Photoresponsive supramolecular polymers

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Chapter 2
Photoinduced Supramolecular Polymerization and the Application in Responsive Organogels

Controlling supramolecular polymerization by external stimuli holds great potential toward the development of responsive soft materials and manipulating self-assembly at the nanoscale. Here we present photoresponsive stiff-stilbene based bis-urea monomers whose trans-isomers that readily form supramolecular polymers in a wide range of organic solvents enabling fast light triggered polymerization and reversible gel formation. Taking advantage of the stability of the cis-isomers and the high photostationary states (PSS) of the cis-trans isomerization, precise control over supramolecular polymerization and in-situ gelation could be achieved with short response times. A detailed study on the temperature-dependent and photoinduced supramolecular polymerization in organic solvent revealed a kinetically controlled nucleation-elongation mechanism. By applying a Volta phase plate to enhanced the phase-contrast method in cryo-EM, unprecedented for non-aqueous solutions, uniform nanofibers were observed in organic solvent.

2.1 Introduction

As highly-organized assemblies, supramolecular polymers play a distinct role in various areas of chemistry, biology and material science,\cite{1-10} and functional systems including application in responsive sensors,\cite{7,9} electronic devices,\cite{8} and biomedical materials.\cite{5,10} They are also ideal candidates for the formation of supramolecular gels,\cite{11-13} which hold great potential based on their intricate properties,\cite{14-17} such as chiral selection,\cite{18} amplification,\cite{19} and microactuation.\cite{20,21} Elegant mathematical models have been developed for different types of polymerization mechanisms,\cite{1-4} e.g. isodesmic,\cite{22} cooperative\cite{23,24} and others,\cite{25,26} revealing the dynamic and tunable nature of synthetic supramolecular systems and providing the tools for controlling their assembly processes.\cite{27-29} Recent advances have focused on manipulating the supramolecular polymerization by using external stimuli, e.g. ultrasound,\cite{30,31} light,\cite{32,33} and chemicals,\cite{34,35} in order to develop responsive and adaptive materials.\cite{5,7,10,36}

Among these stimuli, light has the distinct advantage of allowing direct control of responsive materials through the non-invasive action with high spatiotemporal resolution.\cite{37-41} One of the main approaches to realize reversibility in supramolecular assemblies exploits the photoisomerization of molecular switches,\cite{42-46} such as azobenzenes\cite{43,44,46} and dithienylethenes.\cite{18,19} The majority of the recent studies on supramolecular assemblies focus on the photoregulation of the responsive properties associating with the disassembly and reconfiguration of aggregates,\cite{14-18,47} e.g. gel-sol transition,\cite{43} volume\cite{44} and morphology\cite{46} changes, while limited effort has been devoted to trigger the actual supramolecular polymerization step by using light.\cite{32,33} Notably, Meijer and co-workers reported a cooperative polymerization, where a photoswitchable ligand regulated the fraction of stacked porphyrin monomers.\cite{32} Subsequently, Takeuchi et al. demonstrated a photoregulated living supramolecular polymerization by combining polymerization and photoisomerization of azobenzene derivatives, in which the activation of the monomer was achieved by cis to trans photoisomerization or thermal reversion.\cite{33} However, control on the macroscopic properties of these supramolecular polymers was not discussed, and these photoinduced supramolecular polymerizations were based on azobenzene-monomers\cite{33} or ligands\cite{32}: This photoswitch has the intrinsic disadvantage of cis-trans thermal back-isomerization which limits the bi-stability of the system.

Here we report a light controlled self-assembly process based on a photoresponsive stiff-stilbene bis-urea monomers which forms supramolecular polymers and responsive gels (Figure 2.1). Notably, the thermal isomerization between cis- and trans-isomers of stiff-stilbene is negligible at room temperature due to the high energy barrier for interconversion.\cite{45,49,50} This property offers the opportunity to design a robust bi-stable
system in which supramolecular polymerization can be controlled by irradiation. A series of responsive monomers was obtained based on the stiff-stilbene core bearing two symmetrical urea moieties with different end groups (SG1–SG3). According to the definition of Meijer et al.,\textsuperscript{2,3} the obtained 1 D assemblies qualify as supramolecular polymers. The outstanding ability of the urea groups to self-assemble has been demonstrated in previous studies by our group\textsuperscript{39,51,52} and others.\textsuperscript{53–55} In the present design, bis-ureas form intermolecular hydrogen bonds between the trans-isomers, in contrast to the intramolecular hydrogen bond, formed when the molecule is in its cis-form. Based on these different hydrogen bonding patterns, starting from a cis-isomer (inactive monomer), the polymerization only takes place after conversion to the trans-isomer (active monomer). In other words, the active monomer can be "unlocked" from the dormant state upon irradiation. Hence, we could design a bi-stable supramolecular system benefitting from the high energy barrier between isomers and precisely control its assembly with light in a reversible manner (Figure 2.1). The mechanisms of temperature-dependent polymerization were studied in detail in toluene. We further developed these supramolecular polymers to functional gels with photo-controlled sol-gel transitions.

