Supporting Information

From Photoinduced Supramolecular Polymerization to Responsive Organogels

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1. Materials. All commercial reagents were purchased from Acros, Aldrich, TCI or Merck and were used as received. All solvents used in the reactions were dried using an MBräu SPS-800 solvent purification system or purchased from Acros. Analytical TLC was performed on Merck silica gel 60 F254 plates and visualization was accomplished by UV light or staining with a KMnO₄ solution.

2. General. Column chromatography was performed on a Reveleris X2 Flash Chromatography system. NMR spectra were recorded at 25 °C on Varian AMX400 (¹H: 400 MHz, ¹³C: 101 MHz) and Varian Unity Plus (¹H: 600 MHz, ¹³C: 151 MHz) spectrometers. Chemical shifts (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ¹H NMR [CDCl₃: ¹H(δ) = 7.26 ppm, DMSO-d₆: ¹H(δ) = 2.50 ppm, toluene-d₈: ¹H(δ) = 7.10, 7.02, 6.98 and 2.09 ppm] and ¹³C NMR [CDCl₃: ¹³C(δ) = 77.2 ppm, DMSO-d₆: ¹³C(δ) = 39.5 ppm]. Absolute values of the coupling constants are given in Hertz (Hz), regardless of their sign. Multiplicities are abbreviated as singlet (s), doublet (d), doublet of doublets (dd), triplet (t), triplet of doublets (td), quartet (q), multiplet (m), and broad (br). High-resolution mass spectrometry (HRMS) was performed on an LTQ Orbitrap XL spectrometer with ESI ionization. All reactions were performed under anhydrous conditions under N₂ atmosphere. UV-vis spectra in the part of supramolecular polymerization in toluene were recorded on Analytikjena SPECORD S600 in a 1 mm path length quartz cuvette. Irradiation of samples was carried out at 298 K using a Thorlabs model M365F1 LED (4.1 mW) and M385F1 LED (10.7 mW) positioned at a distance of 1 cm from the samples. The critical gelation concentration (CGC) were tested by the vial-inverting method.¹ Samples of the trans-isomers in the organic solvent were first heated above the critical temperature to form a transparent solution and then cooled to room temperature to form gels. Samples of the trans-isomers in water were heated at 353 K for 10 min and then cooled to room temperature to form gels. CGC was determined as the concentration at which the gel lost its stability when vial was inverted. A FEI T20 cryo-electron microscope equipped with a Gatan model 626 cryo-stage was used to record the morphology of supramolecular polymers, operating at 200 kV under low-dose conditions with a slow-scan CCD camera.
3. Synthesis.

Figure S1. Synthesis of trans-SG1, SG2, and SG3. (cis-SG1 was synthesized by the same method as trans-SG1 starting from cis-1).

**Trans-1 and cis-1**

TiCl₄ (10.8 mL, 98.6 mmol) was added to a suspension of Zn powder (12.9 g, 197.2 mmol) in anhydrous THF (120 mL). After heating at reflux for 2 h, 6-methoxy-1-indanone (8.0 g, 49.3 mmol) was added to the reaction mixture. The mixture was heated at reflux for 16 h, cooled to room temperature and treated with a saturated aqueous solution of NH₄Cl and extracted with EtOAc. The organic layer was washed with brine and dried over Na₂SO₄. The solution was concentrated under reduced pressure and the precipitate was filtered off and washed with pentane to afford trans-1 (3.70 g, 12.6 mmol, 26%) as a yellow solid. The filtrate was concentrated in vacuo and purified by column chromatography (SiO₂, pentane:EtOAc = 98:2) to afford cis-1 (1.60 g, 5.46 mmol, 11%) as a white solid. **cis-1**: ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 2.5 Hz, 2H), 7.22 (d, J = 8.3 Hz, 2H), 6.80 (dd, J = 8.2, 2.4 Hz, 2H), 3.86 (s, 6H), 3.23–3.14 (m, 4H), 3.09–3.02 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 158.8, 141.8, 140.8, 135.6, 125.8, 114.4, 108.5, 55.7, 35.6, 30.4. HRMS (ESI+) calcd. for \([M+H]^+\): 293.1536, found: 293.1537.

**Trans-2 and cis-2**
To *trans*-1 (2.00 g, 6.80 mmol) was added a solution of CH$_3$Mgl (3 M in Et$_2$O) (13.6 mL, 40.8 mmol). The mixture was heated at 140 °C for 16 h, while the solvent was allowed to evaporate via a needle in the septum. After cooling to room temperature, the solid was quenched with ice and an aqueous saturated solution of NH$_4$Cl, then extracted with EtOAc. The organic layer was washed with brine and dried over anhydrous Na$_2$SO$_4$. The solution was concentrated under reduced pressure and the precipitate was filtered off and washed with DCM to afford *trans*-2 (1.10 g, 4.16 mmol, 61%) as a yellow solid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 9.17 (s, 2H), 7.11 (d, $J = 8.1$ Hz, 2H), 7.02 (d, $J = 2.3$ Hz, 2H), 6.63 (dd, $J = 8.1$, 2.2 Hz, 2H), 3.02 (d, $J = 7.3$ Hz, 4H), 2.98–2.91 (m, 4H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) δ 156.0, 143.7, 137.0, 134.9, 125.2, 114.4, 110.9, 31.8, 29.5. HRMS (APCI) calcd. for [M+H]$^+$: 265.1231, found: 265.1225.

