Supplementary Information (SI) for Chemical Communications.

Supporting Information for

Control of Higher-Order Supramolecular Aggregation Driven by Crowding Effects in a PDMS/Oligomer System

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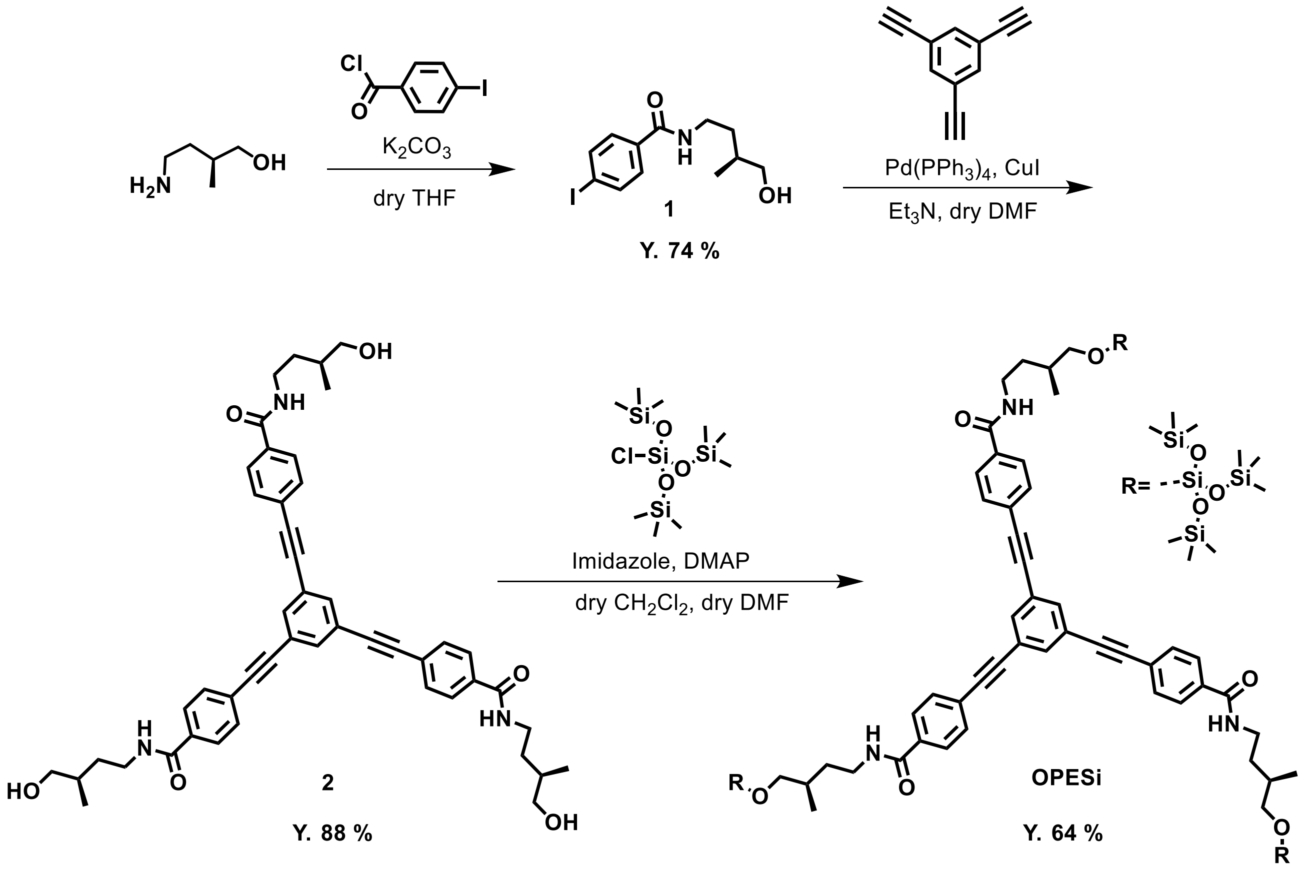
1. Experimental Section

Instrumentation

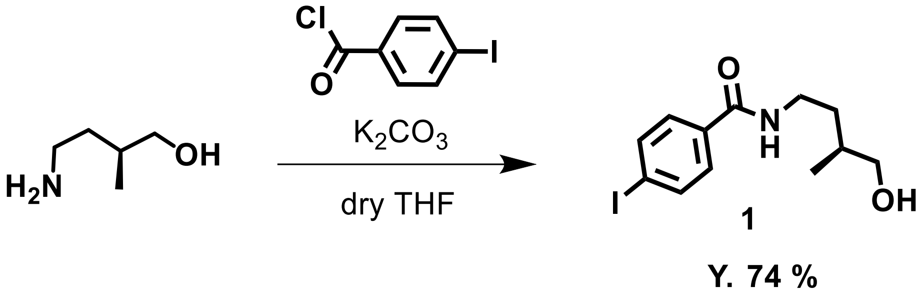
^{1}H and ^{13}C NMR measurements were recorded on a Bruker Avance Neo 400 instrument (^{1}H 400 MHz and ^{13}C 100 MHz). UV–vis spectra were recorded on a JASCO V-750 spectrometer with a JASCO ETCS-761 temperature controller. Circular dichroism (CD) and linear dichroism (LD) spectra were recorded on a JASCO J-1500 spectropolarimeter. Dynamic light scattering (DLS) measurements were performed using a Horiba nano Partica SZ-100-Z instrument. Viscosity measurements were conducted on an Anton Paar MCR 702 rheometer with a coaxial double-cylinder measuring system. Elemental analysis and FAB mass spectroscopy were performed at the Research Institute for Instrumental Analysis, Advanced Science Research Center, Kanazawa University.

Materials.

Unless otherwise noted, all commercially available reagents and solvents were used as received without further purification. Octamethyltrisiloxane (OMTS) used for UV–vis, CD, and LD measurements was distilled prior to use.

