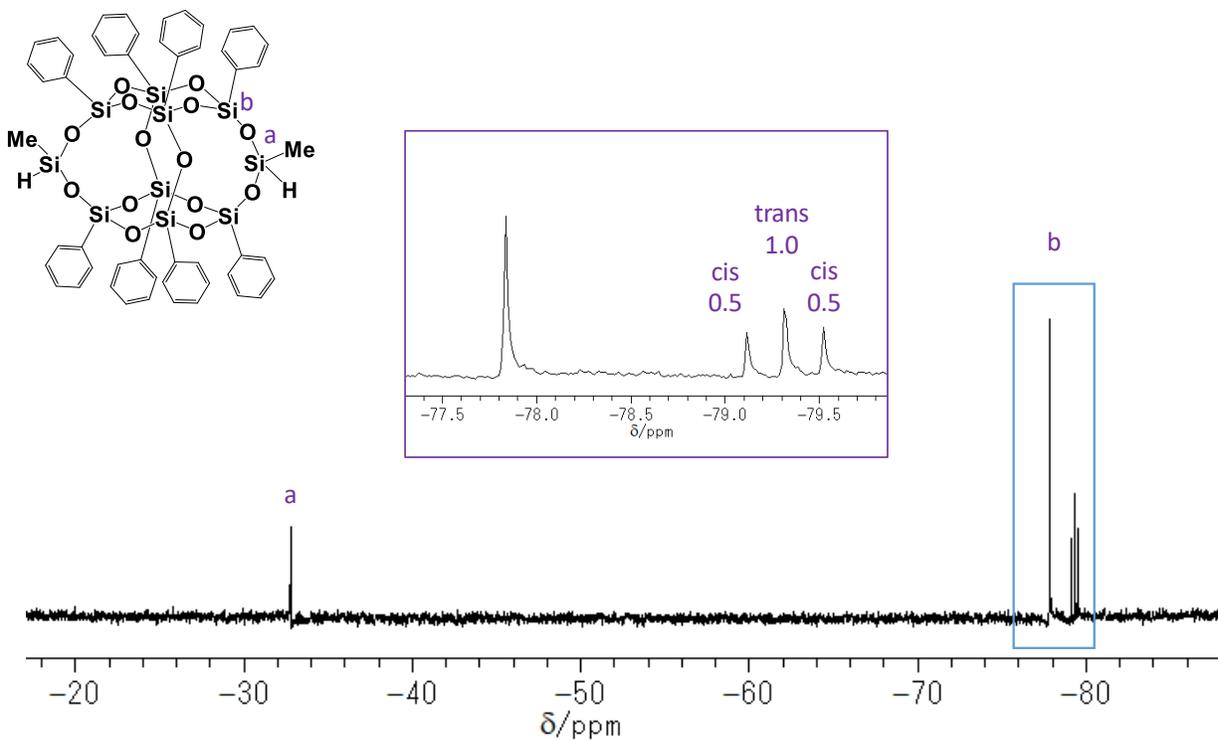
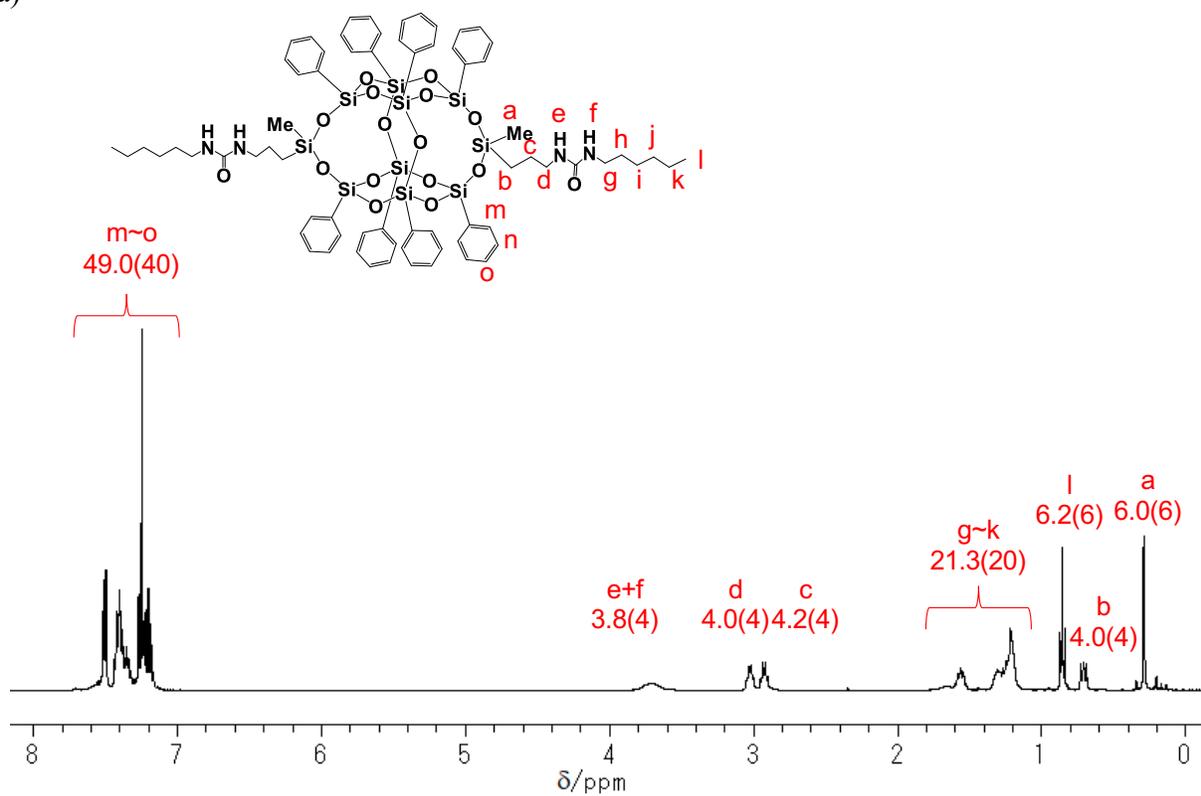
