Electronic Supporting Information for

Aggregation-induced scaffolding: Photoscissable degradable helical polysilane generates circularly polarized luminescent polyfluorene

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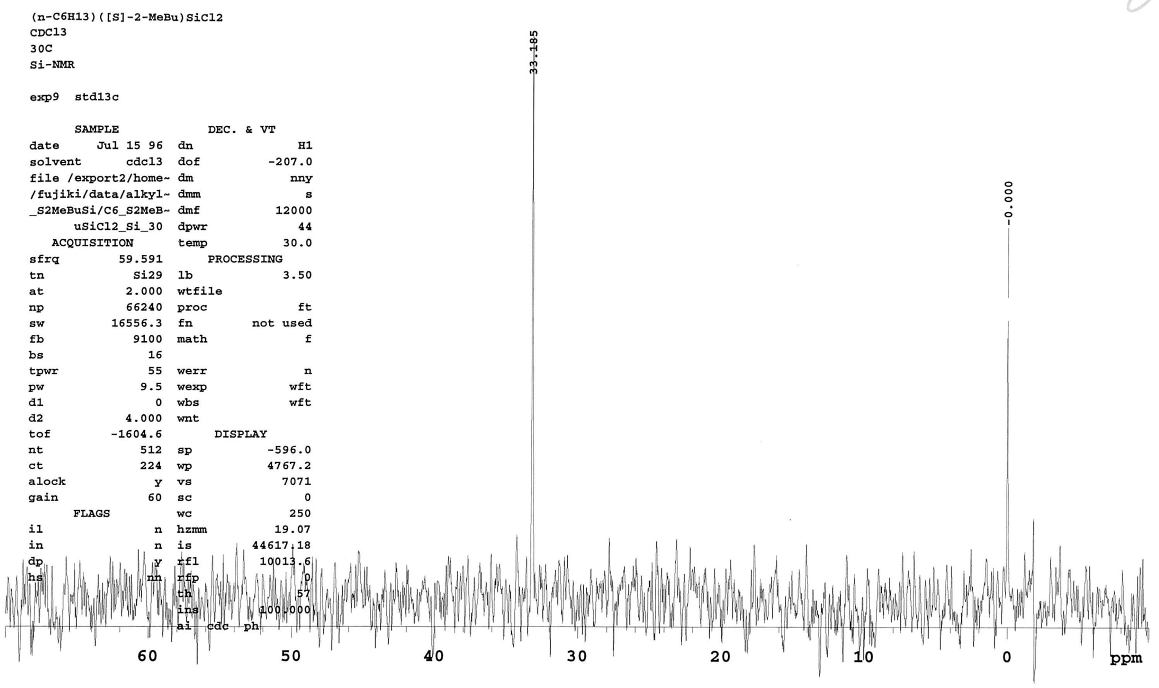
1. Experimental section

1-1. Monomer synthesis

In an analogous method reported previously[S1], *n*-hexyl-(*S*)-2-methylbutylsilanedichloride and *n*-hexyl-(*R*)-2-methylbutylsilanedichloride were prepared.

1-1-1. Synthesis of *n*-hexyl-(*S*)-2 methylbutylsilanedichloride (1*S*)

A fresh Grignard reagent (i.e., (*S*)-2-methylbutylmagnesium chloride) was prepared from 5.0 g (0.217 mol) of Mg turnings (Wako Chemicals (Osaka, Japan)) and (*S*)-2-methylbutylchloride (Tokyo Chemical Industry (TCI), Tokyo, Japan) ($[\alpha]^{24}_{D}$ = 1.44° (neat)). First, Mg and 100 mL of dry THF (Kanto Chemicals (Tokyo, Japan)) were placed in a three-neck flask under pure N_2 gas and the Mg surface was activated by the addition of a few drops of 1,2-dibromoethane (Wako). To this solution, 14.8 g (0.138 mol) of (*S*)-2-methylbutylchloride was added dropwise for 30 min, and the mixture was maintained at 50 °C for 30 min. A coloured solution containing the Grignard reagent was obtained. To a mixture of 51.7 g (0.235 mol)) of *n*-hexyltrichlorosilane (Shin-Etsu Chemical (Tokyo, Japan)) and 50 mL of THF at 55−60 °C in another three-neck flask, the Grignard solution was added dropwise for 2.5 h and maintained at 50 °C for 2 h. The crude monomer was purified by vacuum distillation (bp 79−82 °C/ 0.85 Torr). Yield: 23.3 g (46.6 %). $[\alpha]^{24}_{D}$ = 9.31° (neat). ^{29}Si-NMR ($CDCl_3$, 30 °C, ppm) 33.185, ^{13}C-NMR ($CDCl_3$, 30 °C, ppm) 32.393, 32.180, 31.358, 30.284, 28.174, 22.500, 22.447, 21.865, 21.373, 14.055, 11.211.



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CDCl3
30C
Si-NMR

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at            2.000  wtfile
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bs               16
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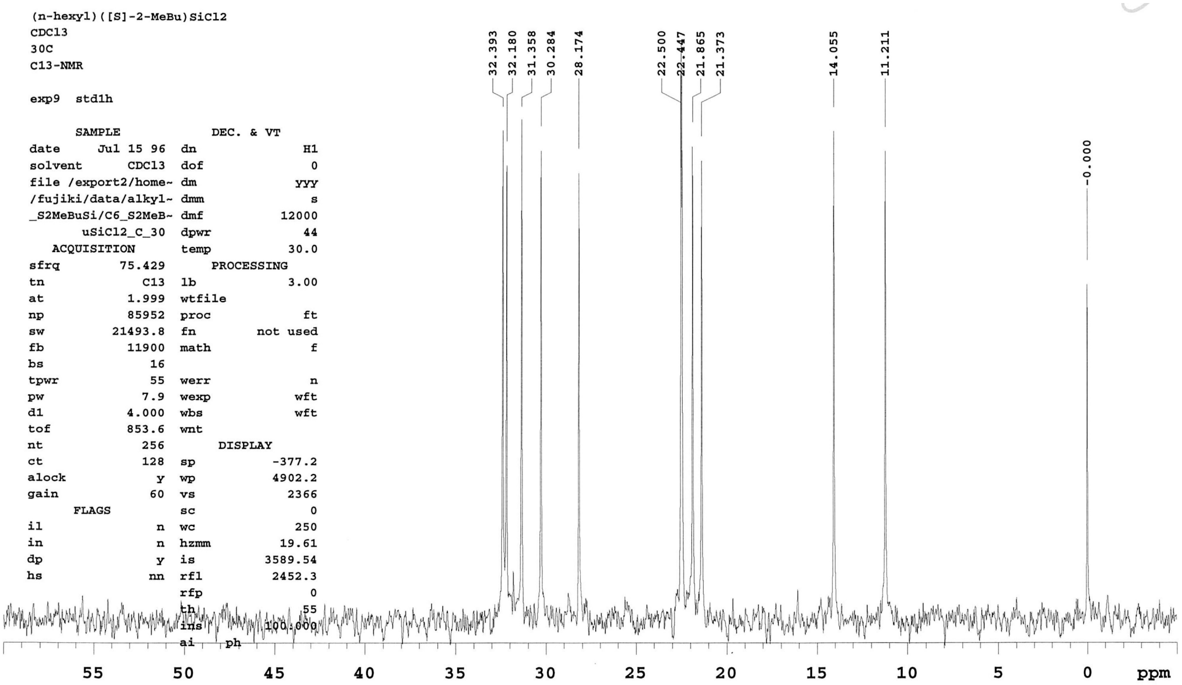
hs               nn  rfp               0
                     th               57
                     ins         100.000
                     ai  cdc  ph
```

Fig. S1. ^{29}Si-NMR spectra of **1*S*** in $CDCl_3$ at 30 °C. ^{29}Si resonances at 33.185 ppm using the Me_4Si ^{29}Si reference peak (0.000 ppm).



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CDCl3
30C
C13-NMR

exp9  std1h

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in               n  hzmm          19.61
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hs              nn  rfl          2452.3
                    rfp               0
                    th               55
                    ins         100.000
                    ai    ph
```
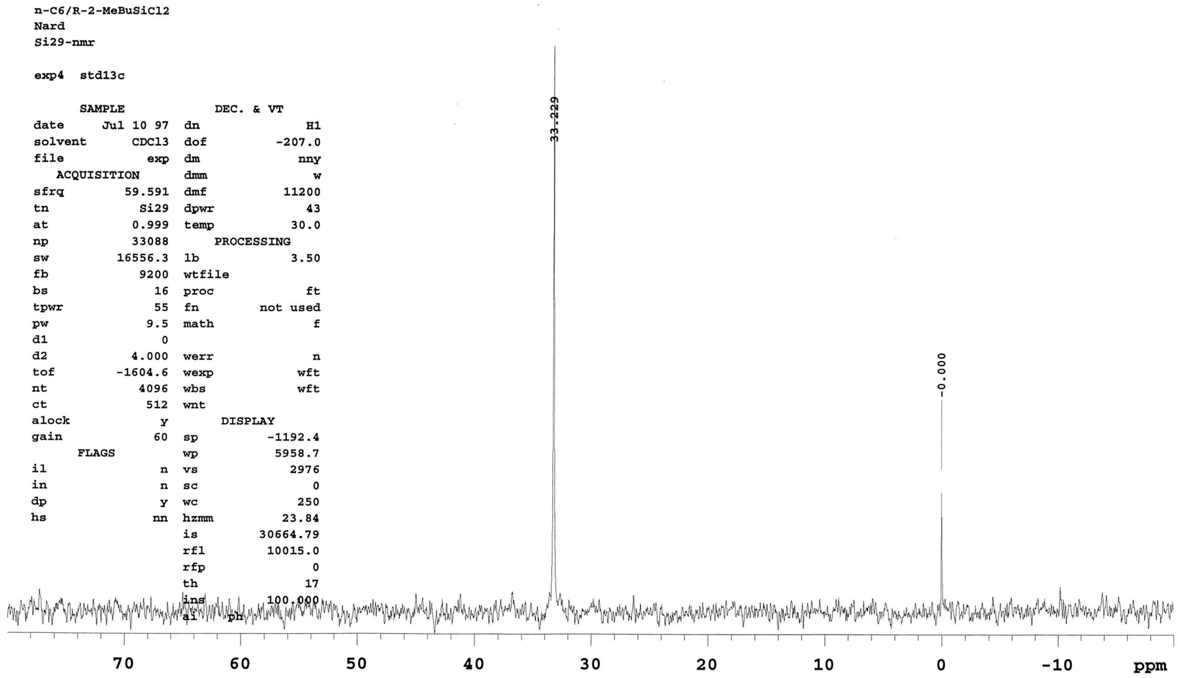

Fig. S2. ^{13}C-NMR spectra of **1*S*** in $CDCl_3$ at 30 °C. ^{13}C resonances at 32.393, 32.180, 31.358, 30.284, 28.174, 22.500, 22.447, 21.865, 21.373, 14.055, 11.211 ppm *vs* Me_4Si ^{13}C reference peak (0.000 ppm).

