Photoresponsive supramolecular assemblies based on H-bonding

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Chapter 3

Motorized Photomodulator: Making A Non-photoresponsive Supramolecular Gel Switchable by Light

Introducing photo-responsive molecules offers an attractive approach for remote and selective control and dynamic manipulation of material properties. However, it remains highly challenging how to use a minimal amount of photo-responsive units to optically modulate materials that are inherently inert to light irradiation. Here we show that the application of a light-driven rotary molecular motor as a “motorized photo-modulator” to endow a typical H-bond-based gel system with the ability to respond to light irradiation creating a reversible sol-gel transition. The key molecular design feature is the introduction of a minimal amount (2 mol%) of molecular motors into the supramolecular network as photo-switchable non-covalent crosslinkers. Advantage is taken of the subtle interplay of the large geometry change during photo-isomerization of the molecular motor guest and the dynamic nature of a supramolecular gel host system. As a result, a tiny amount of molecular motors is enough to switch the mechanical modulus of the entire supramolecular systems. This study proves the concept of designing photo-responsive materials with minimum use of non-covalent light-absorbing units.

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3.1 Introduction

Stimuli-responsive (supra)molecular systems have aroused major attention in recent years as they offer attractive opportunities for designing synthetic materials with dynamic properties and functions. The applied external stimuli could be either physical or chemical e.g., light, temperature, pH, redox to control assembly and responsive behavior. Among them, light has been arguably recognized as one of the most versatile stimuli as it enables remote, selective, programmable and instant control over material properties with high spatiotemporal precision. Major advances have been made by incorporating photoswitches covalently in the materials of interest, such as polymers, frameworks, molecular cages, nanomaterials and surfaces, leading to dynamic control of structure and function in various applications.

Supramolecular gels, a family of soft materials made by noncovalent self-assembly of small molecules (gelators), are among the most attractive soft materials because of their simple structures and dynamic functions (e.g., self-healing properties). Making supramolecular gels responsive to light enables the remote control of phase transitions and mechanical properties of the materials, which has generated several intriguing opportunities to control function. However, the general design principle usually relies on the direct chemical derivation of gelators with photoresponsive units (e.g., azobenzenes, stiff-stilbenes, molecular motors), i.e., using photo-responsive gelators which brings at least three inherent drawbacks, including i) unavoidable inner filter effect, ii) tedious chemical modification procedures and notably often, iii) lack of chemical space for further functional expansion. A more photon-efficient way might be using a tiny amount of photoresponsive units as “photo-modulator” dopants, instead of the major building blocks of these soft materials, to control the global macroscopic properties of a supramolecular gel system that is inherently inert to a light stimulus.

Herein, we demonstrate that the first-generation molecular motor can be applied as such a “motorized photomodulator” that reversibly crosslinks supramolecular polymers, taking advantage of the large geometry change during the photo-isomerization process (Figure 1). The two arms of the molecular motor are modified with H-bonding sites structurally analogous to the small-molecule gelator PC4. The semi-flexible spacer provides geometrical freedom for the molecular motor core to maintain its photo-isomerization function. Racemic metastable cis-S1C2 can engage in multiple intramolecular H-bonds leading to a more compact structure while on the contrary racemic metastable trans-S1C2 is prone to intermolecular H-bonds resulting in an extended structure. The joint effect of the flexible spacer and rigid motor core of S1C2 makes it act as a double-site crosslinker,
instead of a co-monomer, thus leading to the attribute that a minimal amount of S1C2 (2 mol%) can remarkably lower the critical gelation concentration (CGC) because of different crosslinking topologies. As a result, the photoisomerization of S1C2 (2 mol%) can tune the macroscopic mechanical properties of the global supramolecular system and as a consequence can induce reversible sol-gel-sol transition by light irradiation. We envision that this design principle based on a “motorized crosslinker” can be extended to other supramolecular systems, providing opportunities for readily fabricating photo-responsive materials with dynamic functions.

Figure 1. Conceptual illustration of the photo-responsive behavior of molecular motors in our co-assembly system.
Chapter 3

3.2 Results and Discussions

3.2.1 Rotary behavior of S1C2 in solution

The gelator PC4, photomodulator racemic stable trans-S1C2 and stable cis-S1C2 were synthesized and fully characterized by NMR and HR-MS (see experimental details and spectra in SI). The unidirectional rotary behavior of trans-S1C2 was studied by UV-Vis and 1H NMR spectroscopy. A full 360° rotary cycle of a molecular motor contains two photochemical isomerization processes and two subsequent thermal helix inversion (THI) steps (Figure 2a).59 UV-Vis spectra showed that the absorption band of trans-S1C2 decreased upon irradiation at 325 nm, accompanied by the formation of a new absorption maximum at 356 nm (Figure 2b). The clear isosbestic point at 331 nm proved the unimolecular transformation during the photochemical process from stable trans-S1C2 to metastable cis-S1C2 (Figure S1). 1H NMR spectra quantified the photochemical conversion of the E/Z isomers. The downfield shift of the proton signals of Hb and Hd and upfield shift of Ha and Hc indicated the formation of metastable cis-S1C2 (stable trans : metastable cis = 40:60 at the photostationary state (PSS)) in accordance with our earlier functional 1st generation motors45,48. Subsequent warming the solution to 50°C led to the fading of the absorption band at 356 nm and resulted in a new stable absorption band at 310 nm (Figure 2b and S1), attributed to the selective conversion due to the thermal helix inversion (THI) process of unstable cis-S1C2 to stable cis-S1C2. The kinetics of the THI step were monitored in situ by UV-Vis spectroscopy, yielding half-life values of 62 h in THF and 67 h in toluene at 25°C, which are comparable with those reported in our previous studies.44,58 Irradiation of stable cis-S1C2 induced the second photochemical isomerization, which was characterized by 1H NMR with a ratio of 15:85 (stable cis to metastable trans) at -60°C (Figure 2d). After warming to room temperature, the upfield shift of Ha and Hb and the downfield shift of Hc and Hd proved the complete conversion during the fast THI process (Figure 2d). Combining all these data, it can be concluded that S1C2 exhibits the properties of a typical 1st generation molecular motor in solution.
3.2.2 Self-assembly properties of PC4 and S1C2