![Figure 2.1. Schematic illustration of the photo-isomerization of SGs, supramolecular polymerization of trans-SG1, and the process of assembly and disassembly in organic solvents.](image)

### 2.2 Results and Discussion

#### 2.2.1 Molecular design and synthesis

The stiff-stilbene monomers were designed with a photoresponsive core with two urea groups enabling intermolecular (trans-isomers) and intramolecular hydrogen-bonding (cis-isomers, see Figure 2.1). Hexaethylene glycol and hexaethylene glycol methyl ether served as the end group of SG1 and SG2, respectively, and connected to the urea group through
alkyl-linkers. The detailed synthesis routes for trans- and cis-isomers of SGs are summarized in Scheme 2.1, and pure trans-isomers of SG1, SG2, SG3 as well as cis-SG1 were obtained. All the novel structures were confirmed unambiguously by 1H, 13C NMR, and high-resolution ESI-MS.

Scheme 2.1. Synthesis of trans-SG1, SG2, and SG3. (cis-SG1 was synthesized by the same method as trans-SG1 starting from cis-1)
2.2.2 Photoisomerization behavior in solution

The photoresponsive behavior of SG1 was studied in organic solvent by UV-Vis absorption and NMR spectroscopy at 298 K (Figure 2.2). A toluene solution of cis-SG1 (50 µM) has a characteristic strong absorption band at 320–390 nm in the UV-vis spectrum (Figure 2.2a). Upon 385 nm light irradiation for 2 min, the band at 370–390 nm disappeared with an increase of the absorption maxima at 340 and 360 nm, indicating the conversion of cis-SG1 to trans-SG1, in accordance with stiff-stilbene photoisomerization.49,50 A clear isosbestic point at 364 nm confirms the selective unimolecular cis- to trans- photoisomerization process. No further spectral change was observed upon prolonged irradiation, indicating that the photostationary state (PSS385) was attained. The resulting solution showed the reverse switching process upon 365 nm light irradiation (Figure 2.2b).

![Figure 2.2](image.png)

Figure 2.2. Changes in the UV−Vis absorption spectrum (toluene, 298 K) starting from (a) cis-SG1 (50 µM) upon irradiation with 385 nm light for 2 min to PSS385, (b) upon subsequent irradiation with 365 nm light for 1.5 min to reach the PSS365, (c) trans-SG1 (30 µM) upon irradiation with 365 nm light for 1.5 min to PSS365, (d) upon subsequent irradiation with 385 nm light for 3 min to reach the PSS385

For trans-SG1, a band appears at 370–390 nm with a decrease of the absorption at 340–360 nm and a clear isosbestic point at 364 nm upon 365 nm light irradiation for 1.5 min, as a consequence of the photoisomerization process from the trans- to the cis-isomer (Figure 2.2c). A nearly identical spectrum as for trans-SG1 was recovered after subsequent
irradiation with 385 nm light for 3 min (Figure 2.2d). This photoisomerization behavior was also demonstrated in DMSO by UV-Vis absorption spectroscopy (Figure 2.3). It was noted that cis-SG1 showed no significant thermal-induced switching to trans-SG1 after heating at 323 K for 16 h or 313 K for 20 h in toluene and DMSO, respectively (Figure 2.4), indicating excellent thermal stability of cis-SG1.

Figure 2.3. 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 PSS365, and (b) subsequent irradiation with 385 nm light for 80 s to the PSS385.

Figure 2.4. Time-dependent UV–Vis absorption of cis-SG1 (20 µM) at 361 nm and 373 nm in (a) toluene at 323 K for 16 h, (b) DMSO at 313 K for 20 h.

