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Supporting Information

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Confined Synthesis of a Perfect *cis*-Isotactic Ladder Polysilsesquioxane via Pi-stacking and H-bonding Superstructure

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Materials:

All the reagents and solvents were commercially available and of analytical grade. Iodine monochloride was purchased from Acros Company. Tetrahydrofuran (**THF**) and toluene (**TOL**) was distilled from sodium benzophenone complex. 1, 1, 2, 2-tetrachloroethane was dried with molecular sieve overnight and then distilled prior to use. Trichlorosilane and Allyl bromide were distilled before use. 1M HCl was diluted from concentrated HCl by THF. Dicyclopentadienyl platinum dichloride (**Cp_2PtCl_2**) used as hydrosilylation catalyst was prepared according to literature methods (S1). The other reagents were used as received.

Methods

Infrared (IR) spectra were recorded at room temperature on a Bruker EQUINOX55 spectrometer with a maximum resolution of 1 cm^{-1}. ^{1}H-NMR & ^{29}Si-NMR were recorded at room temperature on a JNH-FX100 (JBOX) 300MHz nuclear magnetic resonance spectrometer; for ^{29}Si-NMR, toluene solution of sample was measured with Chromium(？) acetylacetonate as a relaxation reagent. MALDI-TOF-MS measurements were carried out on a BIFLEX ？ MALDI-TOF mass spectrometer(Bruker Analytical System, Inc). Element analysis was measured with a Heraeus CHN-RAPID DATEL System instrument. Powder X-ray diffraction was carried out on a Bruker D8 DISCOVER with a GADDS detector to determine the phase structures of the samples. The X-ray wavelength ? was 0.154 nm. Fluorescence emission spectra were obtained from a Hitachi F-4500 fluorescence spectrometer at room temperature. Transmission electron microscopy (TEM) images

were taken on a JEM-100 operating at 100kV at room temperature. Atomic Force Microscopy (AFM) images were taken on a AFM (Nano Scope ?; Digital Instrument Santa Burbara, CA). Differential scanning calorimetry (DSC) was performed at a Perkin-Elmer DSC7 under N_2 atmosphere at a scanning rate of 10 ?/min.

Light scattering measurements were performed under LLS spectrometer ALV/SP-125 at 23 ?, equipped with a multi-t-correlator (ALV-5000E) and He-Ne Laser (632.8 Å, 22 mw). Determination of differential refractive index increment (*dn/dc*) with a value of 1.412 was made with the differential refractometer, which mainly consists of a laser lighter source, a position-sentive detector, and a temperature-controlled refractometer cuvette with the dV/dn constant as 1.19×10^{-3}. The viscosity was determined with Ubbelohde viscometers using THF as solvent at 25 ?. The flow time of pure solvent was maintained at least 100 s and thus the kinetic correction could be negligible.

Experiments:

Synthesis of 1, 1, 3, 3-tetramethoxyldisiloxane (TMDS)

A mixture of 3.8 mL H_2O and 100 mL THF was drop-wise added into a 250 mL flask containing 58 mL trimethoxylsilane, 50 mL THF and a drop of 1M HCl at room temperature. After that, the reaction solution was stirred for two hours and the titled compound **TMDS** was evaporated under 69 ~ 72 ?/2 ~ 4 mmHg in the yield of nearly 42%.

D_n^{25}: 1.3712?

FTIR (KBr, cm^{-1}): 2947, 2845 (strong, δ?CH_3), 2218 (strong, ν?i-H), 1000-1200 (strong, ν?i-O-Si), 843 (?Si-H)

^{1}H-NMR(dppm, $CDCl_3$, 300 Hz): 4.27 (s, 2H, SiH), 3.56 (d, 12H, OCH_3)?

^{29}Si-NMR (dppm, 300 Hz): -64.7 ppm (H-Si$(OMe)_2$-O-Si$(OMe)_2$-H)?

Synthesis of 2-hydroxy-3-methoxy-6, 7, 1 0, 11-Tetrabutoxy-triphenylene (1)

The compound **1** was prepared by coupling 3, 3', 4, 4'-tetrabutoxy biphenyl and o-methoxy phenol following the similar procedure as described in literature (S2). The crude product was separated by flash chromatography, eluting with 1: 1 dichloromethane/petroleum ether to give the product as a pale yellow solid which was recrystallized from ethanol in 65% yield.

FTIR (KBr, cm^{-1}): 3549 (νOH), 3079, 2955, 2931, 2860 (strong, δCH, aromatic and aliphatic), 1617, 1516, 1435 (strong, νC=C, aromatic ring), 1260 (strong, νC-O-C).