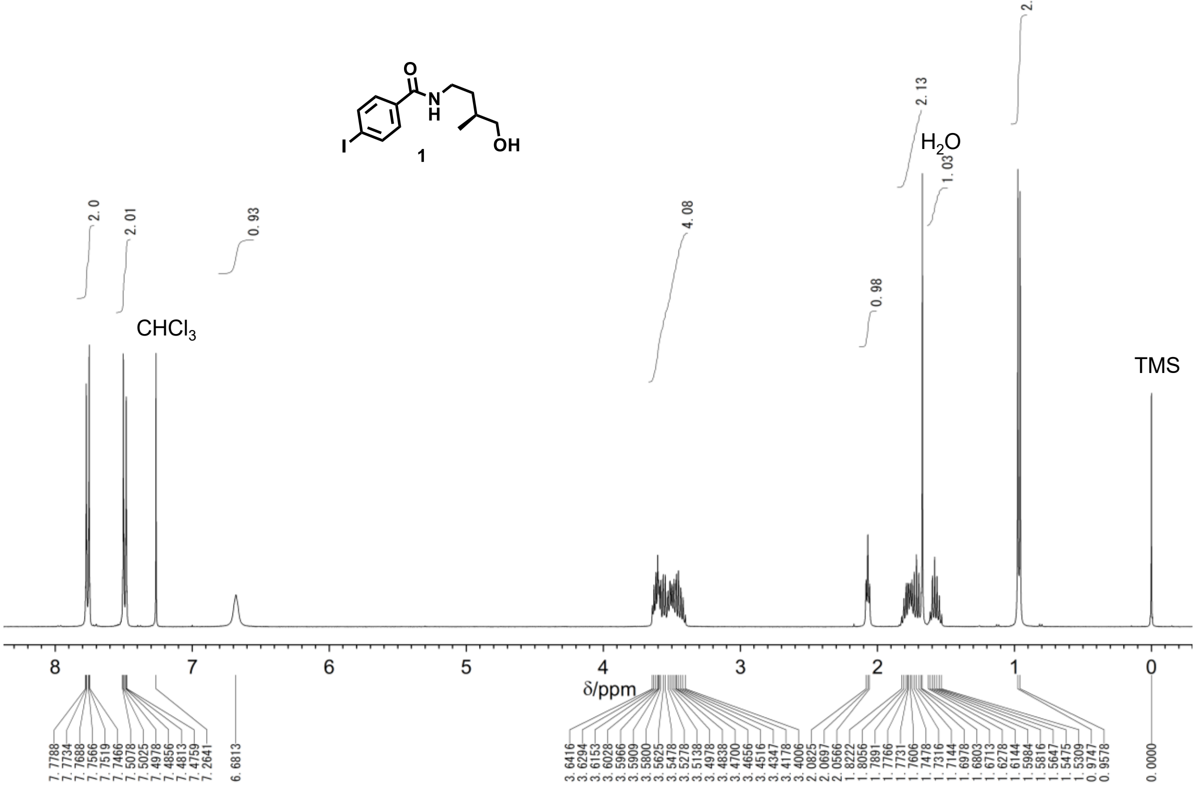


Synthesis of **1**

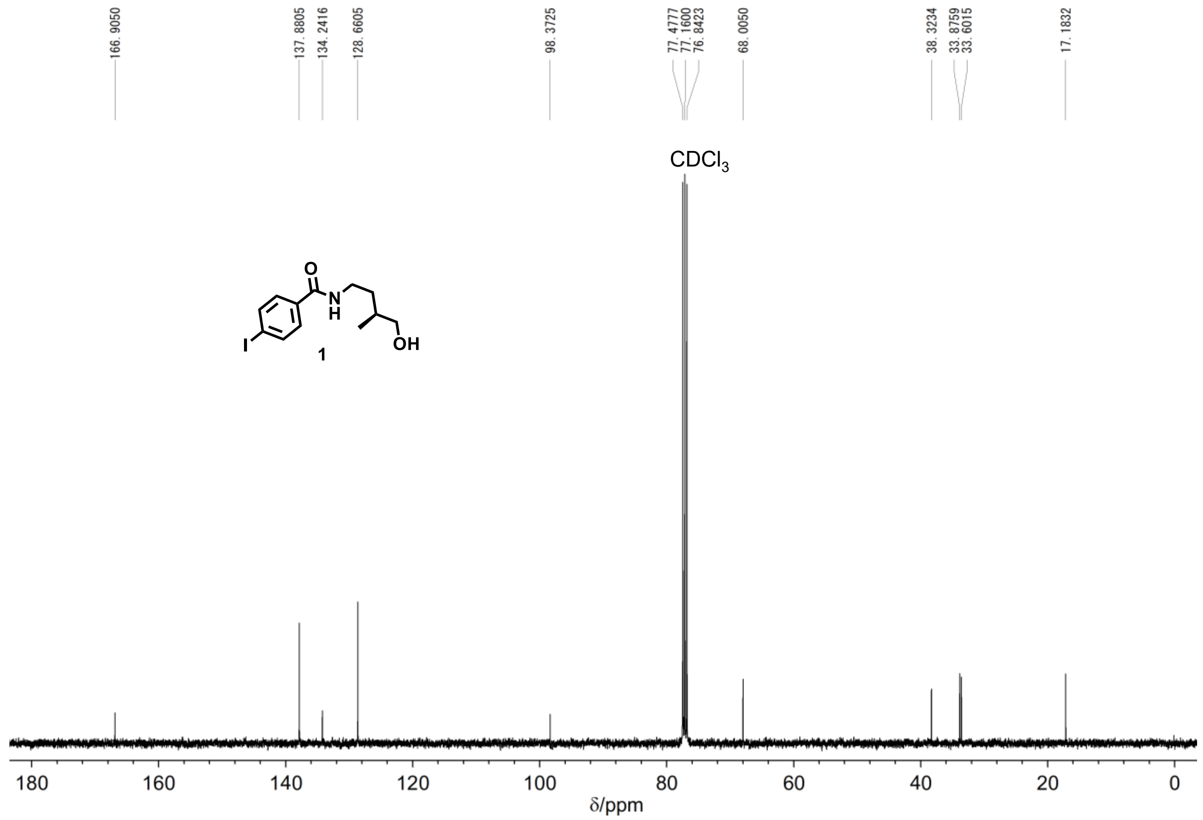


To a mixture of (*R*)-4-amino-2-methyl-1-butanol (515 mg, 5.0 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) in dry THF (10 mL), a solution of 4-iodobenzoyl chloride (1.33 g, 5.0 mmol) in dry THF (5 mL) was slowly added at 0 °C under N_2. After the mixture was stirred overnight at room temperature, it was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous Na_2SO_4, followed by evaporation to dryness. The residue was purified by silica gel column chromatography to obtain **1** as a white solid (1.24 g, 3.7 mmol, 74 %).

^{1}H NMR (400 MHz, $CDCl_3$, TMS standard): δ (ppm) 0.97 (d, *J* = 6.8 Hz, 3 H, C*H*$_3$), 1.53-1.63 (m, 1 H, C*H*$_2$), 1.68-1.82 (m, 2 H, C*H* and C*H*$_2$), 2.07 (t, *J* = 5.2 Hz, 1 H, O*H*), 3.40-3.64 (m, 4 H, C*H*$_2$), 6.68 (brs, 1 H, N*H*), 7.49 (dt, *J* = 8.5, 4.0 Hz, 2 H, Ar*H*), 7.76 (dt, *J* = 8.6, 4.0 Hz, 2 H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$, solvent standard): δ (ppm) 17.18, 33.60, 33.88, 38.32, 68.01, 98.37, 128.66, 134.24, 137.88, 166.91. HRMS(FAB) Calcd for $C_{12}H_{17}INO_2^+$ [$(M+H)^+$]: m/z 334.0299, Found: m/z 334.0308. Elemental analysis: calculated for $C_{12}H_{16}INO_2$: C 43.26, H 4.84, N 4.20, Found: C 43.14, H 4.83, N 4.26.

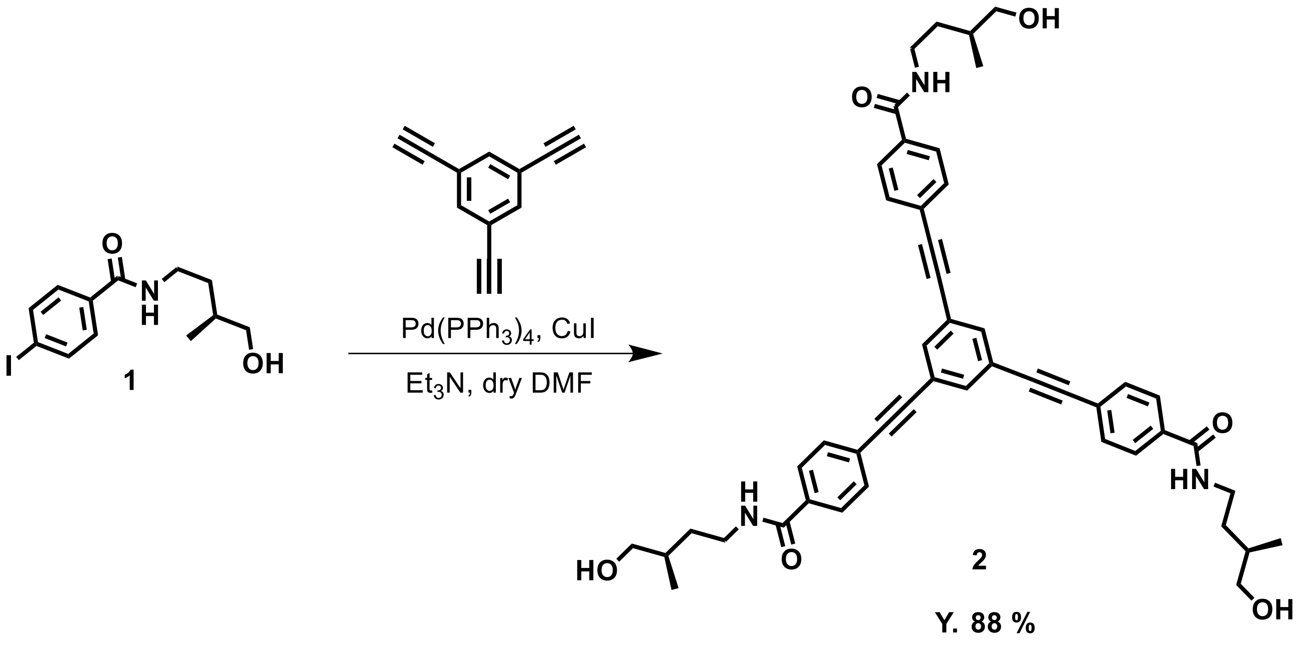


^{1}H NMR spectrum (400 MHz, $CDCl_3$, TMS standard) of **1**.



^{13}C NMR spectrum (100 MHz, $CDCl_3$, solvent standard) of **1**.