*Cis*-1 (500 mg, 1.70 mmol) was converted using the same method. The precipitate was filtered off and washed with DCM to afford *cis*-2 (71.0 mg, 0.269 mmol, 16%). The filtrate was concentrated in vacuo and purified by flash column chromatography (SiO$_2$, EtOAc:pentane = 1:4) to afford cis-2 as a white solid (218 mg, 0.826 mmol, 49%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, $J = 2.3$ Hz, 2H), 7.13 (d, $J = 8.1$ Hz, 2H), 6.71 (dd, $J = 8.1$, 2.3 Hz, 2H), 2.94–2.87 (m, 4H), 2.83–2.76 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.4, 141.9, 141.2, 135.7, 126.0, 115.0, 110.8, 35.3, 29.9. HRMS (ESI+) calcd. for [M$^+$]: 264.1145, found: 264.1149.

*Trans*-3 and *cis*-3

To a suspension of *trans*-2 (1.00 g, 3.80 mmol) in DMF (15 mL) was added 2-(3-bromopropyl) isoindoline-1,3-dione (3.10 g, 11.4 mmol), tetrabutylammonium iodide (4.21 mmol) in DMF and K$_2$CO$_3$ (2.10 g, 15.2 mmol), and the mixture was stirred at 80 °C overnight. After the reaction was complete, deionized water was added and the aqueous phase was extracted with EtOAc. The organic layer washed with brine, dried over Na$_2$SO$_4$ and concentrated in vacuo. The crude product was purified by column chromatography (SiO$_2$, EtOAc:pentane = 1:4) to afford compound *trans*-3 (887 mg, 1.39 mmol 37% yield) as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.84 (dd, $J = 5.4$, 3.1 Hz, 4H), 7.70 (dd, $J = 5.4$, 3.0 Hz, 4H), 7.15 (d, $J = 8.2$ Hz, 2H), 7.04 (d, $J = 2.3$ Hz, 2H), 6.69 (dd, $J = 8.2$, 2.3 Hz, 2H), 4.07 (t, $J = 5.9$ Hz, 4H), 3.94 (t, $J = 6.9$ Hz, 4H), 3.10–2.96 (m, 8H), 2.20 (p, $J = 6.4$ Hz, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.6, 157.91, 144.5, 139.8, 135.9, 134.1, 132.4, 125.3, 123.4, 113.4, 111.3, 66.4, 35.9, 32.6, 30.4, 28.6. HRMS (ESI+) calcd. for [M$^+$]: 638.2411, found: 638.2412.

*Cis*-2 (200 mg, 0.76 mmol) was treated following the same method to afford *cis*-3 as a white solid (135 mg, 0.063 mmol, 28%) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 (dd, $J = 5.5$, 3.1 Hz, 4H), 7.60 (dd, $J = 5.5$, 3.0 Hz, 4H), 7.44 (d, $J = 2.4$ Hz, 2H), 7.12 (d, $J = 8.2$ Hz, 2H), 6.61 (dd, $J = 8.3$, 2.3 Hz, 2H), 3.98 (t, $J = 5.7$ Hz, 4H), 3.89 (t, $J = 7.0$ Hz, 4H), 2.92–2.86 (m, 4H), 2.80–2.74 (m, 4H), 2.15 (p, $J = 6.2$ Hz, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 168.5, 157.3, 141.7, 140.8, 135.5, 133.8, 132.4, 125.6, 123.3, 114.6, 109.3, 66.2, 35.9, 35.5, 30.0, 28.5. HRMS (ESI+) calcd. for [M$^+$]: 638.2411, found: 638.2406.

*Trans*-4 and *cis*-4

To a suspension of *trans*-3 (300 mg, 0.470 mmol) in EtOH (10 mL) was added hydrazine hydrate (50–60%, 4.70 mmol, 0.3 mL), and the suspension was heated at reflux for 2 h. After concentrating in vacuo, the mixture was dissolved in 15% aq. NaOH (15 mL), and extracted with DCM. The organic layer was washed with brine and dried over Na$_2$SO$_4$, and then concentrated in vacuo to afford *trans*-4 (157 mg, 0.415 mmol, 88%) as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20 (d, $J = 8.2$ Hz, 2H), 7.16 (d, $J = 2.5$ Hz, 2H), 6.78 (dd, $J = 8.2$, 2.4 Hz, 2H), 4.09 (t, $J = 6.1$ Hz, 4H), 3.23–2.99 (m, 8H), 2.94 (t, $J = 6.7$ Hz, 4H), 1.96 (p, $J = 6.4$ Hz,
ETOOAc. 26–920.
ed7, 110.–36(%)(81ESI+) calcd. for 134H), 3.44 (t, (520 Hz, 2H), 2.95–2.73 (m, 12H), 1.89 (p, J = 6.3 Hz, 4H). 13C NMR (151 MHz, CDCl3) δ 157.5, 141.8, 140.9, 135.6, 125.8, 114.7, 109.4, 66.4, 42.0, 35.6, 33.3, 30.0. HRMS (ESI+) calcd. for [M + H]+: 379.2380, found: 379.2387.

