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COMMUNICATION

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Dissipative Supramolecular Polymerization Powered by Light

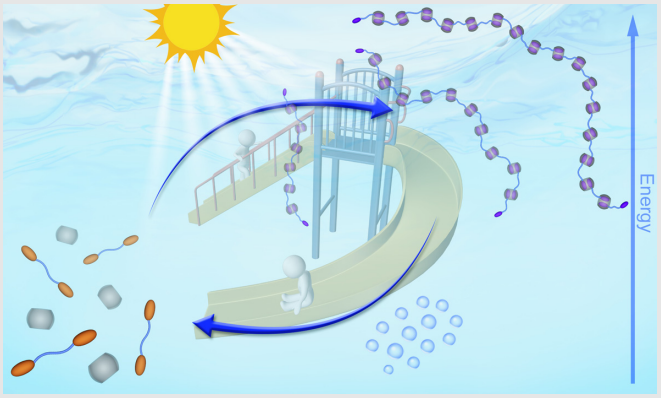
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A new method of light-powered dissipative supramolecular polymerization is established, in which supramolecular polymerization is implemented in the far-from-equilibrium state. A bifunctional monomer containing two viologen moieties was designed. Upon inputting energy by light, the system was driven far from equilibrium, and the monomers were photoreduced and activated to form supramolecular polymers driven by 2:1 host–guest complexation of the viologen cation radical and cucurbit[8]uril. As the system returned to equilibrium, the supramolecular polymers depolymerized spontaneously by air oxidation. This method works in both linear and in cross-linked supramolecular polymerization. The strategy of light-powered dissipative supramolecular polymerization is anticipated to have potential in the fabrication of functional supramolecular materials, especially in creating novel "living" materials.



Keywords: **supramolecular polymer, dissipative self-assembly, supramolecular chemistry, host-guest chemistry, dissipative supramolecular polymerization**

Supramolecular polymers are polymeric arrays of monomers held together by reversible and highly directional noncovalent interactions.[1-9] They have shown attractive potential in fabricating functional supramolecular materials with tailor-made properties such as self-healing, reversibility, stimuli-responsiveness, and easy processability.[10-30] For a long time, supramolecular polymers are mainly fabricated in thermodynamically equilibrium states or kinetically-trapped states.[31-43] If supramolecular polymerization can be implemented far from equilibrium, many unique properties, such as inherent dynamic nature, adaptivity, and spatiotemporal controllability, could emerge.[44-46]