^{1}H NMR (dppm, $CDCl_3$, 300 Hz): 7.96, 7.83, 7.77 (m, 6H, Ar*H*), 5.91 (s, 1H, O*H*), 4.31-4.19 (t, 8H, OCH_2), 4.09(s, 3H, OCH_3), 1.97-1.90 (m, 8H, OCH_2CH_2), 1.58-1.39 { m, 8H, $O(CH_2)_2CH_2$} , 0.97 (t, 12H, CH_3).

Synthesis of 2-Allyloxy-3-methoxy-6, 7, 10, 11-tetrabutoxy-triphenylene (2)

A mixture of 0.7 g (1.0 mmol) of compound **1** and 0.2 mL (2.3 mmol) of allyl bromide was dissolved in dry ethanol mixed with 11.0 g of anhydrous potassium carbonate and refluxed for 30 h under Ar gas atmosphere. The resulting system was cooled and poured into water and extracted with two 100 mL portions of dichloromethane. Then the organic solvent was evaporated to give a white solid **2**, which was recrystallized from ethanol. Yield: 95 %.

FTIR (KBr, cm^{-1}): 3079,2955,2931,2860 (strong, δCH, aromatic and aliphatic), 1648, 1620, 1518, 1430 (strong, νC=C, allyl and aromatic ring), 1262 (strong, νC-O-C).

^{1}H NMR (dppm, $CDCl_3$, 300 Hz): 7.87-7.79 (m, 6H, Ar*H*), 6.32-6.12 (m, 1H, $OCH_2CH=CH_2$), 5.59-5.32 (d, d ,2H, $OCH_2CH=CH_2$), 4.86 (d, 2H, $OCH_2CH=CH_2$), 4.24 (m, 8H, OCH_2), 4.12 (s, 3H, OCH_3), 1.96 (m, 8H, OCH_2CH_2), 1.59 { m, 8H, $O(CH_2)_2CH_2$}, 0.98 (t, 12H, CH_3) .

MALDI-TOF-MS: Cacld. for $C_{38}H_{50}O_6$ [M^+]: m/z=602.4; Found: 602.6

Elemental analysis: Cacld. for $C_{38}H_{50}O_6$ C 75.71, H 8.36; Found C 75.86, H 8.24

Synthesis of 1, 3-Bis-[3-(3-methoxy-6, 7, 10, 11-tetrabutoxy-triphenylen-2-yloxy)-propyl]-1, 1, 3, 3-tetramethoxy-disiloxane (3)

To a 250 mL Schlenk flask were added 15.05 g (25.0 mmol) of compound **2** and 5 mg Cp_2PtCl_2 . The reaction system was vacuumized and refilled with argon, and this process was repeated three times. Under the argon atmosphere, 100 mL dry toluene and 4.95 g (12.5 mmol) of **TMDS** was injected into the system. The reaction mixture was weakly refluxed for 96 h under Ar atmosphere. Then, the residual solvent and **TMDS** were removed by reduced pressure and a brown-yellow solid was obtained in nearly 98% yield.

FTIR (KBr, cm^{-1}): 2958.27, 2870.76(δCH, aromatic and aliphatic), 1618, 1516, 1429 (strong, νC=C, aromatic ring), 1260 (strong, νC-O-C), 1073.85, 1046.82 (strong, νC-O-C, νSi-O-Si).

^{1}H-NMR (dppm, $CDCl_3$, 300 Hz): 7.85-7.79 (m, 12H, Ar*H*), 4.26-4.22 (20H, OCH_2), 4.12 (s, 6H, OCH_3), 3.55 (s, 12H, Si-O-CH_3), 1.96 (16H, OCH_2CH_2), 1.88 (m, 4H, CH_2-CH_2-Si), 1.59 { m, 16H, $O(CH_2)_2CH_2$}, 0.90 (t, 24H, CH_3), 0.73 (t, 4H, CH_2-Si).

^{29}Si-NMR (dppm, 300 Hz): -50.50{R-Si$(OCH_3)_2$-O-Si$(OCH_3)_2$-R}.

MALDI-TOF-MS: Cacld. for $C_{80}H_{114}O_{17}Si_2$ [M^+]: m/z=1402.8; Found : 1403.3

Synthesis of 1, 3-Bis-[3-(3-methoxy-6, 7, 10, 11-tetrabutoxy-triphenylen-2-yloxy)-propyl]-1, 1, 3, 3-tetrahydroxy-disiloxane (4)

The resulting brown-yellow solid **3** was hydrolyzed in the ice/THF/HCl solution for 24 h. The product was extracted with two portions of 100 mL CH_2Cl_2 and washed with distilled water three times. The Combined organic layers were dried by anhydrous $MgSO_4$. Then the solvent was evaporated to give a pale yellow solid, which was purified by flash chromatography with 10: 1 petroleum ether/acetone in 92 % yield.