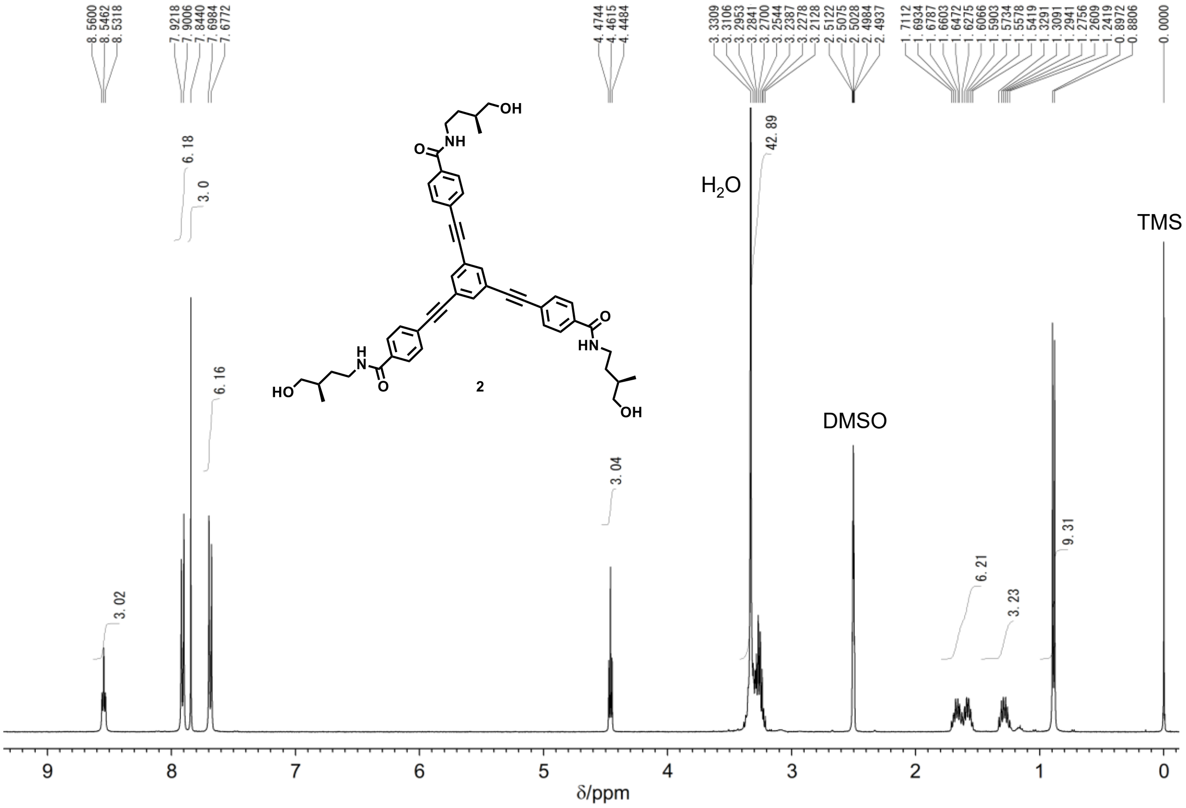
Synthesis of **2**



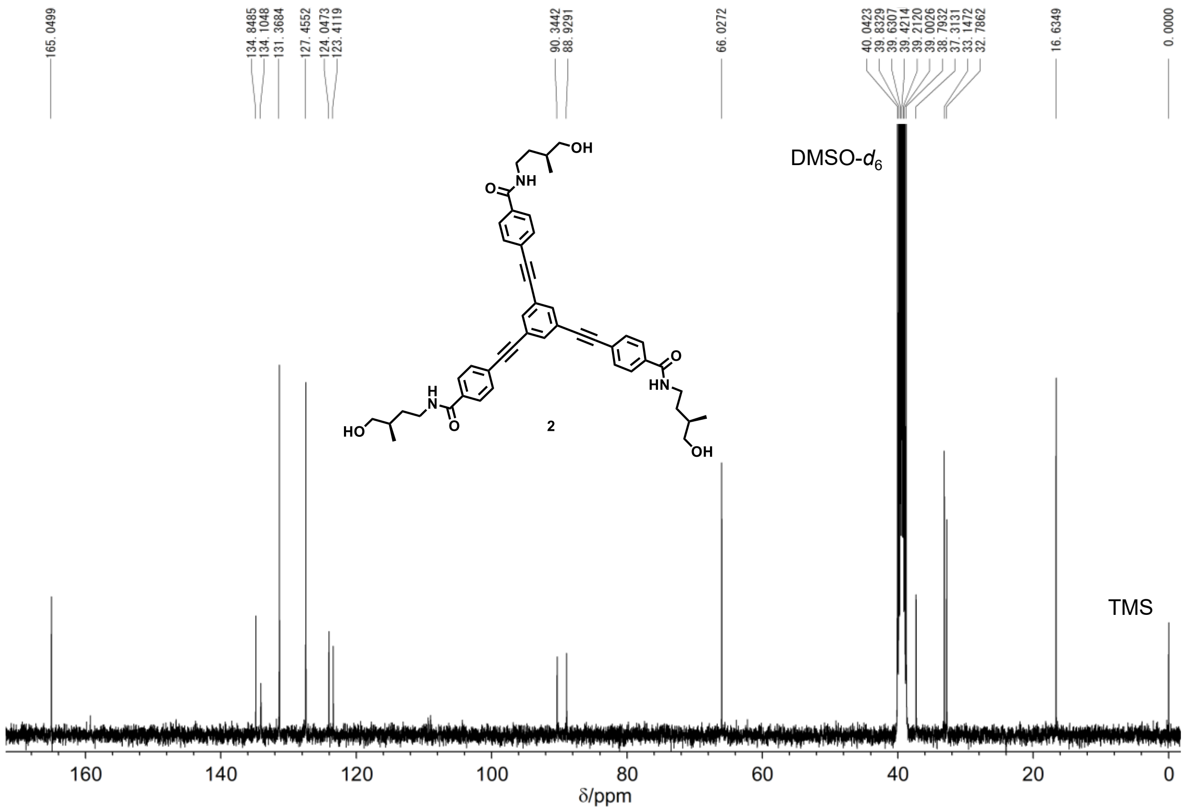
A mixture of compound **1** (430 mg, 1.3 mmol) and triethylamine (5 mL) and dry DMF (5 mL) was bubbled with N_2 for 30 minutes. To the mixture, $Pd(PPh_3)_4$ (18 mg, 0.015 mmol) and CuI (8.9 mg, 0.047 mmol) were added under N_2.

After bubbling with N_2 for 30 minutes, the mixture was stirred at room temperature for 30 minutes, followed by the addition of 1, 3, 5-triethynylbenzene (52 mg, 0.35 mmol). The resulting mixture was heated at 60 °C for 7 hours. After cooling to room temperature, solvents were evaporated under reduced pressure. The crude material was purified by silica gel column chromatography (CH_2Cl_2/MeOH=9/1 to 85/15) to obtain **2** as a white solid (235 mg, 0.31 mmol, 88 %).

^{1}H NMR (400 MHz, DMSO-*d*$_6$, TMS standard): δ (ppm) 0.89 (d, *J* = 6.6 Hz, 9 H, C*H*$_3$), 1.24-1.33 (m, 3 H, C*H*$_2$), 1.54-1.71 (m, 6 H, C*H* and C*H*$_2$), 3.21-3.38 (m, 12 H, C*H*$_2$), 4.46 (t, *J* = 5.2 Hz, 3 H, O*H*), 7.69 (d, *J* = 8.5 Hz, 6 H, Ar*H*), 7.84 (s, 3 H, Ar*H*), 7.91 (d, *J* = 8.5 Hz, 6 H, Ar*H*), 8.55 (t, *J* = 5.6 Hz, 3 H, N*H*). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, TMS standard): δ (ppm) 16.63, 32.79, 33.15, 37.31, 66.03, 88.93, 90.34, 123.41, 124.05, 127.46, 131.37, 134.10, 134.85, 165.05. HRMS(FAB) Calcd for $C_{48}H_{52}N_3O_6^+$ [(M+H)$^+$]: m/z 766.3851, Found: m/z 766.3859.

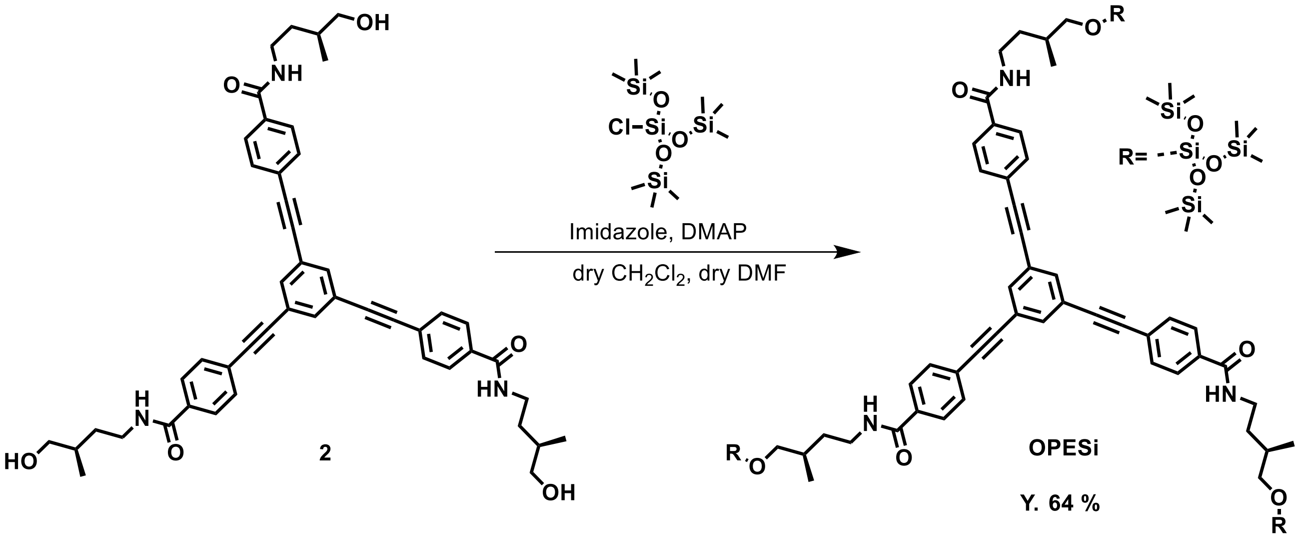


^{1}H NMR spectrum (400 MHz, DMSO-*d*$_6$, TMS standard) of **2**.



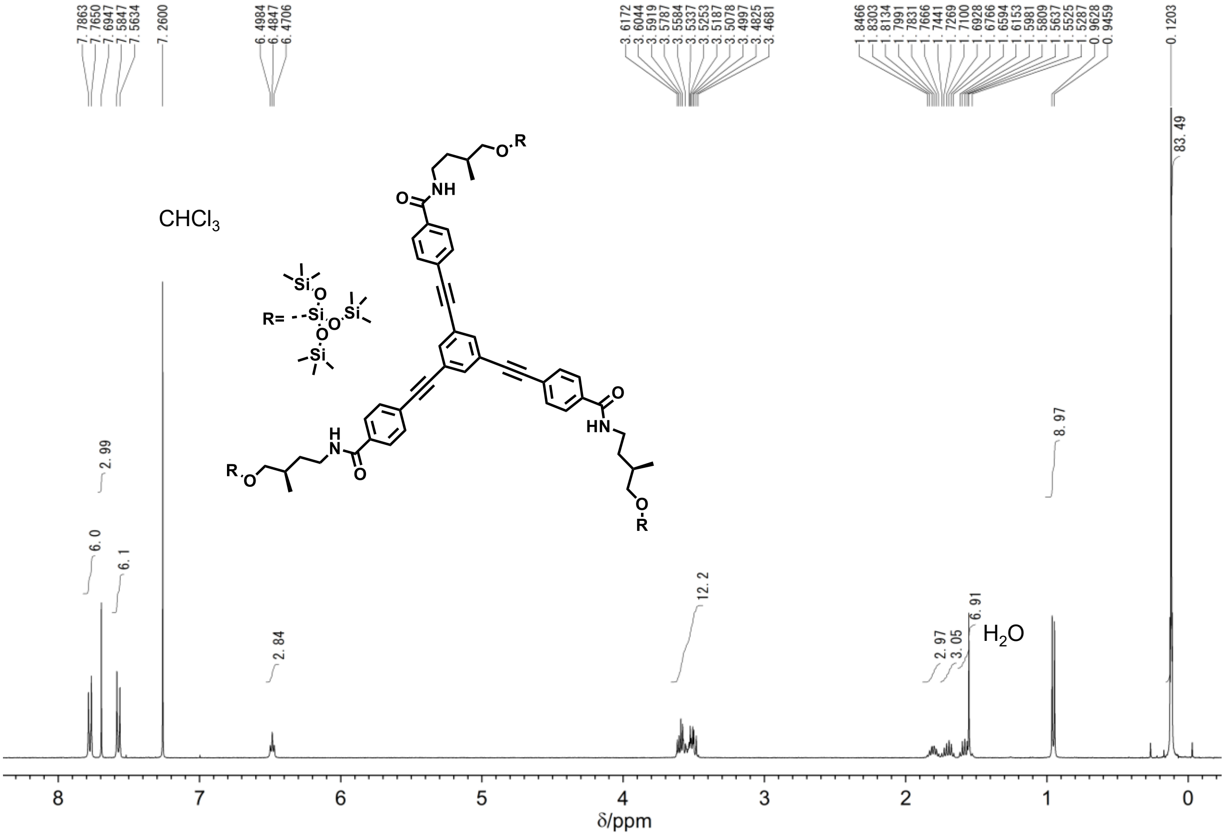
^{13}C NMR spectrum (100 MHz, DMSO-*d*$_6$, TMS standard) of **2**.