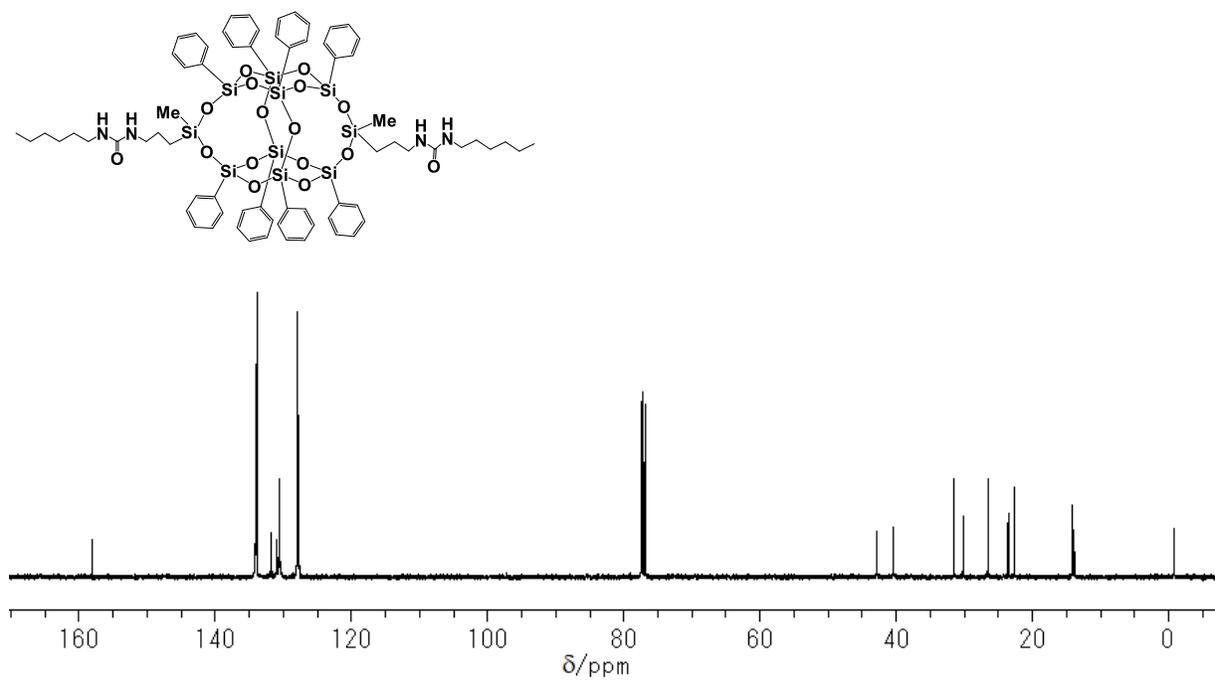