Cis-3 (100 mg, 0.160 mmol) was converted using the same method to afford cis-4 (51.0 mg, 0.135 mmol, 86%) as a yellow solid. 1H NMR (400 MHz, CDCl3) δ 7.65 (s, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.74 (d, J = 8.2 Hz, 2H), 4.01 (t, J = 6.1 Hz, 4H), 2.95–2.73 (m, 12H), 1.89 (p, J = 6.3 Hz, 4H). 13C NMR (151 MHz, CDCl3) δ 157.5, 141.8, 140.9, 135.6, 125.8, 114.7, 109.4, 66.4, 42.0, 35.6, 33.3, 30.0. HRMS (ESI+) calcd. for [M+H]+: 379.2380, found: 379.2386.

To a solution of phenyl chloroformate (91.0 mg, 0.580 mmol) in DCM (3 mL) was added trans-4 (100.0 mg, 0.260 mmol) and N,N-disopropylethylamine (0.1 mL, 0.580 mmol) at 0 °C. After stirring for 16 h, the precipitate was filtered off, washed with DCM and then dried in vacuo to afford trans-5 (140 mg, 0.227 mmol, 86%). 1H NMR (400 MHz, DMSO-d6) δ 7.84 (t, J = 5.5 Hz, 2H), 7.36 (t, J = 8.0 Hz, 4H), 7.24 (d, J = 8.2 Hz, 2H), 7.19 (t, J = 7.4 Hz, 2H), 7.14–7.05 (m, 6H), 6.83 (dd, J = 8.2, 2.3 Hz, 2H), 4.08 (t, J = 6.2 Hz, 4H), 3.29–3.23 (m, 4H), 3.15–3.08 (m, 4H), 3.18–2.94 (m, 4H), 1.95 (p, J = 6.4 Hz, 4H). 13C NMR (151 MHz, DMSO) δ 157.6, 154.4, 151.1, 143.7, 138.9, 135.2, 129.2, 125.3, 124.8, 121.7, 113.9, 110.3, 65.3, 37.6, 31.8, 29.7, 29.1. HRMS (ESI+) calcd. for [M+Na]+: 641.2614, found: 641.2622.

To a suspension of NaH (60%wt in mineral oil) (160 mg, 4.00 mmol) in THF (40 mL) was added hexaethylene glycol monomethyl ether (2.00 g, 6.70 mmol) and 7-bromoheptanoate (1.55 g, 7.40 mmol). The mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with methanol followed by concentration under reduced pressure. The resulting mixture was added to water and extracted with DCM. The organic layer was dried over Na2SO4 and concentrated in vacuo. The crude product was isolated by column chromatography (EtOAc) to obtain 6 (1.10 g, 2.51 mmol, 37%) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 3.67–3.61 (m, 24H), 3.58–3.52 (m, 4H), 3.44 (t, J = 6.7 Hz, 2H), 3.37 (s, 3H), 2.30 (t, J = 7.5 Hz, 2H), 1.65–1.53 (m, 4H), 1.37–1.29 (m, 4H). 13C NMR (151 MHz, CDCl3) δ 174.4, 72.1, 71.5, 70.8, 70.7, 70.3, 59.2, 51.6, 34.2, 29.6, 29.2, 26.0, 25.1. HRMS (ESI+) calcd. for [M+Na]+: 461.2727.

To a solution of compound 6 (1.00 g, 2.30 mmol) in MeOH (20 mL) was added aq. NaOH (4 M; 1.20 mL, 4.80 mmol). After heating at reflux for 4 h, the solution was added to 100 mL deionized water. Then the water solution was adjusted to pH < 7 and extracted with DCM. The organic layer was dried over Na2SO4 and concentrated in vacuo. The crude product was isolated by column chromatography (EtOAc) to obtain 7 (520 mg, 1.23 mmol, 53%) as a colorless oil. NMR (400 MHz, CDCl3) δ 3.68–3.60 (m, 21H), 3.58–3.52 (m, 4H), 3.44 (t, J = 6.6 Hz, 2H), 3.37 (s, 3H), 2.32 (t, J = 7.4 Hz, 2H), 1.67–1.52 (m, 4H), 1.38–1.32 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 178.6, 72.0, 71.4, 70.7, 70.6, 70.2, 59.1, 34.0, 29.5, 29.0, 25.9, 24.8. HRMS (ESI+) calcd. for [M+Na]+: 447.2565, found: 447.2570.