1-1-2. Synthesis of *n*-hexyl-(*R*)-2-methylbutylsilanedichloride (1*R*)

Similarly, a fresh Grignard reagent of (*R*)-2-methylbutylmagnesium chloride was prepared from 2.7 g (0.217 mol) of Mg turnings (Wako) and (*R*)-2-methylbutylchloride (custom made by Chemical Soft Research Co., Kyoto, Japan) ($[\alpha]^{24}_{D}$ = –1.26° (neat)). First, Mg and 75 mL of dry THF (Kanto Chemicals) were placed in a three-neck flask under pure N_2 gas and the Mg surface was activated by the addition of a few drops of 1,2-dibromoethane. To this solution, 10.6 g (0.10 mol) of (*R*)-2-methylbutylchloride was added dropwise for 30 min, and the mixture was maintained at 50 °C for 30 min. A coloured Grignard reagent solution was obtained. To a mixture of *n*-hexyltrichlorosilane (Shin-Etsu Chemical, 60.0 g (0.27 mol)) and THF (150 mL) at 55–60 °C in another three-neck flask, the Grignard solution was added dropwise for 2 h and maintained at 50 °C for 2 h. The crude monomer was purified by vacuum distillation (bp 116–119 °C/ 6 Torr). Yield: 15.0 g (58.8 %). $[\alpha]^{24}_{D}$ = –9.27° (neat). ^{29}Si-NMR ($CDCl_3$, 30 °C, ppm) 33.229, ^{13}C-NMR ($CDCl_3$, 30 °C, ppm) 32.370, 32.170, 31.335, 30.248, 28.109, 22.491, 22.421, 21.847, 21.334, 14.072, 11.228.



```
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Nard
Si29-nmr

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fb             9200  wtfile
bs               16  proc            ft
tpwr             55  fn        not used
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d1                0
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                     rfl        10015.0
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                     th              17
                     ins        100.000
                     ai     ph
```
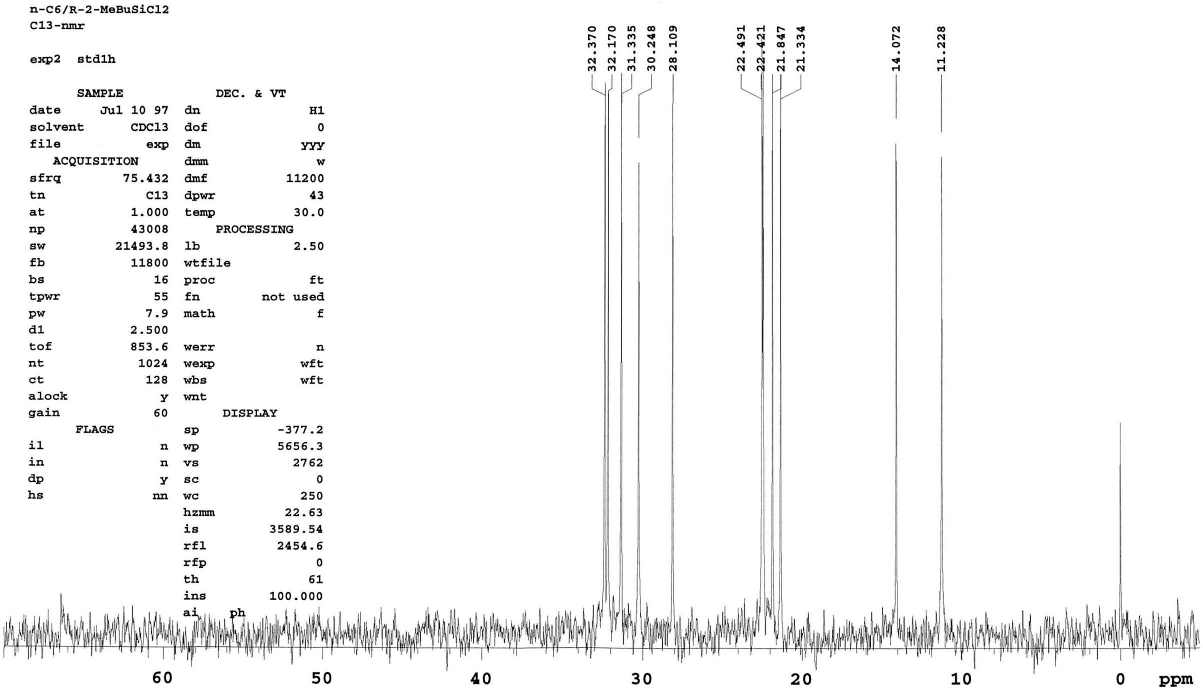

Fig. S3. ^{29}Si-NMR spectra of **1*R*** in $CDCl_3$ at 30 °C. ^{29}Si resonances at 33.229 ppm using the Me_4Si ^{29}Si reference peak (0.000 ppm).



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n-C6/R-2-MeBuSiCl2
C13-nmr

exp2  std1h

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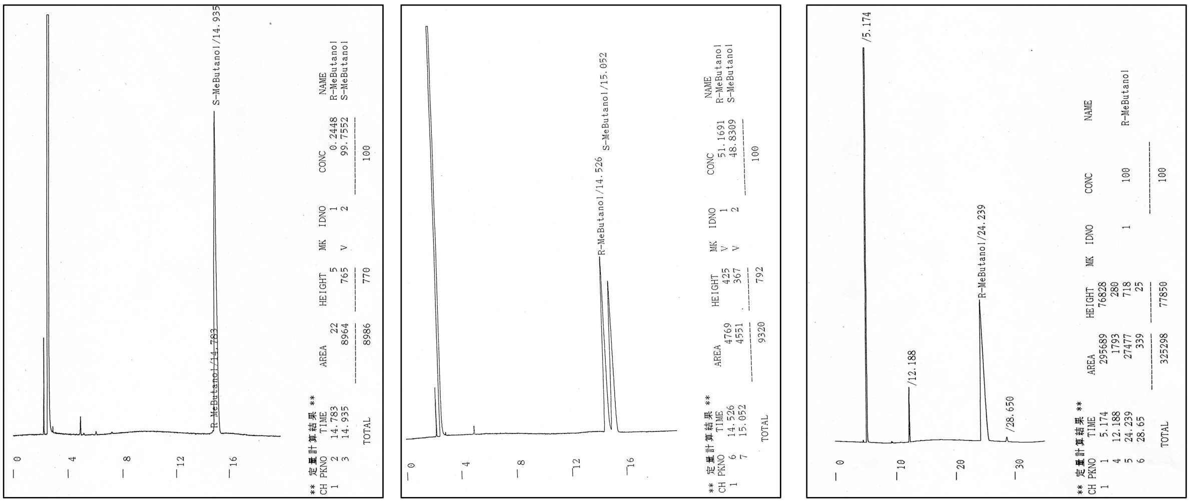
fb            11800  wtfile
bs               16  proc            ft
tpwr             55  fn        not used
pw              7.9  math             f
d1            2.500
tof           853.6  werr             n
nt             1024  wexp           wft
ct              128  wbs            wft
alock             y  wnt
gain             60       DISPLAY
      FLAGS          sp          -377.2
il                n  wp          5656.3
in                n  vs            2762
dp                y  sc               0
hs               nn  wc             250
                     hzmm         22.63
                     is         3589.54
                     rfl         2454.6
                     rfp              0
                     th              61
                     ins        100.000
                     ai     ph
```

Fig. S4. ^{13}C-NMR spectra of **1*R*** in $CDCl_3$ at 30 °C. ^{13}C resonances at 32.370, 32.170, 31.335, 30.248, 28.109, 22.491, 22.421, 21.847, 21.334, 14.072, 11.228 ppm *vs* Me_4Si ^{13}C reference peak (0.000 ppm).

1-1-3. Enantiopurity of (*R*)-2-methylbutylchloride and (*S*)-2-methylbutylchloride

Because (*R*)-2-methylbutylchloride was not available from a naturally occurring substance, Chemical Soft Research Co. synthesized this compound by another route in a nearly ten-step procedure based on the advice from Dr. Akira Tai (Emeritus Prof., University of Hyogo, Japan). Although an enantiopurity (*ee*) check of (*R*)-2-methylbutylchloride and (*S*)-2-methylbutylchloride using several chiral GC columns at the Toray Research Center (TRC) was unsuccessful, these starting chiral alcohols (i.e., (*R*)-2-methyl-1-butanol and (*S*)-2-methyl-1-butanol) as well as their racemic mixture were successfully analysed by *β*-DEX325 (30 m × 0.25 mm ID, Spelco) at the TRC. The enantiopurities of (*R*)-2-methyl-1-butanol and (*S*)-2-methyl-1-butanol were 99.5 % *ee* and 100 % *ee*, respectively.



```
** 定量計算結果 **
CH PKNO   TIME       AREA   HEIGHT   MK  IDNO      CONC   NAME
1     2  14.783        22        5          1    0.2448   R-MeButanol
      3  14.935      8964      765   V      2   99.7552   S-MeButanol
                ----------  -------             ---------
         TOTAL       8986      770                   100
```

```
** 定量計算結果 **
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1     6  14.526      4769      425   V      1   51.1691   R-MeButanol
      7  15.052      4551      367   V      2   48.8309   S-MeButanol
                ----------  -------             ---------
         TOTAL       9320      792                   100
```