The 1H NMR spectrum of trans-SG1 in DMSO-d6 solution (4.0 mM) shows distinctive proton shifts upon photoisomerization. The proton signal of H<sup>a</sup> (δ = 7.10 ppm) shifts downfield to 7.50 ppm, while H<sup>b</sup>, H<sup>c</sup> and H<sup>d</sup> shift upfield upon 365 nm light irradiation for 15 min (Figure 2.5a, 5b), indicating the conversion from trans-SG1 to cis-SG1. Integration of the NMR signals established a PSS<sub>365</sub> ratio of 33:67 (cis:trans). Subsequent irradiation with 385 nm light for 15 min resulted in the full recovery of the initial 1H NMR spectrum of trans-SG1 with a high PSS<sub>385</sub> ratio around 99:1 (trans:cis, Figure 2.5c). Essentially identical photoisomerization processes were observed for SG2 and SG3 (Figure 2.6 and 2.15).
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This photoisomerization behavior was also demonstrated in DMSO by UV-Vis absorption spectroscopy (Figure 2.2d). It was noted that cis-SG1 showed no significant thermal-induced switching to trans-SG1 after heating at 323 K for 16 h or 313 K for 20 h in toluene and DMSO, respectively (Figure 2.2e), indicating excellent thermal stability of cis-SG1.

Figure 2.3. 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 PSS365, and (b) subsequent irradiation with 385 nm light for 80 s to the PSS385.

Figure 2.4. Time-dependent UV−Vis absorption of cis-SG1 (20 µM) at 361 nm and 373 nm in (a) toluene at 323 K for 16 h, (b) DMSO at 313 K for 20 h.

The 1H NMR spectrum of trans-SG1 in DMSO-d6 solution (4.0 mM) shows distinctive proton shifts upon photoisomerization. The proton signal of Hɑ (δ = 7.10 ppm) shifts downfield to 7.50 ppm, while Hb, Hc and Hd shift upfield upon 365 nm light irradiation for 15 min (Figure 2.5a, 5b), indicating the conversion from trans-SG1 to cis-SG1. Integration of the NMR signals established a PSS365 ratio of 33:67 (cis:trans). Subsequent irradiation with 385 nm light for 15 min resulted in the full recovery of the initial 1H NMR spectrum of trans-SG1 with a high PSS385 ratio around 99:1 (trans:cis ≥ 99:1).

Figure 2.5. 1H NMR spectra (DMSO-d6, 298 K, 400 MHz) of trans-SG1 (4 mM), (d) after irradiation with 365 nm light for 15 min to PSS365 (cis:trans = 33:67), as well as (e) after subsequent irradiation with 385 nm for 15 min to PSS385 (trans:cis ≥ 99:1).

Figure 2.6. UV−Vis spectral changes of (a) trans-SG2 upon irradiation with 365 nm light for 120 s to reach PSS365 and subsequent irradiation with 385 nm light for 150 s to obtain PSS385, and (b) trans-SG3 upon irradiation with 365 nm light for 30 s to reach PSS365 and subsequent irradiation with 385 nm light for 90 s to obtain PSS385 (10 µM, DMSO, 298 K).