To a solution of compound 7 (800 mg, 1.89 mmol) in toluene (20 mL) was added diphenylphosphoryl azide (0.490 mL, 2.27 mmol) and triethylamine (0.310 mL, 2.27 mmol) at room temperature under N2 atmosphere.
After stirring for 3 h, the reaction mixture was heated at 70 °C for 2 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo and then purified by column chromatography (SiO2, EtOAc:pentane=9:1) to afford 8 (160 mg, 0.380 mmol, 20%) as a colorless oil. The pure compound was used in the next reaction immediately. 1H NMR (400 MHz, CDCl3) δ 3.67–3.62 (m, 2H), 3.60–3.53 (m, 4H), 3.45 (t, J = 6.6 Hz, 2H), 3.38 (s, 3H), 3.29 (t, J = 6.7 Hz, 2H), 1.63–1.54 (m, 4H), 1.42–1.34 (m, 4H). 13C NMR (151 MHz, CDCl3) δ 72.1, 71.4, 70.8, 70.7, 70.3, 59.2, 43.1, 31.4, 29.7, 26.6, 25.7. HRMS (ESI+) calcd. for [M+H]+: 422.2759, found: 422.2748.

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To a solution of hexaethylene glycol (2.30 g, 8.00 mmol) in 1-BuOH (50 mL) was added 1-BuOK (0.90 g, 8.00 mmol) and 2-(6-bromoethyl)isoindoline-1,3-dione (1.24 g, 8.00 mmol). After heating at reflux for 3 d, water (30 mL) and aq. HCl (1 M; 3 mL) was added to the mixture. The resulting solution was extracted with DCM. The organic layer was dried over Na2SO4 and concentrated in vacuo. The crude product was isolated by column chromatography (EtOAc:pentane = 9:1) to obtain 9 (1.50 g, 2.94 mmol, 37%), as a colorless oil. 1H NMR (400 MHz, CDCl3) δ 7.83 (dd, J = 5.5, 3.1 Hz, 2H), 7.70 (dd, J = 5.5, 3.1 Hz, 2H), 3.78–3.52 (m, 26H), 3.43 (t, J = 6.7 Hz, 2H), 1.72–1.63 (m, 2H), 1.61–1.62 (m, 2H), 1.41–1.30 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 168.6, 134.1, 132.3, 123.3, 72.7, 71.4, 70.8, 70.7, 70.5, 70.2, 61.9, 38.1, 29.6, 28.7, 26.9, 25.8. HRMS (ESI+) calcd. for [M+Na]+: 534.2674, found: 534.2670.

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To a solution of compound 9 (1.00 g, 1.96 mmol) in EtOH (20 mL) was added hydrazine hydrate (50–60%, 20.0 mmol, 1.30 mL), and the suspension was heated at reflux for 4 h. After cooling to room temperature, the mixture was dissolved in 15% aq. NaOH (50 mL), and extracted with DCM. The organic layer was washed with brine and dried over Na2SO4, and then concentrated in vacuo. The crude product was isolated by column chromatography (EtOAc:MeOH = 19:1) to afford 10 (547 mg, 1.52 mmol, 76%) as a colorless oil 1H NMR (400 MHz, CDCl3) δ 3.74–3.55 (m, 26H), 3.45 (t, J = 6.7 Hz, 2H), 2.67 (t, J = 6.9 Hz, 2H), 1.62–1.54 (m, 2H), 1.48–1.40 (m, 2H), 1.37–1.30 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 72.9, 71.4, 70.7, 70.6, 70.4, 70.0, 61.6, 42.1, 33.5, 29.7, 26.8, 26.1. HRMS (ESI+) calcd. for [M+Na]+:382.2799, found: 382.2808.

Trans-SG1 and Cis-SG1
To a solution of trans-4 (30.0 mg, 80.0 μmol) in DCM (3 mL) was added compound 8 (74.0 mg, 17.0 μmol). After stirring for 16 h at room temperature, pentane (8 mL) was added to the solution to induce precipitation. The obtained solid materials was dissolved in DCM (2 mL) and precipitated by adding pentane (8 mL). The precipitation was repeated three times. After drying in vacuo pure trans-SG1 (73.0 mg, 59.8 μmol, 75%) was obtained as a pale yellow solid. 1H NMR (400 MHz, CDCl3) δ 7.19 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 2.3 Hz, 2H), 6.76 (dd, J = 8.2, 2.2 Hz, 2H), 4.81 (t, J = 5.8 Hz, 2H), 4.58 (t, J = 5.7 Hz, 2H), 4.06 (t, J = 5.8 Hz, 4H), 3.64 m, 40H), 3.53 (t, J = 4.8 Hz, 8H), 3.45–3.38 (m, 8H), 3.37 (s, 6H), 3.18–3.08 (m, 8H), 3.07–2.99 (m, 4.3 Hz, 4H), 2.00 (p, J = 6.3 Hz, 4H), 1.54 (p, J = 6.8 Hz, 4H), 1.45 (p, J = 6.6 Hz, 4H), 1.37–1.29 (m, 8H). 13C NMR (151 MHz, CDCl3) δ 158.8, 157.9, 144.5, 139.8, 135.9, 125.4, 113.6, 111.0, 72.1, 71.4, 70.8, 70.7, 70.6, 70.2, 66.3, 59.2, 40.5, 37.9, 32.6, 30.4, 30.2, 30.1, 29.6, 26.7, 25.9. HRMS (ESI+) calcd. for [M+H]+: 1221.7731, found: 1221.7758.