FTIR (KBr, cm^{-1}): 3549 (Si-OH), 2958, 2870 (δCH, aromatic and aliphatic), 1619, 1515, 1427 (strong, νC=C, aromatic ring), 1264 (strong, νC-O-C), 1073, 1046 (strong, νC-O-C, Si-O-Si).

^{1}H-NMR (dppm, $CDCl_3$, 300 Hz): 7.87-7.78 (m, 12H, Ar*H*), 4.27-4.21 (m, 20H, OCH_2), 3.60 (4H, s, Si-OH), 1.96 (m, 16H, OCH_2CH_2), 1.86 (m, 4H, CH_2-CH_2-Si), 1.58 {m, 16H, $O(CH_2)_2CH_2$}, 0.92 (t, 24H, CH_3), 0.70 (t, 4H, CH_2-Si).

^{29}Si-NMR (dppm, 300 Hz): -21.89 (R-Si$(OH)_2$-O-Si$(OH)_2$-R).

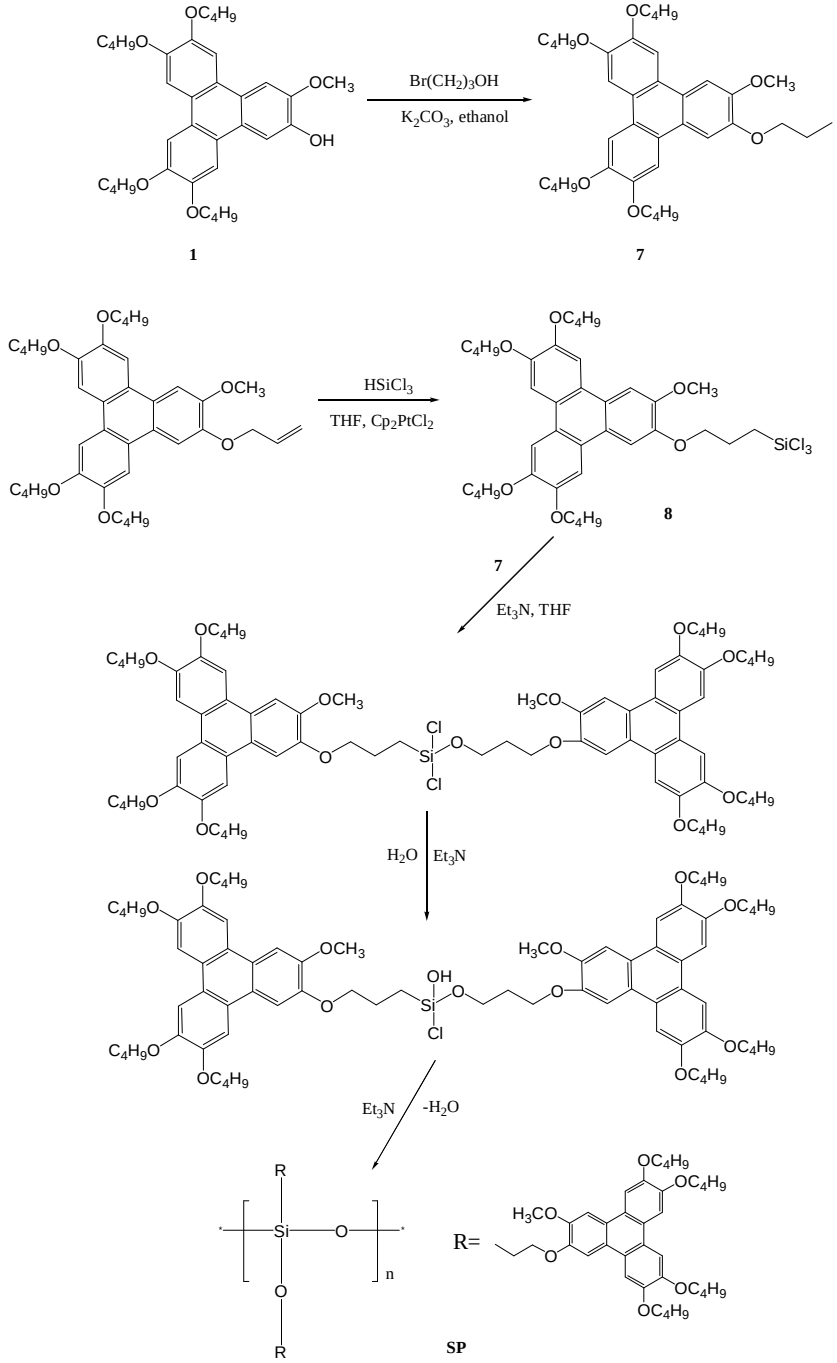
Synthesis of Triphenylene-containing side chain LP (6).