```
** 定量計算結果 **
CH PKNO   TIME       AREA   HEIGHT   MK  IDNO      CONC   NAME
1     1   5.174    295689    76828
      4  12.188      1793      280
      5  24.239     27477      718          1       100   R-MeButanol
      6  28.65        339       25
                ----------  -------             ---------
         TOTAL     325298    77850                   100
```

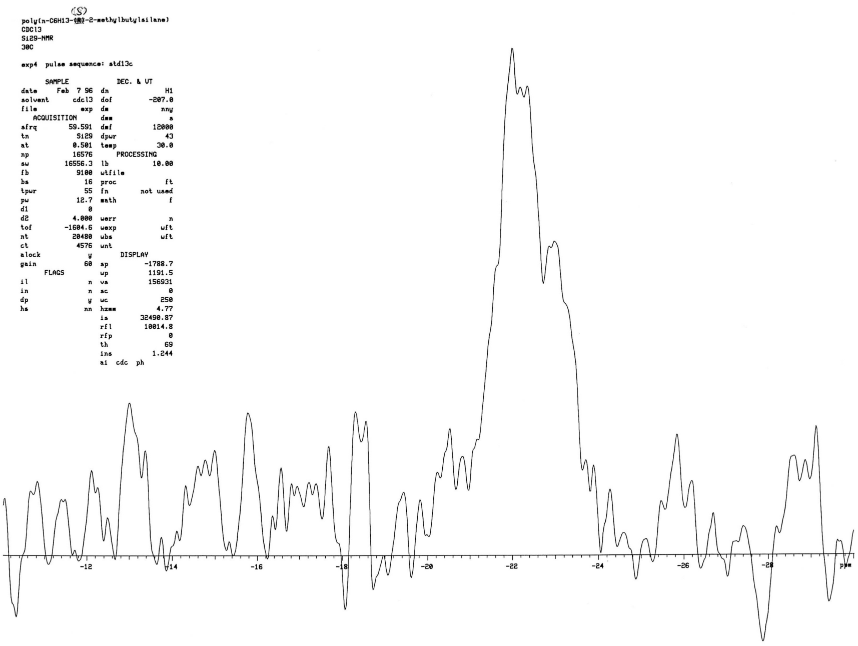
Fig. S5. Gas chromatograms of 2-methyl-1-butanol using a chiral GC technique (HP5890A, He carrier (1.2 mL min^{-1}), *β*-DEX325 (30 m × 0.25 mm ID) at 55 and 50 °C, Spelco). (Left) (*S*)-2-methyl-1-butanal (TCI, Tokyo, Japan) with (*R*)-2-methyl-1-butanol (retention time (*r.t.*) 14.783 min) / (*S*)-2-methyl-1-butanol (*r.t.* 14.935 min) = 0.24/99.76 (%/%). (Centre) A racemic mixture of 2-methyl-1-butanol (TCI, Tokyo, Japan) with (*R*)-2-methyl-1-butanol (*r.t.* 15.052 min) / (*S*)-2-methyl-1-butanol (*r.t.* 14.526 min) = 51.17/48.83 (%/%). (Right) (*R*)-2-methyl-1-butanol (custom made by Chemical Soft Research Co., Kyoto, Japan) with (*R*)-2-methyl-1-butanol (retention time = 24.239 min) = 100.00 (%). No detection of (*S*)-2-methyl-1-butanol. The Toray Research Center (TRC, Shiga, Japan) and Nippon Telegraph and Telephone Corporation (NTT) R&D center (Atsugi–Kanagawa, Japan) [report no. T217601 and T217118] measured and analysed the samples.

1-2. Polymer synthesis

A pair of unfractionated rigid rod-like helical **PSi-*S*** and **PSi-*R*** was prepared according to a previously reported protocol.

1-2-1. Poly(*n*-hexyl-(*S*)-2-methylbutylsilane) (PSi-*S*)

To a mixture containing 50 mL of dry toluene (Wako), 1.0 g (43 mmol) of sodium (Wako), and 0.05 g (0.19 mmol) of 18-crown-6 (Wako) at 120 °C, 5.1 g (20 mmol) of **1*S*** were added dropwise under an N_2 atmosphere. The mixture was slowly stirred at 120 °C for 2 h. The reaction mixture became highly viscous. Additionally, 500 mL of dry toluene was added to reduce the solution viscosity and the resulting mixture was stirred overnight. The hot reaction slurry was passed immediately through 40 μm and 2-μm PTFE filters (Fluoropore F-40 and Fp-200, Sumitomo Electric Co. (Tokyo, Japan)) using the pressure of N_2 gas. To the clear filtrate, ethanol and methanol were carefully added. White precipitates were collected by centrifugation with a Kubota model 5420 centrifuge at 3000 rpm (Kubota Corporation (Tokyo, Japan)) followed by drying overnight at 120 °C under vacuum. The masses of the first (higher-M_w) and second (middle-M_w) fractions were 0.16 g (4.3%) and 0.50 g (13.6%), respectively. In addition, several fractionations from the second fraction were made on the basis of the choice of toluene and poor solvents (IPA, ethanol, methanol and water). For the second fraction, ^{29}Si NMR ($CDCl_3$, 30 °C, ppm) exhibited peaks at –22.2, –22.4 and –23.0, and ^{13}C NMR ($CDCl_3$, 30 °C, ppm) exhibited peaks at 34.1, 31.4 and 23.0.



```
               (S)
poly(n-C6H13-~~(R)~~-2-methylbutylsilane)
CDCl3
Si29-NMR
30C

exp4  pulse sequence: std13c

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at            0.501  temp           30.0
np            16576      PROCESSING
sw          16556.3  lb            10.00
fb             9100  wtfile
bs               16  proc             ft
tpwr             55  fn         not used
pw             12.7  math              f
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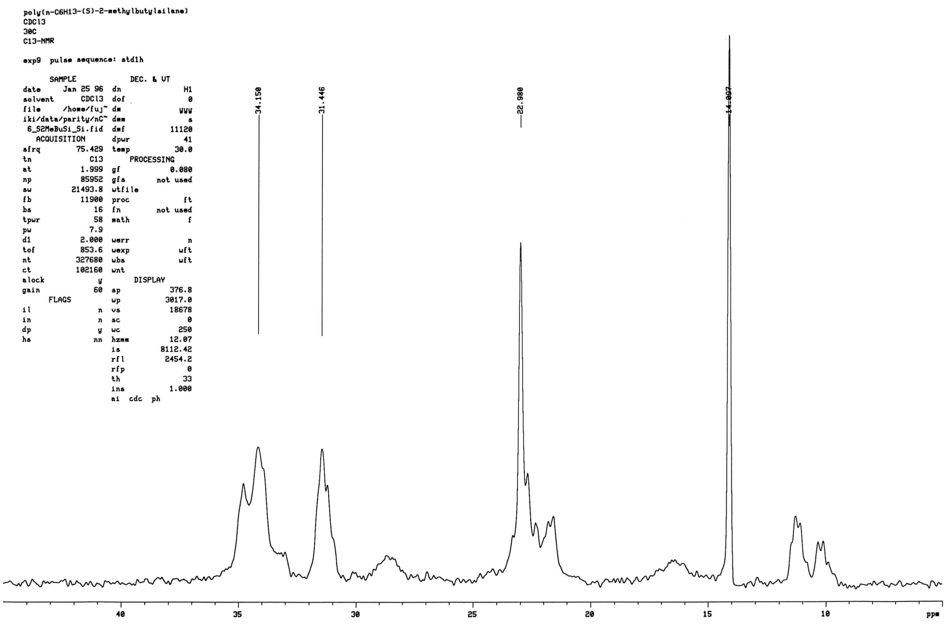
                     th               69
                     ins           1.244
                     ai  cdc  ph
```

Fig. S6. ^{29}Si-NMR spectra of **PSi-*S*** in $CDCl_3$ at 30 °C. ^{29}Si NMR signals exhibit broad resonances at –22.0, –22.2 and –22.7 ppm relative to the Me_4Si ^{29}Si reference peak (0.000 ppm).



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CDCl3
30C
C13-NMR

exp9  pulse sequence: std1h

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tn              C13      PROCESSING
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sw          21493.8  wtfile
fb            11900  proc            ft
bs               16  fn        not used
tpwr             58  math             f
pw              7.9
d1            2.000  werr             n
tof           853.6  wexp           wft
nt           327680  wbs            wft
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                     ins          1.000
                     ai   cdc   ph
```
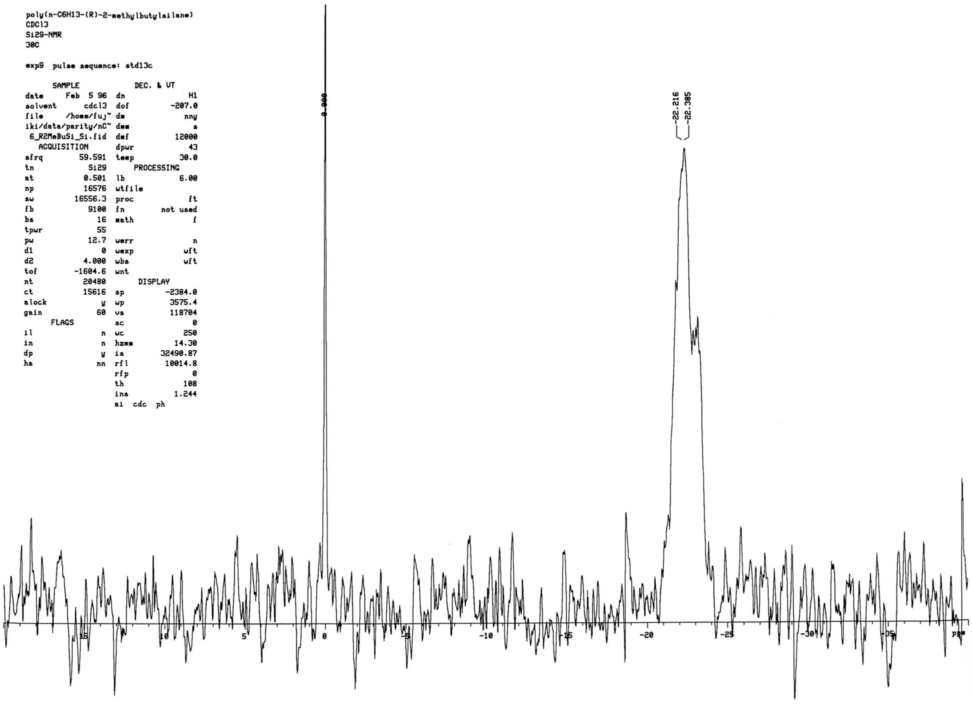

Fig. S7. ^{13}C-NMR spectra of **PSi-*S*** in $CDCl_3$ at 30 °C. ^{13}C NMR signals exhibit broad resonances at 34.1, 31.4 and 23.0 ppm relative to the Me_4Si ^{29}Si reference peak (0.000 ppm).

1-2-2. Poly(*n*-hexyl-(*R*)-2-methylbutylsilane) (PSi-*R*)

Similarly, to a mixture of 25 mL of dry toluene (Wako), 0.80 g (35 mmol) of sodium (Wako) and 0.03 g (0.11 mmol) of 18-crown-6 (Wako) at 120 °C, 2.55 g (10 mmol) of **1*R*** was added dropwise under an N_2 atmosphere. The mixture was stirred at 120 °C for 2 h. The reaction mixture became highly viscous. Additionally, 500 mL of dry toluene were added to reduce the solution viscosity followed by stirring overnight. The hot reaction slurry was passed immediately through 40 μm and 2-μm PTFE filters (Fluoropore F-40 and Fp-200, Sumitomo Electric Co.) using the pressure of the N_2 gas flow. To the clear filtrate, ethanol and methanol were carefully added. The white precipitates were collected by centrifugation using a Kubota 5420 at 3000 rpm and were subsequently died overnight at 120 °C under vacuum. The masses of the first (higher-M_w) and second (middle-M_w) fractions were 0.17 g (9.2 %) and 0.37 g (20.1 %), respectively. Further fractionations from the second fraction were conducted on the basis of the choice of toluene and poor solvents (IPA, ethanol, methanol and water). Three broad ^{29}Si NMR resonance peaks were observed for the second fraction (100 MHz, $CDCl_3$) at –22.0, –22.2 and –22.7. For the second fraction, the ^{29}Si NMR spectrum ($CDCl_3$, 30 °C, ppm) contained peaks at –22.0, –22.2 and –22.7.



```
poly(n-C6H13-(R)-2-methylbutylsilane)
CDCl3
Si29-NMR
30C

exp9  pulse sequence: std13c

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sfrq         59.591  temp          30.0
tn             Si29      PROCESSING
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np            16576  wtfile
sw          16556.3  proc            ft
fb             9100  fn        not used
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                     rfp              0
                     th             108
                     ins          1.244
                     ai  cdc  ph
```

Fig. S8. ^{29}Si-NMR spectra of **PSi-*R*** in $CDCl_3$ at 30 °C. ^{29}Si NMR signals exhibited broad resonances at –22.2, –22.4, and –23.0 ppm relative to the Me_4Si ^{29}Si reference peak (0.000 ppm).