Cis-4 was converted using the same amounts and the same method as for trans-4 to afford cis-SG1 (60.0 mg, 49.2 μmol, 61%) as a pale yellow solid. 1H NMR (400 MHz, CDCl3) δ 7.64 (d, J = 2.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 6.73 (dd, J = 8.3, 2.3 Hz, 2H), 4.00 (t, J = 5.9 Hz, 4H), 3.65–3.61 (m, 40H), 3.58–3.51 (m, 8H), 6.0.
3.43 (t, \( J = 6.6 \) Hz, 4H), 3.37 (m, 10H), 3.12 (t, \( J = 7.1 \) Hz, 4H), 2.95–2.86 (m, 4H), 2.84–2.75 (m, 4H), 2.00–1.92 (m, 4H), 1.56 (p, \( J = 6.6 \) Hz, 4H), 1.45 (p, \( J = 6.8 \) Hz, 4H), 1.34–1.29 (m, 8H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 159.4, 157.3, 141.7, 140.9, 135.6, 125.8, 114.4, 109.7, 72.1, 71.4, 70.8, 70.7, 70.6, 70.2, 65.9, 59.2, 40.3, 37.6, 35.4, 30.4, 30.3, 30.0, 29.6, 26.8, 26.0. HRMS (ESI+) calcd. for [M+H]:1221.7731, found: 1221.7753.

**Trans-SG2**

To a solution of compound 5 (60.0 mg, 97.1 \( \mu \)mol) in DMSO (2 mL) was added compound 10 (81.0 mg, 225 \( \mu \)mol) and triethylamine (30.0 \( \mu \)L, 21.0 \( \mu \)mol). The mixture was stirred at 60 °C for 16 h. After cooling to room temperature, water (5 mL) was added to the solution, followed by extraction with DCM. The organic layer was dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. The resulting viscous oil was dissolved in DCM (2 mL) and precipitated by adding pentane (8 mL). This process was repeated three times. After drying in vacuo pure trans-SG2 (73.0 mg, 61.2 \( \mu \)mol, 63%) was obtained as a pale yellow solid. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.19 (d, \( J = 8.2 \) Hz, 2H), 7.14 (d, \( J = 2.3 \) Hz, 2H), 6.77 (dd, \( J = 8.2, 2.3 \) Hz, 2H), 4.82 (t, \( J = 5.8 \) Hz, 2H), 4.60 (t, \( J = 5.6 \) Hz, 2H), 4.07 (t, \( J = 5.9 \) Hz, 4H), 3.75–3.70 (m, 4H), 3.67–3.58 (m, 40H), 3.55–3.51 (m, 4H), 3.44–3.36 (m, 8H), 3.19–3.10 (m, 8H), 3.07–3.01 (m, 4H), 2.03–1.96 (m, 4H), 1.58–1.05 (m, 4H), 1.50–1.41 (m, 4H), 1.36–1.29 (m, 8H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 159.0, 157.9, 144.5, 139.7, 135.9, 125.4, 113.6, 111.0, 72.8, 71.4, 70.7, 70.6, 70.4, 70.1, 66.3, 61.8, 40.5, 37.9, 32.6, 30.4, 30.2, 30.1, 29.5, 26.7, 25.9. HRMS (ESI+) calcd. for [M+H]: 1193.7418, found: 1193.7401.

**Trans-SG3**

To a solution of trans-4 (50.0 mg, 130 \( \mu \)mol) in DCM (3 mL) was added 1-isocyanatohexane (37.0 mg, 290 \( \mu \)mol). After stirring for 16 h at room temperature, the formed precipitate was filtered off, washed with DCM and then dried in vacuo to afford trans-SG3 (62.0 mg, 99.7 \( \mu \)mol, 77%) as a pale yellow solid. \(^{1}\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 7.23 (d, \( J = 8.3 \) Hz, 2H), 7.09 (d, \( J = 2.3 \) Hz, 2H), 6.81 (dd, \( J = 8.2, 2.2 \) Hz, 2H), 5.86 (t, \( J = 5.8 \) Hz, 2H), 5.78 (t, \( J = 5.7 \) Hz, 2H), 4.00 (t, \( J = 6.3 \) Hz, 4H), 3.18–3.08 (m, 8H), 3.08–2.96 (q, \( J = 6.6 \) Hz, 8H), 1.82 (p, \( J = 6.5 \) Hz, 4H), 1.33 (p, \( J = 6.8 \) Hz, 4H), 1.27–1.20 (m, 12H), 0.88–0.80 (m, 6H). \(^{13}\)C NMR (126 MHz, DMSO-\( d_6 \)) \( \delta \) 157.9, 157.4, 143.4, 138.6, 134.9, 124.8, 113.8, 110.3, 65.8, 36.2, 31.5, 30.6, 29.6, 29.3, 25.6, 21.5, 13.3. HRMS (ESI+) calcd. for [M+H]: 633.4374, found: 633.4376.