Next, the gelation properties of PC4 and S1C2 were studied in various solvents (Table S1 and S2). It is shown that only PC4 has excellent gelation capability with a very low critical gelator concentration (CGC = 0.9 mg/mL, 0.13 wt%) in alkane solvents, thus capable to act as a “super gelator”.48,61 The formed gels are translucent in n-alkanes but visibly transparent in cycloalkanes (Figure 3a). The morphology of the aggregates was determined by TEM (Figure 3c and S7). In n-heptane, PC4 formed wormlike ribbons with widths of 20-100 nm and lengths of hundreds of nanometres. In cyclopentane, the nanofibers were much thinner with a better dispersity (Figure 2c and S13), which explains the less turbid gel at higher concentrations than in n-alkanes. Therefore, cyclopentane was preferably used in this study because it allows for more homogeneous assemblies with less interchain entanglement. The mechanical properties of the resulting gels were investigated by rheology measurements (Figure S12). It is shown that the storage modulus (G’) was significantly larger than the loss modulus (G’’), indicating the nature of a soft gel network.52,63
Interestingly, gelator PC4 also exhibited liquid crystalline (LC) properties in the absence of solvents. Polarizing optical microscopy (POM) images showed a typical liquid-crystal state with a strong birefringence effect in the temperature region ranging from 102 °C to 133 °C, which was further confirmed by differential scanning calorimetric (DSC) analysis. X-ray diffraction (XRD) analysis was performed on PC4 samples prepared by quickly cooling the melt at different temperatures to investigate the different ways of intermolecular packing (Figure S15). The as-prepared PC4 powders show two sharp peaks at 3.96° and 7.93°, with a ratio of 1:2, indicating the lamellar crystalline phase with an interlayer distance of 2.2 nm. Meanwhile, the XRD pattern for the PC4 in the LC state showed multiple low-angle peaks which can be identified as two sets of molecular packing arrangement: one with two peaks at 3.80° and 6.53° with the ratio of 1:v3 attributed to a hexagonal lattice of a columnar structure; and the other containing four peaks at 4.17°, 7.27°, 8.33° and 11.01°, with the ratio of 1:v3:v4:v7.
3.2.3 Co-assembly properties of PC4 and S1C2

Having established the gelator properties, the supramolecular co-assembly of the photomodulator S1C2 with PC4 was investigated. One of the most direct evidence supporting the co-assembly behavior is that the presence of a tiny amount of S1C2 facilitates the gelation of PC4. A typical experiment was performed by adding 1 mol% of S1C2 into a 0.75 mg/mL solution of PC4, resulting in an increase in storage modulus after mixing (Figure 4a). Increasing the ratio of S1C2 led to the formation of gel, until the addition of 17 mol% of S1C2 when precipitates started to form. To investigate the mechanical properties of the resulting gel, rheological measurements were performed (Figure 4b and S15), showing how the mechanical properties varied as a function of the molar ratio of S1C2. In the absence of S1C2, a solution of PC4 (0.75 mg/mL) was observed instead of a gel because of the similar storage/loss modulus. Notably, the addition of S1C2 (from 0.2 mol% to 10 mol%) significantly increased the storage moduli of the system much higher than the loss moduli (Figure S16), confirming the sol-to-gel transition. Higher amounts of S1C2 did not facilitate gelation since the compound started to precipitate, thus yielding lower storage moduli. These results indicated that a tiny amount of S1C2 could act as a guest (non-covalent cross-linker) to facilitate gelation for the supramolecular gel system.

![Figure 4](image-url)

*Figure 4.* (a) Photographs showing the gelation property of PC4 below CGC (0.75 mg/mL) after adding different molar ratios of S1C2, reveal that a minimal amount of S1C2 facilitates the gelation of PC4. (b) The average value of
the storage moduli (G’) of the gel as a function of the molar ratio of S1C2. The comparison of DSC (c) and XRD (d) profiles of the dry gel containing different amounts of S1C2.