2.2.3 Temperature-dependent supramolecular polymerization in toluene.

To investigate the self-assembly process, changes in the UV-Vis absorption spectrum of trans-SG1 (0.4 mM) in toluene were recorded upon cooling from 340 to 270 K at a rate of 1.0 K/min (Figure 2.7a). The absorption maxima at 343 and 359 nm of trans-SG1 decreased in the cooling process with formation of a new red-shifted band appearing around 373 nm, suggesting the formation of well-defined aggregates.2,35 The presence of a clear isosbestic point at 366 nm and the red-shifted spectra are characteristic for the transition from monomeric trans-SG1 to a supramolecular polymer (SP-SG1). To characterize the assembly
morphology of SP-\textbf{SG1} in toluene, a Volta phase-plate was used with cryogenic electron transmission microscopy (cryo-TEM).\textsuperscript{59–61} Because the contrast between carbon-based samples and carbon-based solvents is low, the standard method (without a Volta phase-plate) of defocusing the image to generate phase contrast loses the resolution to see tiny assemblies in organic solvent. With the phase-plate, phase contrast is generated close to the focus resulting in a better resolution. To the best of our knowledge this is the first time a phase-plate was successfully used for non-aqueous samples in cryo-EM. These images show that solutions of SP-\textbf{SG1} (0.4 mM) prepared following an identical procedure as for the UV-Vis studies contained nanofibers with a uniform diameter of 2.5 nm and hundreds of nanometers in length (Figure 2.7b). The diameter (2.5 nm) of the nanofibers is comparable to the molecular axis of the calculated structure (1.8 nm) using an n-layered integrated molecular orbital and molecular mechanics (ONIOM) approach (Figure 2.7c), while the intermolecular distance between two monomers was found to be 3.5 Å. The existence of intermolecular hydrogen bond was further tested by temperature-varied NMR experiments (Figure 2.8). The proton signals of the ureas (H\textsuperscript{1}, H\textsuperscript{2} in Figure 2.8 ) shift upfield upon heating, with $\Delta \delta / \Delta T = -7.99$ ppb/K and -8.17 ppb/K, respectively, which is comparable to the shift reported previously for hydrogen bond formed by urea groups.\textsuperscript{62} Based on these observations, the obtained supramolecular nanofibers of \textit{trans-\textbf{SG1}} are likely built by one-dimensional (1D) stacking of \textit{trans-\textbf{SG1}}. This 1D stacking mode is facilitated by the intermolecular hydrogen bonding of the urea moieties in the designed hydrophobic pockets and by the $\pi-\pi$ interactions between the stiff-stilbene core units (Figure 2.7c).
Figure 2.7. (a) Temperature-dependent changes in the UV-Vis absorption spectrum of trans-SG1 (0.4 mM) in toluene during cooling at a rate of 1.0 K/min. (b) Cryo-TEM image of SP-SG1 formed by trans-SG1 (0.4 mM) after supramolecular polymerization in toluene. (c) Calculated self-assembly structure of trans-SG1 using the ONIOM approach [wB97X-D/def2SVP//wB97X-D/6-31G(d)//UFF]. The distance between the urea groups in one molecule is 1.8 nm. The distance between two monomers is 3.5 Å. (d) Degree of aggregation ($\alpha_{agg}$, estimated from the UV-Vis absorption at 373 nm) of trans-SG1 (cT = 0.4 mM) as a function of temperature upon cooling and heating at different rates (0.5-2.0 K/min). (e) Natural logarithm of the reciprocal cT as a function of the reciprocal Te (van ‘t Hoff plot). (f) Schematic illustration of the nucleation–elongation process of trans-SG1.

Figure 2.8. Temperature-varied N-H chemical shifts belonging to urea moieties of trans-SG1 in $^1$H NMR spectra recorded during heating from 293 K to 363 K (0.5 mM, toluene-$d_8$, 500 MHz).

To identify the polymerization mechanism, we plotted the degree of aggregation ($\alpha_{agg}$), estimated from the absorption at $\lambda = 373$ nm, as a function of temperature. Non-sigmoidal curves were observed for trans-SG1 (0.4 mM) upon cooling and heating with sharp transition at the critical temperatures ($T_e'$ and $T_e$, respectively, Figure 2.7d), indicating a nucleation-elongation process. Notably, we observed a thermal hysteresis for the heating process with the critical temperature distinctly higher than for the cooling process (Figure 2.7d, 2.9 and 2.10). For instance, the critical temperature $T_e'$ (cooling process) was 303 K at 1.0 K/min, while $T_e$ (heating process) was observed at 333 K, which is much higher than $T_e'$ (Figure 2.7d, circles). Furthermore, the value of $T_e'$ was decreased from 307 to 301 K upon increasing the cooling rate from 0.5 to 2.0 K/min (Figure 2.7d, blue scatters). These data imply that the supramolecular polymerization of trans-SG1 proceeds under kinetic control.
Figure 2.9. 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, 1.0 K/min).