4. Isomerization behavior.

The photo-responsive behavior was studied by steady-state UV-Vis absorption and \(^{1}\)H NMR spectroscopy. The solvents, DMSO, toluene, and DMSO-\( d_6 \) were degassed by purging with argon for 30 min prior to use in the photoisomerization experiments followed by UV-vis absorption and NMR spectroscopy measurements.
Figure S2. UV-Vis absorption spectral changes of a sample of *cis*-SG1 (50 µM in toluene, 298 K) after irradiation with 385 nm light for 2 min to reach PSS$_{385}$ and upon subsequent irradiation with 365 nm light for 1.5 min to reach the PSS$_{365}$ (pink curve).

Figure S3. UV-Vis absorption spectral changes of a sample of *trans*-SG1 (30 µM in toluene, 298 K) after irradiation with 365 nm light for 1.5 min to reach the PSS$_{365}$ and upon subsequent irradiation with 385 nm light for 3 min to reach the PSS$_{385}$.

Figure S4. UV-Vis absorption spectral changes of a sample of *trans*-SG1 (10 µM in DMSO, 298 K) upon (a) irradiation with 365 nm light for 60 s to the PSS$_{365}$, and (b) subsequent irradiation with 385 nm light for 80 s to the PSS$_{385}$. 
Figure S5. Time-dependent UV−Vis absorption of cis-SG1 (30 µM) at 361 nm and 373 nm in toluene at 323 K for 16 h. No significant changes were observed during heating, indicating excellent thermal stability of cis-SG1 in toluene.

Figure S6. Time-dependent UV−Vis absorption of cis-SG1 (20 µM) at 361 nm and 373 nm in DMSO at 313 K for 20 h. No significant changes were observed during heating, indicating excellent thermal stability of cis-SG1 in DMSO.

Figure S7. UV−Vis spectral changes of (a) trans-SG2 upon irradiation with 365 nm light for 120 s to reach PSS_{365} and subsequent irradiation with 385 nm light for 150 s to obtain PSS_{385}, and (b) trans-SG3 upon irradiation with 365 nm light for 30 s to reach PSS_{365} and subsequent irradiation with 385 nm light for 90 s to obtain PSS_{385} (10 µM, DMSO, 298 K).
Figure S8. $^1$H NMR spectra (DMSO-$d_6$, 298 K, 400 MHz) of trans-SG2 (blue), a PSS$_{365}$ mixture ($cis:trans = 31:69$) of trans- and cis-SG2 after irradiation with 365 nm light for 20 min (green), and a PSS$_{385}$ mixture ($trans:cis \geq 99:1$) after subsequent irradiation with 385 nm light for 20 min (red).

5. Temperature-dependent supramolecular polymerization and data fitting with cooperative model.

Figure S9. Temperature-dependent degree of aggregation ($\alpha_{agg}$, estimated from the apparent absorption coefficients at $\lambda = 373$ nm) of trans-SG1 at different total concentrations ($c_T$) during the polymerization (cooling process, 1 K/min).
**Figure S10.** Temperature-dependent degree of aggregation \((\alpha_{agg})\) of trans-SG1 estimated from the apparent absorption coefficients at \(\lambda = 373\) nm at different total concentrations \((c_T)\) in toluene upon heating (1 K/min). The curves show fits calculated according to the cooperative model proposed by Meijer and co-workers.\(^4,5\)

**Table S1.** Molecular enthalpy \((\Delta H_e)\) during the elongation process of supramolecular polymerization and the critical elongation temperature \((T_e)\) of trans-SG1 at different total concentrations \((c_T)\) in toluene, resulting from fitting to a cooperative model.\(^4,5\)

| Concentration \((c_T)\) (mM) | 0.2  | 0.3  | 0.4  | 0.5  | 0.6  |
|-----------------------------|------|------|------|------|------|
| \(T_e\) (K)                 | 325.9489 | 329.5737 | 333.7055 | 335.5201 | 337.0752 |
| \(\Delta H_e\) (J mol\(^{-1}\)) | -40824.2309 | -42535.5892 | -47994.5302 | -57832.9615 | -65778.2513 |

The \(T_e\) values obtained from fitting (Table S1) are comparable to the ones in the van’t Hoff plots (Figure 3e, 325, 329, 332.5, 335.5, 338, respectively) obtained by the method proposed by Sugiyasu and co-workers.\(^6\) \(\Delta H_e\) in the cooperative model is the molecular enthalpy release due to the noncovalent interactions between monomers during elongation.\(^5\) The interaction between molecules and solvents are not included in \(\Delta H_e\). However, toluene has an effect on the assembly process\(^7\) to an extent that possibly affects \(\Delta H^o\) obtained from the van’t Hoff plot (\(-77\) kJ mol\(^{-1}\)).
6. $^1$H NMR dilution experiments.