Synthesis of **OPESi**

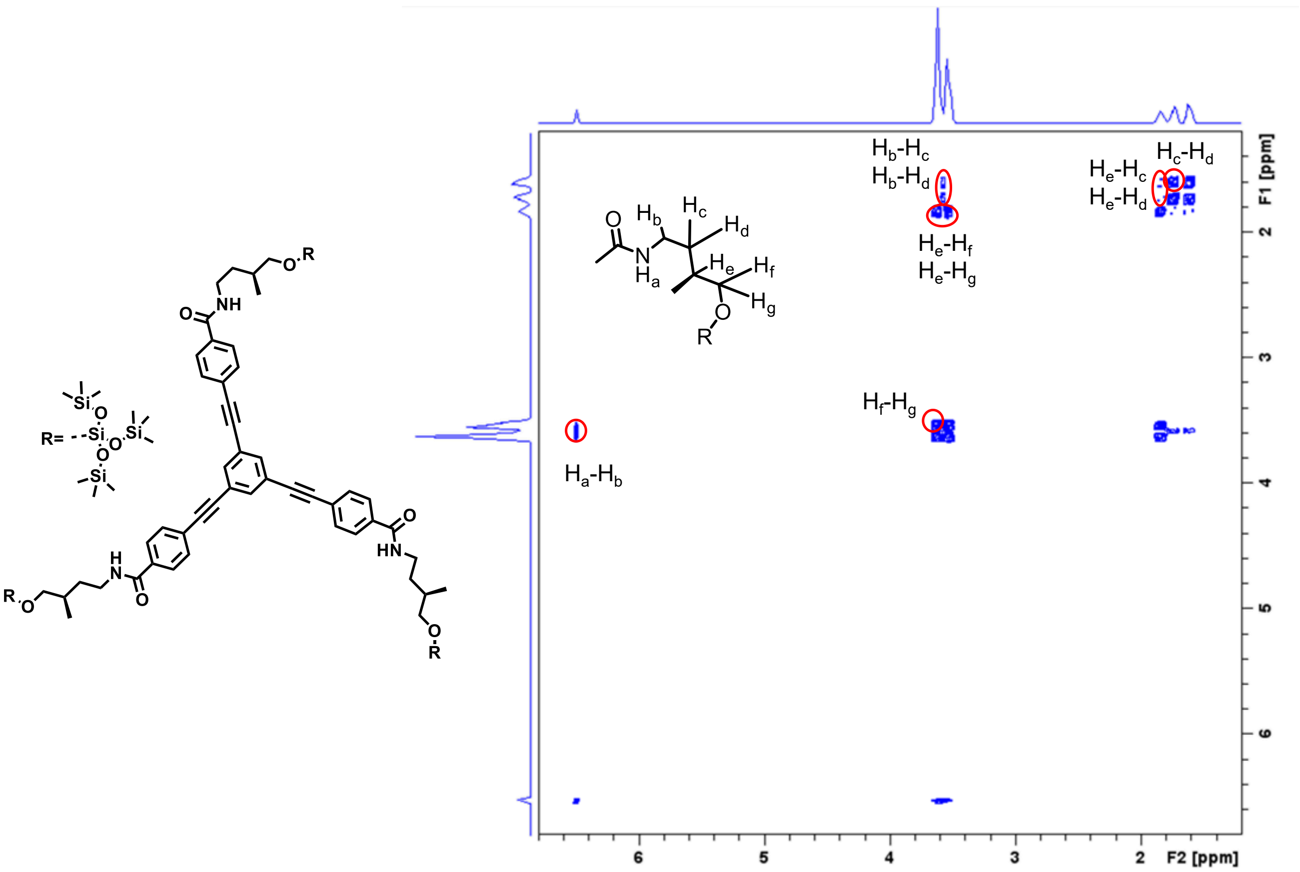


To a solution of compound **2** (168 mg, 0.22 mmol), 4-dimethylaminopyridine (5 mg, 0.04 mmol) and imidazole (107 mg, 1.58 mmol) in dry DMF (3.5 mL) and dry CH_2Cl_2 (3.5 mL), tris(trimethylsiloxy)chlorosilane (261 mg, 0.78 mmol) was slowly added at 0 °C under N_2. After the mixture was stirred at room temperature for 4 hours, it was poured into water and extracted with hexane/EtOAc (1/1). The organic layer was washed with water and dried over anhydrous Na_2SO_4, followed by evaporation to dryness. The residue was purified by column chromatography (CH_2Cl_2/MeOH=98/2) to obtain **OPESi** as a white solid (232 mg, 0.14 mmol, 64 %).

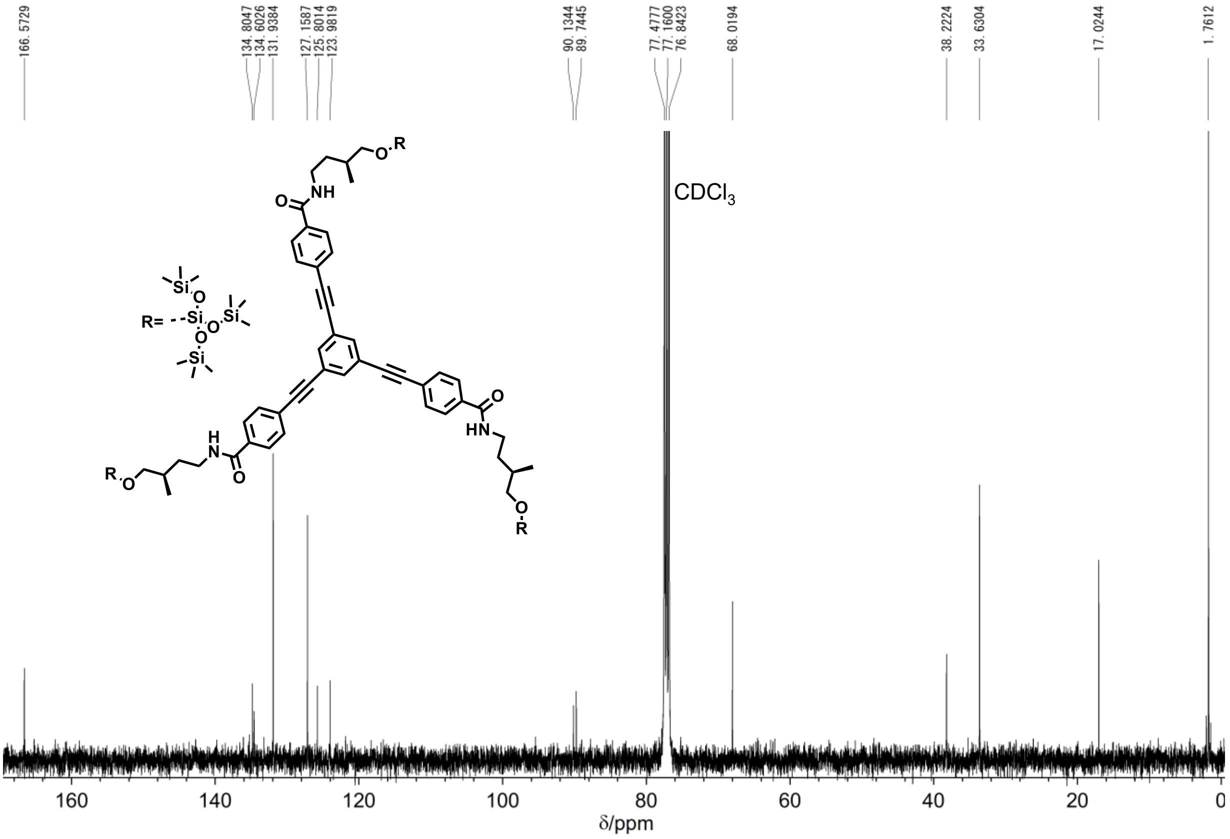
^{1}H NMR (400 MHz, $CDCl_3$, solvent standard): δ (ppm) 0.12 (s, 81 H, SiC*H*$_3$), 0.95 (d, *J* = 6.8 Hz, 9 H, C*H*$_3$), 1.53-1.62 (m, 3 H, C*H*$_2$), 1.66-1.74 (m, 3 H, C*H*$_2$), 1.77-1.85 (m, 3 H, C*H*), 3.47-3.62 (m, 12 H, C*H*$_2$), 6.48 (t, *J* = 5.6 Hz, 3 H, N*H*), 7.57 (d, *J* = 8.5 Hz, 6 H, Ar*H*), 7.69 (s, 3 H, Ar*H*), 7.78 (d, *J* = 8.5 Hz, 6 H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$, solvent standard): δ (ppm) 1.76, 17.02, 33.63, 38.22, 68.02, 89.74, 90.13, 123.98, 125.80, 127.16, 131.94, 134.60, 134.80, 166.57. HRMS(FAB) Calcd for $C_{75}H_{130}N_3O_{15}Si_{12}^+$ [$(M+H)^+$]: m/z 1648.6728, Found: m/z 1648.6776.



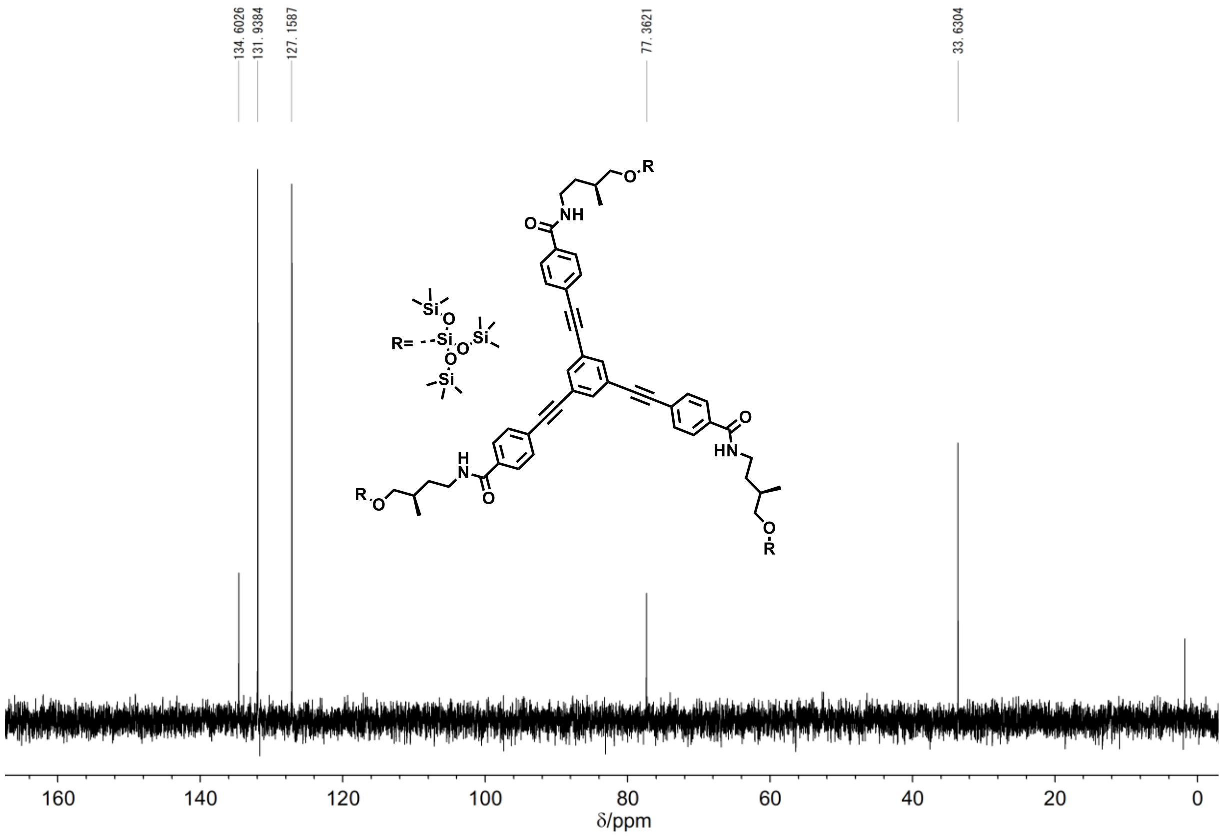
^{1}H NMR spectrum (400 MHz, $CDCl_3$, solvent standard) of **OPESi**.