Figure 2.10. 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 (1.0 K/min). The curves show fits calculated according to the cooperative model proposed by Meijer and co-workers.\textsuperscript{24,23} On the contrary, we did not observe any notable effect of the heating rate on $T_e$, indicating that the disassembly process occurs under thermodynamic control (Figure 2.7d, orange scatters). We fitted the $\alpha_{agg}$ as a function of temperature with the cooperative model proposed by Meijer and coworkers,\textsuperscript{24,35} resulting in an elongation enthalpy value of $\Delta H_e = -48$ kJ mol$^{-1}$ (Figure 2.10). The degree of aggregation ($\alpha_{agg}$) at increasing total concentrations ($c_T$) was recorded as a function of temperature to afford a van ‘t Hoff plot, in which the natural logarithm of the reciprocal $c_T$ shows a linear relationship with reciprocal $T_e$ (Figure 2.7e). Standard enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) associated to the process are $-77$ kJ mol$^{-1}$ and $-165$ J mol$^{-1}$ K$^{-1}$, respectively, resulting in a Gibbs free energy ($\Delta G^\circ$) value of $-28$ kJ mol$^{-1}$ at 293 K, comparable to a known cooperative supramolecular polymerization driven by
hydrogen bond formation.\textsuperscript{33} The $\Delta H^\circ$ ($\sim$77 kJ mol$^{-1}$) value obtained from the van 't Hoff plot is more negative compared to $\Delta H_e$ ($\sim$48 kJ mol$^{-1}$) resulting from the cooperative model fitting. This discrepancy might be attributable to the interaction between toluene molecules and monomers\textsuperscript{64} that possibly affect $\Delta H^\circ$ from the van 't Hoff plot but not the $\Delta H_e$ in the cooperative model fitting. The unfavorable entropic term ($-T\Delta S > 0$) parallels the loss of degrees of freedom of the monomers upon polymer formation. Overall, these data suggest that the fibers of \textit{trans-SG1} were formed through a cooperative (nucleation-elongation) process.

2.2.4 Photoinduced supramolecular polymerization

In stark contrast to \textit{trans-SG1}, a toluene solution of \textit{cis-SG1} (0.4 mM) did not produce any aggregate observable via cryo-TEM. Moreover, \textit{cis-SG1} shows excellent solubility in toluene and possibly is monomeric, demonstrated by the constant chemical signal of urea moieties in well-resolved $^1$H NMR spectra of the compound at different concentrations (Figure 2.11). To clarify the reason for the difference, we performed FTIR measurements on the toluene solution of \textit{cis-} and \textit{trans-SG1} (Figure 2.12). \textit{Trans-SG1} shows a strong vibrational band centered at 3333 cm$^{-1}$, attributed to hydrogen-bonded N-H in urea moieties.\textsuperscript{55,65} \textit{Cis-SG1} shows a broader band centered at 3396 cm$^{-1}$, at higher wavenumbers than the band of \textit{trans-SG1} but lower than the free N-H stretching vibration (ca. 3445 cm$^{-1}$).\textsuperscript{66} These results suggest a different hydrogen-bonding pattern for N-H in the two photoisomers. The presence of intramolecular urea hydrogen bonds (revealed by DFT calculations, Figure 2.13d) might explain the lower ability of the \textit{cis}-isomer to form a supramolecular polymer compared to the \textit{trans}-form (Figure 2.17). The distances between either nitrogen and the oxygen were 3.016 Å and 3.108 Å, respectively, in the energy minimized structure of \textit{cis}-isomer, which is comparable to those observed for other bis-urea derivatives.\textsuperscript{39}
Figure 2.11. $^1$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).

Figure 2.12. FTIR spectra of trans-SG1 and cis-SG (0.5 mM) in toluene at 25 °C.
Consequently, it should be possible to initiate the supramolecular polymerization upon photoisomerization of the cis- to the trans-form (Figure 2.13e). To prove this concept, we irradiated a toluene solution of cis-SG1 (0.4 mM) with 385 nm light for 3 min to reach PSS. The solution was kept in the dark at 298 K to achieve supramolecular polymerization. The spectral changes upon irradiation, revealed a typical cis- to trans- photoisomerization in toluene (Figure 2.13a, purple curve). After irradiation, the spectra remained unchanged for 2 min, indicating no apparent formation of intermediates. The present lag time is associated with the nucleation process. Subsequently, an characteristic increase in absorption around 373 nm with an isosbestic point at 366 nm signaled the formation of aggregates, implying an elongation process (Figure 2.13a, green curves). Cryo-TEM images showed the presence of fibers with a uniform diameter of 2.5 nm and hundreds of nanometers in length (Figure 2.13b), confirming the formation of supramolecular polymers. The morphology of the photoinduced supramolecular polymers was identical to those formed by cooling a solution of trans-SG1 (vide supra).