Furthermore, DSC was used to determine the thermal properties of the co-assemblies of PC4 and S1C2. The dry gel of PC4 showed an endothermic peak at 133 °C attributed to a phase transition from crystalline to isotropic. Upon co-assembly with 1 mol% of S1C2, the peak shifted to 129 °C, and further shifted to 125 °C with 10 mol% of S1C2. At the ratio of 50 mol%, the first peak at 61°C corresponding to the phase transition of S1C2 from crystalline to isotropic phase indicated the precipitation of S1C2. Further XRD analysis was also performed on these co-assemblies (Figure 4c), showing a collection of diffraction peaks consistent with the original PC4 after mixing with a minimal amount of S1C2, which supports the notion that the introduction of S1C2 did not affect the supramolecular packing of PC4. The shifted phase transition peaks in DSC and retained XRD diffraction peaks jointly indicate that S1C2 acts as a noncovalent crosslinker that does not affect the homo-assembly of PC4. To further understand the co-assembly, a reference motor molecule S1 was synthesized (see details in Section 3.6), featuring a more rigid and shorter spacer than present in S1C2. A control experiment was performed using S1 to co-assemble with PC4 (Figure S17) indicating that, different from S1C2, the addition of S1 did not facilitate the gelation of PC4 but only resulted in the formation of precipitates. This control experiment suggested the significance of the two ethylene linkages in S1C2 for the gelation behavior, which might be attributed to the enhanced flexibility and decreased steric hindrance in the supramolecular co-assembling system.

Based on the combined experimental results, it could be reasonably inferred that S1C2 acts as a supramolecular double-site crosslinker in the gel system (Figure S18 and 5a). Due to the introduction of the ethylene spacer, the S1C2 molecule is flexible and able to adjust its conformation for intra/inter- molecular co-assembly, i.e., the π-π stacking between phenyl moieties and the H-bonding between amide groups allow for the favored interactions of S1C2 with (assembled) PC4 molecules, thus functioning as a supramolecular crosslinker. On the contrary, due to the rigid structure of S1, the interactions between (assembled) PC4 molecules and S1 are not favored to form well-defined assemblies, resulting in precipitation from the solvent.

The quantification of “molecularly dissolved” S1C2 in the co-assembly system was investigated by UV-Vis spectroscopy. According to the Lambert-Beer law (\(A = K \cdot l \cdot c\)), the concentration of S1C2 can be quantified in co-assemblies. Figure S20b shows the data of prepared concentration (C_pre) and calculated concentration (C_cal) of S1C2 in co-assemblies, as the calculated maximum concentration (C_max) of co-assembled S1C2 in cyclopentane is \(3 \times 10^{-5}\) M (4.3×10^{-2} mg/mL). The solubility of S1C2 in cyclopentane is \(3 \times 10^{-7}\) M. Remarkably,
the solubility of $S1C2$ in cyclopentane is enhanced 100 times after dissolving $PC4$ indicating the $PC4$-fibre works as a solubilizer to dissolve $S1C2$.

3.2.4 Photoresponsive properties of the co-assemblies

UV-Vis spectroscopy was used to monitor the photochemical properties of molecular motor $S1C2$ in the co-assembled gel system (Figure 5c and 5d). After irradiating a thin layer of gel in a quartz cuvette with 325 nm UV light, a characteristic new absorption band at 352 nm appears with a clear isosbestic point at 330 nm ($trans$ to $cis$ isomerization), which is consistent with the observations in monomeric solution in THF (Figure 2b), indicating the formation of the metastable $cis$-isomer. This process was also accompanied with the visible decrease in viscosity of the gel sample in the cuvette, reaching a fluid solution at PSS (Figure 5b). Subsequent irradiation by 365 nm led to the disappearance of the absorption at 352 nm, with the same isosbestic point at 330 nm, confirming the inverse isomerization process, i.e., $cis$-to-$trans$ transition, which also restores the gelation process in the system. All these observations support the reversible switching capability of the supramolecular system under the control of irradiation.

Rheology measurements were performed to further characterize the switchable mechanical properties before and after light irradiation. The effect of the molar ratio of the dopant $S1C2$ was first investigated (Figure S22-24). The minimal amount of $S1C2$ was 2 mol% to make a notable change in which the $G'$ decreased from 3.5 Pa to 0.5 Pa after 10 min irradiation. When the amount of $S1C2$ was increased to 3 mol%, the $G'$ can be switched from 5.5 to 0.5 Pa (Figure 5e), showing the optimal modulation (factor of 10) of the mechanical properties. The inverse transition was performed by 365 nm irradiation and subsequent aging. Meanwhile, the $G'$ could be recovered to 7.8 Pa, indicating the complete recovery of the mechanical properties, consistent with the observation in the monomer solution (Figure 5f and S25).
Figure 5. (a) Representation of the packing behavior of PC4 and S1C2 in the co-assembly gel. (b) Photos of gel towards UV light of distinct wavelength. Changes in UV-Vis spectra of formed gel under irradiation (c) at 325 nm and (d) then 365 nm. (e) The change of G' with the irradiation time for different ratios of M_{S1C2} %. (f) The rheological measurement of gel before irradiation (black), after 10 min of 325 nm irradiation (red) and then irradiation at 365 nm (blue).

3.3 Conclusions

In summary, we successfully demonstrated the concept that using a minimal amount of molecular motors (2 mol%) functionalized with structural units related to a low-molecular-weight gelator, can endow an intrinsically non-photoresponsive supramolecular
gel system with light-controllable properties. Taking advantage of the large geometry change of the 1st-generation molecular motor during its photoisomerization process, the key design here is to use it as a supramolecular crosslinker to manipulate the crosslinking density in the supramolecular network. Rheology measurements showed that the mechanical properties of the co-assembled materials could be precisely tuned by light. This principle provides a conceptually novel strategy to design light-responsive supramolecular systems using molecular switches and motors. The use of a tiny amount of photo-responsive units are solving a few inherent issues that cannot be readily overcome in current systems, e.g., the low light penetration percentages due to the inner filter effect, and the bulk use of multifunctional elaborate monomer structures. Many future opportunities towards responsive systems can be envisioned such as the amplification of mechanical effects from a minimal amount of molecular motors, responsive liquid crystal elastomers and smart materials.