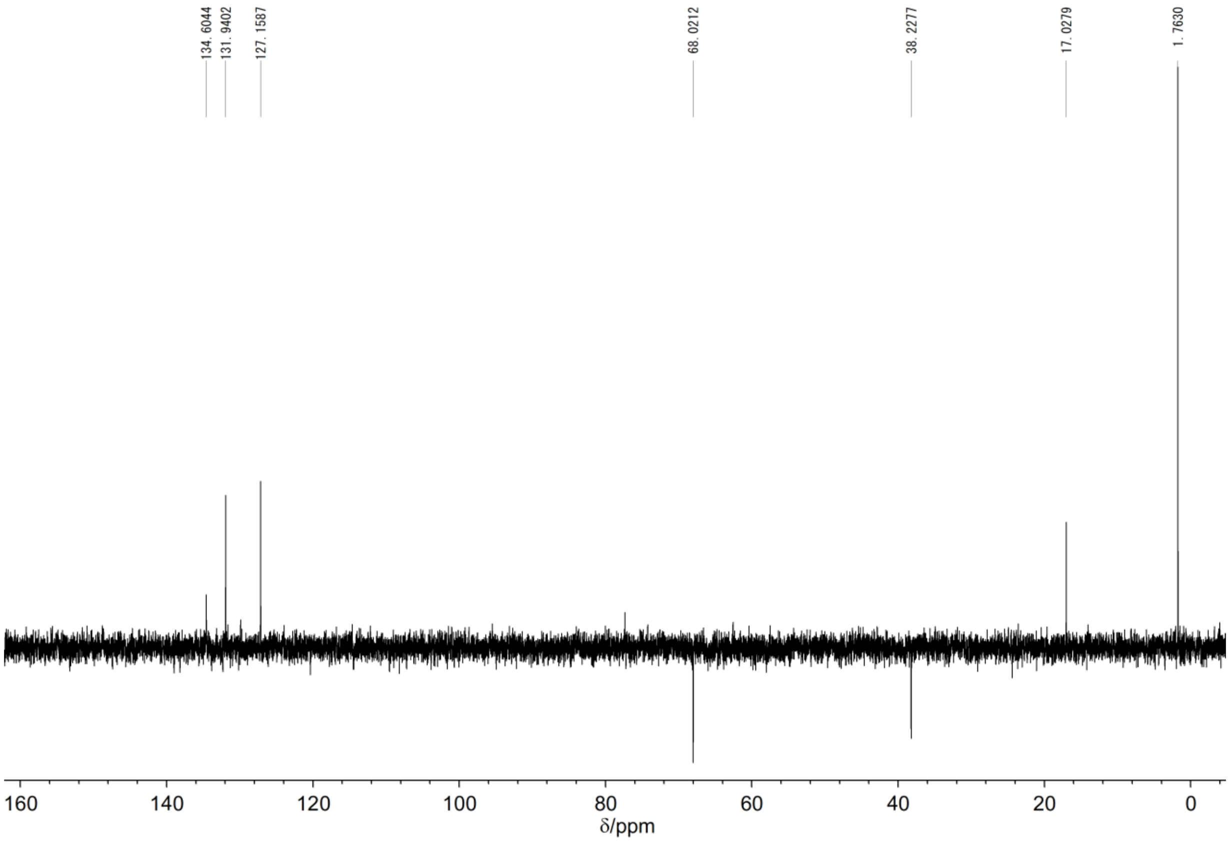
^{1}HH-COSY NMR spectrum (400 MHz, CDCl$_3$) of a selected region of **OPESi**.



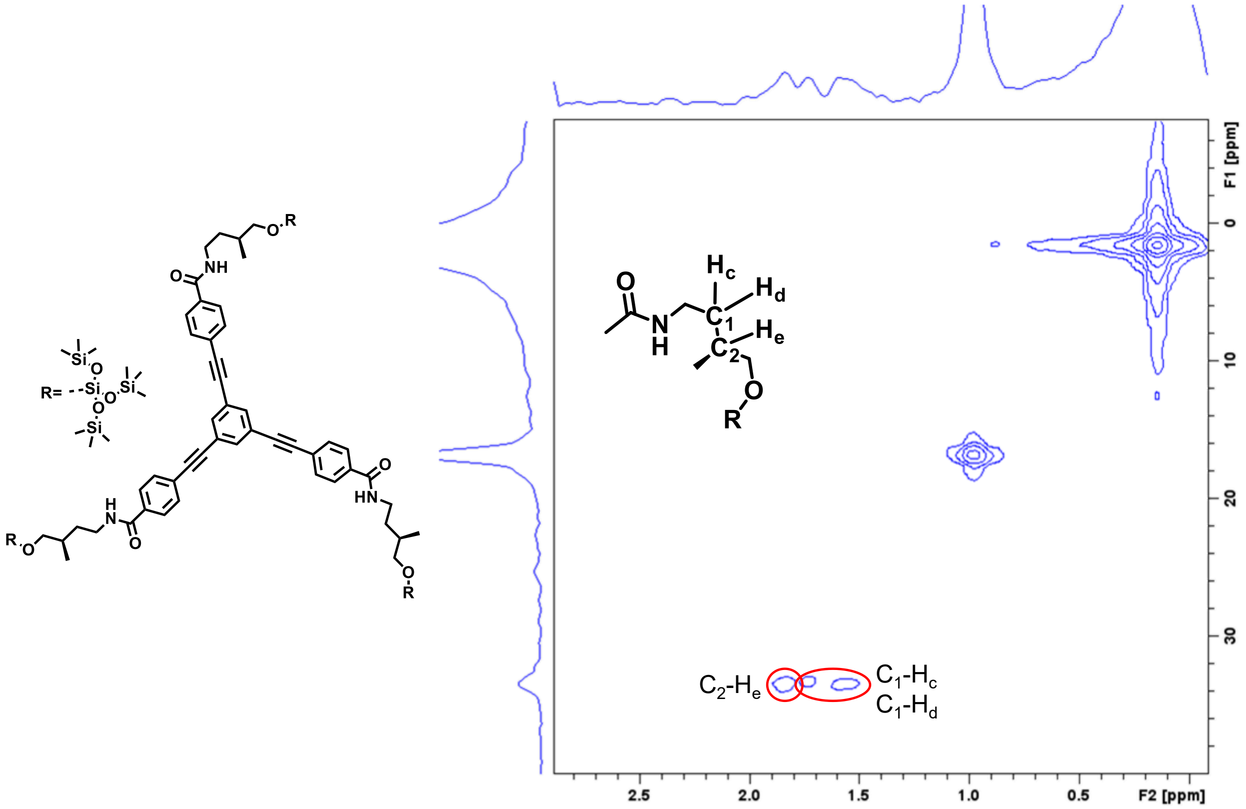
^{13}C NMR spectrum (100 MHz, CDCl$_3$, solvent standard) of **OPESi**.



^{13}C (DEPT90) NMR spectrum (100 MHz, CDCl$_3$) of **OPESi**.



^{13}C (DEPT135) NMR spectrum (100 MHz, CDCl$_3$) of **OPESi**.



^{1}H, ^{13}C-HMQC NMR spectrum ($CDCl_3$) of a selected region of **OPESi**.

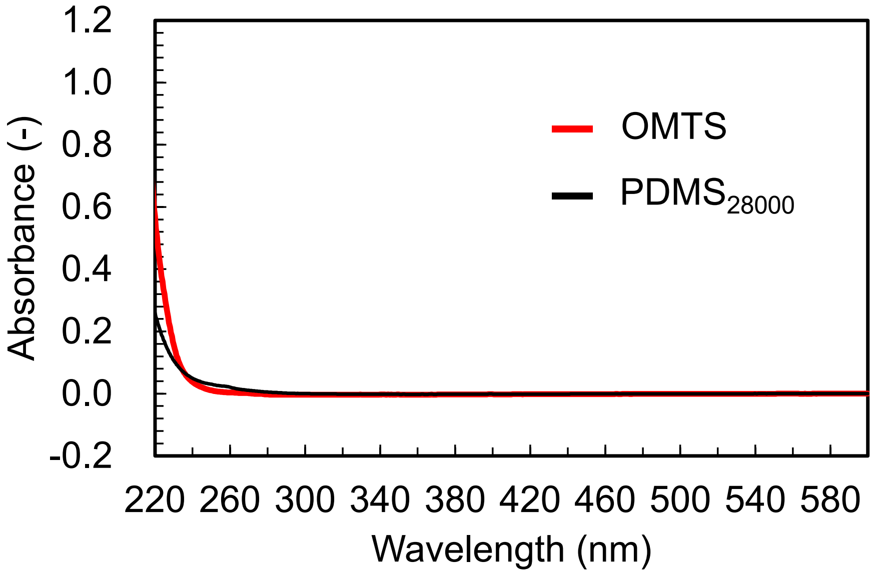


Fig. S1 UV–vis spectra of OTMS and $PDMS_{28000}$ (path length = 10 mm).