To further understand the mechanism of photoinduced supramolecular polymerization, we analyzed the time-resolved UV-Vis traces at 373 nm of cis-SG1 in toluene at different concentrations (Figure 2.13c). With lower concentrations (0.2 mM and 0.4 mM), absorption at 373 nm first decreased due to cis- to trans- photoisomerization, and then increased after a lag time (19 min and 2 min, respectively), showing a sigmoidal transition, which is characteristic for an elongation process. These features confirmed that the photoinduced assembly process followed the cooperative (nucleation-elongation) polymerization mechanism. At the highest concentration (0.6 mM), the lag time is too short to be monitored (Figure 2.13c). The lag time for the polymerization of monomeric trans-isomers to the supramolecular polymer dramatically decreased with increasing concentration, indicating that polymerization is under kinetic control, which is in accordance with the study on the temperature-dependent process (vide supra). In conclusion, the supramolecular polymerization in this system is successfully triggered by light and these experiments confirm the cooperative (nucleation-elongation) mechanism in toluene (Figure 2.13e).
2.2.5 Gelation ability and solvent screening

Having established the supramolecular polymerization of trans-SG1 in toluene, we continued our investigation towards the development of a supramolecular gel in different solvents. To our delight, trans-SG1 showed excellent gelation ability in a wide range of solvents (Table 2.1, for more details, see the Experimental Section 2.5.1). As shown in Table 2.1, the critical gelation concentration (CGC) of trans-SG1 ranges from 1.3 mg/mL in toluene to 3.0 mg/mL in THF. Trans-SG1 can hence be categorized as a 'supergelator'.\textsuperscript{39,68,69} To explore the influence with respect to gelation ability of end groups with different polarity,\textsuperscript{56,70} trans-SG2 and -SG3 bearing hexaethylene glycol and alkyl chains were also investigated. The CGC values for trans-SG2 are relatively high (from 2.5 mg/mL to
7.5 mg/mL), which might be attributed to the higher polarity of trans-SG2. Trans-SG3 bearing only alkyl side chain formed gels in a range of organic solvent. Long fibers with a uniform diameter of 2.5 nm were observed by cryo-TEM in toluene (Figure 2.18). It should be emphasized that the incorporation of oligoethylene glycol in trans-SG1 and trans-SG2 in contrast to trans-SG3 enable these molecules to gelate not only in organic solvents but also in water. This property could be beneficial for these structures to be applied in the area of smart biomedical materials.6,1

### Table 2.1 Solubility and critical gelation concentrations of trans-SG1, SG2 and SG3 in different solvents.

<table>
<thead>
<tr>
<th>trans-isomer</th>
<th>wa</th>
<th>et</th>
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<th>chlor</th>
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<th>p-xylene</th>
<th>cyclohexane</th>
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<td>1.0</td>
<td>2.0</td>
<td>i</td>
<td>1.8</td>
</tr>
</tbody>
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a: mg/mL; i: insoluble during heating; s: soluble at room temperature; gp: gel-like precipitate

#### 2.2.6 In-situ gelation and gel-sol transition behavior

As the supramolecular gel is formed by non-covalent interactions, it offers the opportunity to realize macroscopic changes triggered by light.14–16 A toluene solution of cis-SG1 (1.5 mg/mL) was irradiated with 385 nm light for 3 min in a quartz cuvette at room temperature (Figure 2.14a). After irradiation, the sample gelated within 10 min (Figure 2.14b) and cryo-TEM images of the resulted gel showed the presence of fibers (Figure 2.14e), which are identical to that formed by temperature-dependent and photoinduced supramolecular polymerization (vide supra). The solution and gel samples were characterized by 1H NMR in CDCl3 after drying (Figure 2.14c,d). The signals of cis-SG1 (e.g., H4=7.64) had almost disappeared and a distinct set of signals (e.g., Ha = 7.13) belonging to the trans-isomer was observed, indicating a trans:cis ratio at PSS385 of 99:1. Upon subsequent irradiation with 365 nm light for 30 min, the gel transformed to sol again. The lower speed of trans to cis photoisomerization in the gel state compared to solution, where the PSS was reached within 15 min, is likely due to the confined space of molecules in the self-assembled fiber.15,71 To establish the ratio of trans- to cis-isomer after the gel-to-sol process, a gel formed by pure trans-SG1 (1.5 mg/mL) was irradiated to sol using the same procedure and characterized by 1H NMR in CDCl3 after drying (Figure 2.16). The ratio of trans- to cis-isomer in the sol sample was 95:5, indicating that already a small extent of trans- to cis-isomerization caused a gel-sol phase transition in this supramolecular system.72

In other words, the photo-triggered changes in macroscopic properties of the gel system based on this responsive supramolecular polymer were readily achieved through a switchable photoisomerization.
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2.3 Conclusion