3.4 Acknowledgements

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3.5 Author Contributions

Y.S., J.S., Q.Z., and B.L.F. conceived the project and designed molecules of S1C2 and PC4. B.L.F. and D.-H.Q. guided the research. Y.S. and J.S. synthesized all compounds and performed on UV-Vis, 1H NMR. Y.S. J.S. and Q.Z. wrote the manuscript. D.-H.Q. and B.L.F. revised and finalized the manuscript.
3.6 Experimental Data

3.6.1 General Information

Chemicals were purchased from Aldrich, TCI or Merck and were used as received. Solvents for extraction and chromatography were technical grade. All solvents used in reactions were freshly distilled from appropriate drying agents before use. All reactions were performed under inert atmosphere (Ar). Analytical TLC was performed with Merck silica gel 60 F254 plates and visualization was accomplished by UV light. Flash chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM). Solvents for spectroscopic studies were of spectrophotometric grade (UVASOL Merck). Compounds 5,5′-(butane-1,4-diylbis(oxy))disopthalic acid (1), 5-(2-bromoethoxy)isophthalic acid (2) and (2,2′,4,4′,7,7′-hexamethyl-2,2′,3,3′-tetrahydro-[1,1′-biindenylidene]-6,6′-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) were prepared according to procedures described in the literature.68-70

Nuclear magnetic resonance (NMR) spectra were recorded on Varian AMX400 (\(^{1}H\): 400 MHz, \(^{13}C\): 100 MHz) and Varian Unity Plus (\(^{1}H\): 500 MHz, \(^{13}C\): 125 MHz) spectrometers. The deuterated solvents (CD\(_2\)Cl\(_2\) and CDCl\(_3\)) were treated with Na\(_2\)CO\(_3\), molecular sieves (4 Å) and degassed by argon prior to use. Chemical shifts are denoted in parts per million (ppm) relative to the residual solvent peak (CD\(_2\)Cl\(_2\): \(^{1}H\) δ = 5.32 ppm, \(^{13}C\) δ = 53.84 ppm; CDCl\(_3\): \(^{1}H\) δ = 7.26 ppm, \(^{13}C\) δ = 77.0 ppm). The splitting parameters are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets.

High-resolution mass spectrometry (HRMS) was performed on an LTQ Orbitrap XL spectrometer with ESI ionization.

UV-Vis absorption spectra were recorded on a Hewlett-Packard HP 8543 diode array with a Peltier heating/cooling element. The irradiation experiments were performed by fiber-coupled LEDs obtained from Thorlabs Inc.

Polarized optical microscopy (POM) investigations were performed using a microscope BX51 (Olympus).

Transmission electron microscopy (TEM) was used to image the morphology of gels on a FEI Tecnai T20 electron microscope, operating at 200 kV under low-dose conditions with a slow-scan CCD camera. The samples were vitrified in liquid nitrogen using the vitrobot.

Differential scanning calorimetry (DSC) was carried out on a TA Instruments DSC Q1000 calorimeter in a dry nitrogen atmosphere. Samples were cycled from 10 °C to 200 °C at a rate of 5 °C/min.

Rheological tests were performed on a TA Instruments Discovery HR-2 rheometer. The gel samples were placed under a 20-mm-diameter parallel plate with a gap of 0.2 mm at 20°C. X-ray diffraction (XRD) experiments were performed using a rotating anode X-ray powder diffractometer (18KW/D/max2550VB/PC) equipped with a copper target 18 KW (450 mA), a fully automated curved (plate) crystal graphite monochromator and a programmable variable slit system.
3.6.2 Synthesis and characterizations

Scheme S1. The synthesis route to PC4.

5,5’-(butane-1,4-diylbis(oxy))bis(N1,N3-didodecylisophthalamide) (PC4).

5,5’-(butane-1,4-diylbis(oxy))diisophthalic acid (1.1 g, 2.4 mmol) and triphenylphosphine (4.0 mg, 15.3 μmol) were suspended in thionyl chloride (12 mL). The mixture was heated at reflux for 1 h. The excess of thionyl chloride was removed in a stream of nitrogen. The resulting residue was cooled to RT. Dodecylamine (2.2 g, 12 mmol) was dissolved in dichloromethane (20 mL) and added to the residue. The solution was cooled to 0 °C and triethylamine (3.63 mL, 25.9 mmol) was added with stirring. The mixture was continued to stir for 12 h and the solution was concentrated under reduced pressure. The crude product was dissolved in dichloromethane (50 mL) and washed with water (2 × 50 mL). The organic solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, dichloromethane : methanol, 100:1 to 10:1) to give PC4 as a white solid (1.8 g, 68%). 1H NMR (400 MHz, CDCl3) δ 7.62 (s, 2H), 7.36 (d, J = 1.4 Hz, 4H), 6.63 (t, J = 5.7 Hz, 3H), 4.06 (s, 4H), 3.43 (q, J = 6.7 Hz, 8H), 1.93 (s, 4H), 1.65 – 1.54 (m, 13H), 1.25 (m, 77H), 0.87 (t, J = 6.6 Hz, 12H). 13C NMR (101 MHz, CDC13) δ 164.74, 137.10, 136.15, 127.28, 110.71, 110.49, 39.38, 31.51, 29.44, 29.30, 29.28, 29.25, 29.09, 28.96, 26.69, 22.20, 13.08. HRMS (ESI pos) calcd C68H119NaO6[M+H]+: 1087.9124, found 1087.9103.
Scheme S2. The synthesis route to racemic stable trans-S1C2 and stable cis-S1C2.