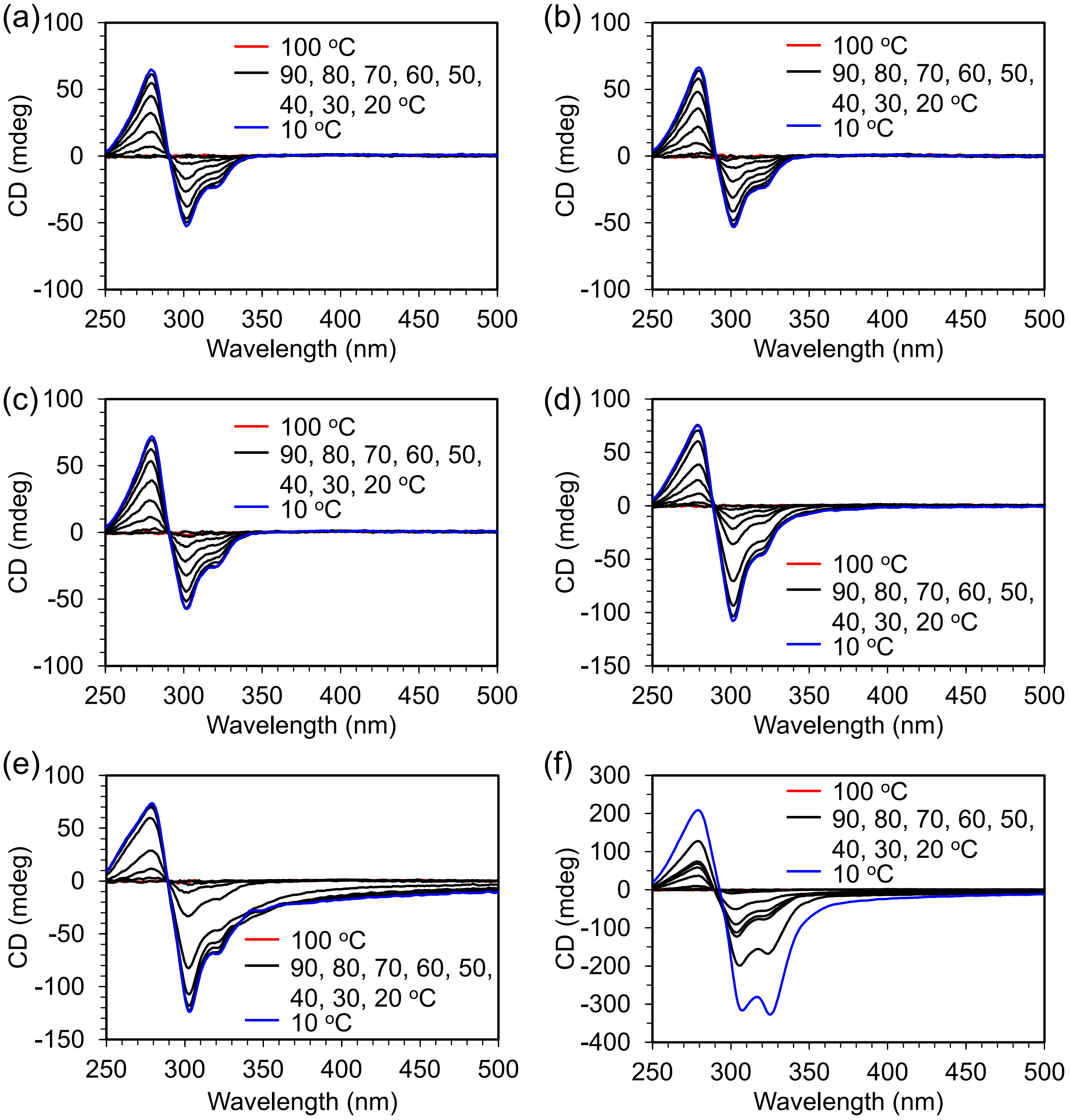


Fig. S2 Temperature-dependent CD spectra of **OPESi** in (a) pure OMTS and (b) 6, (c) 8, (d) 10, (e) 12.5, and (f) 15 wt% PDMS$_{28000}$/OMTS solutions ([**OPESi**] = 5 × 10^{-5} M, path length = 2 mm, cooling rate = 1 °C/min).

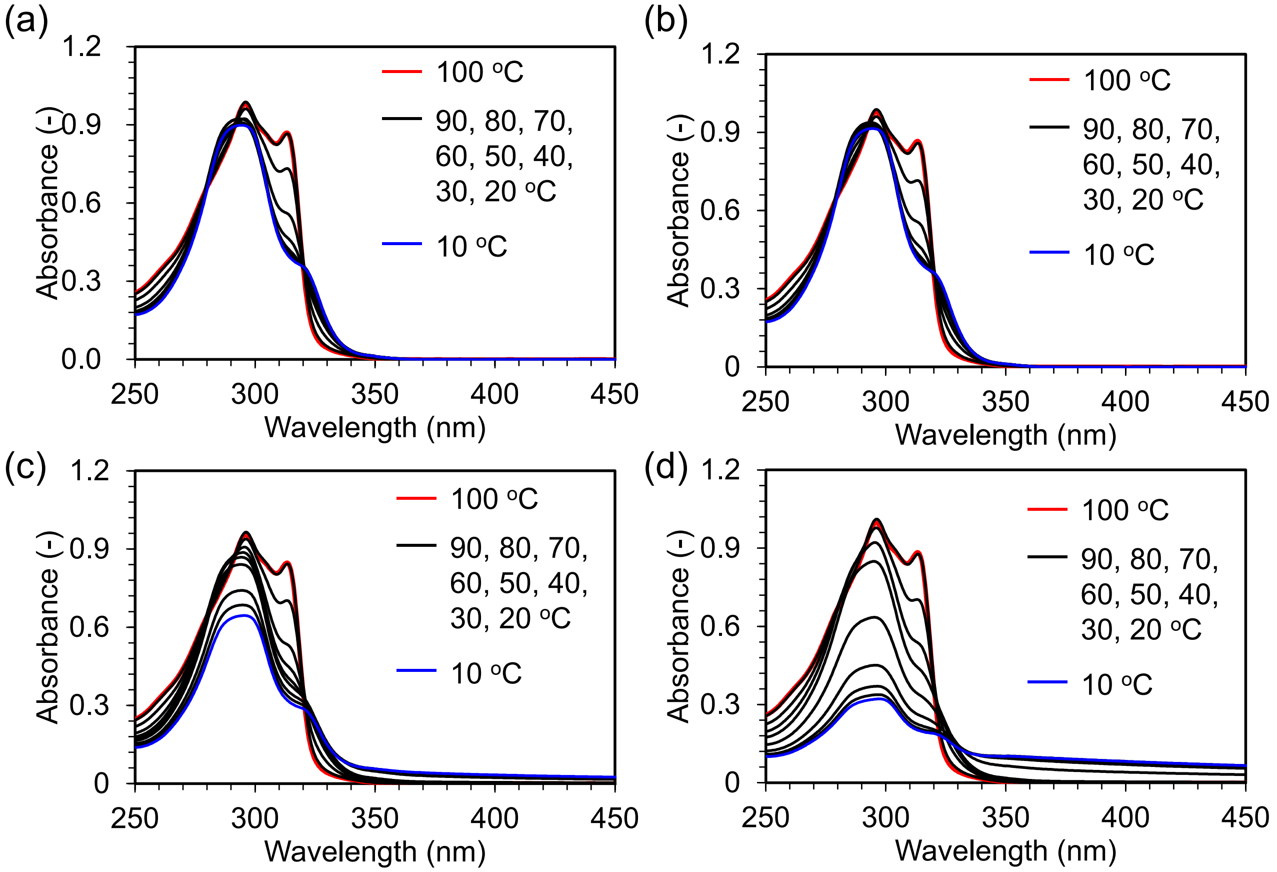


Fig. S3 Temperature-dependent UV–vis absorption spectra of **OPESi** in (a) 6, (b) 8, (c) 10, and (d) 12.5 wt% PDMS$_{28000}$/OMTS solutions ([**OPESi**] = 5 × 10^{-5} M, path length = 2 mm, cooling rate = 1 °C/min).

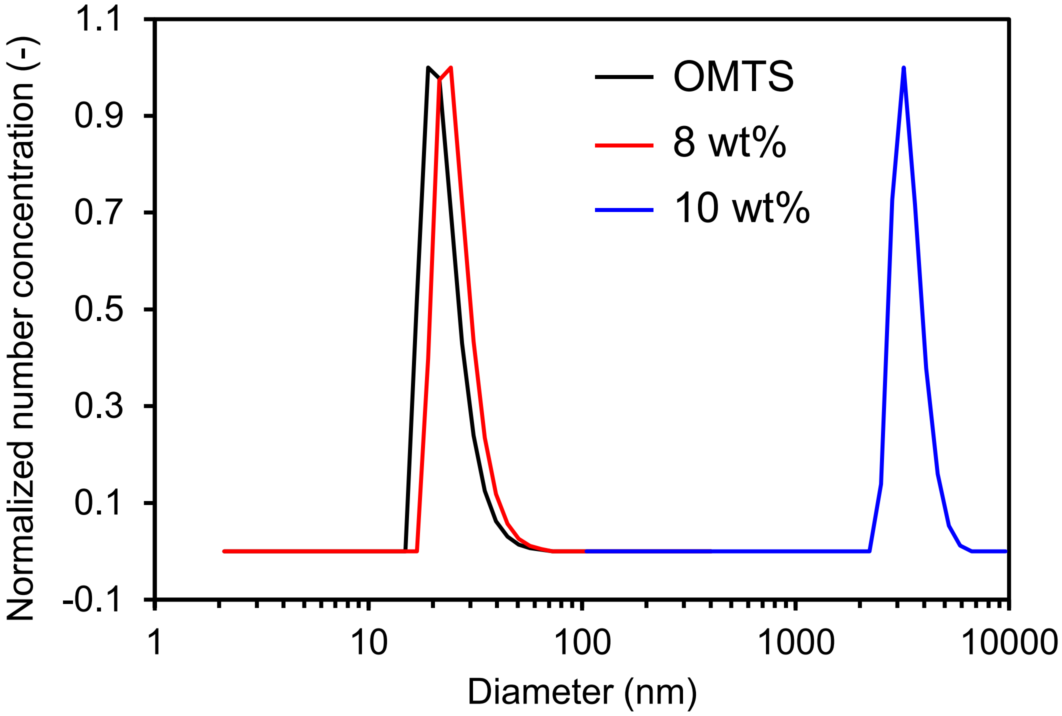


Fig. S4 Hydrodynamic diameter distributions of the assembled structures obtained by DLS measurements. Black line: pure OMTS; red line: 8 wt% $PDMS_{28000}$/OMTS solution; blue line: 10 wt% $PDMS_{28000}$/OMTS solution ([**OPESi**] = 5 × 10^{-5} M, 20 °C).

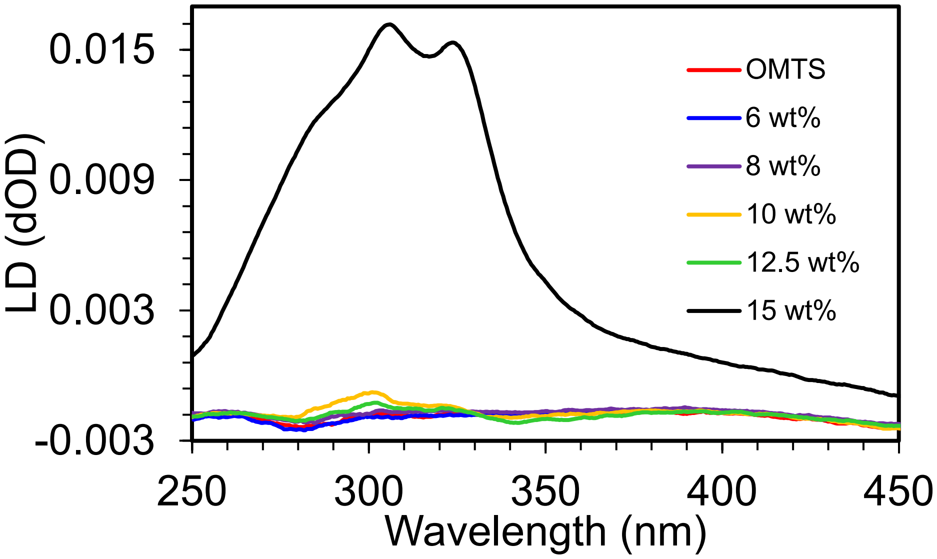


Fig. S5 Linear dichroism (LD) spectra of **OPESi** in pure OMTS and 6, 8, 10, 12.5, and 15 wt% $PDMS_{28000}$/OMTS solutions at 10 °C ([**OPESi**] = 5 × 10^{-5} M, path length = 2 mm).