In conclusion, we developed three stiff-stilbene based bis-urea monomers, characterized by cis-isomers acting as inactive monomers, while the trans-isomers serve as the active monomers for supramolecular polymerization. Thermodynamic studies on the polymerization and depolymerization of the active monomer (trans-SG1) demonstrated a cooperative supramolecular polymerization in toluene, which was under kinetic control. Due to the high energy barrier of thermal cis to trans isomerization, this supramolecular polymerization can be precisely triggered by light to form trans monomers at room temperature. The photoinduced polymerization followed the nucleation-elongation (cooperative) mechanism. Both processes, temperature dependent and photoinduced polymerization, were monitored by absorption spectroscopy and cryo-TEM with a Volta phase-plate. The present study established the precise photo-control on the supramolecular polymerization. The resulting polymers show remarkable gelation ability in various organic solvents and reversible changes in macroscopic properties, i.e. sol-gel transition, which creates opportunities for many potential applications in the field of smart and responsive materials.

2.4 Acknowledgements

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2.5 Experimental section

2.5.1 Materials and methods

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 MBraun 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. 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.³⁹ 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.
2.5.2 Synthesis and characterization

Trans-1 and cis-1\textsuperscript{23}

\(\text{TiCl}_4\) (10.8 mL, 98.6 mmol) was added to a suspension of \(\text{Zn}\) powder (12.9 g, 197.2 mmol) in anhydrous THF (120 mL). After heating at reflux for 2 h, 6-methoxy-1-indanone (8.00 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 \(\text{NH}_4\text{Cl}\) and extracted with \(\text{EtOAc}\). The organic layer was washed with brine and dried over \(\text{Na}_2\text{SO}_4\). 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 chromatograph (SiO\(_2\), pentane:EtOAc = 98:2) to afford cis-1 (1.60 g, 5.46 mmol, 11%) as a white solid. cis-1: \(\text{H}^1\) NMR (400 MHz, \(\text{CDCl}_3\)) \(\delta\) 7.70 (d, \(J = 2.5\) Hz, 2H), 7.22 (d, \(J = 8.3\) Hz, 2H), 6.80 (dd, \(J = 8.2, 2.5\) Hz, 2H), 3.81 (s, 6H), 2.99–2.92 (m, 4H), 2.89–2.82 (m, 4H). \(\text{C}^{13}\) NMR (101 MHz, \(\text{CDCl}_3\)) \(\delta\) 158.2, 141.8, 140.8, 135.6, 125.8, 114.4, 108.5, 55.7, 35.6, 30.1. Trans-1: \(\text{H}^1\) NMR (400 MHz, \(\text{CDCl}_3\)) \(\delta\) 7.22 (d, \(J = 8.2\) Hz, 2H), 7.18 (d, \(J = 2.4\) 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). \(\text{C}^{13}\) NMR (151 MHz, \(\text{CDCl}_3\)) \(\delta\) 158.8, 144.6, 139.6, 136.0, 125.4, 113.0, 110.4, 55.8, 32.7, 30.4. HRMS (ESI+) calcd. for \([\text{M}+\text{H}]^+: 293.1536, \text{found: 293.1537.}

Trans-2 and cis-2

To trans-1 (2.00 g, 6.80 mmol) was added a solution of \(\text{CH}_3\text{MgI}\) (3 M in \(\text{Et}_2\text{O}\)) (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 \(\text{NH}_4\text{Cl}\), then extracted with \(\text{EtOAc}\). The organic layer was washed with brine and dried over anhydrous \(\text{Na}_2\text{SO}_4\). 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. \(\text{H}^1\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 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). \(\text{C}^{13}\) NMR (151 MHz, DMSO-\(d_6\)) \(\delta\) 156.0, 143.7, 137.0, 134.9, 125.2, 114.4, 110.9, 31.8, 29.5. HRMS (APCI) calcd. for \([\text{M}+\text{H}]^+: 265.1231, \text{found: 265.1225.}\)