Figure S11. $^1$H NMR spectra of cis-SG1 in toluene-$d_8$ at different concentrations, diluting from 1.0 mM to 0.3 mM (500 MHz, 293 K).

The spectra showed no obvious chemical shift for the protons of urea moieties at 5.8 and 5.5 ppm as the concentration decreased, indicating that cis-SG1 is likely monomeric in toluene.
7. Temperature-varied $^1$H NMR experiments.

Figure S12. (a) Temperature-varied $^1$H NMR spectra of trans-SG1 in toluene-$d_8$ recorded during heating from 293 K to 363 K (500 MHz, 0.5 mM). (b) Temperature-dependent N-H chemical shifts of urea.

8. FTIR studies

Toluene solution of trans- and cis-SG1 were measured on a PerkinElmer Spectrum 400 in a CaF$_2$ cell with 1.0 mm path length. Background correction was recorded for solvent and cell absorption.
Figure S13. FTIR spectra of trans-SG1 and cis-SG (0.5 mM) in toluene at 25 °C.

7. Computational study.
Structure optimizations of cis-SG1 and trans-SG1 in toluene (solvent model: IEFPCM) were performed in Gaussian 16 (B3LYP, 6-31G+(d,p)) using the GaussView 5.0 add-on. The dimer of trans-SG1 was optimized with ONIOM at the wB97X-D/def2SVP//wB97X-D/6-31G(d)/UFF level. The high level was modelled on the stilbene core, including the ureas and the atoms connecting the urea moieties and the photocwitch. The medium level was selected to be the methylene proximal to the ureas. All the remaining atoms were modelled with the low level. Figure 4d and S14 a shows the optimized geometry.

Figure S14. DFT energy minimized structures of trans-SG1.

8. Cryo-TEM study.
A toluene solution of trans-SG1 (0.4 mM) was cooled from 340 to 270 K at a rate of 1 K/min to form supramolecular polymer (SP-SG1). A toluene solution of cis-SG1 (0.4 mM) was prepared by in-situ irradiation for 3 min and then keeping in dark at 293 K for 1 h to afford SP-SG1. A few micro litter of each sample solution were placed on holey carbon-coated copper grids (Quantifoil 3.5/1, Quantifoil Micro Tools,
Jena, Germany). Grids with sample were vitrified in liquid nitrogen⁸ (Vitrobot, FEI, Eindhoven, The Netherlands) and transferred to a FEI Talos Arctica cryo-electron microscope operating at 200 keV with a postcolumn energy filter (Gatan) in zero-loss mode, with a 20-eV slit. A volta phase-plate was used with a phase shift of around $\frac{1}{4}\lambda$ to generate sufficient contrast between the organic solvent (toluene) and the organic supramolecular fibers. Typically, defocus around $-500$ nm was used for the measurements. Movies were recorded under low-dose conditions with a K2 summit direct electron detector (Gatan). Images were corrected for drift during the recording.

The supramolecular polymer (0.4 mM) is hundreds of nanometers in length with a uniform diameter of 2.5 nm (Figure 3b, main text). The cryo-TEM of a gel (1.5 mg/mL=1.2 mM, Figure 5e) did not show any noticeable changes in the diameter and length compared to the sample that formed supramolecular polymers but did not gelate (Figure 3b). Therefore, the size of the supramolecular polymer might not be the critical point for gelation. As the gelation happens above specific concentrations (Table 1), we assume the critical point is associated with the concentration of supramolecular polymers.

**Figure S15.** Cryo-TEM image of toluene gel formed by *trans-SG3* (1 mg/mL).
9. ^1^H NMR study on gel-sol transition.

![Figure S16](image)

**Figure S16.** ^1^H NMR (CDCl₃, 298 K, 400 MHz) spectral changes of a gel sample (trans-SG1, 1.5 mg/mL) before irradiation (red), after 365 nm light irradiation for 30 min to a sol sample (green) (trans:cis = 95:5). Samples were characterized after drying from toluene.

**Notes**

(1) In Figure 4c, the “polymerization” happened after the cis- to trans- isomerization with a specific lag time, suggesting no competition between the “polymerization” and cis- to trans- isomerization. As described in the review, “Once a critical concentration/temperature is reached, the nuclei start to grow and larger assemblies are formed” (Ref 4), turning points of nucleation to elongation are temperature or concentration.

(2) The distance between either nitrogen and the oxygen of cis-SG1 are 3.016 Å and 3.108 Å, which is slightly smaller than the distance (3.216 Å) of the cis-isomer in Ref 38. The minor difference might be attributed to the position of the urea group in the molecules. In that case, the urea group is attached directly to a robust overcrowded alkene-based core, which restricts the movement and the interaction between both urea groups. In our case, the urea groups are connected to the stilbene through a C3 alkyl chain linker, which offers more flexibility for the formation of intramolecular bonding with a slightly smaller distance.