The above mentioned **4** was dissolved in 30 mL of 1, 1, 2, 2-tetrachloroethane to form **LS 5** and polymerized at 60~80 ？ with slightly stir for 48 hours using a drop of 10% Me_4NOH solution as catalyst, and then the solvent and released water were gradually evaporated with the temperature elevated to 100 ？ in vacuum to give a pale yellow solid, and the polycondensation continued in solid state for 24 h with temperature gradually elevated to 130 ？ in vacuum. When cooled down, the brown product was dissolved in petroleum ether and fractionated using 1:1 methanol/ethanol as precipitation agent, and finally a brown solid **LP 6** was obtained.

FTIR (KBr, cm^{-1}): 2961, 2934, 2861(δCH, aromatic and aliphatic), 1618, 1513, 1428 (strong, νC=C, aromatic ring), 1261 (strong, νC-O-C), 1089, 1033(strong, νC-O-C, Si-O-Si).

^{29}Si-NMR (dppm, 300 Hz): d = -18.67 ($RSiO_{3/2}$).

Synthesis of single chain polysiloxane (SP)



Synthetic route of **SP**

Synthesis of 3-(2, 3, 6, 7-tetrabutoxy-10-methoxytriphenylen-11-yloxy) propan-1-ol (7)

The synthesis process of **7** is similar with that of compound **2** and it was recrystallized from ethanol in 90% Yield.

FTIR (KBr, cm^{-1}): 3499 (strong, νOH), 2957, 2932, 2868 (strong, δCH, aromatic and aliphatic), 1617, 1516, 1435 (strong, νC=C, aromatic ring), 1262, 1170, 1069, 1037 (strong, νC-O-C).

^{1}H NMR (dppm, $CDCl_3$, 300 Hz): 7.87-7.80 (m, 6H, Ar*H*), 4.65(m, 2H, OC$H_2$$CH_2$OH), 4.26-4.23 (t, 8H, OCH_2), 4.09(s, 3H, OCH_3), 1.95-1.91(m, 8H, OCH_2CH_2), 1.58-1.39{ m, 8H, $O(CH_2)_2CH_2$} , 1.07-1.03 (t, 12H, CH_3).

Synthesis of (3-(2, 3, 6, 7-tetrabutoxy-10-methoxytriphenylen-11-yloxy)propyl)trichlorosilane (8)

To a 250 mL Schlenk flask were added 15.05 g (25.0 mmol) of compound **2** and 5mg Cp2PtCl2 . The reaction system was vacuumized and refilled with argon, and this process was repeated three times. Under the argon atmosphere, 100mL dry THF and 3.0mL (30.0 mmol) of HSiCl3 was injected into the system. The reaction mixture was stirred for 36 h at 60 ? under Ar atmosphere. Then, the residual solvent and HSiCl3 were removed under reduced pressure and a white solid was obtained in nearly 98% yield.

FTIR (KBr, cm^{-1}): 2959, 2872(δCH, aromatic and aliphatic), 1618, 1514, 1426 (strong, νC=C, aromatic ring), 1260, 1077, 1049 (strong, νC-O-C).

^{1}H-NMR (dppm, $CDCl_3$, 300 Hz): 7.86-7.77(m, 6H, Ar*H*), 4.26-4.22 (10H, OCH_2), 4.09 (s, 3H, OCH_3)), 1.96 (8H, OCH_2CH_2), 1.88-1.86 (m, 2H, CH_2-CH_2-Si), 1.59 {m, 8H, $O(CH_2)_2CH_2$}, 0.95-0.90 (t,12H, CH_3), 0.70 (t, 2H, CH_2-Si).

Synthesis of single chain polysiloxane (SP)

The Si-H addition product **8** was dissolved in 50mL THF. A mixture solution of **7** (15.50 g, 25 mmol), 3.5mL Et_3N and 50 mL THF was slowly added into the solution of **8** over 6 h under room temperature. After that, the reaction mixture was continued to stir for several hours. Then another mixture solution of 0.4 mL H_2O, 3.5 mL Et_3N and 100 mL THF was slowly dropwise under ice bath over about 10 h. The white precipitate solid salt was filtered carefully under argon atmosphere and the clear solution was slowly warmed up to reflux for 24 h to condensate. The condensation product was dissolved in petroleum ether (30-60 ?) and fractionated using 1:1 methanol/ethanol as precipitation agent, and finally a white solid was obtained.