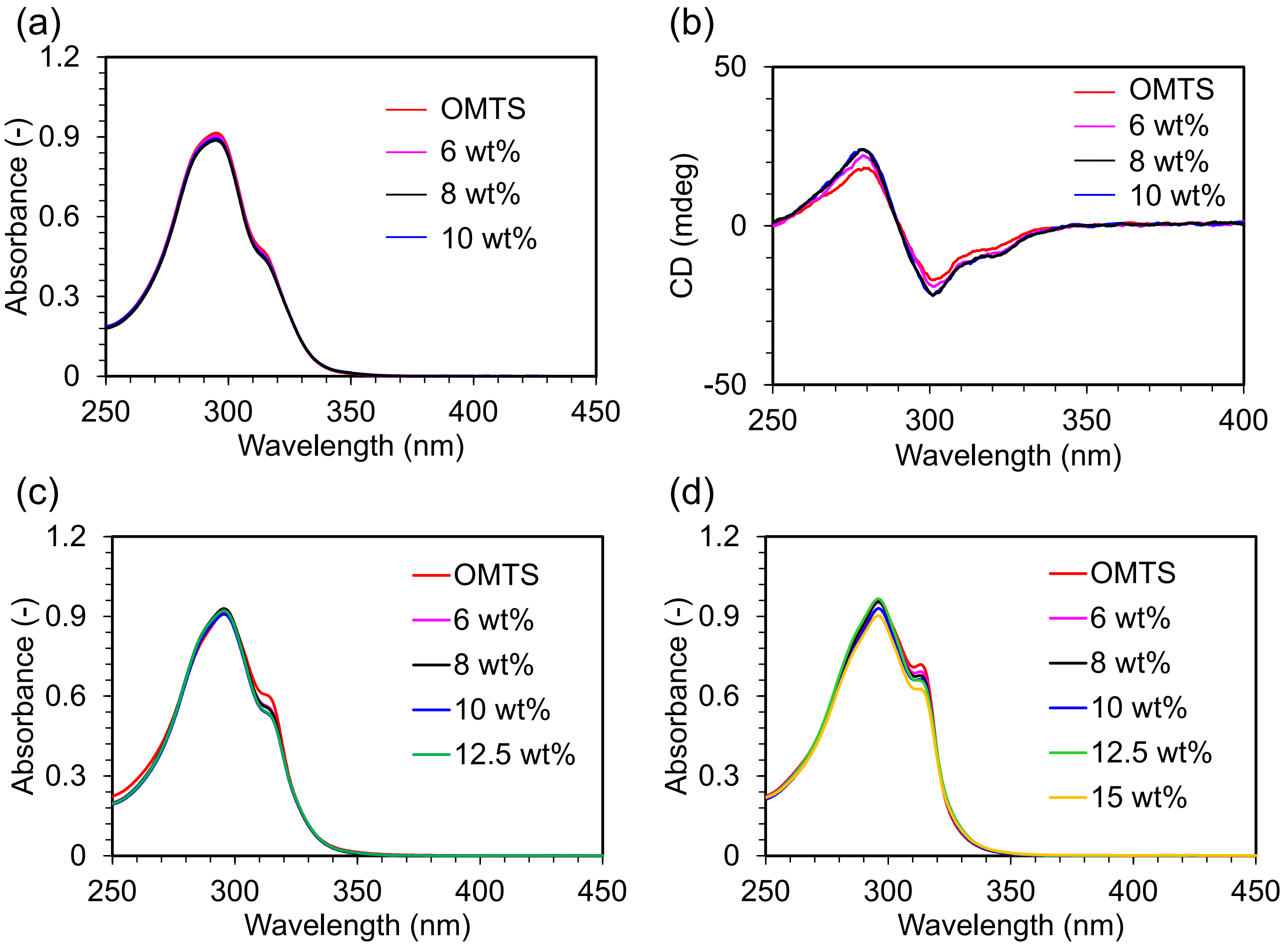


Fig. S6 UV–vis absorption (a, c, d) and CD spectra (b) of **OPESi** in pure OMTS and PDMS$_{28000}$/OMTS solutions at (a, b) 60 °C, (c) 70 °C, and (d) 78 °C ([**OPESi**] = 5 × 10^{-5} M, path length = 2 mm).

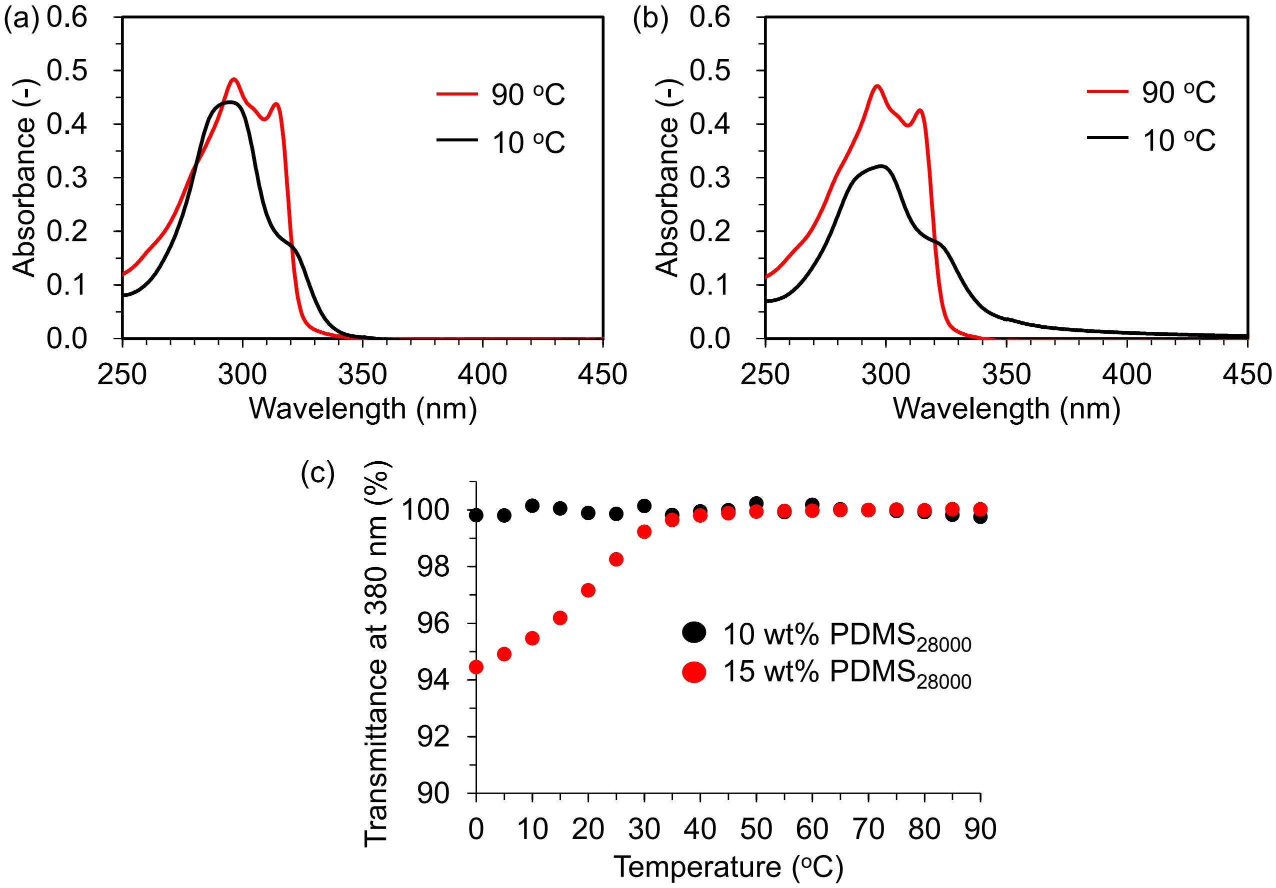


Fig. S7 Temperature-dependent UV–vis absorption spectra of 5 × 10^{-6} M **OPESi** in (a) 10 and (b) 15 wt% PDMS$_{28000}$/OMTS solutions (path length = 10 mm, cooling rate = 1 °C/min). (c) Temperature-dependent transmittance of 5 × 10^{-6} M **OPESi** in 10 and 15 wt% PDMS$_{28000}$/OMTS solutions.