1-3. Chain rigidity of PSi-*S* and PSi-*R*

The degree of polysilane stiffness was confirmed by the high viscosity index observed in the viscometric data (α) in the Kuhn-Mark-Houwink-Sakurada plots ($[\eta] = \varkappa \cdot M^{\alpha}$, where $[\eta]$ is the intrinsic viscosity, M is the molecular mass, $\varkappa$ is a constant, and α is the viscosity index) in toluene at 70 °C. The viscometric measurement has been well established as a physico-chemical method for the characterisation of floppy chain-like polymers in dilute solution. The α values of **PSi-*S*** and **PSi-*R*** were 1.24 and 1.52, respectively.

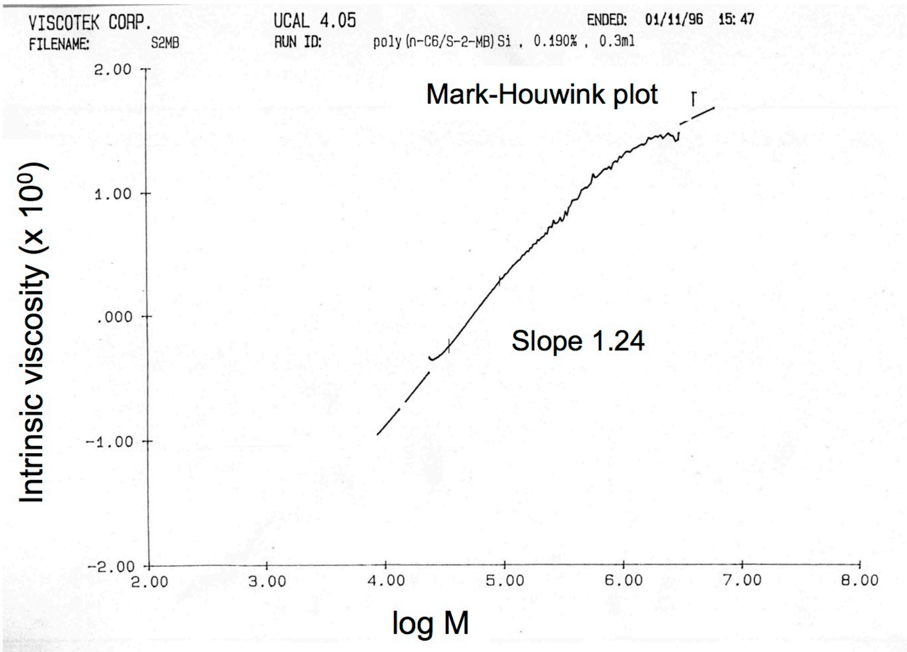


Fig. S9. Raw data of log[η] as a function of log$M$ for **PSi-*S*** in toluene at 70 °C using a Waters model 150C GPC system (three GMH$_{XL}$ columns (30 cm × 8 mm ID, Tosoh (Tokyo, Japan) equipped with a Viscotek H502a detector) at a flow rate of 0.97 mL min^{-1}. The TRC and NTT R&D centre measured and analysed the samples (file no. TRC-T111433).

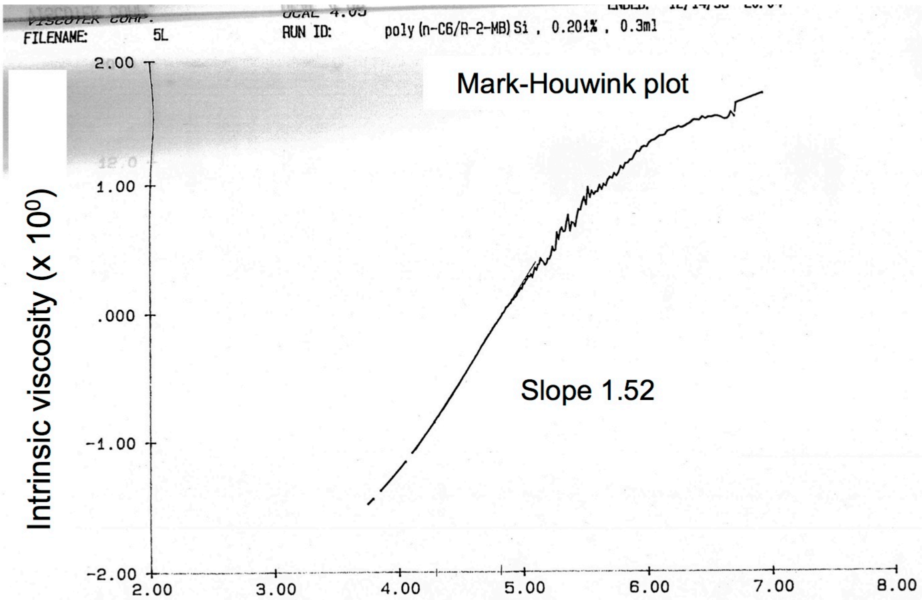


Fig. S10. Raw data of log[η] as a function of log$M$ for **PSi-*R*** in toluene at 70 °C using a Waters model 150C GPC system (three GMH$_{XL}$ columns (30 cm × 8 mm ID, Tosoh (Tokyo, Japan) equipped with a Viscotek H502a detector) at a flow rate of 0.97 mL min^{-1}. The TRC and NTT R&D centre measured and analysed the samples (file no. TRC-T111093).

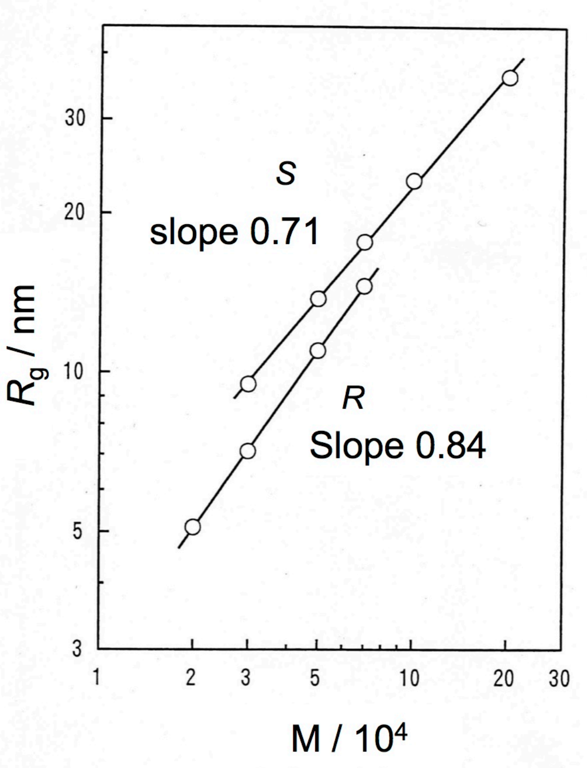


Fig. S11. R_g value as a function of *M* for **PSi-*R*** and **PSi-*S*** in toluene at 70 °C. The analysis was performed by the TRC, file no. TRC-T111433 T111433/ T111093.

2. Supporting Figures

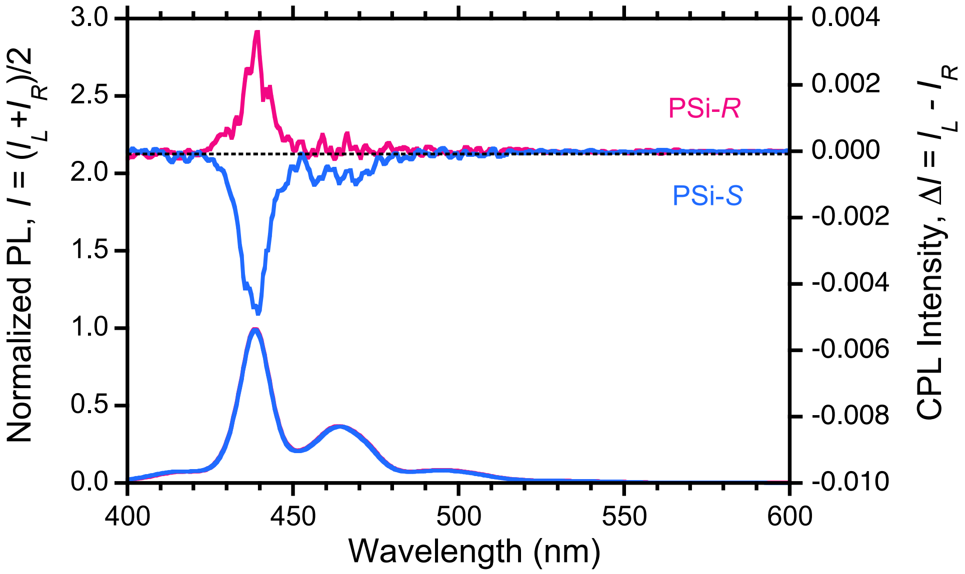


Fig. S12. CPL and PL spectra of the as-prepared **PSi** and **PF8** (= 2:1 ratio) hetero-aggregate in toluene-methanol (1.5/1.5 (v/v)).

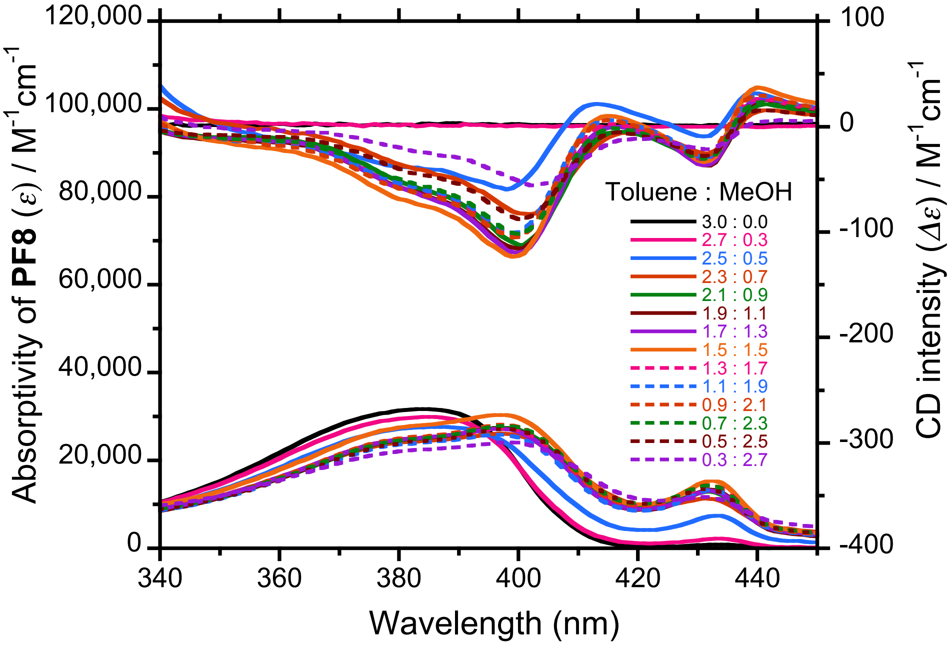


Fig. S13. CD and UV-Vis spectra of hetero-aggregates of **PSi-*S*** and **PF8** with various amount toluene-methanol cosolvent (v/v) with [**PF8**] = 2.5 × 10^{-5} M and [**PSi-*S***] = 5.0 × 10^{-5} M as their repeating units. The M_w values of **PSi-*S*** and **PF8** were 75,800 and 78,800, respectively.

