



Recent progress in photoreactive crosslinkers in polymer network materials toward advanced photocontrollability

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Abstract

Photochemically adaptable polymer materials, which change shape and physical properties under light irradiation, are widely used in the fields of medicine, electronics, and engineering due to their precise and remote processability. This processability is attributed to the photocleavage of chemical bonds introduced into the polymer materials. In particular, the efficient photolytic cleavage of the crosslinking points in the network induces rapid softening and degradation of the materials. Recently, diverse designs of light-responsive units have been developed to fabricate various photocontrollable materials with low-energy, rapid, and reversible photoreactivity. Furthermore, multiple stimuli-responsive materials have been demonstrated to control photodegradation reaction rates and photoreactivity by combining light with another stimulus, leading to advanced photocontrollable capabilities. This paper reviews the recent progress in developing photochemically adaptable polymer network materials by designing photoresponsive units, focusing on the chemical structures of cleavable moieties.

Introduction

Photochemically adaptable polymeric materials have gained importance in industrial fields as a photocontrolling technology because their shape and physical properties can be fine-tuned under light irradiation [1–6]. Their photocontrollability enables precise and remote microscale tuning over a large area and has diverse applications in process engineering [7, 8] and biomaterials [9–12]. This photoresponsive phenomenon is primarily attributed to the photolytic cleavage of covalent bonds in polymer materials. In particular, the cleavage of the crosslinking points in three-dimensional polymer network structures induces rapid softening and degradation of the materials (Fig. 1a)

[13–15]. Moreover, the partial cleavage of crosslinkers allows fine control of material characteristics based on the degree and scale of light irradiation, demonstrating the high spatiotemporal control of photochemically adaptable polymeric materials [16, 17].

Various photochemically adaptable materials can be developed based on novel designs of photocleavable crosslinkers. The photoreactivity, which involves the degradation rate and response wavelength, can be freely controlled by modifying the chemical structures of the crosslinkers [18–20]. Recently, various photoresponsive crosslinking points have been developed, realizing new concepts and applications of photoactive materials. Novel photocontrollable materials with low-energy light reactivities and rapid and reversible photoreactivities have been reported. Furthermore, compared with conventional materials that undergo monotonic degradation in response to light, advanced photocontrollable materials that combine multiple stimuli sequentially or simultaneously exhibit stepwise, gradual, and on/off-switchable photodegradation (Fig. 1b). This Focus Review summarizes recent studies on photodegradable and photocontrollable materials that utilize the chemical cleavage of 3D polymeric network structures, focusing on their molecular designs.

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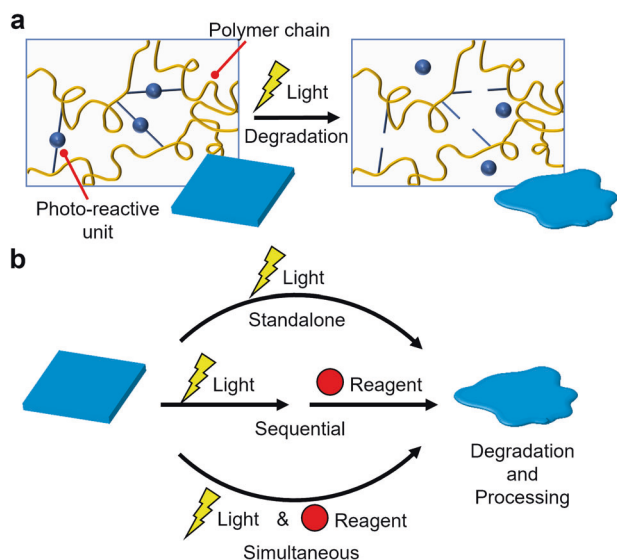


Fig. 1 **a** Schematic of photodegradation of polymer network materials with photoreactive units and **b** categories of photodegradation in this Focus Review; sole stimulus of light and sequential or simultaneous stimuli of light and reagent

Photodegradable materials developed via photocleavage of crosslinkers

Photolabile materials responsive to UV light

Hydrogels, which comprise polymer networks swelled in water (which is used as a solvent), are widely utilized as biocompatible materials for medical supplies and cell media. In 2009, Anseth et al. reported a new class of hydrogels that introduced efficient photoreactive moieties as crosslinkers in polymer network materials [21]. They focused on the photocleavage of *o*-nitrobenzyl ester derivatives to produce benzyl ketones and carboxylic acids under 365 nm UV light irradiation (Fig. 2a) [22–24]. Photocontrollable hydrogels were fabricated by incorporating an *o*-nitrobenzyl ester derivative as a crosslinker for poly(ethylene glycol) chains. The elasticity of the hydrogels decreased under 365 nm UV light irradiation via photocleavage of the *o*-nitrobenzyl ester-based crosslinkers, which softened and degraded the hydrogels (Fig. 2b).