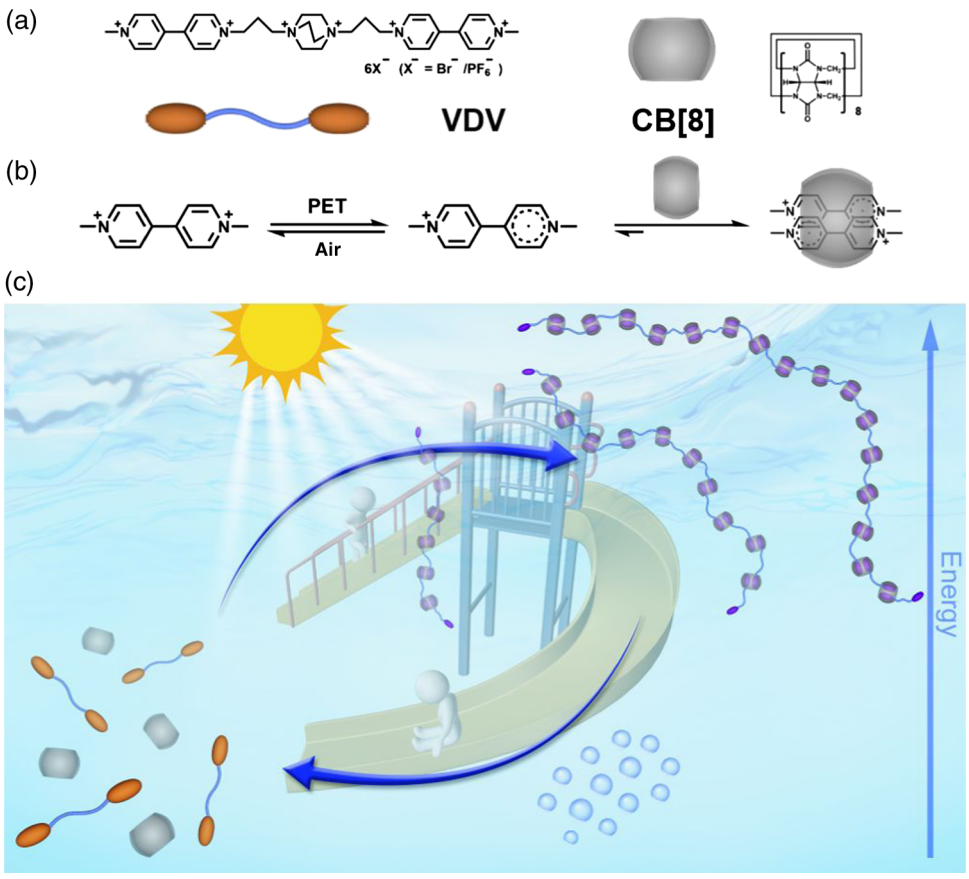
It is notable that far-from-equilibrium state is exactly where self-assembly systems in life operate and undertake crucial functions. These far-from-equilibrium systems, such as microtubule and actin filament, are fabricated through energy consuming processes, that is, dissipative self-assembly.[47] Owing to the energy dissipating nature, thermodynamically unreachable states can be realized, and unique properties not observed in equilibrium states emerge.[47-49] Through dissipative self-assembly, fascinating properties have been realized in man-made systems, such as lifetime control of transient materials, dynamic formation of patterns, and energy-driving motion.[47-60] Considering the advantages of far-from-equilibrium

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CCS Chem. **2019**, *1*, 335–342

systems, combining energy-dissipating process with supramolecular polymerization to achieve dissipative supramolecular polymerization becomes attractive. The dissipative supramolecular polymerization system could, in principle, be reversibly regulated between diverse states from equilibrium to far from equilibrium. Taking advantage of such a system which undergoes a continuous regulation process and can return to equilibrium spontaneously, it is hopeful to obtain supramolecular polymers with abundant properties and fruitful functions. This may open up a new way to mimic dissipative self-assembly in life and fabricate "living" materials closer to highly functional and precisely regulated supramolecular materials in nature.

Herein, we introduce a method of light-powered dissipative supramolecular polymerization in which supramolecular polymerization is implemented in far-from-equilibrium state. Light is a clean and controllable energy source to drive a system far from equilibrium.[57-60] Using light as energy source, it is easy to achieve temporal and spatial control over the dissipative supramolecular polymerization. What's more, the intensity and the wavelength of light can be easily controlled. To enable dissipative supramolecular polymerization, the following conditions should be simultaneously met: First, energy input is required to drive the system far from equilibrium wherein the monomers are activated to be supramolecularly polymerizable. Second, noncovalent interactions between activated monomers should be strong enough to promote supramolecular polymerization. Third, the inputted energy should be dissipated via a monomer deactivation process at a rate lower than that of the monomer activation process. Therefore, the far-from-equilibrium supramolecular polymer can not only form and exist with continuous energy supply, but also depolymerize when the energy source is removed and the system returns to equilibrium.