FTIR (KBr, cm^{-1}): 2961, 2934, 2861(δCH, aromatic and aliphatic), 1618, 1513, 1428 (strong, νC=C, aromatic ring), 1261 (strong, νC-O-C), 1089, 1033(strong, νC-O-C, Si-O-Si).

^{29}Si-NMR (dppm, 300 Hz): d = -21.40 ($RSiO_{3/2}$).

Hydrogen-deuterium (H-D) exchange experiments: The experimental methodology of H-D exchange study was similar with that reported by Mong (S3). The sample was stored at room temperature under vacuum for 1 day to remove the residual solvent and water and [D6]-Acetone was fully dried with 3 $\mathring{A}$ molecular sieves for 3 days. A solution of 6.7 mg (5×10^{-3} mmol) **4** in [D6]-Acetone (0.50 mL) was prepared in a pre-dried NMR tube. 5μL D_2O was then added by means of a microsyringe and a series of ^{1}H-NMR spectra was recorded at regular time intervals (10 min per spectrum). From the relative integrals thus obtained, a pseudo first-order rate constant for the PDX process of a particular H-D exchangeable functionality was computed, from which an exchange half-life $t_{1/2}$ (time for 50% of the protons in such a functionality to be exchanged) was evaluated. The experiments processes of the two model compounds are similar with that mentioned above.

Table and Figures

Table S1. Degree of polymerization (DP) and intrinsic viscosity $[h]$ of three different molecular weight polymers.

No.	$\overline{M_w}$	DP	[?]
1	8.2×10^5	602	45.8
2	5.5×10^5	403	27.9
3	2.7×10^5	198	11.6

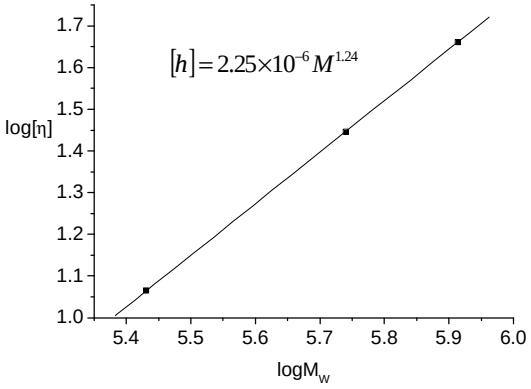


Figure S1: Molecular weight dependent of intrinsic viscosity $[h]$ of polymer.

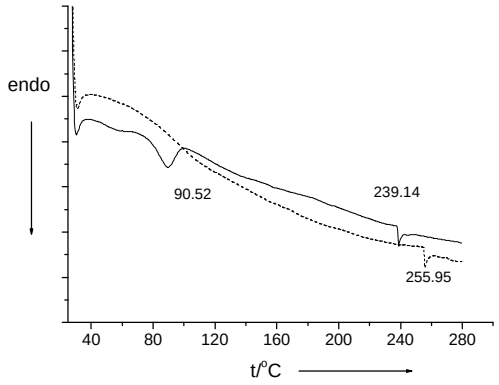


Figure S2: DSC curves of **LP**: the real line for the first scan with the speed as 10 ？/min, and

another for the second scan.

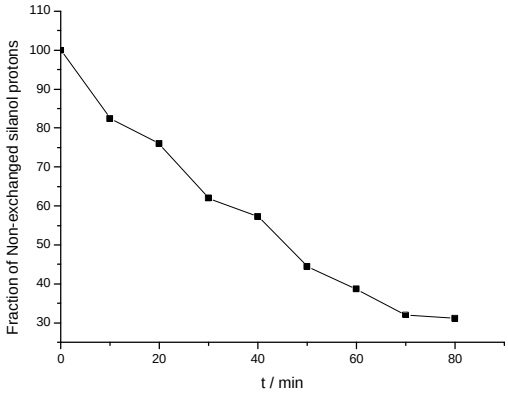


Figure S3 Fraction of non-exchanged silanol protons in **LS** in [D6]-Acetone solution

Supporting References

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S2. N. Boden, R. J. Bushby, Q. Liu, O. R. Lozman, *J. Mater. Chem.* **2001**, *11*, 1612-1617.

S3. T. K.-K. Mong, A. Niu, H.-F. Chow, C. Wu, L. Li, R. Chen, *Chem. Eur. J.* **2001**, *7*, 686-699.