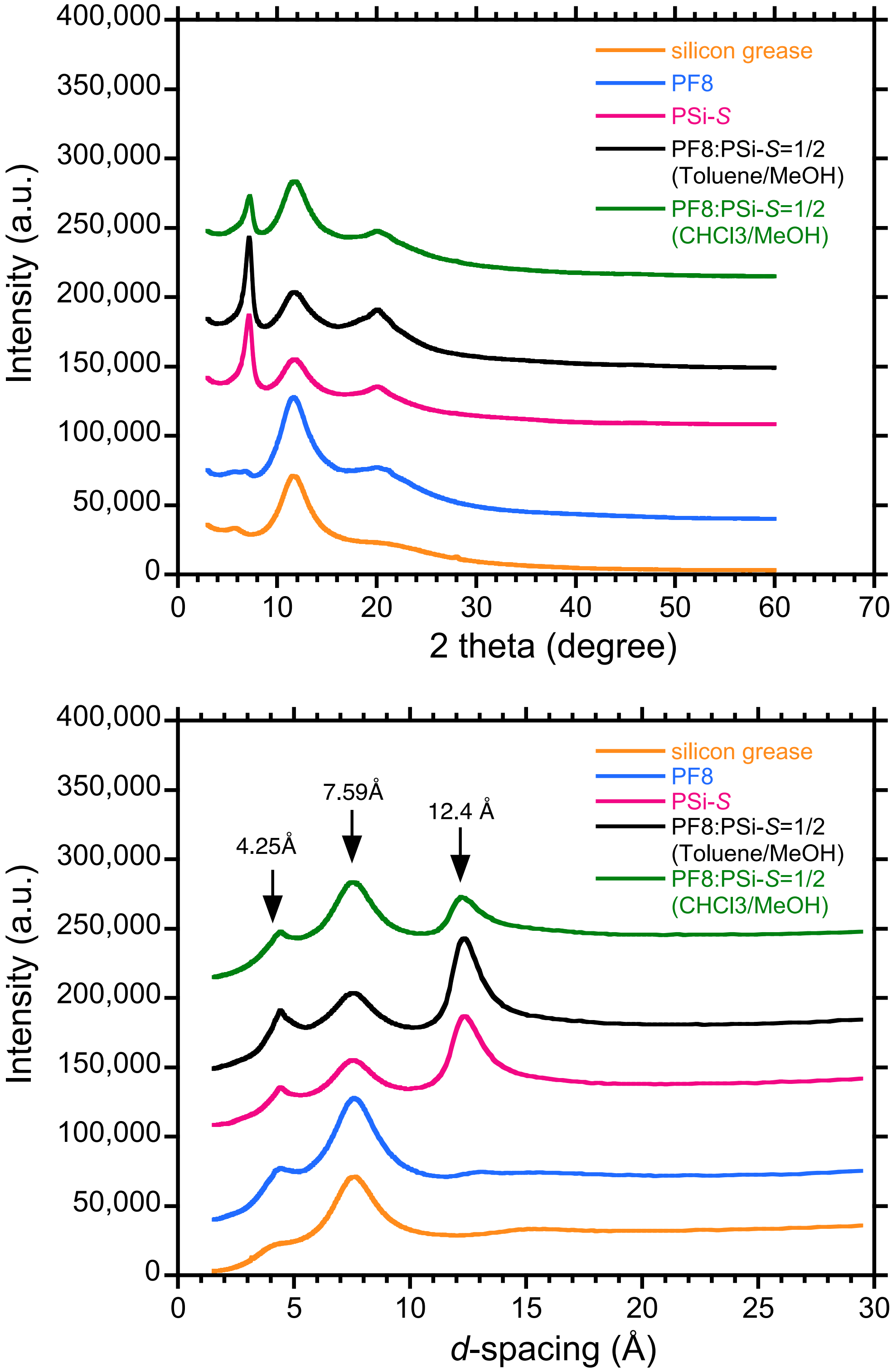


Fig. S14. WAXD data of high-vacuum silicone grease (Dow-Corning-Toray), **PF8** (M_n = 78,800), **PSi-*S*** (M_n = 75,800) and their **PSi-*S*-PF8** (= 2:1) aggregate from chloroform and methanol (1/1 (v/v)) and from toluene and methanol (1/1 (v/v)) embedded to silicone grease onto an Si-crystal substrate as functions of (top) diffraction angle (2θ) and (bottom) *d*-spacing.

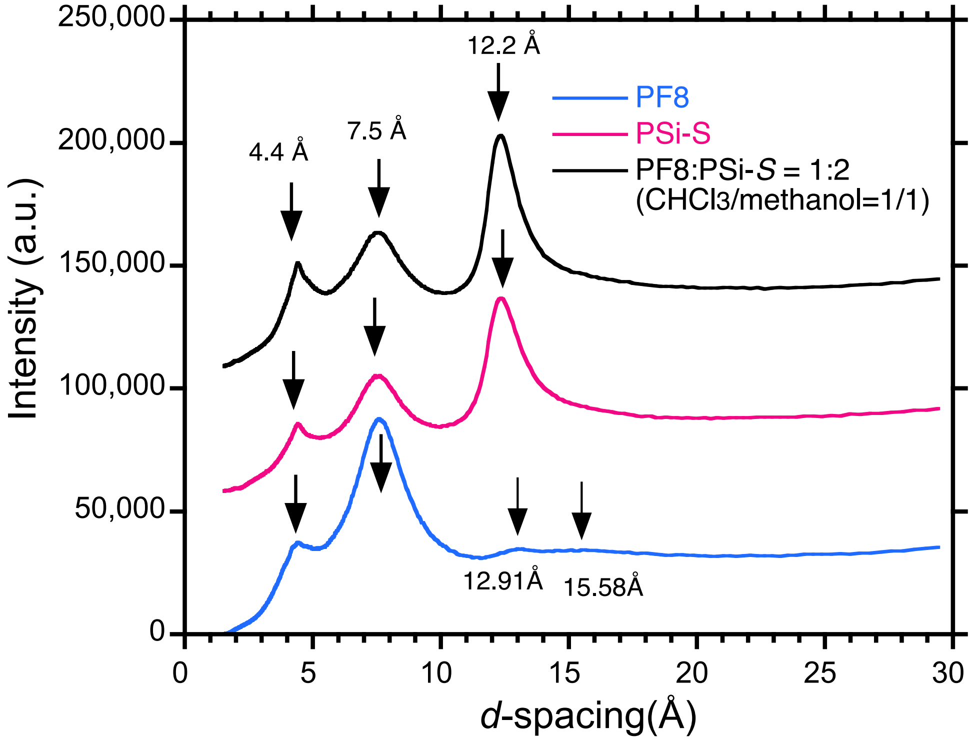


Fig. S15. WAXD of **PF8** (M_n = 78,800), **PSi-*S*** (M_n = 75,800) and **PSi-*S*-PF8** (= 2:1) aggregate from chloroform and methanol (1/1 (v/v)) subtracted with WAXD data of the silicone grease.

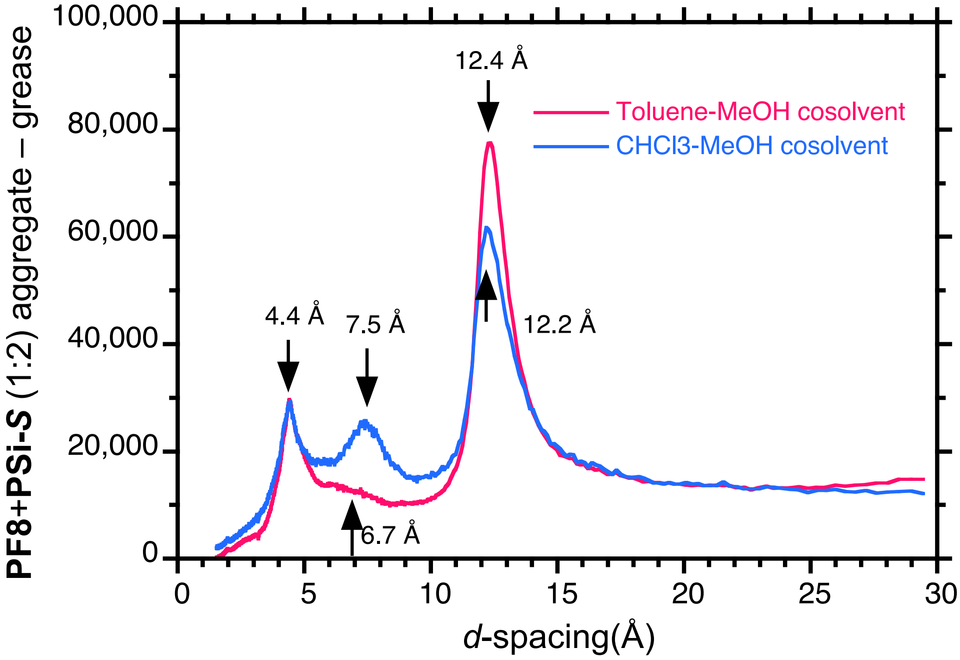


Fig. S16. Comparison of WAXD between **PSi-*S*-PF8** (= 2:1) aggregates from chloroform and methanol (1/1 (v/v)) and from toluene and methanol (1/1 (v/v)) subtracted with WAXD data of the silicone grease.

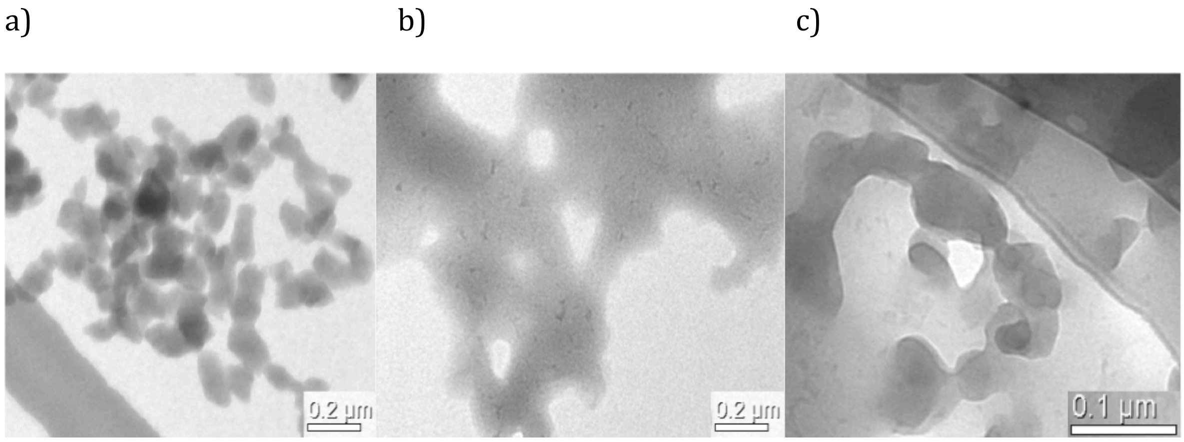


Fig. S17. Cryo-TEM images on carbon-coated copper grid (200 mesh) of a) **PF8** homo-aggregates, b) **PSi-*S*** homo-aggregates and c) **PSi-*S*-PF8** (= 2:1) hetero-aggregates.

