Electronic Supplementary Information

Transfer and Amplification of Cyanostilbene Molecular Function to Advanced Flexible Optical Paints through Self-Crosslinkable Side-Chain Liquid Crystal Polysiloxanes

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Experimental Section

Materials

4-Hydroxybenzaldehyde (97 %, Sigma-Aldrich), 5-bromo-1-pentene (95 %, TCI), 4-hydroxybenzyl cyanide (99 %, TCI), 1-bromobutane (98 %, Sigma-Aldrich), poly(methylhydrosiloxane) (PMHS, average M_n 1700~3200, Sigma-Aldrich), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt's catalyst, in xylene Pt ~ 2 %, Sigma-Aldrich), 1-ethynyl-1-cyclohexanol (inhibitor, 98 %, TCI), potassium carbonate (K_2CO_3, 99.5 %, Showa), 18-crown-6-ether (98 %, TCI), sodium hydroxide (NaOH, 93 %, Showa), sodium sulfate (Na_2SO_4, 99 % , Showa), tetrahydrofuran (THF, 99.5 %, Showa), N,N-dimethylformamide (DMF, 99.5 %, Showa), ethyl acetate (EA, 99.5 %, Samchun Chemical), *n*-hexane (95 %, Samchun Chemical), chloroform ($CHCl_3$, 99 %, Showa), methanol (MeOH, 99.8 %, Showa), ethanol (EtOH, 99 %, Sigma-Aldrich), silica gel (63-200, Merck) were used as received.

Synthesis

4-(pent-4-en-1-yloxy)benzaldehyde (1): 4-Hydroxybenzaldehyde (1.0 g, 8.18mmol) and K_2CO_3 (2.0 g, 14.47 mmol) were stirred in DMF (30 mL). The solution was heated at 80 °C and 5-bromo-1-pentene (1.5 g, 10.06 mmol) was slowly added. After 12 h the reaction mixture was cooled to room temperature and poured into 200 mL of cold distilled water. The mixture was extracted with EA (50 mL × 3 times) and the combined organic phase was subsequently dried over Na_2SO_4. The crude product was purified by column chromatography with silica gel using EA:n-hexane = 1:4 to afford 1 as low viscous oil (Yield: 74 %, 1.16 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 7.82 (d, 2H), 6.98 (d, 2H), 5.85 (m, 1H), 5.05 (m, 2H), 4.05 (t, 2H), 2.28 (m, 2H), 1.92 (m, 2H).

2-(4-butoxyphenyl)acetonitrile (2): 4-Hydroxybenzyl cyanide (1.0 g, 7.51 mmol), K_2CO_3 (2.0 g, 14.47 mmol) and 18-crown-6-ether (0.2 g, 7.60×10^{-4}mol) in THF (30 mL) were heated to 65 °C. 1-bromobutane (1.3 g, 9.49 mmol) in THF (5 mL) was slowly added for 60 min and the solution was stirred overnight. The reaction mixture was cooled at room temperature and the solvent was evaporated. The mixture was extracted with EA (50 mL × 3 times) and the combined organic phase was dried over Na_2SO_4. The crude product was purified by column chromatography with silica gel using EA:n-hexane = 1:3 to afford 2 as viscous oil. (Yield: 72 %, 1.03 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, 2H), 6.89 (d, 2H), 3.96 (t, 2H), 3.68 (s, 2H), 1.75 (m, 2H), 1.48 (m, 2H), 0.98 (t, 3H).

(Z)-2-(4-butoxyphenyl)-3-(4-(pent-4-en-1-yloxy)phenyl)acrylonitrile (CSM) : Compound 1 (1.1 g, 5.78 mmol) and compound 2 (1 g, 5.28 mmol) were dissolved in EtOH (40 mL) and NaOH (0.4 g, 10 mmol) was subsequently added. The reaction mixture was stirred for 24 h. After the reaction, the solvent was evaporated and extracted with $CHCl_3$ (50 mL × 3 times). The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by precipitation with MeOH to afford pure product as ivory solid (Yield: 61 %, 1.16 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, 2H), 7.57 (d, 2H), 7.34 (s, 1H), 6.94 (t, 4H), 5.80-5.92 (m, 1H), 4.99-5.12 (m, 2H), 4.02 (m, 4H), 2.26 (m, 2H), 1.92 (m, 2H), 1.78 (m, 2H), 1.50 (m, 2H), 0.98 (t, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 160.8, 159.9, 139.9, 137.8, 131.0, 127.1, 126.8, 120.3, 115.5, 115.0, 114.9, 108.2, 68.0, 67.5, 31.3, 30.1, 28.4, 19.3, 13.9.

Synthesis of Si-CSM : (Z)-2-(4-butoxyphenyl)-3-(4-(pent-4-en-1-yloxy)phenyl)acrylonitrile (CSM, 0.9 g, 2.49 mmol) and PMHS (0.3 g, 1.22×10^{-4} mol) were dissolved in toluene (20 mL) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (20 µL) was subsequently added. The reaction mixture was stirred and heated to 60 °C with reflux for 48 h under nitrogen atmosphere. After solvent evaporation, the reactant and catalyst were removed through the flash column chromatography with THF and n-hexane solution. The crude product was purified by precipitation with cold MeOH to afford Si-CSM as waxy solid. (Yield: 86 %, 1.03 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ =

7.72 (s, 2H), 7.45 (s, 2H), 7.21 (s, 1H), 6.84 (s, 4H), 4.74 (s, 1H), 3.90 (s, 4H), 1.75 (s, 4H), 1.46 (s, 6H), 0.96 (s, 3H), 0.60 (s, 2H), 0.15 (d, 6H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ = 160.8, 159.9, 139.9, 131.0, 127.0, 126.7, 119.0, 114.9, 114.7, 108.2, 68.1, 67.8, 31.3, 29.6, 29.1, 23.0, 19.3, 17.4, 14.1, 1.4, -0.3; FT IR (CaF_2 window): *v* = 2923, 2859 (C-H), 2211 (C≡N), 2165 (Si-H), 1604, 1512, 1467 (Ar), 1256 (C-H), 1180 (C-H in Ar), 1115 (Si-O-Si), 1024 (C-H in Ar), 902 (Si-H), 796 (Si-C) cm^{-1}.

Preparation of Si-CSM paint

Si-CSM (100 mg) was dissolved in $CHCl_3$ (250 µL). 1-ethynyl-1-cyclohexanol solution (1.5 mg) was added and mixed for 5 min using vortex mixer. Next, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex solution (7.5 µL) was added and mixed again in the same way. The prepared paint can be coated by various methods and amount of the solvent can be controlled for a desirable viscosity. 1-Ethynyl-1-cyclohexanol introduced as an inhibitor of self-crosslinking reaction prevent an undesirable fast reaction before finishing coating process. The curing at room temperature takes several days and the curing rate is accelerated at the higher temperature. Additionally, the crosslinking density of the paint can be controlled by the concentration of catalyst. In this study, the optimized amount of catalyst was used for free standable, stretchable and relatively robust Si-CSM paint.