5-(2-bromoethoxy)-$N^1,N^3$-didodecylisophthalamide (3)

Compound 3 was synthesized by the same procedure as PC4. 5-(2-bromoethoxy)isophthalic acid (2.1 g, 3.5 mmol) and triphenylphosphine (3.0 mg, 11.5 $\mu$mol) were suspended in thionyl chloride (10 mL). The mixture was heated at reflux for 1 h. The excess of thionyl chloride was removed in a stream of nitrogen. The resulting residue was cooled to RT. Dodecylamine (1.9 g, 10.5 mmol) was dissolved in dichloromethane (20 mL) and added to the residue. The solution was cooled to 0 °C and triethylamine (2.5 mL, 17.8 mmol) was added with stirring. The mixture was continued to stir for 12 h and the solution was concentrated under reduced pressure. The crude product was dissolved in dichloromethane (50 mL) and washed water (2 x 50 mL). The organic solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, dichloromethane/methanol, 100:1 to 50:1) to give 3 as a white solid (1.8 g, 86%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73 (s, 1H), 7.45 (d, $J$ = 1.4 Hz, 2H), 6.20 (t, $J$ = 5.7 Hz, 2H), 4.41-4.38 (m, 2H), 3.44 (q, $J$ = 6.7 Hz, 4H), 1.61 (t, $J$ = 7.4 Hz, 4H), 1.25 (m, 36H), 0.87 (t, $J$ = 6.7 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.5, 158.4, 136.3, 120.0, 118.3, 117.9, 116.1, 68.2, 52.5, 40.4, 40.3, 31.9, 29.6, 29.5, 29.3, 28.9, 28.7, 27.0, 22.7, 14.1. HRMS (ESI pos) calcd C$_{34}$H$_{59}$BrN$_2$O$_3$[M+H]$^+$: 623.37818, found 623.37736.
Motorized Photomodulator: Making A Non-photoresponsive Supramolecular Gel Switchable by Light

5,5’-(((2S,E)-2,2’,4,4’,7,7’-hexamethyl-2,2’,3,3’-tetrahydro-[1,1’-biindenylidene]-6,6’-diyl)bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(N1,N3-didodecylisophthalamide) (racemic trans-S1C2)

Under nitrogen atmosphere, Cs₂CO₃ (1.6 g, 4.2 mmol, 6 eq) and compound 3 (1.3 g, 2.1 mmol, 3 eq) were placed in a 30 mL reaction vial with a stirring bar before the addition of the racemic stable trans-diol⁷¹,⁷² (0.25 g, 0.7 mmol, 1 eq) in dry DMF (5 mL). Then, the resulting mixture was allowed to be heated at 80 °C overnight. The reaction mixture was diluted with DCM (100 mL) and water (100 mL). The organic phase was dried over MgSO₄ and concentrated in vacuum to give a brown oil. The crude was purified by flash chromatography (silica gel, dichloromethane/methanol, 100:1 to 20:1) to obtain the pure product as a white solid (545 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, 2H), 7.55 (s, 4H), 6.62 (s, 2H), 6.24 (d, J = 4.8 Hz, 4H), 4.50 (s, 4H), 4.42 - 4.37 (m, 4H), 3.48 (q, J = 6.2 Hz, 8H), 2.90 (t, J = 6.3 Hz, 2H), 2.62 (dd, J = 10.24, 4.2 Hz 2H), 2.31 (s, 6H), 2.22 (s, 6H), 2.18 (d, J = 10.9 Hz, 2H), 1.64 (t, J = 5.8 Hz, 8H), 1.30 (m, 76H), 1.09 (d, J = 5.0 Hz, 6H), 0.90 (t, J = 4.9 Hz, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 166.4, 159.2, 155.7, 142.6, 141.7, 136.5, 134.7, 131.4, 120.8, 117.4, 116.0, 111.5, 67.4, 67.1, 42.2, 40.3, 38.4, 31.9, 29.6, 29.5, 29.3, 27.0, 22.7, 19.2, 18.7, 16.2, 14.1. HRMS (ESI pos) calcd C₆₈H₁₁₉N₄O₆[M+H]⁺: 1434.10569, found 1434.10124.