The high spatial resolution of light enables the precise control of material properties, including shape and stiffness. The hydrogels crosslinked with an *o*-nitrobenzyl ester derivative were degraded under 365 nm light irradiation with a photomask to realize micrometer-scale patterning (Fig. 2c). Moreover, the inner space of the hydrogel was selectively degraded via the two-photon absorption of *o*-nitrobenzyl ester derivatives by focusing on the inside of the material under 740 nm laser irradiation (Fig. 2d). Spatially processable hydrogels were then used as platforms for controlling cells. Cell migration was controlled in the inner

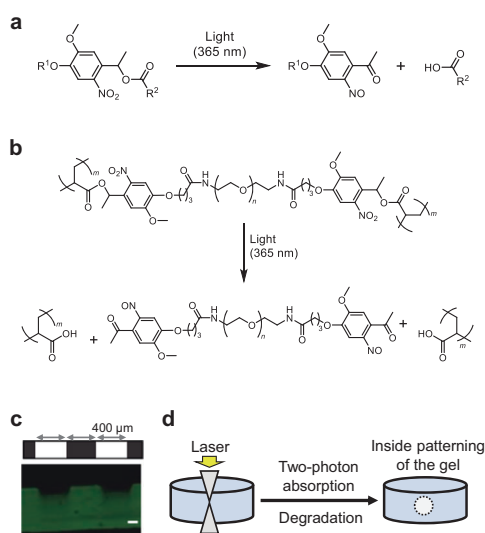


Fig. 2 **a** Photocleavage reaction of an *o*-nitrobenzyl ester derivative. **b** Photodegradation of polymer networks crosslinked by an *o*-nitrobenzyl ester derivative. **c** Image of micrometer-scale hydrogel patterning with a photomask (scale bar, 100 μm). Adapted with permission from ref. [21]. Copyright 2009 AAAS. **d** Illustration of the internal photopatterning of the gels achieved by controlled rastering of the laser focus

processed area of the hydrogels because the cell mobility increased by decreasing the crosslinking density of the hydrogel networks. These results demonstrate that the photocontrollability of hydrogels is a promising tool for controlling cells in microenvironments.

In 2014, Anseth et al. reported a material composed of a coumarinyl methyl ester as a photoresponsive moiety [25]. The coumarinyl methyl ester was cleaved under 365 nm light irradiation, which generated the corresponding coumarinyl methyl alcohol and carboxylic acid [26–28]. This photoresponsive moiety was incorporated into a poly(ethylene glycol)-based network as a crosslinker to obtain a photodegradable gel (Fig. 3a). Furthermore, in 2017, Weder et al. demonstrated the utility of azo groups as photoreactive crosslinkers in poly(vinyl alcohol)-based networks [29]. The organogels decomposed to the sol state through photocleavage of crosslinkers with 320–390 nm light (Fig. 3b) [30]. This photoreactivity was applied to adhesives for the lap joining of glass, which could be immediately debonded under light irradiation. Thus, various photocleavable moieties have been incorporated into polymer network materials as crosslinkers to develop photochemically adaptable materials and their applications.

Visible and near-infrared light-responsive materials utilizing ruthenium complexes

The diversification of light wavelengths for photoreactions has been extensively studied for the application of