Charaterization

The chemical structure and purity of intermediates and Si-CSM were confirmed by nuclear magnetic resonance (NMR, JEOL, JNM-ECZ500R) in deuterated chloroform. Chemical shifts were quoted in part per million (ppm) with a reference of solvent peak. NMR spectroscopy was also used to analyze photoisomerization and self-crosslinking of Si-CSM. The molecular weight of Si-CSM was characterized by gel permeation chromatography (GPC, Waters, ACQUITY APC). In addition, Successful hydrosilylation reaction of PMHS and CSM was identified by Fourier transform infrared spectroscopy (FT-IR, Shimadzu, IRTracer-100). All samples for FT-IR analysis were prepared by spin coating of 1.5 wt% solution on CaF_2 window. Optical textures at different temperatures were observed with a cross-polarized optical microscope (POM, Nikon, ECLIPSE E600POL) coupled with a METTLER TOLEDO FP90 heating stage. The phase transition behaviors were monitored using differential scanning calorimetry (DSC, Perkin Elmer, DSC 4000). Thermal degradation temperature of Si-CSM was confirmed by the thermogravimetric analysis (TGA, TA Instruments, US/TA5000). Wide-angle X-ray diffraction (WAXD, Bruker, D8 DISCOVER) were conducted using a CuKα radiation generator and a diffractometer. Density of differently self-assembled Si-CSM was measured using NaCl solution at 20 °C. Absorption and emission properties of Si-CSM were investigated by the ultraviolet-visible light spectrometer (Scinco, S-3100) and the spectro-fluorophotometer (Shimadzu, RF-6000). Photoluminescence quantum yield measurement was conducted using absolute PL quantum yield spectrometer (Hamamatsu, C9920-02). Surface morphology of solution casted and annealed Si-CSM film were observed by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss, SUPRA 40VP) and atomic force microscopy (AFM, Bruker, Multimode-8). Dynamic mechanical tests of Si-CSM paint film were conducted by dynamic mechanical analyzer (DMA, TA Instruments, Q800). The width and thickness of all samples for mechanical tests are 5.30 mm and 0.25 mm, respectively.

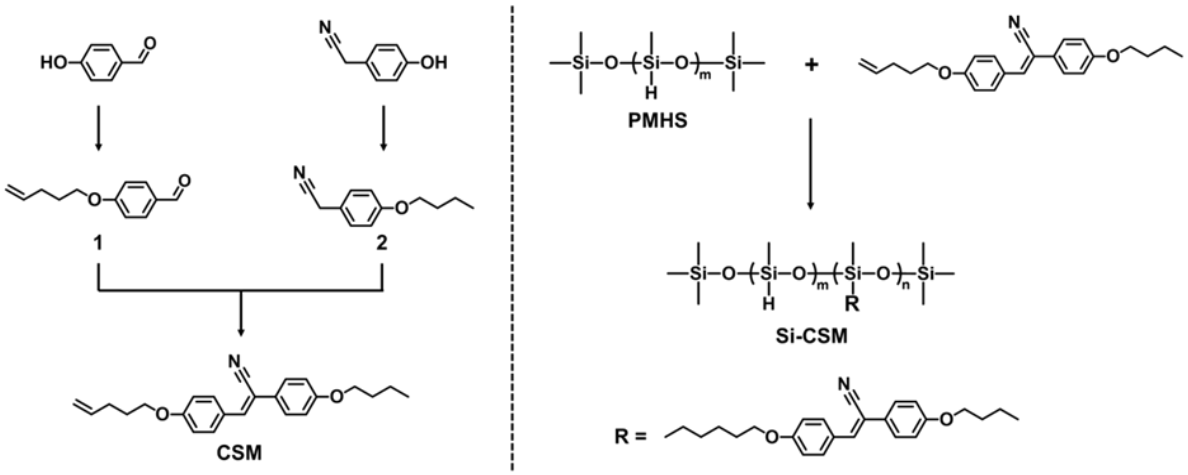


Fig. S1 Synthetic procedure of Si-CSM

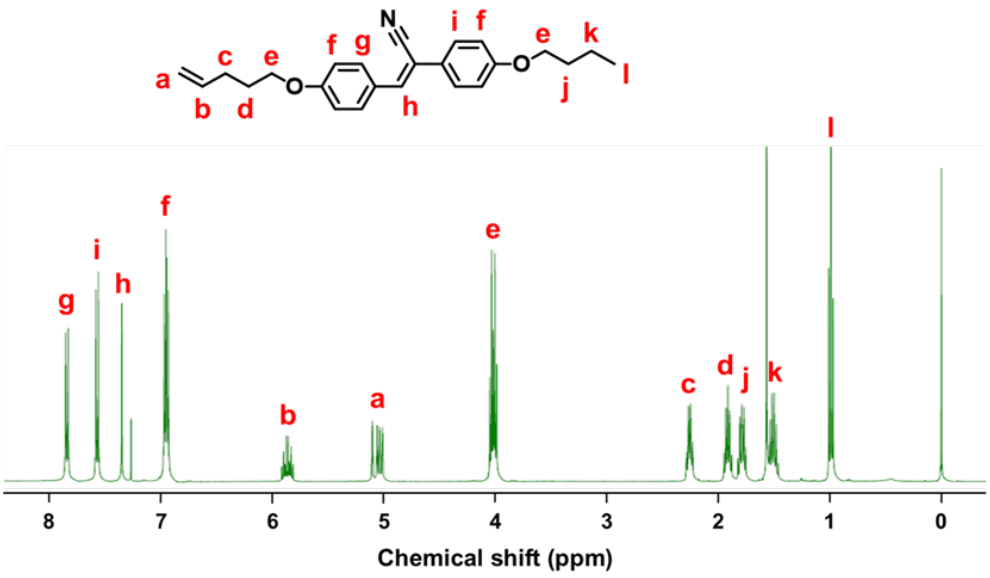


Fig. S2 ^{1}H-NMR spectrum of CSM.

