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Molecular Motors

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

Yahan Shan, Qi Zhang, Jinyu Sheng, Marc C. A. Stuart, Da-Hui Qu,* and Ben L. Feringa*

Abstract: 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 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 and create 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.

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.^[1] The applied external stimuli could be either physical or chemical e.g. light, temperature,

pH, redox to control assembly and responsive behavior.^[2] 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.^[3] Major advances have been made by incorporating photo-switches covalently in the materials of interests, such as polymers, frameworks, molecular cages, nanomaterials and surfaces, leading to dynamic control of structure and function in various applications.^[4]

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).^[5] Making supramolecular gels responsive to light enables the remote control of phase transitions and mechanical properties of the materials,^[6] 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),^[7] i.e. using photo-responsive gelators which at least brings 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 photo-responsive 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.^[8]

Herein, we demonstrate that the first-generation molecular motor^[9] can be applied as such a “motorized photo-modulator” 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 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)

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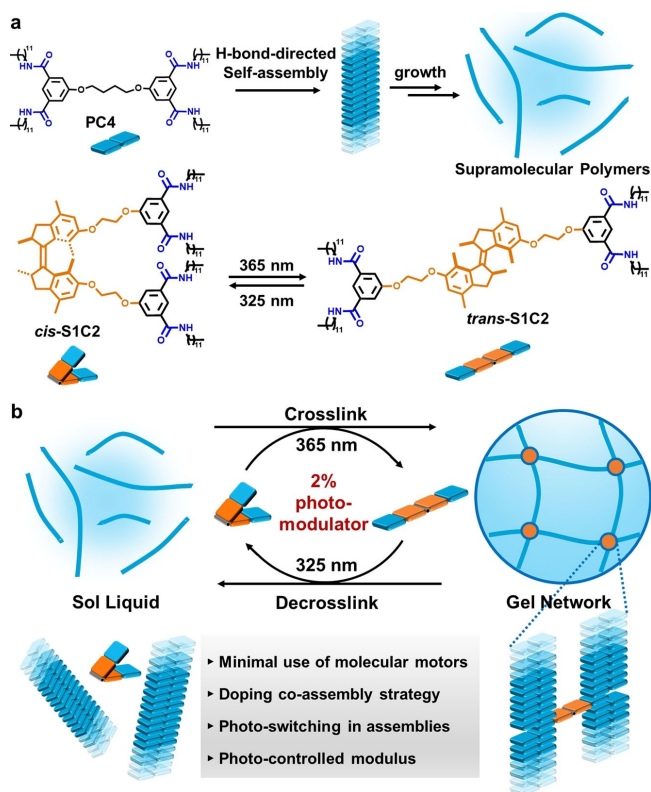


Figure 1. Conceptual illustration of the photo-responsive behavior of molecular motors in our co-assembly system.

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 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.

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 molecular motor contains two photochemical isomerization processes and two subsequent thermal helix inversion (THI) steps (Figure 2a).^[10] UV/Vis spectra showed that the absorption band of *trans*-**S1C2** decreased upon irradiation at 325 nm, accompanied with 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 H^b and H^d and upfield shift of H^a and H^c indicated the formation of metastable *cis*-**S1C2** (stable *trans*:metastable *cis*=40:60 at the photostationary

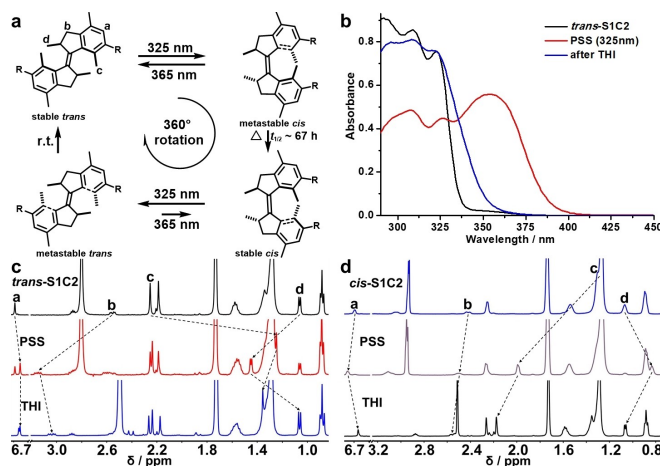


Figure 2. a) The unidirectional rotary cycle of molecular motor **S1C2**. b) UV/Vis spectra of stable *trans*-**S1C2** (black spectrum, 5×10^{-5} M, THF, 293 K), PSS₃₂₅ (metastable-*cis* state, red spectrum), and after THI (stable-*cis* state, blue spectrum). Partial ^1H NMR spectra (d_8 -THF, 3 mM) monitoring the unidirectional rotary cycle from (c) stable *trans*-**S1C2** (253 K) and (d) stable *cis*-**S1C2** (213 K).

state (PSS)) in accordance with our earlier functional 1st generation motors.^[7d,g] 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 in situ monitored 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.^[4c,11] 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 H^a and H^b and the downfield shift of H^c and H^d 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.