To this end, a bifunctional monomer, which contains two viologen moieties as end groups and a 1,4-diazabicyclo[2.2.2]octane (DABCO) moiety as a rigid linker [Viologen-DABCO-Viologen (VDV) in brief, Scheme 1], was designed. In an aqueous solution of equimolar amounts of VDV and cucurbit[8]uril (CB[8]), no supramolecular polymers could be formed because of the



Scheme 1 | *(a) Chemical structures of monomer VDV and CB[8], (b) redox reaction of viologen, and host–guest complexation of viologen cation radical and CB[8], (c) schematic diagram of dissipative supramolecular polymerization powered by light. VDV, viologen-DABCO-viologen; CB[8], cucurbit[8]uril; PET, photoinduced electron transfer.*

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CCS Chem. **2019**, *1*, 335–342

stable 1:1 host–guest complexation between viologen moiety and CB[8].[61–63] However, upon input of light energy, the system could be driven far from equilibrium, and the viologens could be reduced to viologen cation radicals ($V^{+\cdot}$) via photoinduced electron transfer (PET).[64–66] As $V^{+\cdot}$ can form a stable dimer inside the cavity of CB[8], the 1:1 complexation between viologen and CB[8] could be converted to a 2:1 complexation between $V^{+\cdot}$ and CB[8].[63,67–69] In this way, VDV could be activated to be supramolecularly polymerizable, and supramolecular polymers might be obtained far from equilibrium. Moreover, this far-from-equilibrium system may return to equilibrium upon removing the light energy, since $V^{+\cdot}$ are unstable in air and can be oxidized back to viologen by oxygen. This oxidation would convert the binding stoichiometry back to 1:1. Consequently, VDV could be deactivated and the supramolecular polymers disappear. By controlling the light intensity, the generation of $V^{+\cdot}$ can be made to occur faster than the oxidation process. We therefore envisioned that, based on the photoreduction of viologen and the dimerization of $V^{+\cdot}$ inside the cavity of CB[8], a dissipative supramolecular polymerization system could be realized with this approach.

We synthesized dimethyl viologen diiodide ($MV^{2+}2I^-$) as a model compound to confirm the photoreduction of viologen and the dimerization of $V^{+\cdot}$ inside the cavity of CB[8]. MV^{2+} was reduced via PET in aqueous solution using *N*-methyliminodiacetic acid (MIDA) as the electron donor (see Supporting Information).[64] Ultraviolet-visible