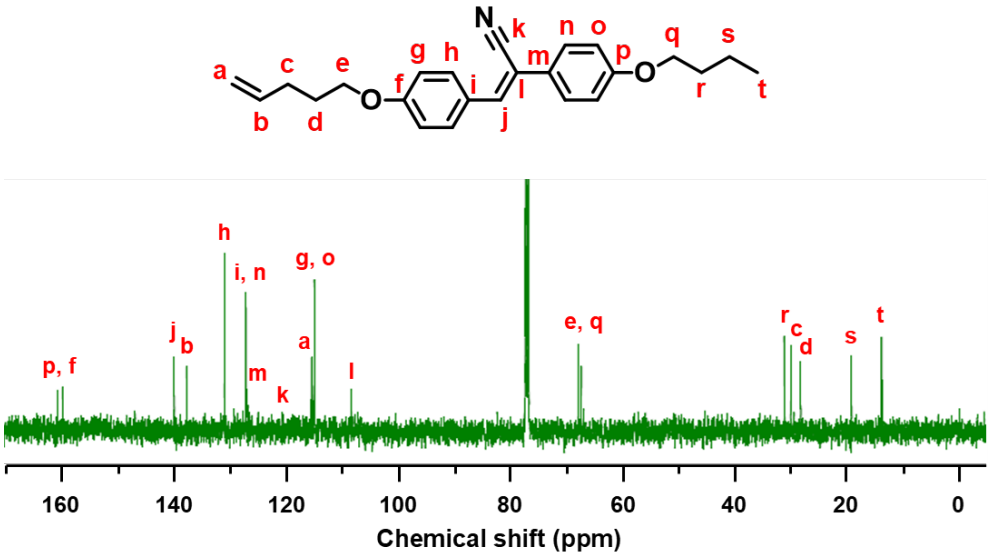


Fig. S3 ^{13}C-NMR spectrum of CSM.

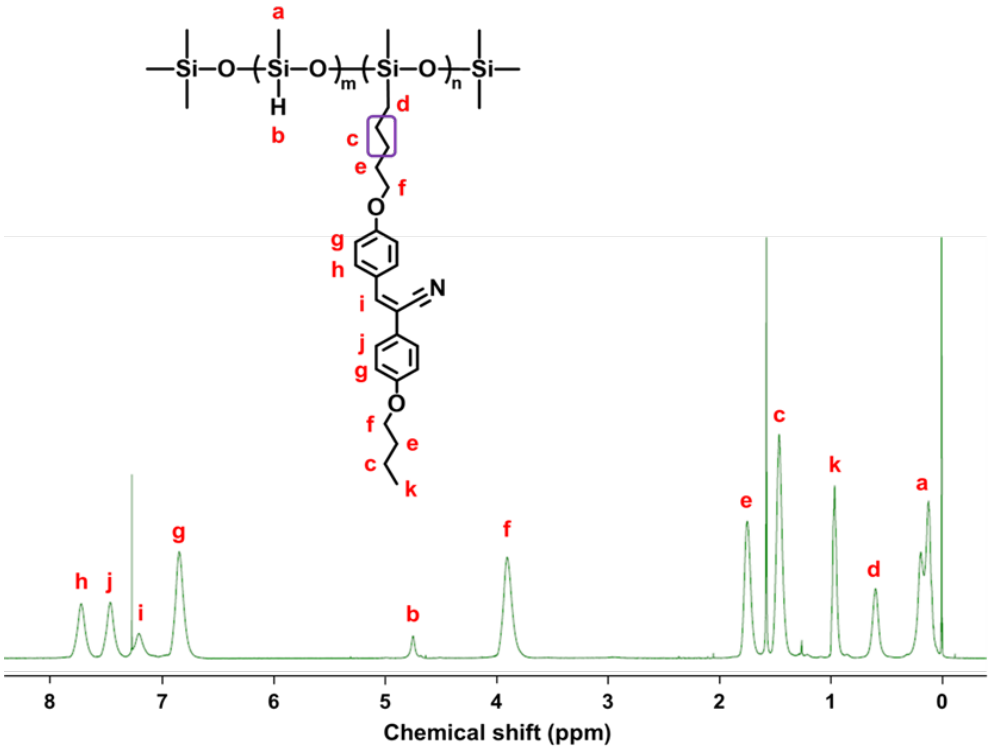


Fig. S4 ^{1}H-NMR spectrum of Si-CSM.

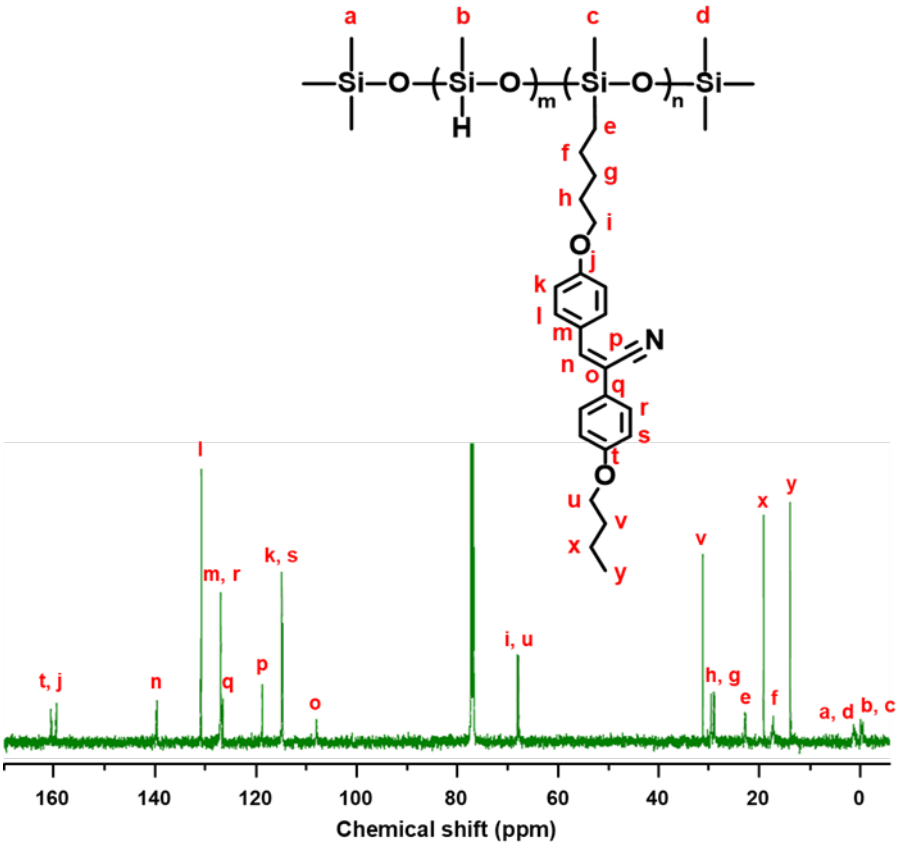


Fig. S5 ^{13}C-NMR spectrum of Si-CSM.