Figure S4 ^{29}Si -NMR spectrum of *mix*-DDSQ-2SiH in CDCl_3 .

(a)



(b)



(c)

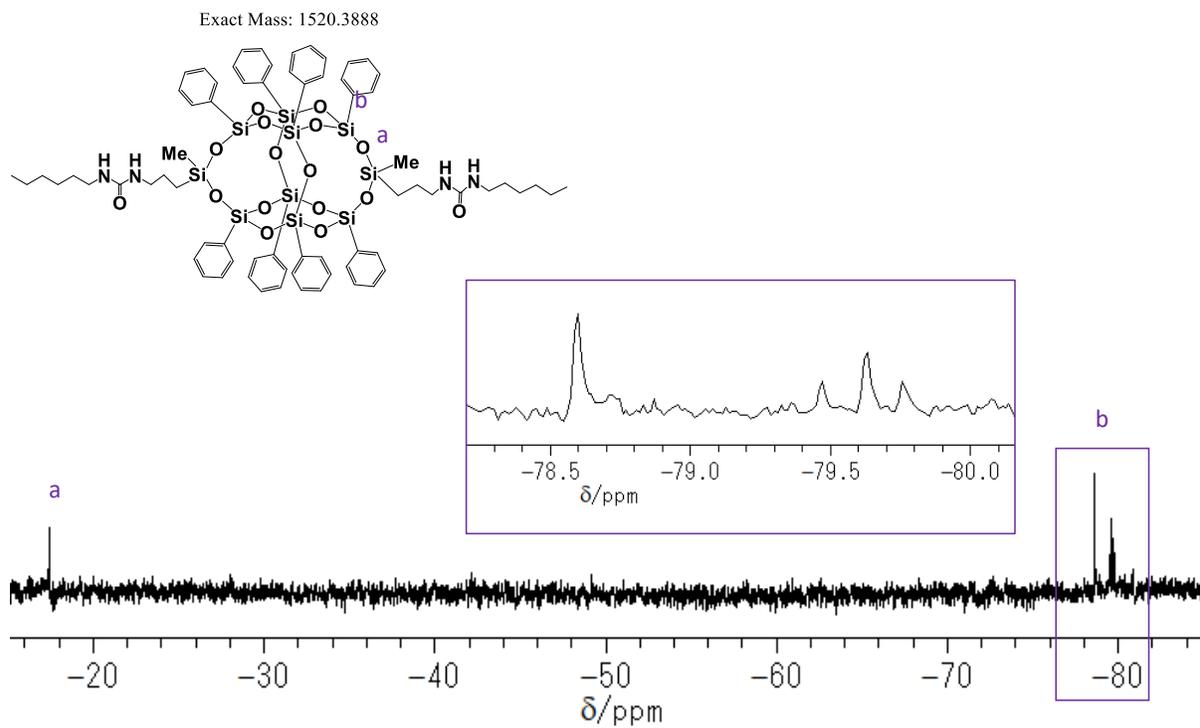


Figure S5 (a) ^1H -, (b) ^{13}C -, and (c) ^{29}Si -NMR spectra of *mix-2* in CDCl_3 .