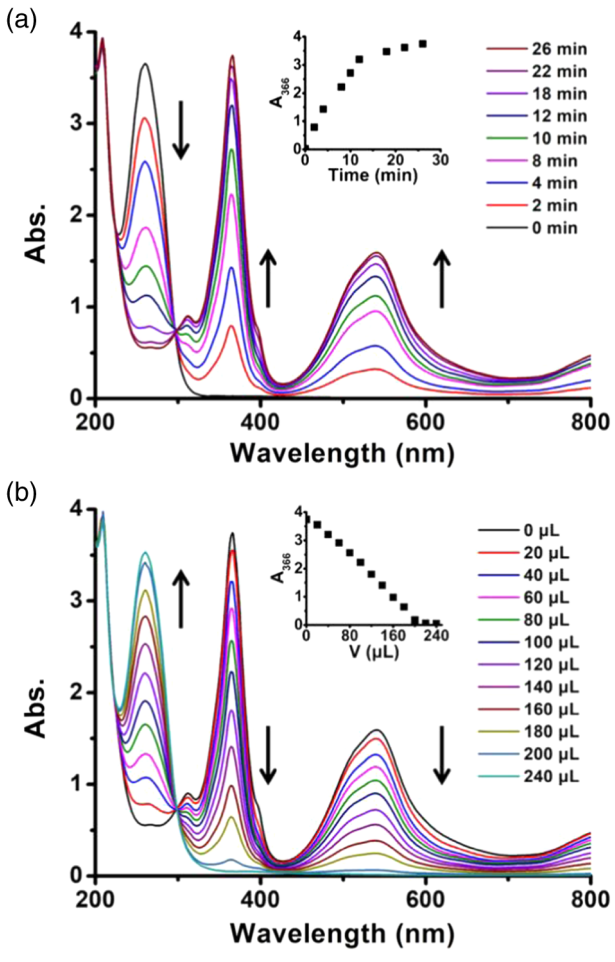


Figure 1 | *Ultraviolet-visible (UV–vis) spectra of VDV (1.0 mM) (a) by 254 nm UV irradiation at different times (inset: absorbance at 366 nm vs irradiation time), (b) when different volume of air was injected into the cuvette after irradiation (inset: absorbance at 366 nm vs volume of injected air). (CB[8]: 1.0 mM, MIDA: 20 mM, and pH 11.0.) VDV, viologen-DABCO-viologen; MIDA,* N*-methyliminodiacetic acid.*

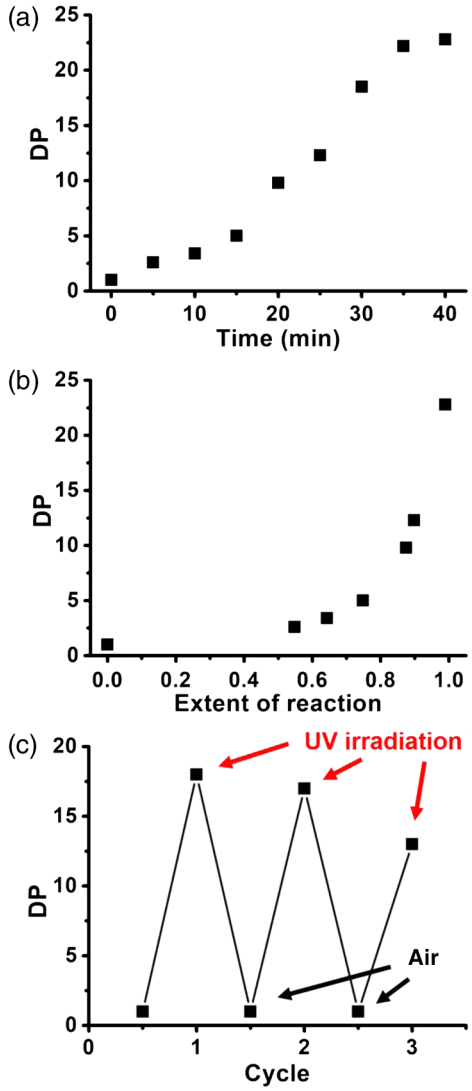


Figure 2 | *Degree of polymerization (DP) of the supramolecular polymer (a) versus UV irradiation time, (b) versus extent of reaction (calculated from the integral of* ^{1}*H NMR spectra), and (c) in multiple photoreduction–oxidation cycles (VDV: 1.0 mM, CB[8]: 1.0 mM, MIDA: 20 mM, and pH 11.0). VDV, viologen-DABCO-viologen; MIDA,* N*-methyliminodiacetic acid.*

DOI: 10.31635/ccschem.019.20190013
CCS Chem. **2019**, *1*, 335–342

(UV–vis) spectra and proton nuclear magnetic resonance (^{1}H NMR) spectra (Supporting Information Figures S9 and S10) indicated that MV^{2+} was reduced completely to dimethyl viologen cation radical (MV^{+}) via PET, and most MV^{+} existed in the dimeric form with 0.5 equivalent of CB[8]. This high conversion from viologen to $V^{+\cdot}$ dimer could facilitate the supramolecular polymerization process. Electron paramagnetic resonance (EPR) results (Supporting Information Figure S11) confirmed that almost all $MV^{+\cdot}$ existed as dimers with 0.5 equivalent of CB[8]. Taking both UV–vis spectra and EPR results into account, the apparent dimerization constant of $MV^{+\cdot}$ inside the cavity of CB[8] was estimated to be greater than 10^6 M^{-1}, which is high enough to drive the formation of supramolecular polymers with a high degree of polymerization. Therefore, the photoreduction of viologen and the dimerization of $V^{+\cdot}$ inside the cavity of CB[8] can act as the driving force for the dissipative supramolecular polymerization.