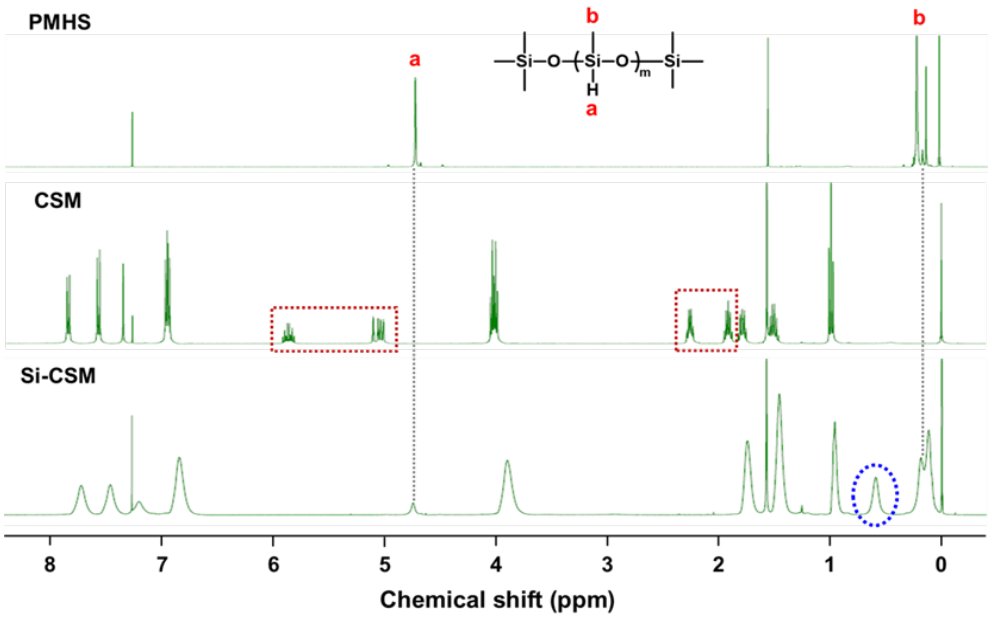
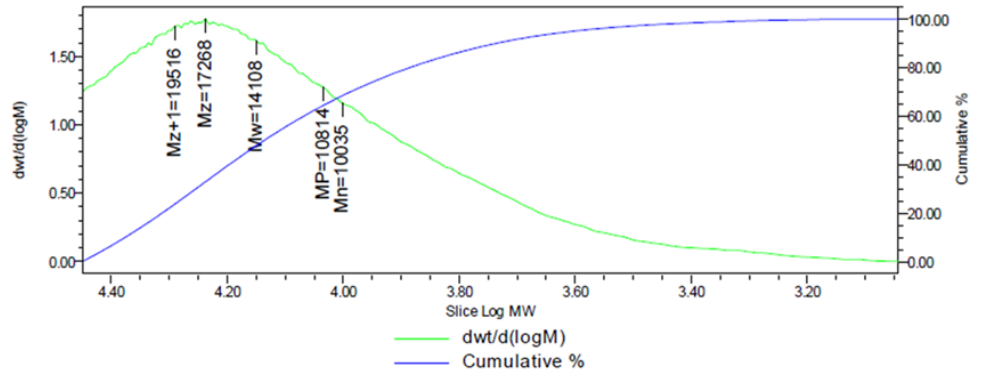


Fig. S6 ^{1}H-NMR spectrum comparison of PMHS, CSM, and Si-CSM.



GPC Sample Result					
Retention Time (min)	M_n	M_p	M_w	M_z	Poly-dispersity
1.887	10,035	10,814	14,108	17,268	1.406

Fig. S7 GPC data and result table of Si-CSM.

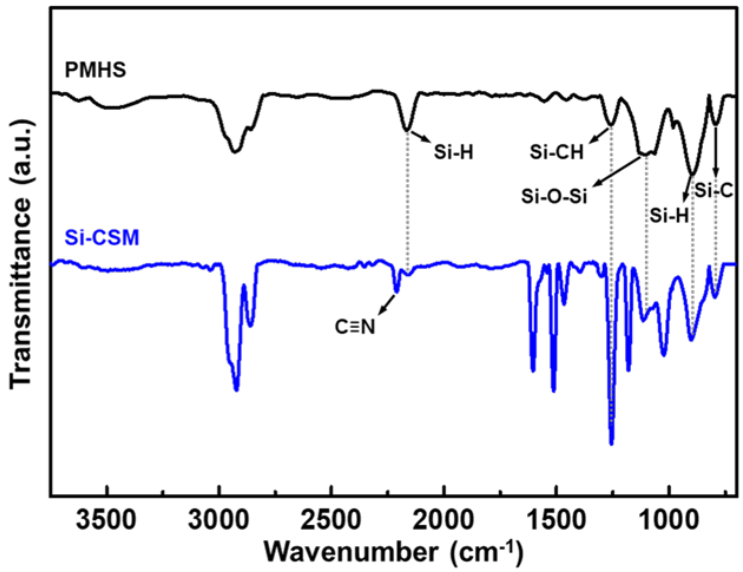


Fig. S8 FT-IR spectrum comparison of PMHS and Si-CSM.

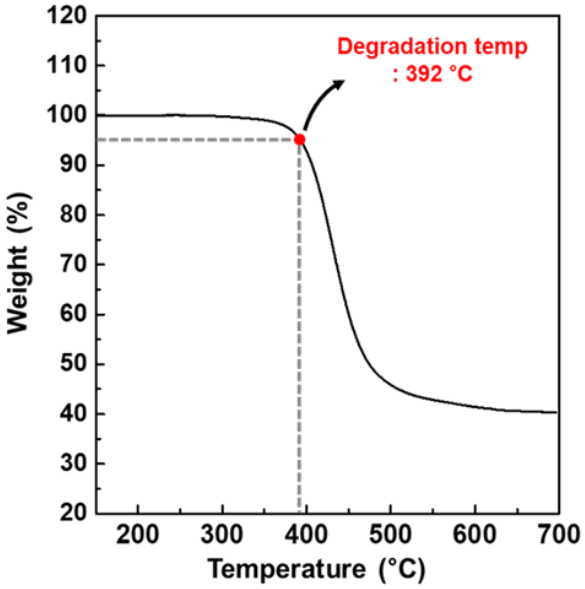


Fig. S9 TGA data of Si-CSM.

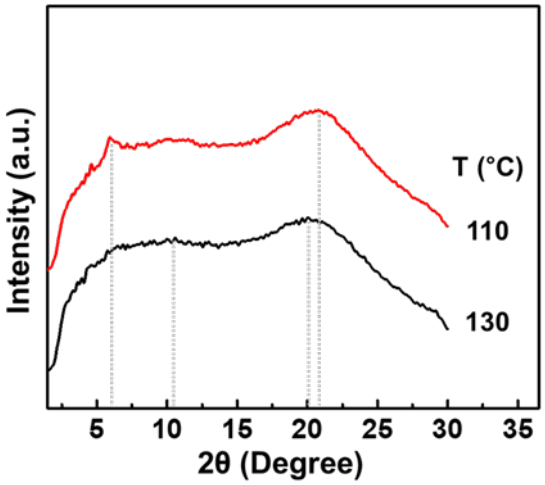


Fig. S10 1D WAXD data of Si-CSM at different temperatures of 130 °C (isotropic state) and 110 °C (LC phase).