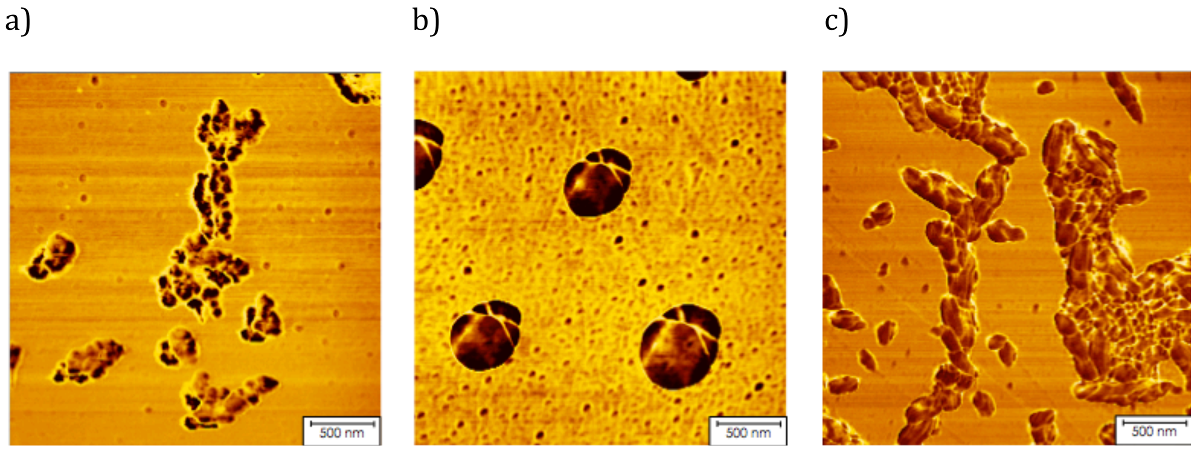


Fig. S18. Dynamic force mode (DFM) AFM images with SI-DF20 (f = 132 KHz, R = 15 nm, D = 12.5 μm, C = 13 N m^{-1}) on HOPG. Specimens were a) **PSi-*S*** homo-aggregates, b) **PF8** homo-aggregates and c) **PSi-*S*-PF8** (= 2:1) hetero-aggregates. All specimens were produced by a drop-cast of 10^{-4} M aggregates suspension in toluene-methanol (1/1 (v/v)) cosolvent.

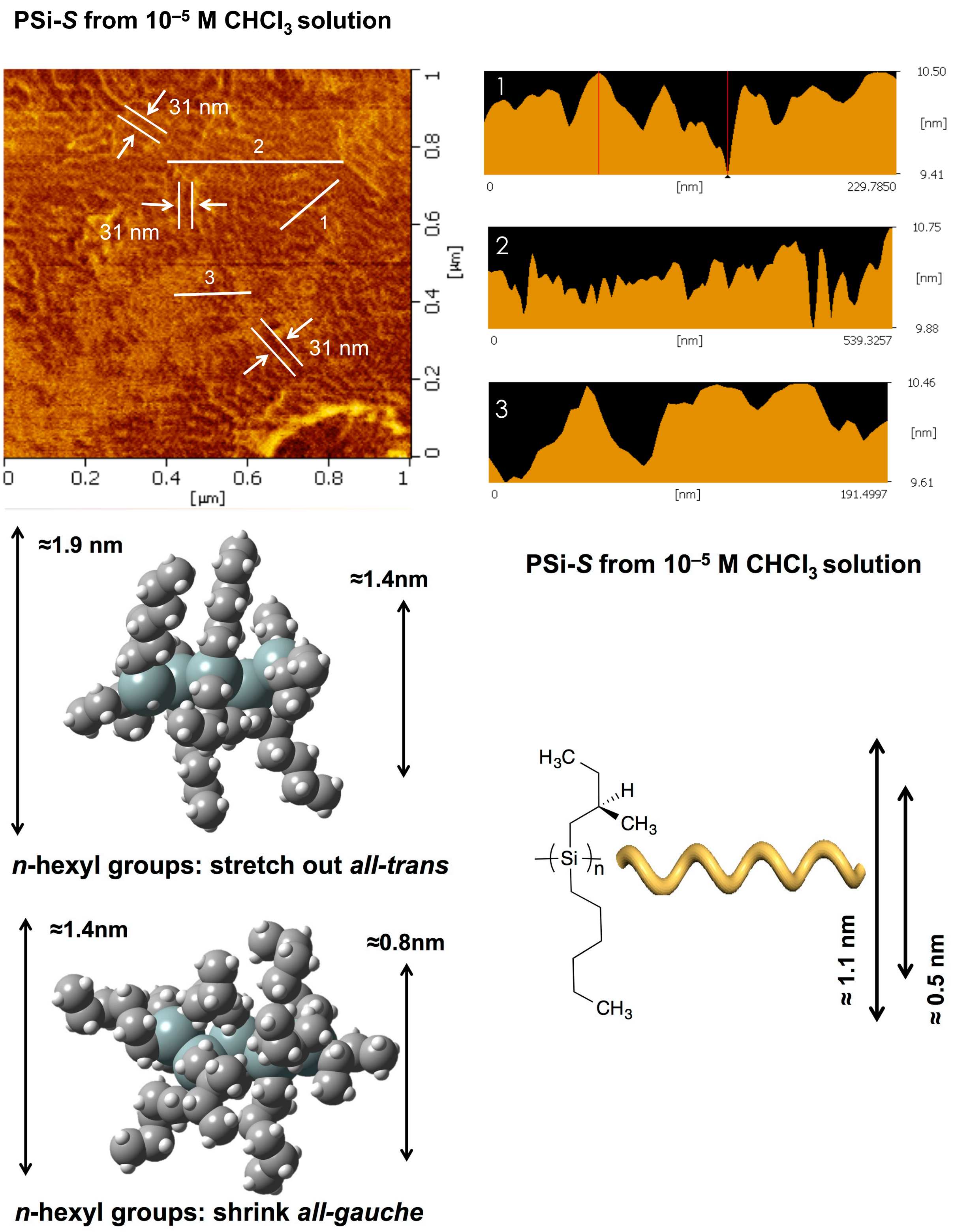


Fig. S19. (Top) DFM AFM image and height profile with SI-DF20S (coated with Al, *f* = 129 KHz, *R* = 2–5 nm, *D* = 12.5 *μ*m, *C* =12 N m^{-1}) on HOPG casting from 1 x 10^{-5} M chloroform solution of **PSi-*S*** (M_n = 75,800). (Bottom) Two representative models of *n*-hexyl structures with stretch out (*all-trans*) and shrink (*all-gauche*) forms.

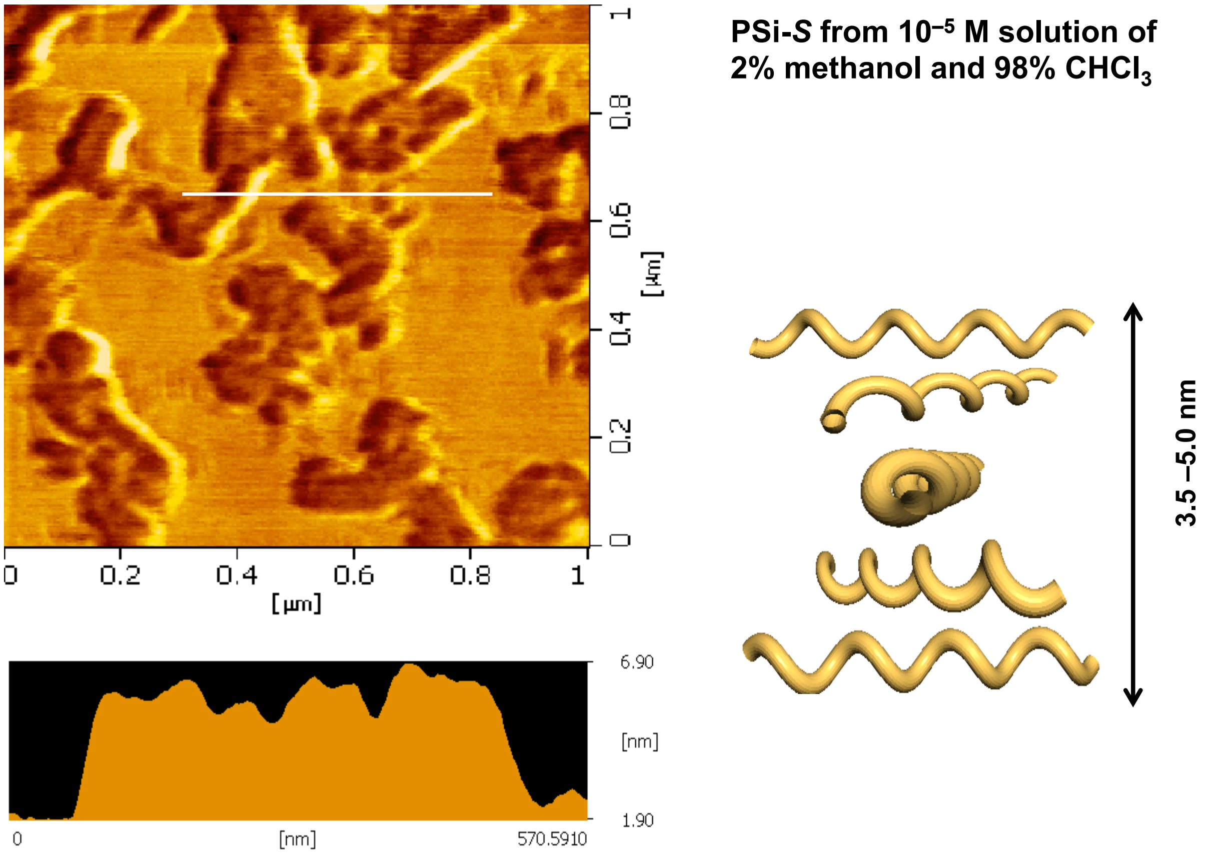


Fig. S20. (Left) DFM AFM image and height profile with SI-DF20S (coated with Al, f = 129 KHz, R = 2–5 nm, D = 12.5 μm, C =12 N m^{-1}) on HOPG casting from 1 x 10^{-5} M in 2% methanol and 98 % chloroform solution of **PSi-*S*** (M_n = 75,800). (Right) Schematic model of 7_3-helical **PSi-*S*** aggregate on HOPG.