The activation and deactivation of the bifunctional monomer, VDV, were monitored by UV–vis spectroscopy. As the UV irradiation time increased, the absorbance of viologen at 261 nm moiety decreased, whereas the absorbance of $V^{+\cdot}$ dimer at 366 and 540 nm increased, suggesting that VDV could be activated with high radical-to-cation ($V^{+\cdot}$) conversion (Figure 1). The absorbance of the $V^{+\cdot}$ dimer reached a maximum after 26 min of irradiation in a degassed system. Owing to the dimerization of $V^{+\cdot}$ inside the cavity of CB[8], the activated VDV became supramolecularly polymerizable. When air was injected into the cuvette, the absorbance of the $V^{+\cdot}$ dimer disappeared while the absorbance of viologen moiety recovered gradually (Figure 1b), indicating that $V^{+\cdot}$ could be oxidized back to viologen. It should be noted that the activation of VDV was also observed by UV irradiation under air (Supporting Information Figure S13), although a longer time (34 min) was needed compared to the condition under nitrogen atmosphere (26 min). This result suggests that the rate of the activation of VDV is much higher than that of the deactivation of VDV, which is a critical condition for keeping the system in the far-from-equilibrium state. Therefore, the activation and deactivation of VDV are highly reversible processes with high viologen-to-radical/radical-to-viologen conversion. Supramolecular polymers could be formed in the activation process, whereas depolymerized in the deactivation process.

Diffusion-ordered NMR spectroscopy (DOSY) was employed to characterize the supramolecular polymers that were formed. As shown in Figure 2a and Supporting Information Figure S14, the diffusion coefficient of the species in the solution decreased gradually from