5,5’-(((2R,2’R,Z)-2,2’,4,4’,7,7’-hexamethyl-2,2’,3,3’-tetrahydro-[1,1’-biindenylidene]-6,6’-diyl)bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(N¹,N³-didodecylisophthalamide) (racemic cis-S1C2)

Racemic stable cis-S1C2 was synthesized from racemic stable cis-diol (100 mg, 0.28 mmol) by using the same method as for trans-S1C2. The cis-S1C2 was obtained as a white solid (210 mg, 51%). ¹H NMR (400 MHz, CDCl₃) δ 7.67 (s, 2H), 7.39 (s, 4H), 6.61 (d, J = 5.0 Hz, 6H), 4.31 (m, 2H), 4.22 (s, 6H), 3.43-3.34 (m, 10H), 3.06 (dd, J = 11.8, 3.2 Hz, 2H), 2.41 (d, J = 11.7 Hz, 2H), 2.27 (s, 6H), 1.60 (m, 13H), 1.38-1.27 (m, 81H), 1.10 (d, J = 5.3 Hz, 6H), 0.90 (t, J = 5.3 Hz, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 166.7, 166.4, 159.2, 159.0, 155.3, 142.6, 142.3, 140.9, 137.1, 136.5, 136.4, 130.7, 123.0, 117.4, 116.1, 116.0, 113.2, 67.7, 67.4, 67.1, 41.7, 40.3, 38.4, 38.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 27.1, 27.0, 22.7, 20.5, 19.2, 18.8, 18.7, 16.2, 14.5, 14.1. HRMS (ESI pos) calcd C₆₈H₁₁₉N₄O₆[M+H]⁺: 1434.10569, found 1434.10174.
Figure S1. UV-Vis spectra changes of trans-S1C2 (THF, 20 °C, 5×10⁻⁵ M) (a) upon irradiation at 325 nm for 30 min to reach the PSS state, (b) subsequent irradiation at 365 nm, (c) warming the sample at 60 °C for 5 h to finish the THI process. (d) Cis-S1C2 (THF, 20 °C, 6×10⁻⁵ M) upon irradiation with 325 nm for 40 min to reach the PSS state.
**Figure S2.** In situ $^1$H NMR monitored spectra of **trans-S1C2** (3 mM) under irradiation of 325 nm at 253 K in THF-$d_8$, black spectrum to red spectrum. A PSS ratio of stable **trans** : metastable **cis** = 20:80 was obtained.

**Figure S3.** In situ $^1$H NMR monitored spectra of stable **cis-S1C2** (3 mM) under irradiation of 325 nm at 213 K in THF-$d_8$, black spectrum to blue spectrum. A PSS ratio of stable **cis** : metastable **trans** = 15:85 was obtained.
Figure S4. Time-dependent absorption changes at 353 nm during the THI process of metastable cis-S1C2 in (a) THF and (c) toluene. The linear fitting of ln (k/T) by 1/T calculated by Eyring equation of metastable cis-S1C2 in (b) toluene and (d) THF, and (e) the summary of calculated thermodynamic parameters.

<table>
<thead>
<tr>
<th>solvent</th>
<th>$t_{1/2}$ (h)</th>
<th>$\Delta^\circ G^\circ$ (kJ/mol)</th>
<th>$\Delta^\circ H^\circ$ (kJ/mol)</th>
<th>$\Delta^\circ S^\circ$ (kJ/mol)</th>
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<tr>
<td>toluene</td>
<td>67</td>
<td>102.83</td>
<td>97.94</td>
<td>-16.68</td>
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<tr>
<td>THF</td>
<td>62</td>
<td>102.66</td>
<td>88.39</td>
<td>-43.43</td>
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Figure S5. UV-Vis spectra of stable \textit{trans-S1C2} in THF (black spectrum, $5 \times 10^{-5}$ M) under irradiation of 325 nm at (a) 313 K, (d) 318 K, (g) 323 K, (j) 328 K, (m) 333 K until the PSS state (metastable \textit{cis-S1C2}, pink spectrum) and the corresponding THI process at (b) 313 K, (e) 318 K, (h) 323 K (k) 328 K, (n) 333 K until the stable \textit{cis-S1C2} (blue spectrum). Time-
dependent absorption changes and the fitting line at (c) 313 K, (f) 318 K, (i) 323 K, (l) 328 K, (o) 333 K.

Figure S6. UV-Vis spectra of stable trans-S1C2 in THF (black spectrum, 5×10^{-5} M) under irradiation of 325 nm at (a) 328 K, (d) 333 K, (g) 338 K, (j) 343 K, (m) 348 K until the PSS state (metastable cis-S1C2, pink spectrum) and the corresponding THI process at (b) 328 K, (e)
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333 K, (h) 338 K (k) 343 K, (n) 348 K until the stable cis-S1C2 (blue spectrum). Time-dependent absorption changes and the fitting line at (c) 328 K, (f) 333 K, (i) 338 K, (l) 343 K, (o) 348 K.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>State (CGC)</th>
<th>Solvent</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
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<td>I</td>
<td>methylcyclohexane</td>
<td>P</td>
</tr>
<tr>
<td>n-hexane</td>
<td>G (1.2 mg/mL)</td>
<td>THF</td>
<td>S</td>
</tr>
<tr>
<td>n-heptane</td>
<td>G (0.9 mg/mL)</td>
<td>ethyl acetate</td>
<td>P</td>
</tr>
<tr>
<td>n-octane</td>
<td>G (0.9 mg/mL)</td>
<td>toluene</td>
<td>P</td>
</tr>
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<td>n-dodecane</td>
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<td>G (1.1 mg/mL)</td>
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<td>P</td>
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<tr>
<td>cyclohexane</td>
<td>G (3.0 mg/mL)</td>
<td>acetonitrile</td>
<td>I</td>
</tr>
</tbody>
</table>

Table S1. Summary of gelation properties of PC4 in organic solvents.

The number in brackets means the critical gelation concentration (CGC); G: gel; S: solution; P: precipitate; and I: insoluble.