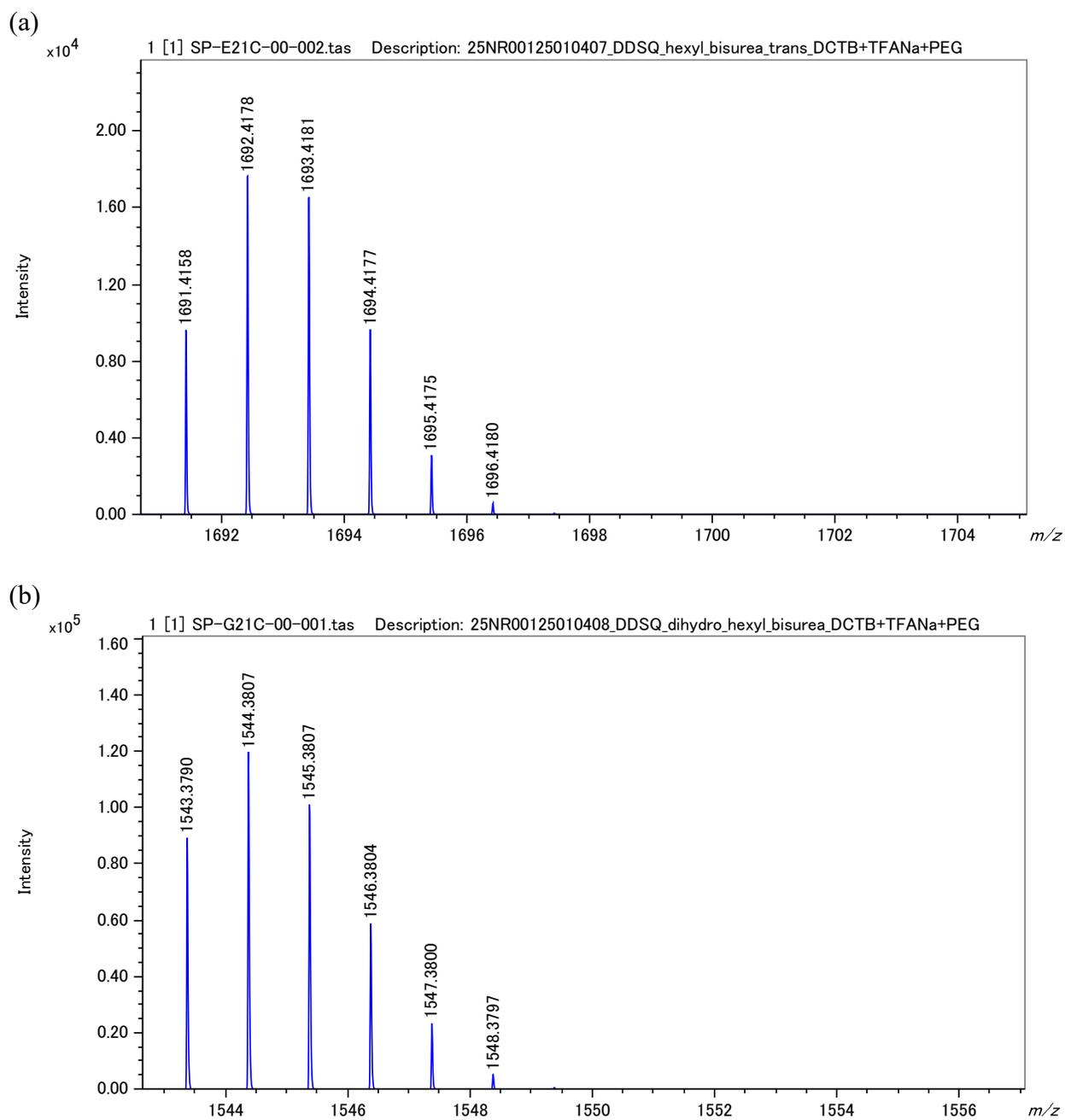
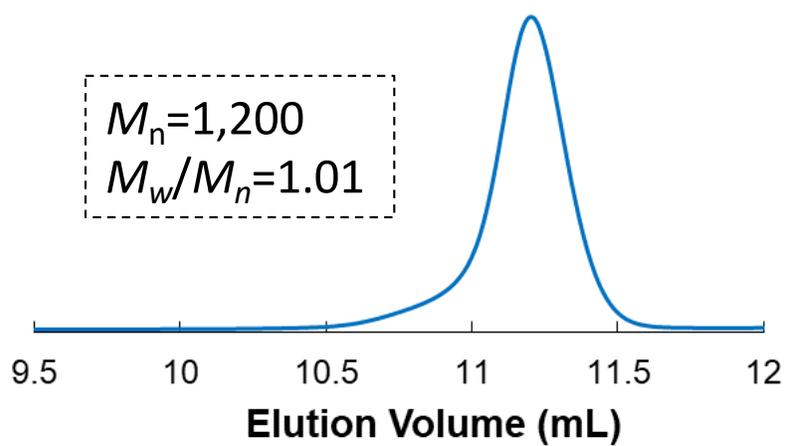