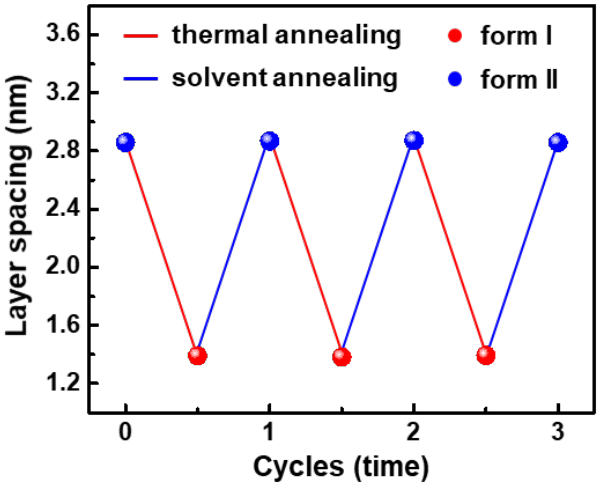


Fig. S11 Reversible phase transition behavior of Si-CSM through two different annealing processes.

NaCl wt% in NaCl soln	Thermally annealed	Solvent annealed
10	Settle	Settle
11	Settle	Settle
12	Settle	Float (slow)
13	Settle	Float
14	Settle (slow)	Float
15	Float (slow)	Float

Density of thermally annealed Si-CSM = 1.11 g/cm^3

Density of solvent annealed Si-CSM = 1.08 g/cm^3

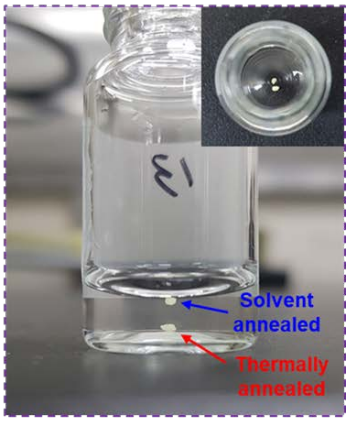


Fig. S12 Density measurement of the differently prepared Si-CSM samples and result table

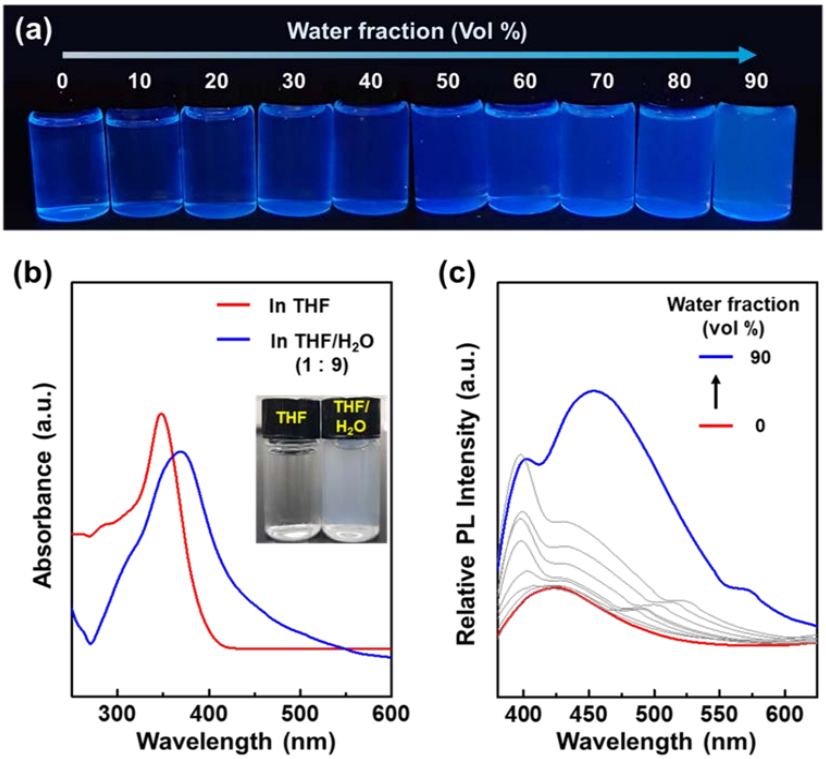


Fig. S13 Aggregation-induced emission properties of Si-CSM: (a) Photographs under UV light, (b) UV-Vis spectra, and (c) PL spectra with different water fractions in THF/H_2O solution (concentration: 0.005 % (w/v), λ_{ex}= 350 nm).

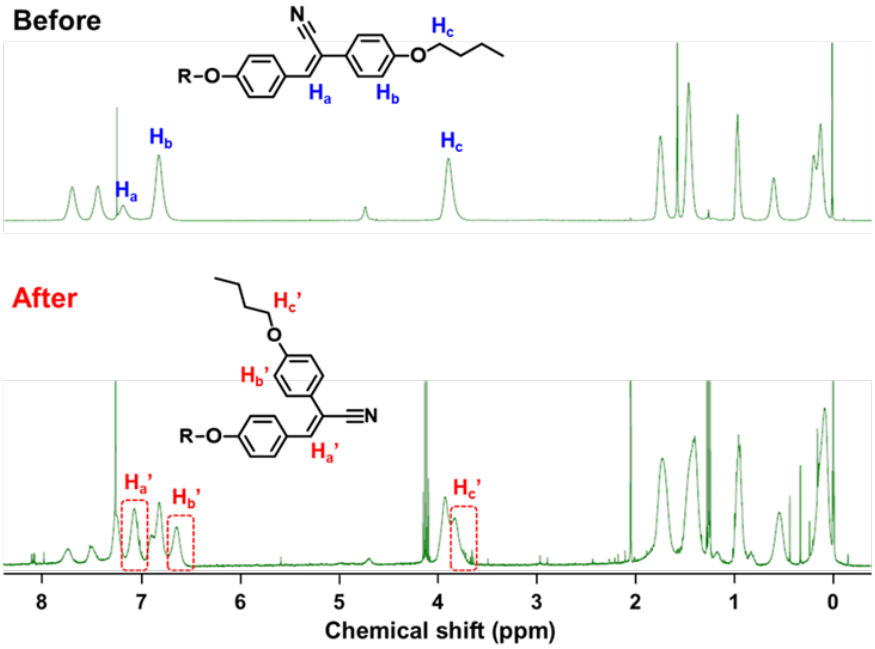


Fig. S14 ^{1}H-NMR spectra of Si-CSM before and after UV irradiation (UV intensity: 10 mW/cm^2, irradiation time: 15 min).