Figure S7. The formed gels of PC4 in different solvents at CGC. The solvent is indicated on the vial. The formed gels are translucent in n-alkanes while visibly transparent in cycloalkanes.
Table S2. Solubility of trans-S1C2 and cis-S1C2 in tested solvents.

<table>
<thead>
<tr>
<th>solvents</th>
<th>trans-S1C2</th>
<th>cis-S1C2</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>cyclopentane</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>n-heptane</td>
<td>I</td>
<td>I</td>
</tr>
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<td>S</td>
</tr>
<tr>
<td>ethanol</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

S: solution; P: precipitate; and I: insoluble.

Figure S8. Photos of trans-S1C2 at the concentration of (a) 10 mg/ml (c) 5 mg/mL after cooling to room temperature in toluene. Cryo-TEM images of trans-S1C2 at (b) 10 mg/ml (d) 5 mg/mL. The scale bar is 500 nm.

The solubility of trans-S1C2 and cis-S1C2 were summarized in Table S2. None of them could form gel in all tested solvents. The formed floc-like precipitates in toluene (10 mg/mL) were measured by cryo-TEM. As shown in Figure S8, particles with ~500 nm diameter were discovered. No clear morphology was observed after decreasing the concentration to 5
mg/mL. The formed particles can be attributed to the aggregation of trans-S1C2. All in all, the trans-S1C2 molecule cannot form ordered self-assembly in present experiments. In addition, cis-S1C2 shows better solubility (higher than 10 mg/mL) in toluene, methylcyclohexane and cyclopentane. However, no gel was obtained in the tested solvent system.

The formation of intermolecular H-bond:

The $^1$H NMR chemical shift of the amide NH signal has a relationship with the formation of H-bond. The formation of intermolecular H-bond can be proved by variable-temperature $^1$H NMR measurement. The $\delta_{N-H}$ can be measured at different temperatures. The plots of $\delta_{N-H}$ vs T can be fitted by $y = A + Bx$, where the parameter B represents the $-\Delta\delta_{N-H}/\Delta T$ (ppb/K). The intermolecular/intramolecular H-bond exists if the value of B is higher than 4.

![Figure S9.](image)

(a) The molecular structure of PC4, the amide hydrogen which can form intermolecular H-bond is labeled in red. (b) The summary of $-\Delta\delta_{N-H}/\Delta T$ (ppb/K) at different
concentrations. Even in a low concentration of 0.05 mM, the value of $-\Delta \delta_{N-H}/\Delta T$ (ppb/K) is higher than 4, demonstrating the formation of intermolecular H-bond which gives an evidence for the low CGC of PC4. (c) Plots of $^1$H NMR chemical shifts of $\delta_{N-H}$ with increasing temperature at different concentrations. The black line is the fitting line. The $^1$H NMR spectra in CDCl$_3$ from 243 K (wine) to 283 K (red) at (d) 0.05 mM (e) 2 mM and (f) 20 mM. The $C_{max}$ of PC4 in CDCl$_3$ is 20 mM, so a higher concentration than 20 mM cannot be obtained.

**Figure S10.** (a) The molecular structure of trans-S1C2, the amide hydrogen which can form intermolecular H-bond is labeled in red. The summary of $-\Delta \delta_{N-H}/\Delta T$ (ppb/K) at different concentrations. Only at the concentration higher than 20 mM, the value of $-\Delta \delta_{N-H}/\Delta T$ (ppb/K) is higher than 4. (b) Plots of $^1$H NMR chemical shifts of $\delta_{N-H}$ with increasing temperature at
different concentrations. The black line is the fitting line. The $^1$H NMR spectra from 243 K (wine) to 283 K (red) at (c) 0.05 mM, (d) 2 mM, (e) 20 mM and (f) 50 mM.

Figure S11. (a) The molecular structure of cis-S1C2, the amide hydrogen which can form intramolecular H-bond is labeled in red, and a summary of $-\Delta\delta_{N-H}/\Delta T$ (ppb/K) at different concentrations. At the concentration of 0.05 mM, the value of $-\Delta\delta_{N-H}/\Delta T$ (ppb/K) is higher than 4 and does not change at 2 mM, which implies the formation of intramolecular H-bond. (b) Plots of $^1$H NMR chemical shifts of $\delta_{N-H}$ with increasing temperature at different
concentrations. The black line is the fitting line. The $^1$H NMR spectra from 243 K (wine) to 283 K (red) at (c) 0.05 mM, (d) 2 mM, (e) 20 mM and (f) 50 mM.

Based on the $^1$H NMR results, it can be concluded$^{74}$:

<table>
<thead>
<tr>
<th>molecule</th>
<th>H-bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC4</td>
<td>Inclined to form intermolecular H-bond even in low concentration</td>
</tr>
<tr>
<td>trans-S1C2</td>
<td>Only could form intermolecular H-bond in high concentration</td>
</tr>
<tr>
<td>cis-S1C2</td>
<td>Inclined to form intramolecular H-bond</td>
</tr>
</tbody>
</table>

Figure S12. Rheological properties of PC4 in cyclopentane at (a) 0.5 mg/mL, (b) 0.75 mg/mL, (c) 1.1 mg/mL at 20 °C. From the curves, the higher value of G’ than G” at the concentration of 1.1 mg/mL proved the gel state and CGC (critical gelation concentration) in cyclopentane.