Figure S6 MALDI-TOF-MS spectra of *trans*-1 (a) and *mix*-2 (b).

(a)



(b)

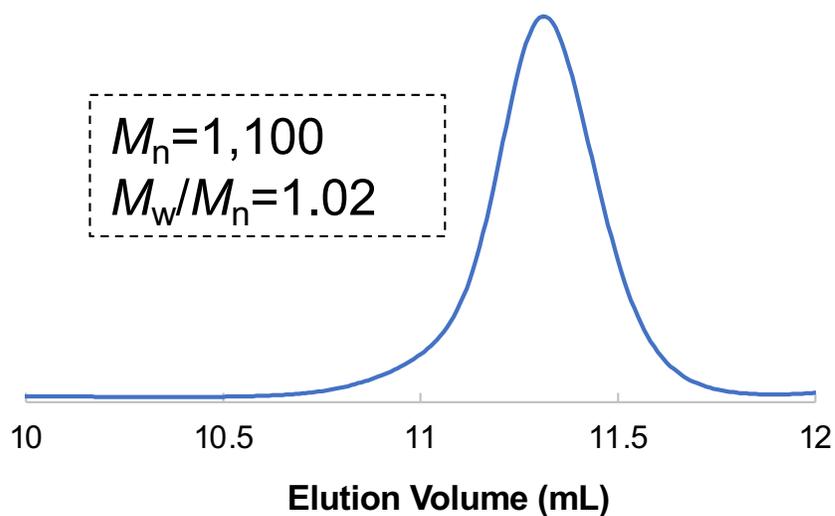


Figure S7 SEC traces of *trans-1* (a) and *mix-2* (b) measured by Shodex KF-803 column using THF as an eluent with RI detection.