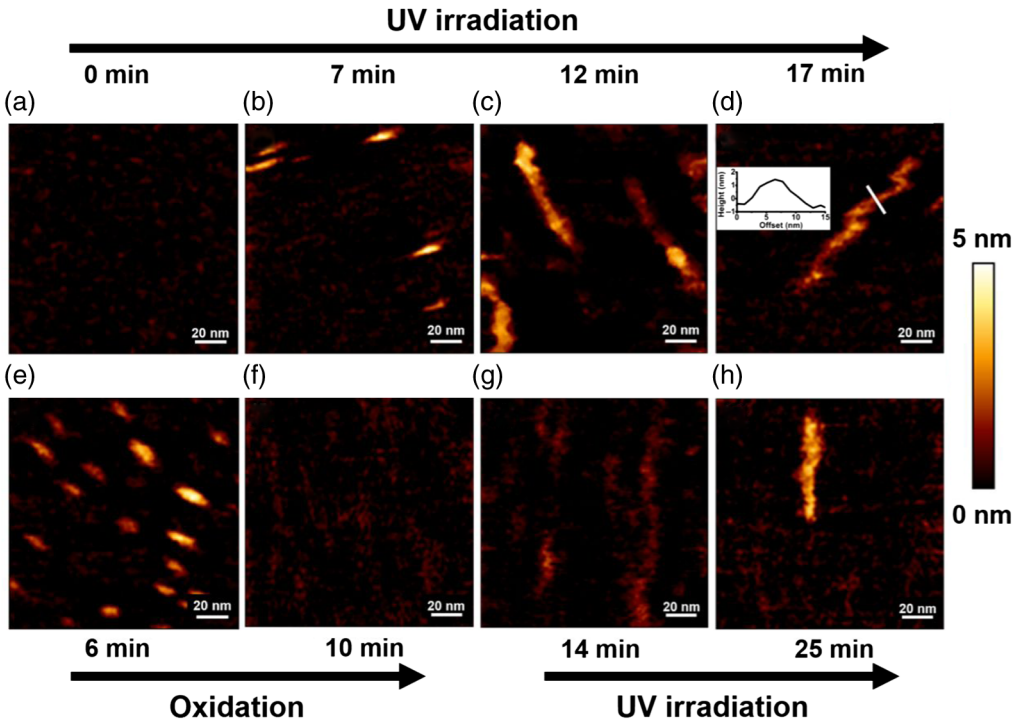


Figure 3 | *Atomic force microscopy (AFM) images during the dissipative supramolecular polymerization process. AFM images before irradiation (a), and after (b) 7 min, (c) 12 min, and (d) 17 min irradiation [inset in (d): height measurement of the fiber]. AFM images after stopping irradiation for (e) 6 min and (f) 10 min, then being irradiated again for (g) 14 min and (h) 25 min (VDV: 1.0 mM, CB[8]: 1.0 mM, MIDA: 20 mM, and pH 10.5). VDV, viologen-DABCO-viologen; MIDA,* N*-methyliminodiacetic acid.*

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CCS Chem. **2019**, *1*, 335–342

1.8×10^{-10} $m^2 \cdot s^{-1}$ to 0.63×10^{-10} $m^2 \cdot s^{-1}$ as the UV irradiation time increased from 0 to 40 min, indicating an increase in the degree of polymerization (DP) of the supramolecular polymer. According to the Stokes-Einstein equation, the largest DP was calculated to be about 23 (Figure 2a and Supporting Information Table S1). By fitting the DP with the extent of reaction, it was observed that the DP rose slowly when the extent of reaction was lower than 80% and rose rapidly when the extent of reaction was higher than 80%. This trend is in accordance with the rule of stepwise polymerization (Figure 2b). The supramolecular polymer depolymerized after being oxidized by air. Interestingly, it could reform upon reapplying UV irradiation, which was confirmed by DOSY (Figure 2c). The photoreduction-oxidation cycle could be repeated at least three times, indicating that the polymerization and the depolymerization processes were indeed reversible. Therefore, supramolecular polymers with controllable DP can be fabricated by regulating the UV irradiation time.

Atomic force microscopy (AFM) was utilized to directly observe the dissipative supramolecular polymerization process. A reactant mixture consisting of equimolar amounts of VDV and CB[8], as well as MIDA, was placed onto a quartz coverslip to which a much smaller mica disc was glued. When exposed to UV radiation, the positively charged supramolecular polymer was generated in the solution and presumed to adsorb onto the negatively charged mica, which would be observable with AFM. Before the UV irradiation, the mica disc showed a flat and clean surface (Figure 3a). Upon UV irradiation of the solution under air, fibers with increasing length, ranging from 20-120 nm, were observed as the irradiation time increased from 7-17 min (Figure 3b–d). The height of the fiber was measured to be ~2.0 nm (Figure 3d, inset), which was consistent with the size of a unimolecular CB[8]. When the irradiation was stopped, the fibers were rapidly degraded to about 20 nm after 6 min (Figure 3e) and disappeared spontaneously within 10 min (Figure 3f). When the UV radiation was reapplied to the solution (Figure 3g,h), the fibers reformed and again elongated with time, indicating that the fibrous structure could be fabricated reversibly. The AFM images confirmed that the fibrous structures were supramolecular polymers fabricated through dissipative supramolecular polymerization. We can conclude that the supramolecular polymers, which exist in far-from-equilibrium state and depolymerize spontaneously without energy input, can be prepared through light-driven dissipative supramolecular polymerization.