Figure S13. Rheological property of PC4 in n-heptane (1.5 mg/mL, 20 °C).
**Figure S14.** TEM images of dry PC4-gel formed in n-heptane (scale bar = 200 nm). The concentration of sample is 1.5 mg/mL.

**Figure S15.** (a) DSC profile (20-200 °C, 5 °C/min) of PC4. (b) Pictures for showing the preparation of samples of LC-PC4 and I-PC4. (c) XRD results of PC4 in 3 states. **PC4 powder:** the pristine state (as-prepared). **LC-PC4:** heating to 120 °C (liquid crystal state) and cooling to room temperature. The corresponding 2θ are labeled, one set is labeled as purple, and the other set is labeled as black. **I-PC4:** heating to 134 °C (isotropic state) and cooling to room temperature.
Figure S16. Rheological properties of PC4 in cyclopentane with different mole ratio of S1C2 (\(M_{S1C2}\% (n \text{ mol}) = \frac{n_{S1C2}}{n_{S1C2} + n_{PC4}}\)) of (a) 0\%, (b) 0.2\%, (c) 1\%, (d) 1.5\%, (e) 2\%, (f) 3\%, (g) 5\%, (h) 9\%, (i) 17\%, (j) 33\%, and (k) a summary of \(G'\). The concentration of PC4 for each sample is 0.75 mg/mL.
**Figure S17.** Molecular structure of S1. Pictures of a mixture of PC4 (0.75 mg/mL) and S1 in cyclopentane with 3.2 mol% of n$_{S1}$ (n$_{PC4}$: n$_{S1}$ = 30:1) under (a) daylight and (b) 365 nm UV light.

**Figure S18.** Schematic illustration of the proposed crosslinker and unfavored co-monomer behavior of trans-S1C2 in PC4 assemblies and incapable co-assembly between trans-S1 and PC4. The proposed intermolecular interactions between trans-S1C2 and PC4 are indicated by blue dash (H-bonding) and grey dot (π-π stacking) lines.
Figure S19. (a) UV-Vis spectra of S1C2 in THF at different concentrations. (b) Linear fitting of the absorption at 323 nm with the concentration. According to the Lambert-Beer law: $A = K \cdot l \cdot c$, the $K_{323}$ is calculated to be $1.56 \times 10^4$ L/mol/cm.

Figure S20. (a) UV-Vis spectra of S1C2 with a reference of PC4 (0.75 mg/mL) in cyclopentane. According to the Lambert-Beer law, the concentration of S1C2 dissolved in cyclopentane can be calculated ($C_{cal}$) by the absorbance. (b) The points of prepare concentration ($C_{pre}$) vs calculation concentration ($C_{cal}$) of S1C2 in co-assemblies and the line of $C_{cal} = C_{pre}$. Starting from $30 \times 10^{-6}$ M, the points begin to deviate from the line of $C_{cal} = C_{pre}$, demonstrating the maximum concentration ($C_{max}$) of S1C2 in 1 mg/mL PC4 of cyclopentane is $3 \times 10^{-5}$ M ($4.3 \times 10^{-2}$ mg/mL). (c) UV-Vis spectra of S1C2 in cyclopentane. The sample for measurement was prepared by heating and cooling to RT and then shaking overnight. The spectra show no change when the added S1C2 is higher than $20 \times 10^{-6}$ M proving the limitation of solubility. The solubility of S1C2 in cyclopentane is calculated as $3 \times 10^{-7}$ mol/L ($4.3 \times 10^{-4}$ mg/mL).
Figure S21. (a) UV-Vis spectra of S1C2 with a reference of PC4 (0.75 mg/mL) in THF. (b) $C_{\text{cal}}$: the added S1C2 in 0.75 mg/mL of THF. $C_{\text{cal}}$: the calculated concentration by Beer-Lambert law with the value of absorption shown in the spectra. $C_{\text{cal}}$ is the same as $C_{\text{pre}}$ proving that S1C2 is dissolved in THF.

Figure S22. Rheological properties of the formed co-gel of S1C2 (0.01 mg/mL, 1 mol% of MS1C2) and PC4 (0.75 mg/mL) (a) before irradiation and after (b) 5 min, (c) 10 min, (d) 20 min and (e) 40 min irradiation. (f) Summary of change between average value of $G'$ and irradiation time.
Figure S23. Rheological properties of the formed co-gel of S1C2 (0.02 mg/mL, 2 mol% of M5S1C2) and PC4 (0.75 mg/mL) (a) before irradiation and after (b) 5 min, (c) 10 min, (d) 20 min and (e) 40 min irradiation. (f) The summary of change between the average value of $G'$ and irradiation time.

Figure S24. Rheological properties of the formed co-gel of S1C2 (0.03 mg/mL, 3 mol% of M5S1C2) and PC4 (0.75 mg/mL) (a) before irradiation and after (b) 5 min, (c) 10 min, (d) 20 min and (e) 40 min irradiation. (f) The summary of change between the average value of $G'$ and irradiation time.
Figure S25. Rheological properties of the formed co-gel of S1C2 (0.03 mg/mL, 1 mol% of M51C2) and PC4 (0.75 mg/mL) after 325 nm irradiation for 10 min then 5 min irradiation of 365 nm, (a) measured immediately, (b) heating at 40 °C for 20 min and aging for overnight at room temperature.
3.7 References

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