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”.^[7g,12] 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 width of 20–100 nm and length 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 rheol-

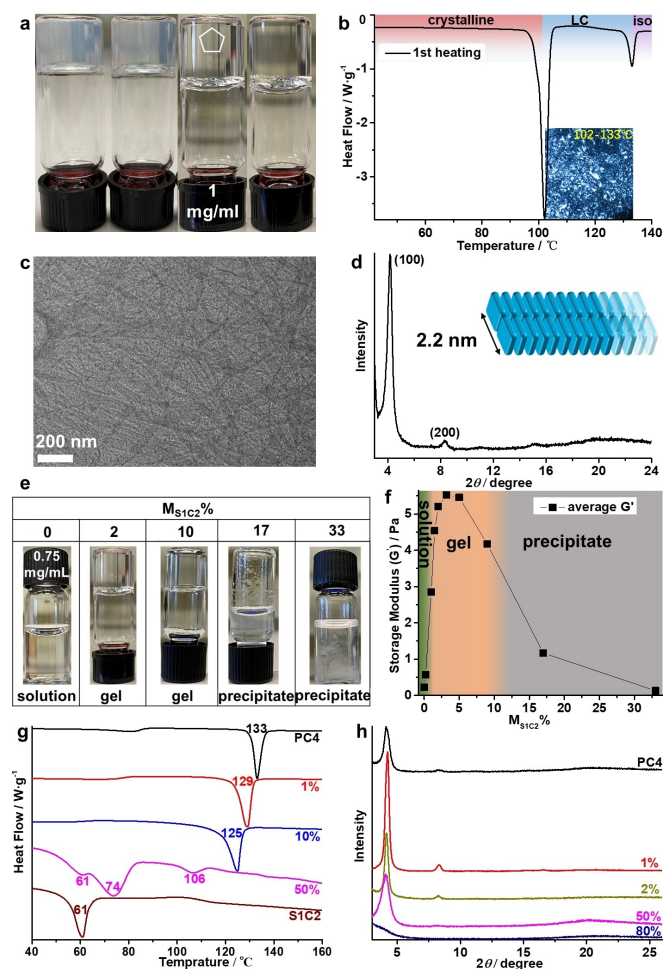


Figure 3. a) Photographs of the resulting organic gel of **PC4** in different solvents. b) DSC profile of **S1C2** powders showing the phase transition temperatures. The inset image shows the LC-phase pattern under POM. c) Representative TEM image of **PC4** gel in cyclopentane. d) XRD profile of the dry gel. The inset Scheme shows the lamellar packing and the corresponding d value. e) Photographs showing the gelation property of **PC4** below CGC (0.75 mg/mL) after adding different mole ratios of **S1C2**, reveal that a minimal amount of **S1C2** facilitates the gelation of **PC4**. f) The average value of the storage moduli (G') of the gel as a function of the molar ratio of **S1C2**. Comparison of the DSC (g) and XRD (h) profiles of the dry gel containing different amounts of **S1C2**.

ogy 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.^[13]

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 the ratio of 1:2, indicating the lamellar crystalline phase with an interlayer distance of 2.2 nm.^[14] 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 $1:\sqrt{3}$ 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 $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$.

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 3e). 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 3f 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.

Furthermore, DSC was used to determine the thermal properties of the co-assemblies of **PC4** and **S1C2**.^[15] 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 3h), 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 Supporting Information), 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 result 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-assembly 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 4a). 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 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 3×10^{-5} M (4.3×10^{-2} mg/mL). The solubility of **S1C2** in cyclopentane is 3×10^{-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**.

UV/Vis spectroscopy was used to monitor the photochemical properties of molecular motor **S1C2** in the co-assembled gel system (Figure 4c and 4d). 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 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 4b). 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–S24). 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, 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

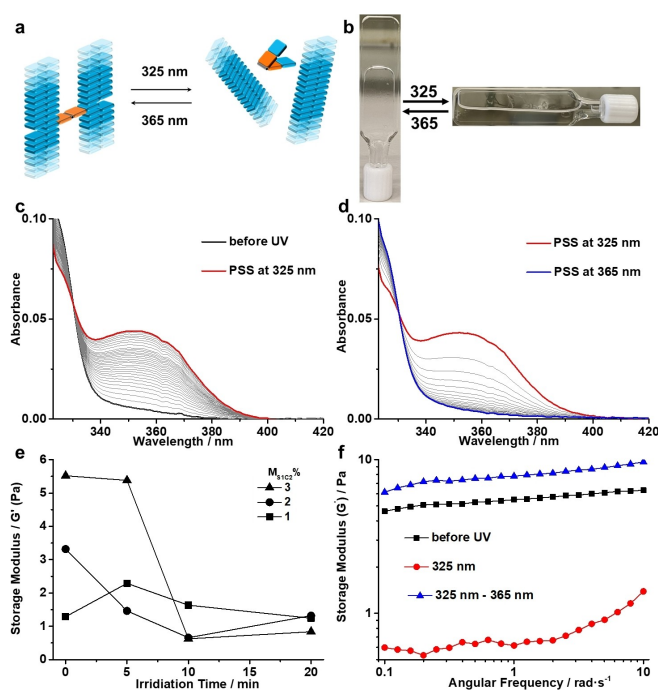


Figure 4. a) Representation of the packing behavior of **PC4** and **S1C2** in the co-assembly gel. b) Photos of gel towards UV light of distinct wavelength. Changes in UV/Vis spectra of the formed gel under irradiation (c) at 325 nm and (d) then 365 nm. e) The change of G' with the irradiation time 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).

recovery of the mechanical properties, consistently with the observation in monomer solution (Figure 2 and S25).

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-photo-responsive supramolecular gel system with light-controllable properties. Taking advantage of the large geometry change of 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 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.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Dynamic Systems · Molecular Motor · Organic Gel-Sol Transition · Photomodulator · Supramolecular Assembly

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