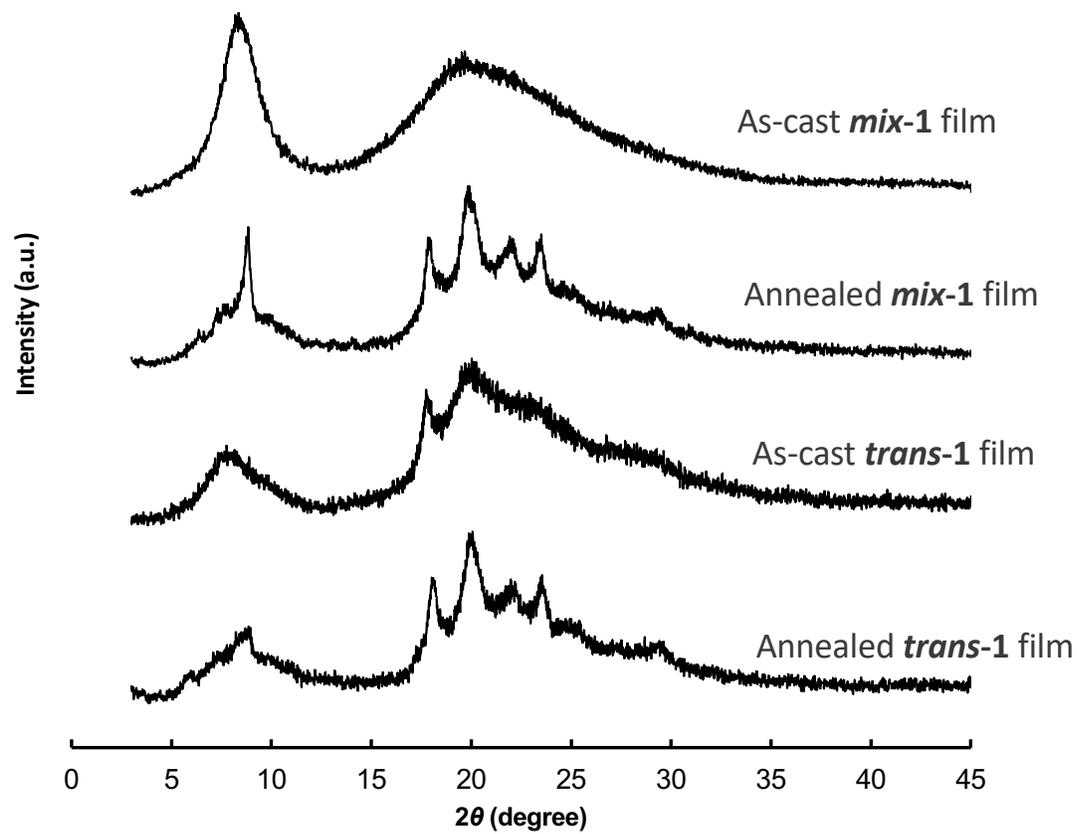


Figure S8 XRD patterns of the as-cast and annealed *mix-1* films and the as-cast and annealed *trans-1* films.

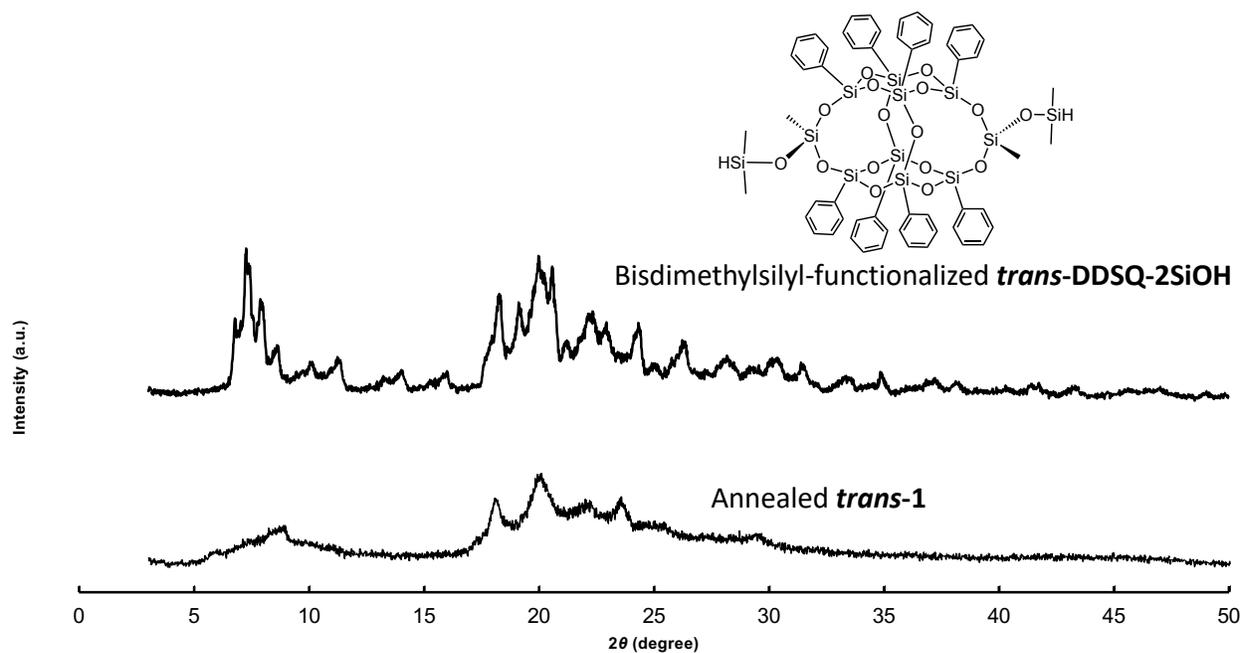


Figure S9 XRD patterns of bisdimethylsilyl-functionalized *trans*-DDSQ-2SiOH and the annealed *trans*-1 films.