The strategy of light-powered dissipative supramolecular polymerization applied not only to dissipative linear supramolecular polymerization, but also to dissipative cross-linked supramolecular polymerization, which has additional potential in the fabrication of functional materials. To realize the cross-linked supramolecular polymerization, methyl viologens were introduced to the carboxyl groups of carboxymethylcellulose sodium salt (CMC) to form a side-chain polymer with a CMC backbone and linked with viologen moieties (CMC–MV, in brief, Figure 4a). Using CMC–MV as a multifunctional monomer, we obtained cross-linked supramolecular polymers in the far-from-equilibrium state with light energy input. In a typical experiment, CMC–MV (0.75%; w/w) was dissolved together with CB[8] and MIDA. By applying UV irradiation to the solution mixture under air, dissipative cross-linked supramolecular polymerization occurred, with the formation of a transient hydrogel, as shown in Figure 4b. The hydrogel formed in the far-from-equilibrium state was unstable in air. As the system returned to equilibrium, the cross-link was gradually destroyed, as observed by the hydrogel dissolving and the solution settling at the bottom of the cuvette. This sol–gel transition could occur at least three times, indicating the reversibility of the dissipative cross-linked

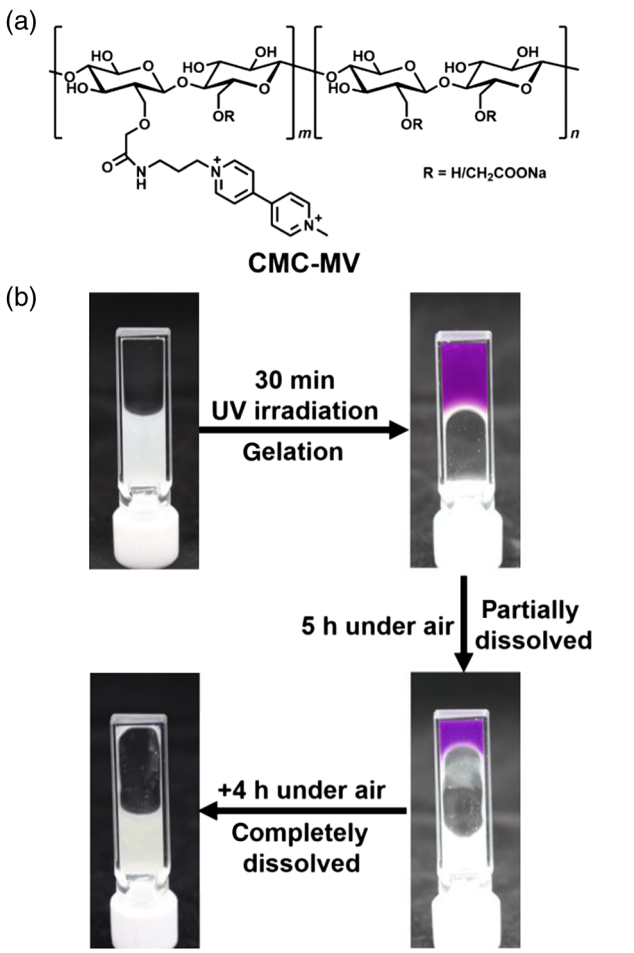


Figure 4 | *(a) Chemical structure of CMC–MV and (b) sol–gel transition of the transient hydrogel formed by dissipative cross-linked supramolecular polymerization. CMC–MV, methylviologen modified carboxymethylcellulose.*

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CCS Chem. **2019**, *1*, 335–342

supramolecular polymerization. Therefore, transient materials, which only function with energy supply and break down spontaneously without energy input, may be fabricated through dissipative supramolecular polymerization.

In conclusion, we have successfully established a method of light-powered dissipative supramolecular polymerization. By transferring the preparation of supramolecular polymers from equilibrium state to far-from-equilibrium state, supramolecular polymers with diverse structures unreachable in equilibrium could be fabricated, and more abundant properties and fruitful functions of supramolecular polymers are hopeful to emerge, thus opening new horizons for supramolecular polymers. Various energy sources, such as mechanical force and electric energy, are also likely to drive dissipative supramolecular polymerization and will require further investigation. We anticipate that the strategy of light-powered dissipative supramolecular polymerization will continue to be of broad interest in the fabrication of functional supramolecular assemblies, in particular in the creation of novel "living" materials.

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Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting Information is available, including experimental details, synthesis of compounds, UV–vis spectra, EPR spectra, and calculation details.

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