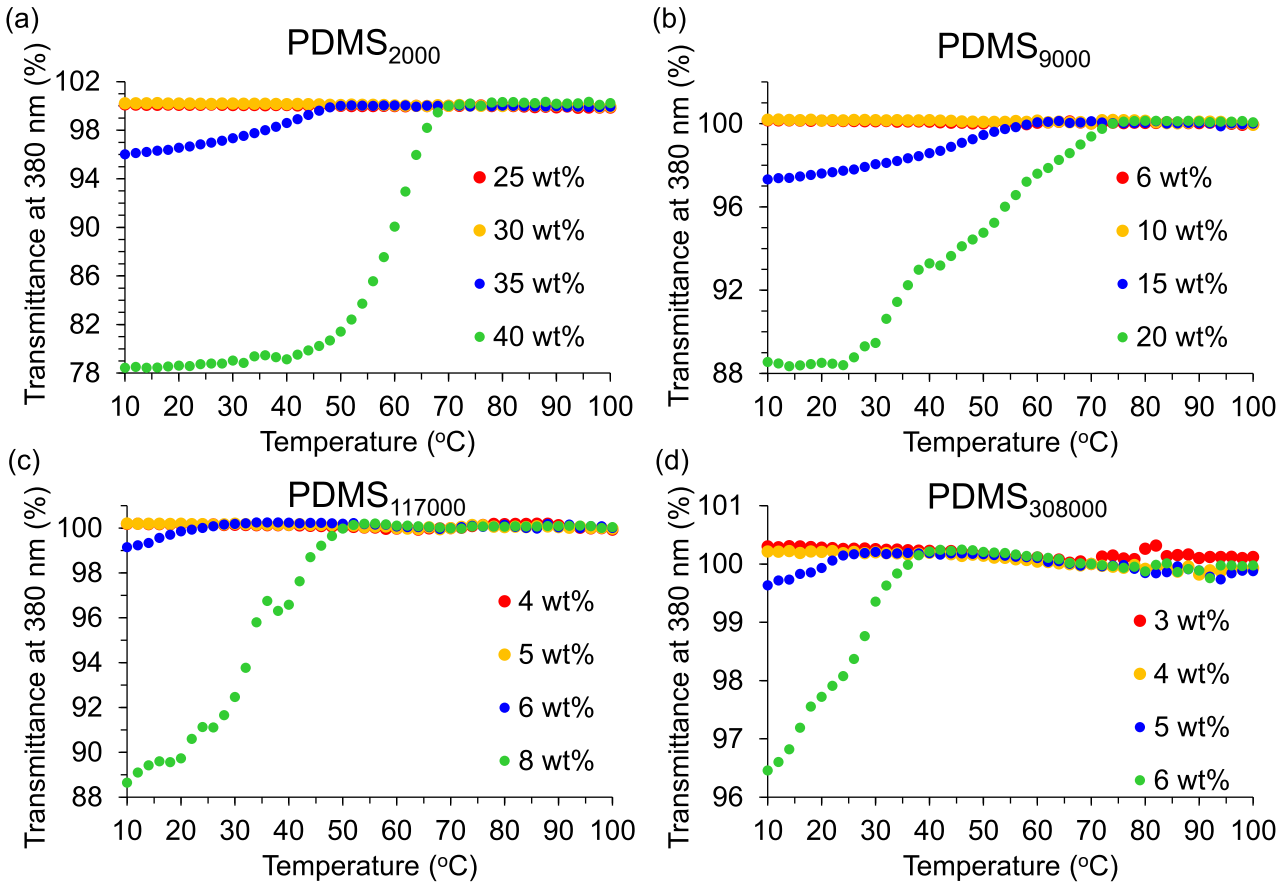


Fig. S8 Temperature-dependent transmittance of 5 × 10^{-5} M **OPESi** in (a) $PDMS_{2000}$, (b) $PDMS_{9000}$, (c) $PDMS_{117000}$, and (d) $PDMS_{308000}$/OMTS solutions (path length = 2 mm, cooling rate = 1 °C/min).

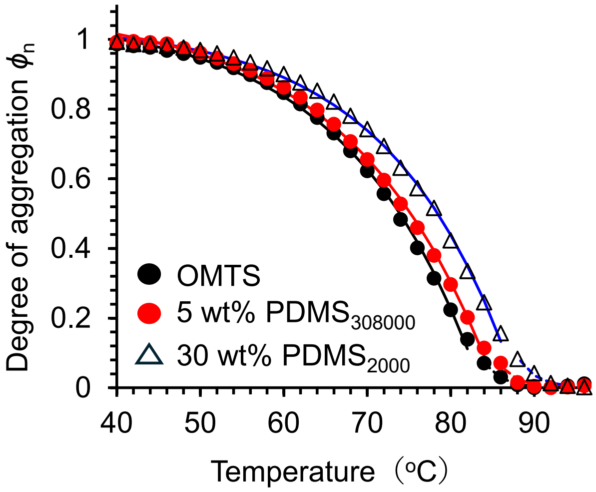


Fig. S9. Temperature-dependent degree of aggregation for **OPESi** in pure OMTS, 5 wt% $PDMS_{308000}$, and 30 wt% $PDMS_{2000}$. The solid and dotted lines are the fitted curves in the elongation and nucleation regimes, respectively.

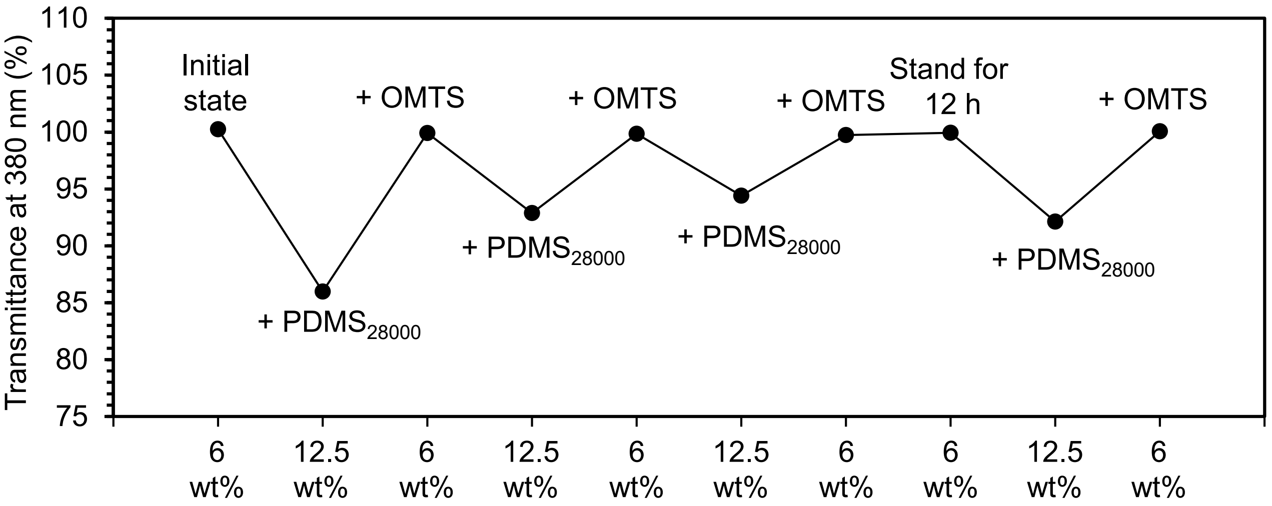


Fig. S10. Reversible changes in the transmittance of the **OPESi** solution in OMTS ([**OPESi**] = 5 × 10^{-5} M, path length = 2 mm) upon varying the $PDMS_{28000}$ concentration at room temperature. The initial concentration of $PDMS_{28000}$ was 6 wt%, and this concentration was increased to 12.5 wt% by the addition of further $PDMS_{28000}$, with simultaneous addition of a 1 × 10^{-4} M **OPESi** solution in OMTS to maintain a constant **OPESi** concentration. Subsequently, the mixture was diluted with a 5 × 10^{-5} M solution of **OPESi** in pure OMTS to restore the $PDMS_{28000}$ concentration to 6 wt%. This cycle of transmittance decrease and complete recovery was reproducibly repeated.

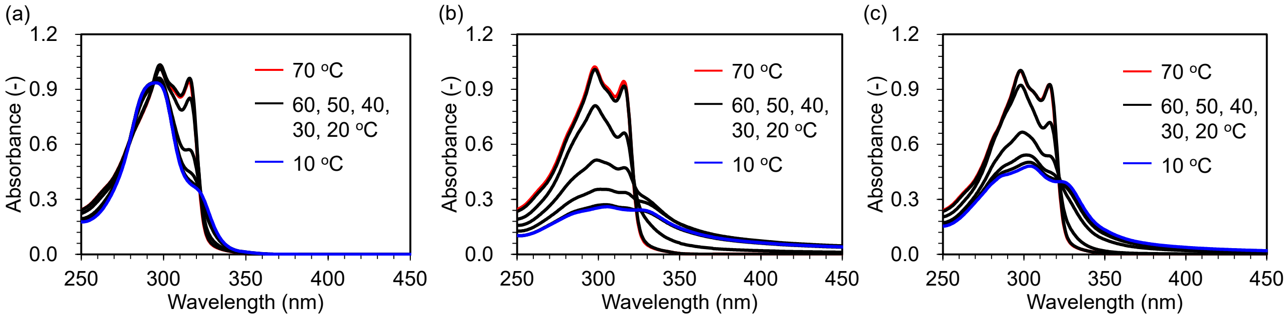


Fig. S11. Temperature-dependent UV–vis spectra of **OPESi** in (a) pure MCH, (b) a 15 wt% $PDMS_{28000}$/MCH solution and (c) a 10 wt% poly(isobutylene) (M_n = 200,000)/MCH solution ([**OPESi**] = 5 × 10^{-5} M, path length = 2 mm, cooling rate = 1 °C/min).

Table S1. Viscosities of pure OMTS and PDMS/OMTS solutions with varying PDMS concentrations at room temperature.

	Viscosity (mPa · s)		Viscosity (mPa · s)		Viscosity (mPa · s)		Viscosity (mPa · s)		Viscosity (mPa · s)
OMTS	0.8	6 wt% $PDMS_{9000}$	1.4	6 wt% $PDMS_{28000}$	1.7	4 wt% $PDMS_{117000}$	2.7	3 wt% $PDMS_{308000}$	3.5
25 wt% $PDMS_{2000}$	1.6	10 wt% $PDMS_{9000}$	1.7	8 wt% $PDMS_{28000}$	2.2	5 wt% $PDMS_{117000}$	3.4	4 wt% $PDMS_{308000}$	5.0
30 wt% $PDMS_{2000}$	1.8	15 wt% $PDMS_{9000}$	2.4	10 wt% $PDMS_{28000}$	2.6	6 wt% $PDMS_{117000}$	4.1	5 wt% $PDMS_{308000}$	7.0
35 wt% $PDMS_{2000}$	2.1	20 wt% $PDMS_{9000}$	3.2	12.5 wt% $PDMS_{28000}$	3.3	8 wt% $PDMS_{117000}$	6.1	6 wt% $PDMS_{308000}$	9.5
40 wt% $PDMS_{2000}$	2.4			15 wt% $PDMS_{28000}$	4.1				

The degree of aggregation (ϕ_n) was analyzed based on a nucleation–elongation model using Eq. S1 and Eq. S2

$$\phi_\mathrm{n} = \phi_\mathrm{SAT}(1 - \exp\left[\frac{-h_\mathrm{e}}{RT_\mathrm{e}^2}(T - T_\mathrm{e})\right]) \qquad \text{Eq. S1}$$

$$\phi_\mathrm{n} = K_a^{1/3}\exp\left[(2/3K_a^{-1/3} - 1)\frac{h_\mathrm{e}}{RT_\mathrm{e}^2}(T - T_\mathrm{e})\right] \qquad \text{Eq. S2}$$

where ϕ_SAT is the parameter necessary to equate ϕ_n / ϕ_SAT to unity, h_e is the enthalpy released during elongation, T_e is the elongation temperature, R is the gas constant and K_a is the dimensionless equilibrium constant of the activation step at T_e. The ϕ_n values were calculated from absorbance at 315 nm using Eq. S3

$$\phi_\mathrm{n} = \frac{A_\mathrm{Max} - A}{A_\mathrm{Max} - A_\mathrm{Min}} \qquad \text{Eq. S3}$$

where A_Max, A_Min, and A are the maximum absorbance, the minimum absorbance, and the absorbance at a given temperature, respectively, measured at 315 nm.

Table S2. Thermodynamic parameters for the self-assembly of **OPESi** in OMTS, 5 wt% PDMS_{308000}, and 30 wt% PDMS_{2000}.

	T_e (°C)	h_e (kJmol^{-1})	K_a (-)
OMTS	84	-68	5.3×10^{-4}
5 wt% PDMS_{308000}	85	-65	4.8×10^{-4}
30 wt% PDMS_{2000}	88	-74	6.9×10^{-4}