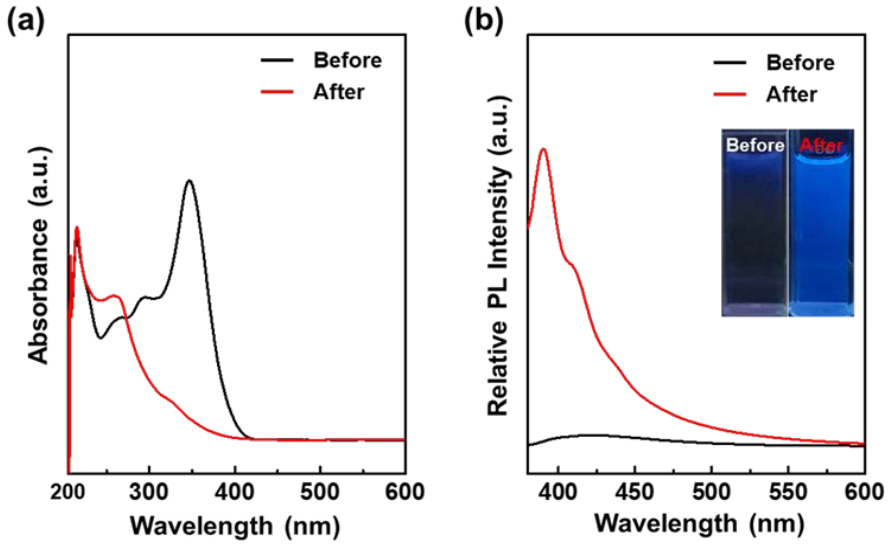
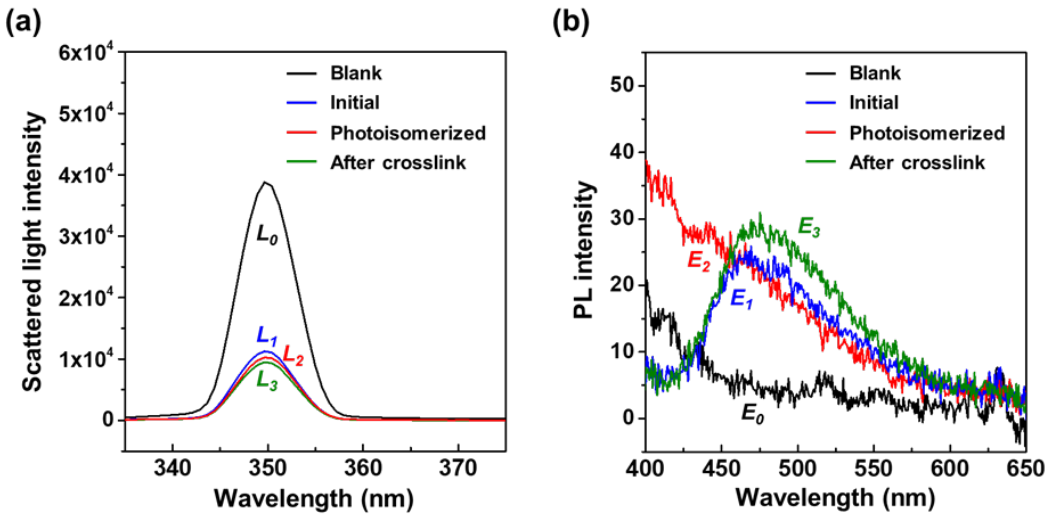


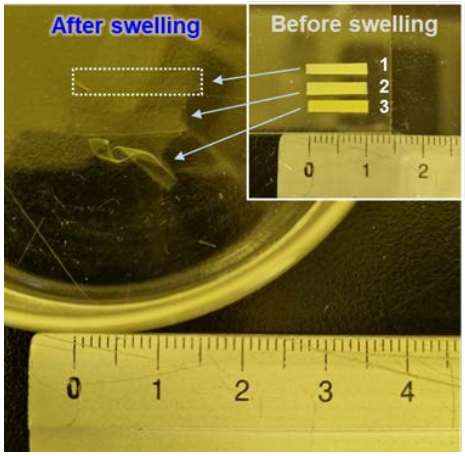
Fig. S15 Photophysical changes of Si-CSM in THF upon UV irradiation: (a) UV-Vis spectra and (b) PL spectra (concentration: 0.005 % (w/v), UV intensity: 10 mW/cm^2, irradiation time: 15 min, λ_{ex}= 350 nm).



(c)

State	L_n	L_0	E_n	E_0	QY (%)
Initial	83692.15	285247.92	2746.94	704.39	1.01
Photoisomerized	76906.12	285247.92	3787.61	937.78	1.37
After crosslink	73513.94	285247.92	3159.10	704.39	1.16

Fig. S16 The photoluminescence quantum yield of Si-CSM in different states: (a) the scattering and (b) emission spectra, and (c) a summary table for quantum yield measurement.



Swelling test result	
Sample number	Change in length (ΔL)
1[a]	1.5
2[b]	1.35
3[c]	1.2

[a] The amount of catalyst in sample 1 is half of that in sample 2.

[b] Sample 2 is the proposed Si-CSM paint.

[c] Sample 3 has the 1.5 times higher catalyst than sample 2.

Fig. S17 Swelling test result of three samples with different catalyst concentrations.

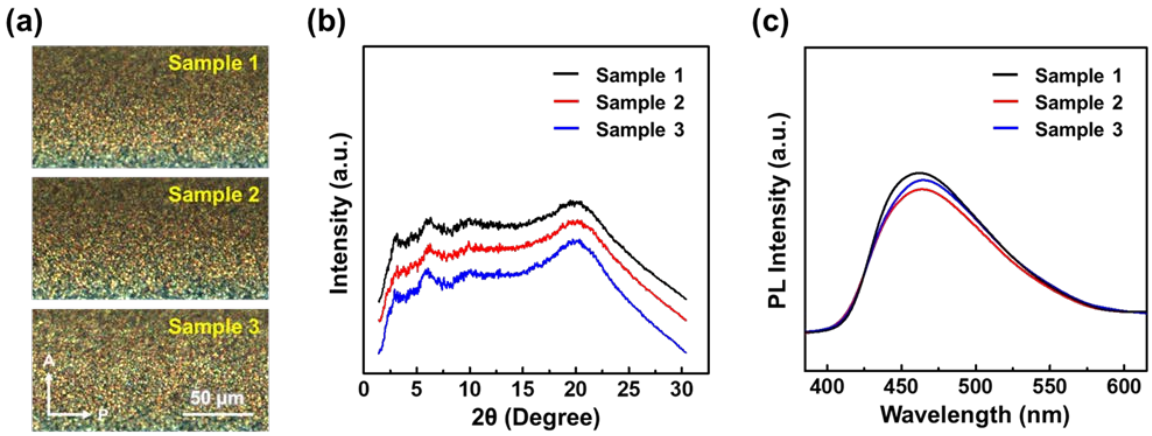


Fig. S18 (a) POM, (b) 1D WAXD and (c) PL spectra of three samples with different crosslinking density.