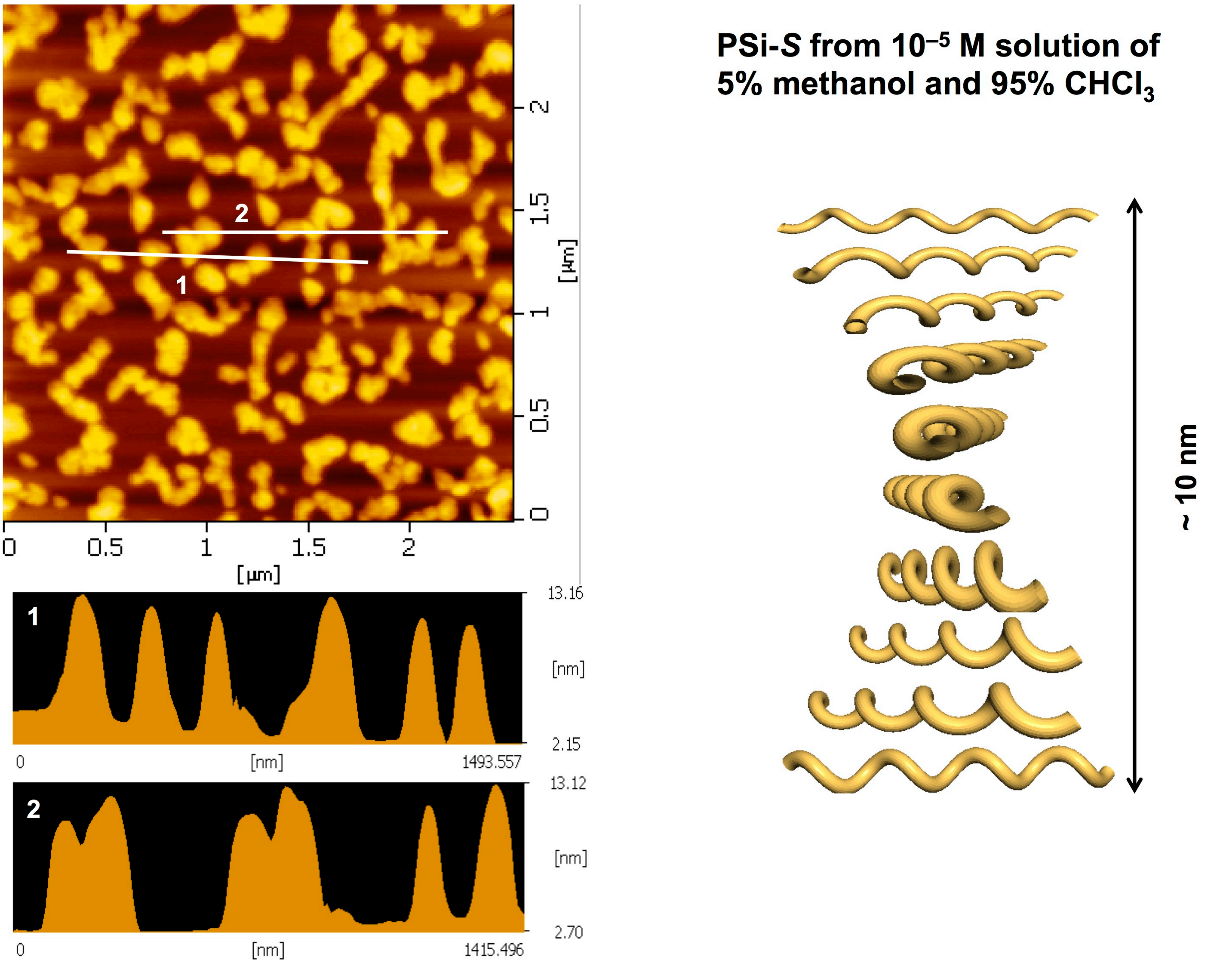
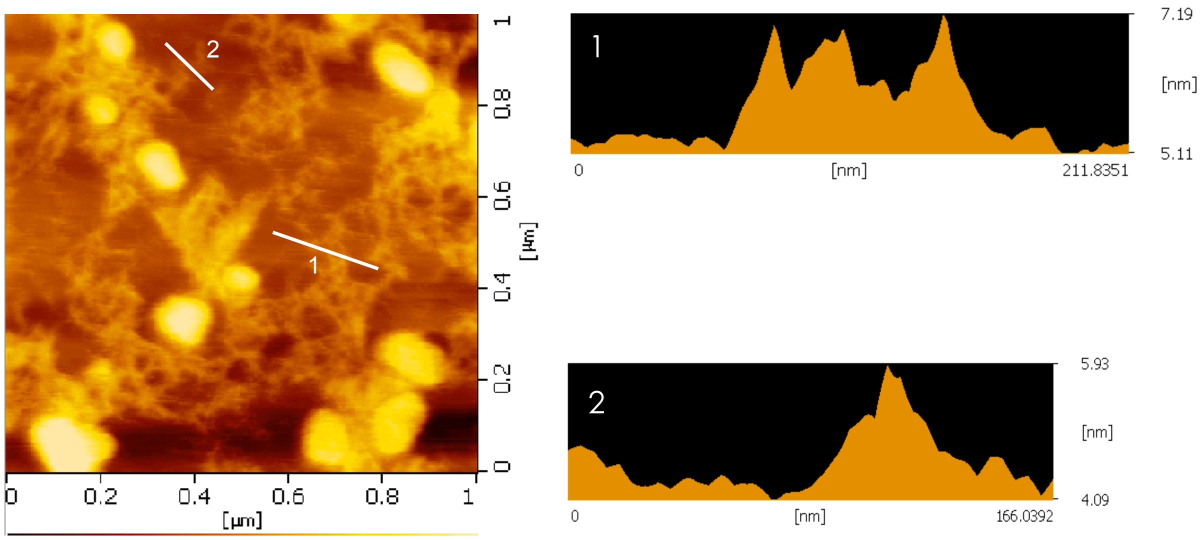


Fig. S21. (Left) DFM AFM image and height profile with SI-DF20S (coated with Al, *f* = 129 KHz, *R* = 2–5 nm, *D* = 12.5 μm, *C* =12 Nm^{-1}) on HOPG casting from 5% methanol and 95 % chloroform solution (1 x 10^{-5} M) of **PSi-*S*** (M_n = 75,800). (Right) A schematic model of 7_3-helical **PSi-*S*** aggregate on HOPG.

PSi-*S* from 10^{-5} M solution of 5% methanol and 95% $CHCl_3$



PF8 from $CHCl_3$ ($5x10^{-6}$ M)

***M*n = 78,400 *DP*n = 212**
End-to-end distance of an ideal rod ≈ 169 nm

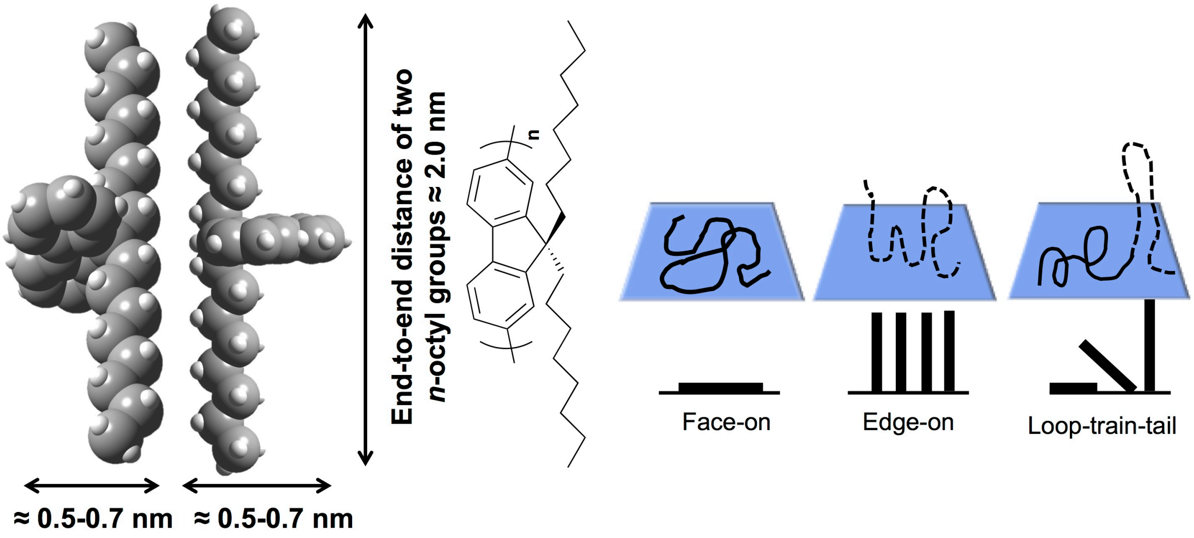
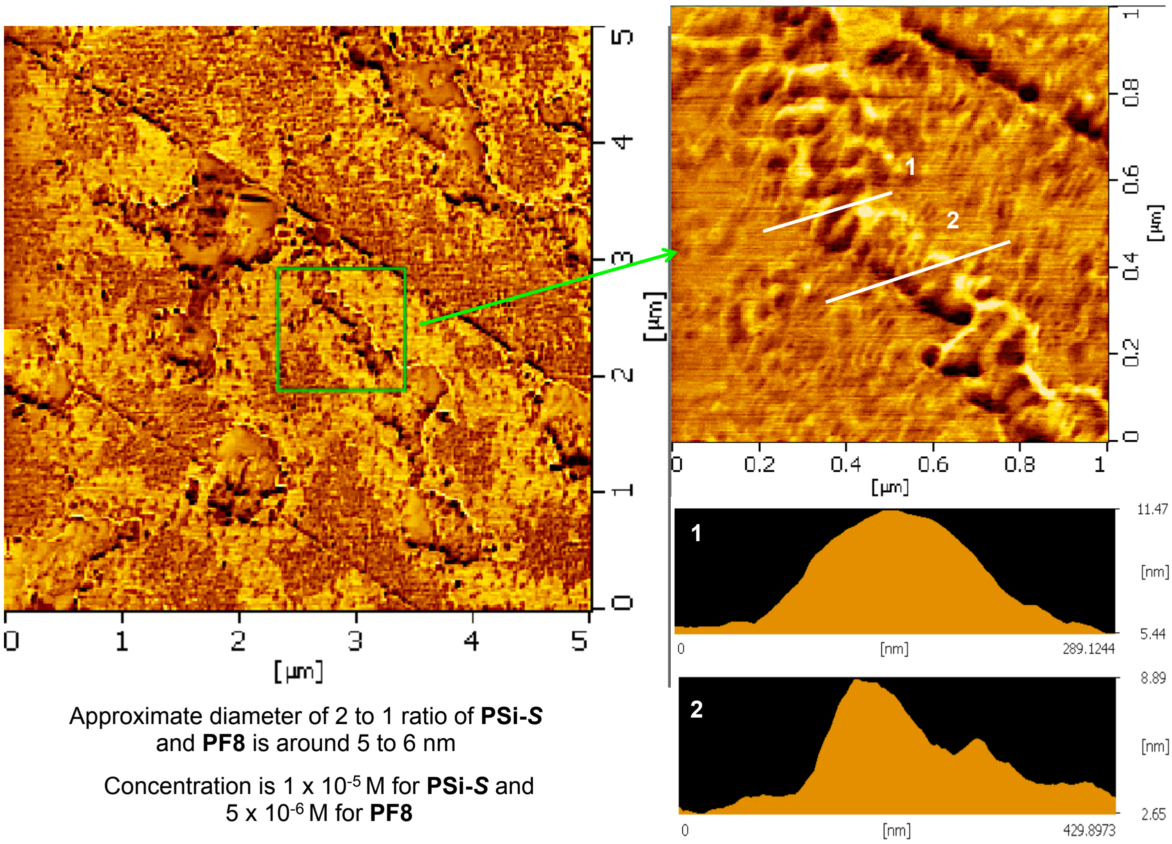


Fig. S22. (Top) DFM AFM image and height profiles with SI-DF20S (coated with Al, f = 129 KHz, R = 2–5 nm, D = 12.5 μm, C = 12 N m^{-1}) on HOPG casting from 5 x 10^{-6} M chloroform solution of **PF8** (M_n = 78,400). (Bottom) A representative model of two *n*-octyl groups with stretch out form and several orientations of **PF8** at HOPG.