Cis-1 (500 mg, 1.70 mmol) was converted using the same method. The precipitate was filtered off and washed with DCM to afford trans-2 (71.0 mg, 0.269 mmol, 16%). The filtrate was concentrated in vacuo and purified by flash column chromatography (SiO\(_2\), \(\text{EtOAc}:\text{pentane} = 1:4\)) to afford cis-2 as a white solid (218 mg, 0.826 mmol, 49%). \(\text{H}^1\) NMR (400 MHz, \(\text{CDCl}_3\)) \(\delta\) 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$_3$) $\delta$ 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 g, 11.4 mmol) and K$_2$CO$_3$ (2.10 g, 15.2 mmol), and the mixture was stirred at 80 $^\circ$C overnight. After the reaction was complete, deionized water was added and the aqueous phase was extracted with EtOAc. The organic layer was washed with brine, dried over Na$_2$SO$_4$, and then 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 pale a 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, 0.663 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, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.2, 144.6, 139.7, 135.9, 125.4, 113.6, 111.1, 66.4, 39.5, 33.4, 32.7, 30.4. 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. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 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-diisopropylethylamine (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%). $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 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). $^{13}$C NMR (151 MHz, DMSO) $\delta$ 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 Na$_2$SO$_4$ 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. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 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). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 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]$^+$: 461.2721, found: 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 Na$_2$SO$_4$ 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, CDCl$_3$) $\delta$ 3.68–3.60 (m, 21H), 3.58–3.52 (m, 4H), 3.44 (t, $J = 6.6$ Hz, 2H), 3.37 (s, 3H), 2.33 (t, $J = 7.5$ Hz, 2H), 1.66–1.53 (m, 4H), 1.37–1.29 (m, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 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]$^+$: 461.2721, found: 461.2727.
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.

8

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 ºC 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, 20H), 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.

9

To a solution of hexaethylene glycol (2.30 g, 8.00 mmol) in 1BuOH (50 mL) was added 1BuOK (0.90 g, 8.00 mmol) and 2-(6-bromohexyl)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., 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.

10

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), 1.63–1.54 (m, 4H), 1.42–1.34 (m, 4H).
2H), 1.48–1.40 (m, 2H), 1.37–1.30 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 72.9, 71.4, 70.7, 70.6, 70.4, 70.2, 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 $\mu$mol) in DCM (3 mL) was added compound 8 (74.0 mg, 17.0 $\mu$mol). 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 $\mu$mol, 75%) was obtained as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 2.3 Hz, 2H), 6.76 (dd, J = 8.2, 2.3 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), 2.00 (p, J = 6.6 Hz, 4H), 1.54 (p, J = 6.8 Hz, 4H), 1.45 (p, J = 6.6 Hz, 4H), 1.37–1.29 (m, 8H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 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 $\mu$mol, 61%) as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19 (d, J = 8.2 Hz, 2H), 6.76 (dd, J = 8.2, 2.3 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), 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, 66.9, 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, 210 $\mu$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
Trans-SG3

To a solution of trans-4 (50.0 mg, 130 μmol) in DCM (3 mL) was added 1-isocyanatoctane (37.0 mg, 290 μmol). 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 μmol, 77%) as a pale yellow solid. 1H NMR (400 MHz, DMSO-d6) δ 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). 13C NMR (126 MHz, DMSO-d6) δ 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.

2.5.3 UV-vis spectroscopy study on photoisomerization

The photoresponsive behavior was studied by steady-state UV-Vis absorption. UV-vis spectra were recorded on a Hewlett-Packard HP 8543 Diode Array. The solvents, DMSO, and toluene, were degassed by purging with argon for 30 min prior to use in the photoisomerization experiments.
2.5.4 $^1$H NMR study on photoisomerization

Figure 2.15. $^1$H NMR spectra (DMSO-d$_6$, 298 K, 400 MHz) of trans-SG$_2$ (blue), a PSS$_{365}$ mixture (cis:trans = 31:69) of trans- and cis-SG$_2$ after irradiation with 365 nm light for 20 min (green), and a PSS$_{385}$ mixture (trans:cis ≥ 99:1) after subsequent irradiation with 385 nm light for 20 min (red).

Figure 2.16. $^1$H NMR (CDCl$_3$, 298 K, 400 MHz) spectral changes of a gel sample (trans-SG$_1$, 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.
2.5.5 FTIR studies

Toluene solution of trans- and cis-SG1 were measured on a PerkinElmer Spectrum 400 in a CaF2 cell with 1.0 mm path length. Background correction was recorded for solvent and cell absorption.

2.5.6 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 urea 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.8 Figure 4d and S14 a shows the optimized geometry.

![DFT energy minimized structures of trans-SG1.](image)

2.5.7 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 ¼ λ 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.
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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 2.1), we assume the critical point is associated with the concentration of supramolecular polymers.

Figure 2.18. Cryo-TEM image of toluene gel formed by trans-SG3 (1 mg/mL).
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 2.1), we assume the critical point is associated with the concentration of supramolecular polymers.

2.6 References


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