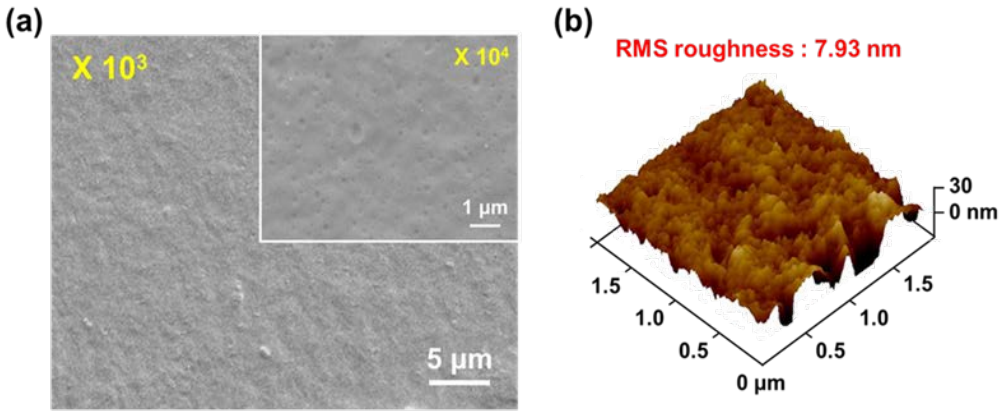


Fig. S19 Surface morphology of the self-crosslinked Si-CSM film: (a) SEM images (top view) and (b) AFM surface topography.

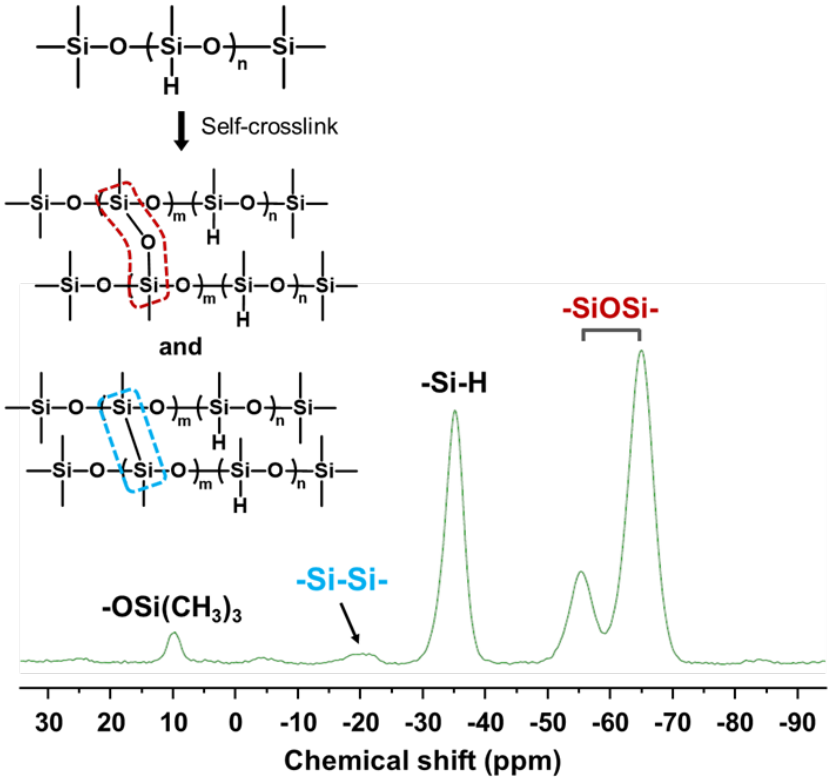


Fig. S20 Solid-state ^{29}Si NMR spectrum of PMHS.

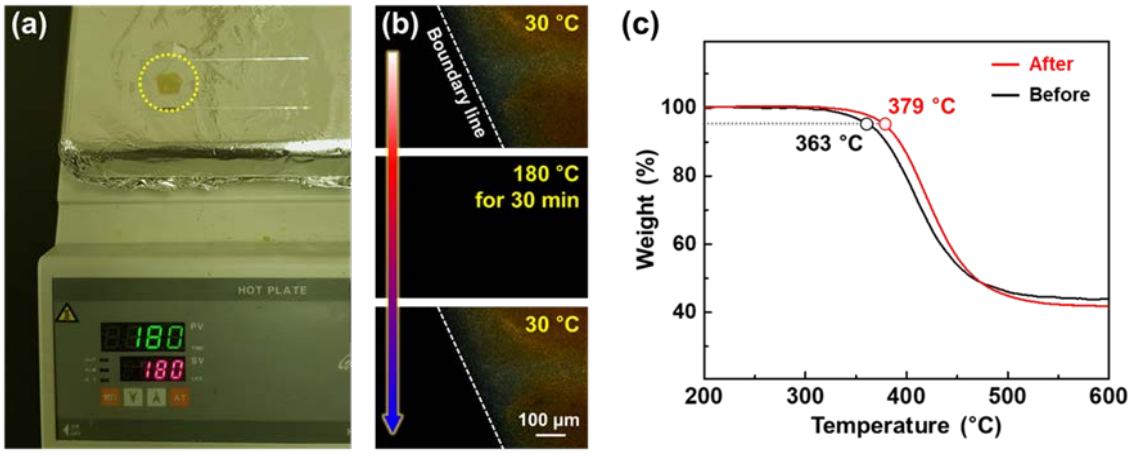


Fig. S21 Thermal stability tests of the self-crosslinked Si-CSM film: (a) a photograph of the film on hot plate, (b) POM images at different temperatures, and (c) TGA data before and after immersion.