From PSi-*S* (1×10^{-5} M) and PF8 (0.5×10^{-5} M) solution of 5% methanol and 95% $CHCl_3$



Approximate diameter of 2 to 1 ratio of **PSi-*S*** and **PF8** is around 5 to 6 nm

Concentration is 1 x 10^{-5} M for **PSi-*S*** and 5 x 10^{-6} M for **PF8**

Fig. S23. DFM AFM images and height profiles with SI-DF20S (coated with Al, f = 129 KHz, R = 2–5 nm, D = 12.5 μm, C = 12 N m^{-1}) on HOPG casting from **PF8** (0.5 x 10^{-5} M) and **PSi-*S*** (1.0 x 10^{-5} M) (2:1 ratio) from solution of 5% methanol and 95% $CHCl_3$.

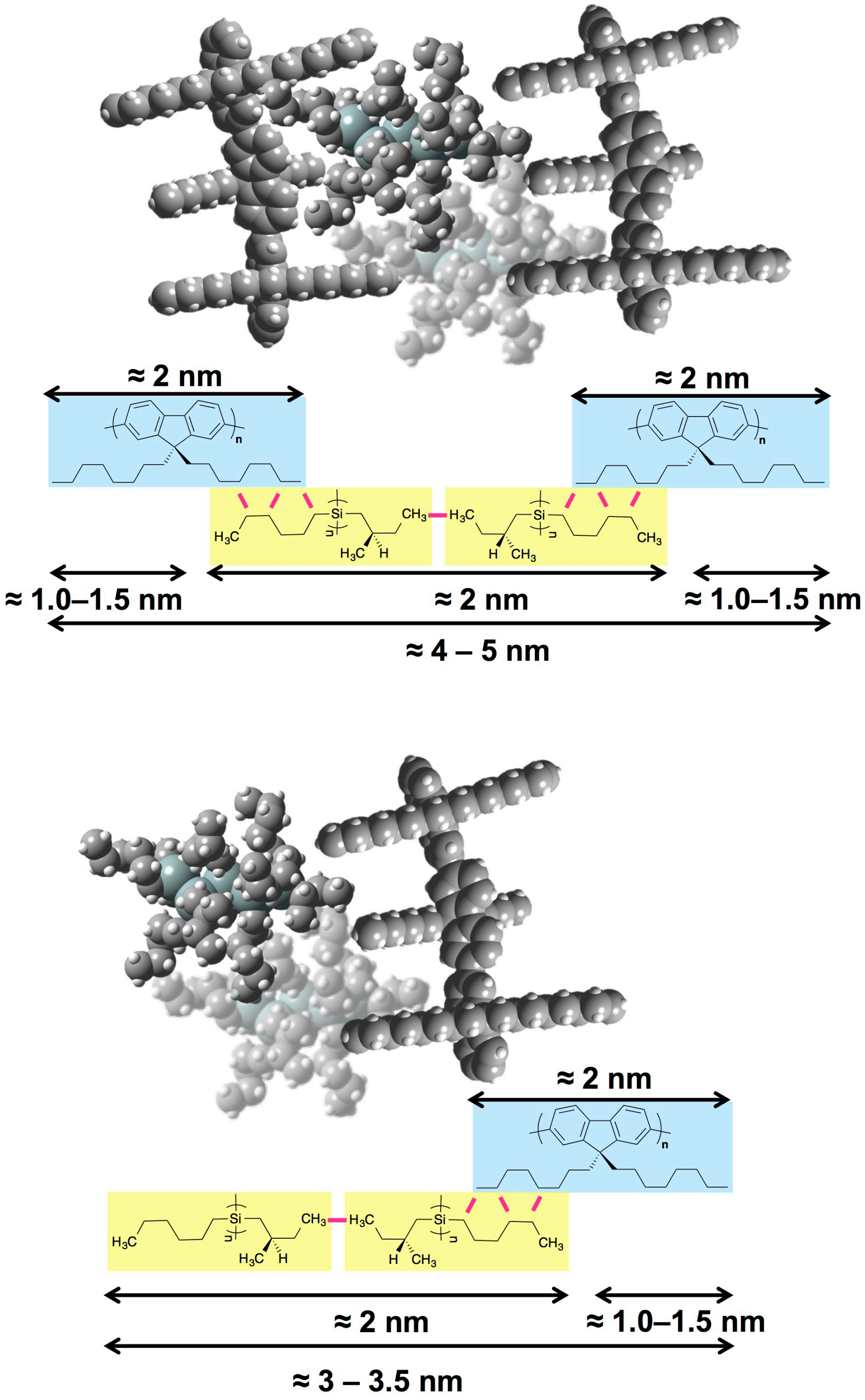


Fig. S24. Speculated cross-section and computer generated models of **PSi-*S*-PF8** (= 2:1) ratio) hetero-aggregate to explain height profile (diameter of the aggregate) in Fig. S23. Red lines are possible attractive C-H/H-C interactions, causing an interdigitation between several alkyl side chains of **PSi-*S*** and **PF8**. (Top) Height of ≈ 6 nm arises from two helical **PSi-*S*** chains with shrink *n*-hexyl groups and two **PF8** chains with stretch-out *n*-octyl groups. (Bottom) Height of ≈ 5 nm comes from two **PSi-*S*** chains with shrink *n*-hexyl groups and one **PF8** chain with stretch-out *n*-octyl groups.

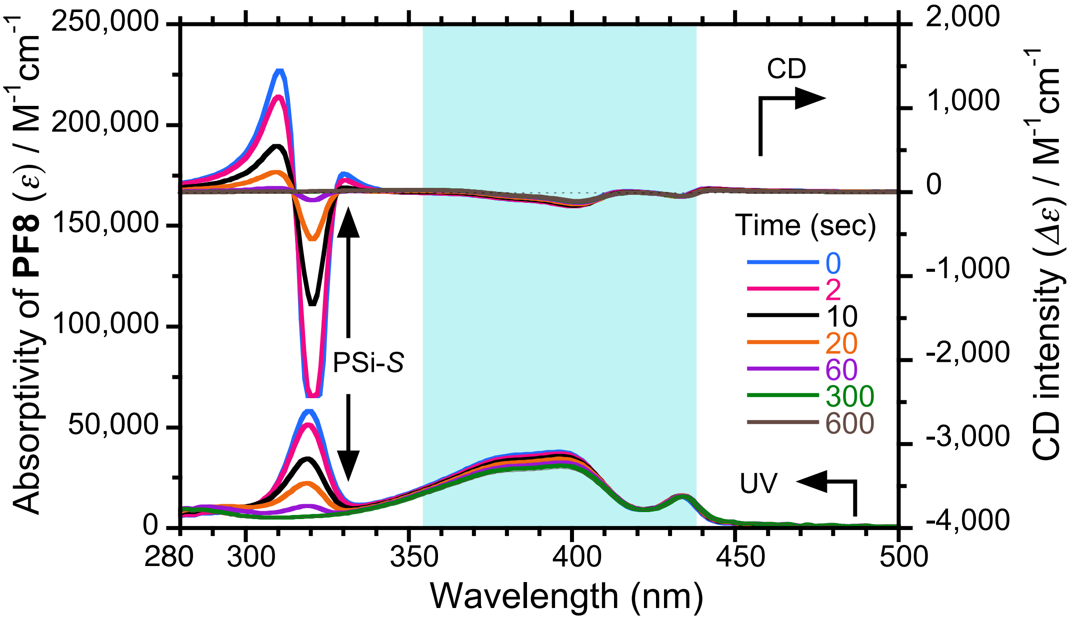


Fig. S25. CD and UV-Vis spectra of hetero-aggregates under photochemical decomposition of **PSi-*S*** and **PF8** with a 2-to-1 ratio produced in a toluene-methanol cosolvent (1.5/1.5 (v/v)) with [**PF8**] = 2.5 × 10^{-5} M and [**PSi-*S***] = 5.0 × 10^{-5} M as their repeating units. The M_w values of **PSi-*S*** and **PF8** were 40,500 and 78,400, respectively.

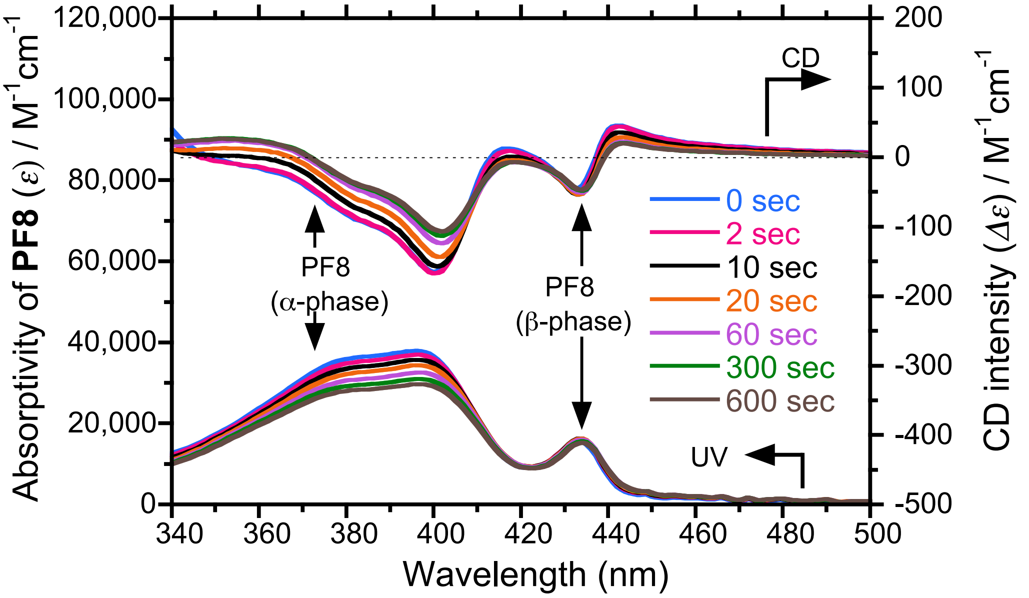


Fig. S26. CD and UV-Vis spectra of hetero-aggregates under photochemical decomposition of **PSi-*S*** and **PF8** (enlarge) with a 2-to-1 ratio produced in a toluene-methanol cosolvent (1.5/1.5 (v/v)) with [**PF8**] = 2.5 × 10^{-5} M and [**PSi-*S***] = 5.0 × 10^{-5} M as their repeating units. The M_w values of **PSi-*S*** and **PF8** were 40,500 and 78,400, respectively.

3. References

S1) a) M. Fujiki, *Jpn. Kokai Tokkyo Koho*, 1993, JP 05-202528; b) M. Fujiki, *J. Am. Chem. Soc.*, 1994, **116**, 6017; c) M. Fujiki, *Appl. Phys. Lett.*, 1994, **65**, 3251; d) Y. Nakano, F. Ichiyanagi, M. Naito, Y. Yang and M. Fujiki, *Chem. Commun.*, 2012, **48**, 6636; e) M. Fujiki, *Symmetry*, 2010, **2**, 1625.