(3) The theoretical analysis was performed on the temperature-dependent degree of aggregation (α_{agg}) in the heating process, which is an established method to study the mechanism of polymerization (Ref 23,33). There are no effects of the heating rate on the critical temperature (Figure 3d). Hence, this process is equilibrated. The discrepancy pointed out by the referee can also be found in other studies (Ref 32). ΔH_c in the cooperative model is the molecular enthalpy release due to the noncovalent interactions between monomers during elongation (Ref 23). The interaction between molecule and solvents is not included in ΔH_c. However, toluene has a non-negligible effect on the assembly process (Ref 61) that possibly affects ΔH° from the van’t Hoff plot but not the ΔH_c in the cooperative model fitting.
10. NMR spectra.

Figure S17. $^1$H NMR spectrum of trans-1 (CDCl$_3$, 25 °C, 400 MHz).

Figure S18. $^{13}$C NMR spectrum of trans-1 (CDCl$_3$, 25 °C, 151 MHz).
Figure S19. $^1$H NMR spectrum of cis-1 (CDCl$_3$, 25 °C, 400 MHz).

Figure S20. $^{13}$C NMR spectrum of cis-1 (CDCl$_3$, 25 °C, 101 MHz).
Figure S21. $^1$H NMR spectrum of trans-2 (DMSO-$d_6$, 25 °C, 400 MHz).

Figure S22. $^{13}$C NMR spectrum of trans-2 (DMSO-$d_6$, 25 °C, 151 MHz).
Figure S23. $^1$H NMR spectrum of cis-2 (CDCl$_3$, 25 °C, 400 MHz).

Figure S24. $^{13}$C NMR spectrum of cis-2 (CDCl$_3$, 25 °C, 101 MHz).
Figure S25. $^1$H NMR spectrum of trans-3 (CDCl$_3$, 25 °C, 400 MHz).

Figure S26. $^{13}$C NMR spectrum of trans-3 (CDCl$_3$, 25 °C, 101 MHz).
Figure S27. $^1$H NMR spectrum of cis-3 (CDCl$_3$, 25 °C, 400 MHz).

Figure S28. $^{13}$C NMR spectrum of cis-3 (CDCl$_3$, 25 °C, 101 MHz).
Figure S29. $^1$H NMR spectrum of trans-4 (CDCl$_3$, 25 °C, 400 MHz).

Figure S30. $^{13}$C NMR spectrum of trans-4 (CDCl$_3$, 25 °C, 151 MHz).
Figure S31. $^1$H NMR spectrum of cis-4 (CDCl$_3$, 25 °C, 400 MHz).

Figure S32. $^{13}$C NMR spectrum of cis-4 (CDCl$_3$, 25 °C, 151 MHz).
Figure S33. $^1$H NMR spectrum of 5 (DMSO-$d_6$, 25 °C, 400 MHz).

Figure S34. $^{13}$C NMR spectrum of 5 (DMSO-$d_6$, 25 °C, 151 MHz).
Figure S35. $^1$H NMR spectrum of compound 6 (CDCl$_3$, 25 °C, 400 MHz).

Figure S36. $^{13}$C NMR spectrum of compound 6 (CDCl$_3$, 25 °C, 151 MHz).
Figure S37. $^1$H NMR spectrum of compound 7 (CDCl$_3$, 25 °C, 400 MHz).

Figure S38. $^{13}$C NMR spectrum of compound 7 (CDCl$_3$, 80 °C, 101 MHz).
Figure S39. $^1$H NMR spectrum of compound 8 (CDCl$_3$, 25 °C, 400 MHz).

Figure S40. $^{13}$C NMR spectrum of compound 8 (CDCl$_3$, 25 °C, 151 MHz).
Figure S41. $^1$H NMR spectrum of compound 9 (CDCl$_3$, 25 °C, 400 MHz).

Figure S42. $^{13}$C NMR spectrum of compound 9 (CDCl$_3$, 25 °C, 101 MHz).
Figure S43. $^1$H NMR spectrum of compound 10 (CDCl$_3$, 25 °C, 400 MHz).

Figure S44. $^{13}$C NMR spectrum of compound 10 (CDCl$_3$, 25 °C, 101 MHz).
Figure S45. $^1$H NMR spectrum of trans-SG1 (CDCl$_3$, 25 °C, 400 MHz).

Figure S46. $^{13}$C NMR spectrum of trans-SG1 (CDCl$_3$, 25 °C, 151 MHz).
Figure S47. $^1$H NMR spectrum of cis-SG1 (CDCl$_3$, 25 °C, 400 MHz).

Figure S48. $^{13}$C NMR spectrum of cis-SG1 (CDCl$_3$, 25 °C, 151 MHz).
Figure S49. $^1$H NMR spectrum of trans-SG2 (CDCl$_3$, 25 °C, 400 MHz).

Figure S50. $^{13}$C NMR spectrum of trans-SG2 (CDCl$_3$, 25 °C, 151 MHz).
Figure S51. $^1$H NMR spectrum of trans-SG3 (DMSO-$d_6$, 25 °C, 400 MHz).

Figure S52. $^{13}$C NMR spectrum of trans-SG3 (DMSO-$d_6$, 80 °C, 126 MHz).
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