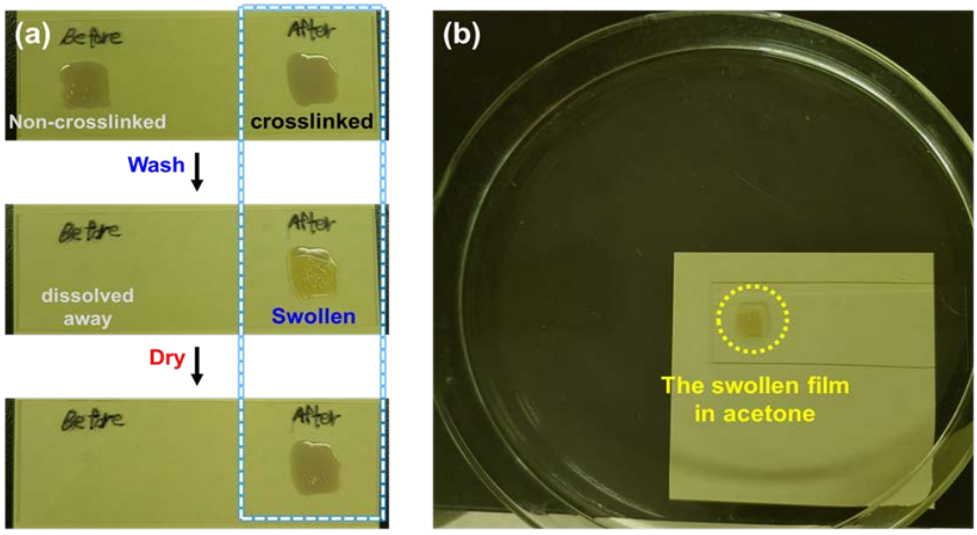


Fig. S22 Chemical resistance of the self-crosslinked Si-CSM film: (a) Comparison of non-crosslinked and crosslinked film after solvent rinsing with chloroform, and (b) an acetone immersion test for 30 min.

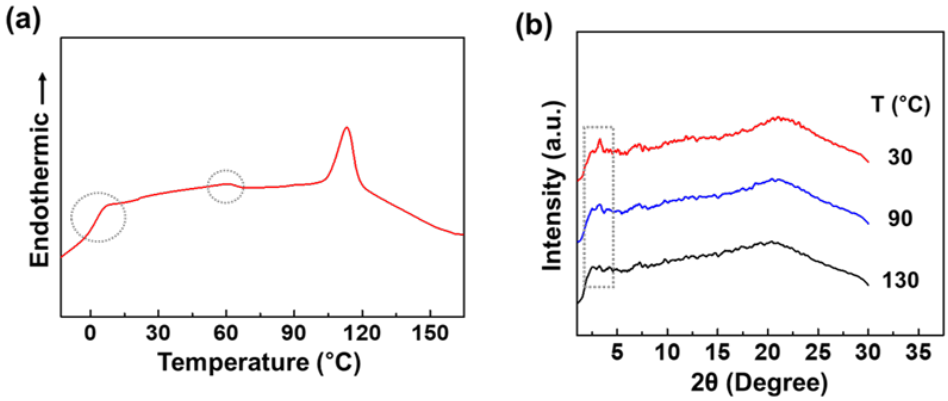


Fig. S23 Thermal analyses of the self-crosslinked Si-CSM: (a) DSC data, and (b) 1D XRD data at different temperatures.

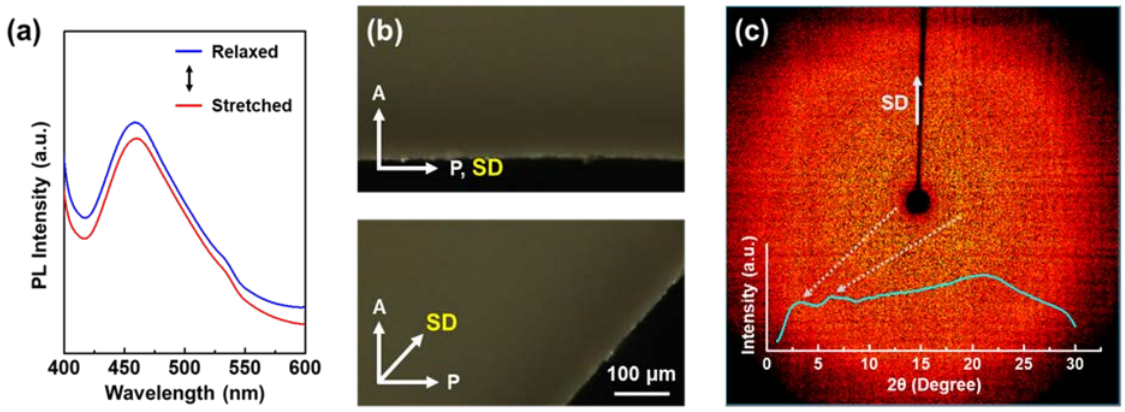


Fig. S24 (a) PL spectra of the stretched and relaxed Si-CSM paint film, (b) POM observations with the angles of 0° and 45° between polarizer (P) and stretching direction (SD) and (c) WAXD data of the stretched film.

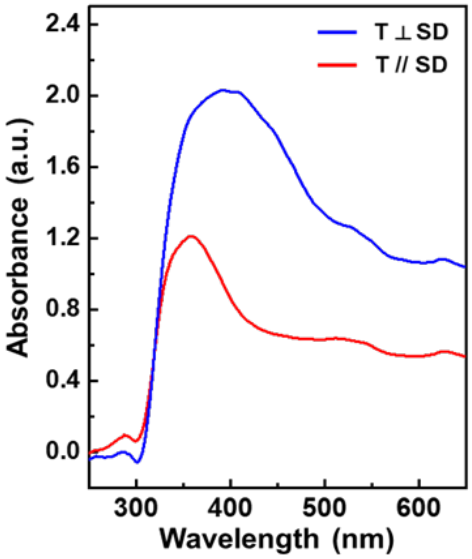


Fig. S25 Polarized UV-Vis absorption of the uniaxially oriented and self-crosslinked Si-CSM paint film.

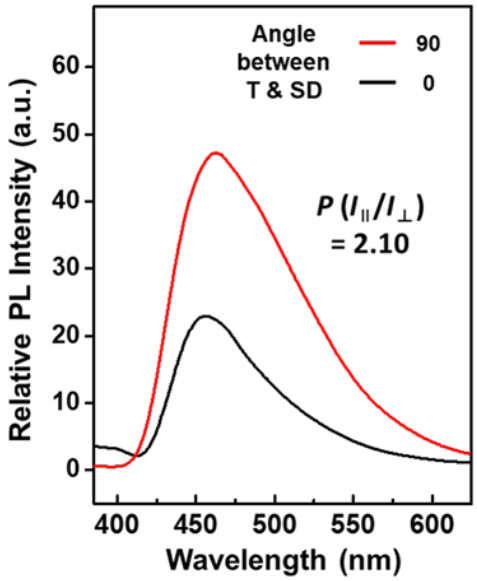


Fig. S26 Polarized PL spectra of the uniaxially oriented Si-CSM paint film before self-crossliking.