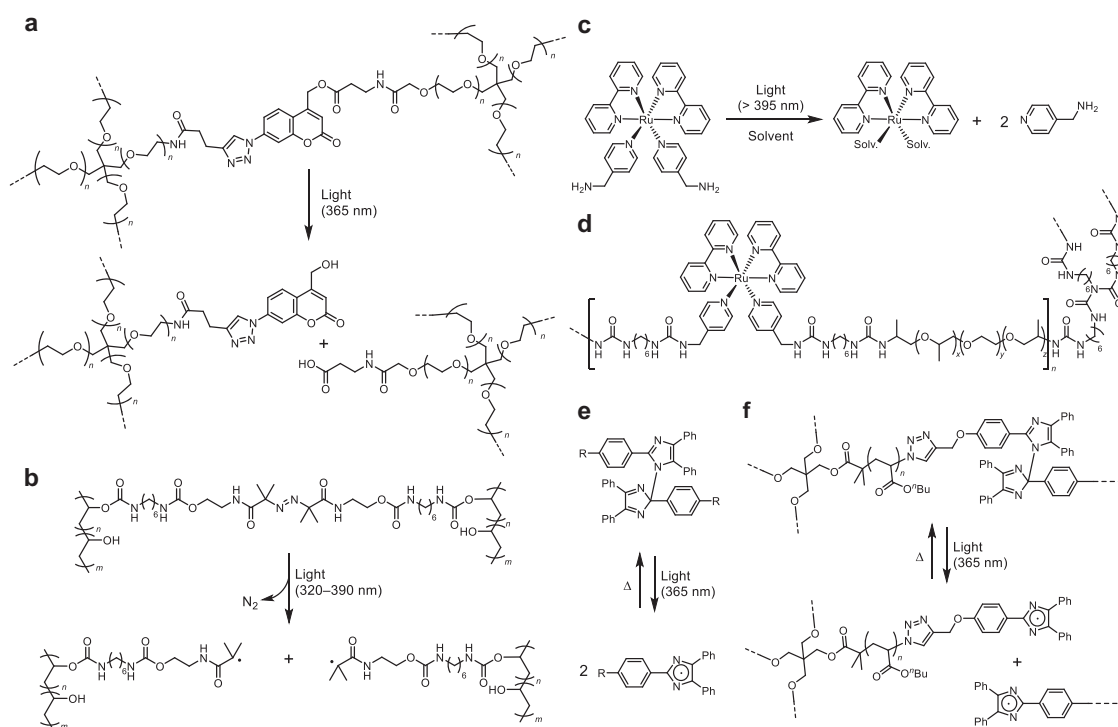


Fig. 3 Schemes of the photodegradation of polymer network materials with **a** coumarinyl ester and **b** azo moieties [25]. **c** Photocleavage reaction of a ruthenium complex. **d** Chemical structure of the polymer networks crosslinked by ruthenium complexes [32]. **e** Reversible

reaction between hexaarylbiimidazole and triphenylimidazolyl radicals. **f** Photocleavage and subsequent recoupling of a polymer network based on a hexaarylbiimidazole moiety [39]

photochemically adaptable materials in various fields. Shortwavelength light enables fine processing, whereas longwavelength light serves as a low-energy light processing technology. In particular, photoreactions within the near-infrared wavelength region, which is referred to as the biological window with high biotransparency, are indispensable for use in drug delivery and biological imaging technologies [31].

In 2017, Monkowius, Teasdale and coworkers developed a photodegradable gel that was responsive to visible and near-infrared light by introducing a photolabile ruthenium complex as a crosslinking point in a polyurea-based network [32, 33]. They utilized the coordination bond of 4-aminomethylpyridine with the ruthenium(II) bis(2,2'-bipyridine) complex, which was efficiently cleaved under 460 nm excitation by a metal-to-ligand charge transfer (MLCT) transition (Fig. 3c) [34]. The polymer material crosslinked with the ruthenium complex degraded into a solution state through the dissociation of the pyridine ligand connected to the polymer chains under light irradiation (Fig. 3d). Photodegradation of the organogels and hydrogels proceeded with acetonitrile and water as solvents, respectively. Moreover, near-infrared laser irradiation at a wavelength of 800 nm was applied to the photocontrollable hydrogels via two-photon absorption in a ruthenium complex. As a result, the use of a ruthenium complex as a

crosslinker enabled the photocontrol of polymer network materials using longwavelength irradiation, encompassing both visible and near-infrared light.

Reversible and rapid photoresponsive materials

Reforming photocleaved crosslinkers into original crosslinkers can produce reversible or reusable photocontrollable materials. In 2008, Iwamura et al. incorporated hexaarylbiimidazole derivatives as crosslinking moieties and reported a polymer network material [35]. These hexaarylbiimidazole derivatives were cleaved into two triphenylimidazolyl radicals under light irradiation (Fig. 3e) [36–38]. In 2017, Honda and Toyota reported a hexaarylbiimidazole-crosslinked polymer material using a star-network system, which enabled rapid and reversible photoreactivity [39]. In the network, the hexaarylbiimidazole crosslinkers were cleaved only during light irradiation. The crosslinkers were reversibly regenerated immediately after irradiation (Fig. 3f). Based on this unique responsiveness, the glass transition temperature of network materials comprising poly(*n*-butyl acrylate) or polydimethylsiloxane chains crosslinked with hexaarylbiimidazole moieties decreased during light irradiation, changing from the solid to the liquid state. After irradiation, the material returned to the solid state, demonstrating rapid

and reversible conversion between the solid and liquid states with light irradiation. More recently, Honda et al. demonstrated a photodetachable adhesive material by utilizing the reversible reactivity of hexaarylbiimidazole moieties [40].

Photoresponsive materials utilizing self-assembled metal complexes

Self-assembled capsules have been used as the crosslinking points of polymer network materials because they provide unique features to the materials. Johnson et al. reported supramolecular polymer network materials comprising metal–organic capsules as network junctions [41]. Coumarin- or poly(ethylene glycol)-functionalized *m*-benzenedicarboxylate ligands (L) were coordinated to Cu(II) ions to form cuboctahedral capsules ($\text{Cu}_{24}\text{L}_{24}$) as the junction points of gels. During photoirradiation, the Cu(II) ions were reduced to Cu(I) and Cu(0) species, and the junction capsules were degraded, resulting in a gel–sol phase transition. Furthermore, the resultant Cu(I) and Cu(0) were reoxidized by O_2 to provide a reversible sol–gel phase transition of the supramolecular system.

In 2018, Johnson et al. reported a novel method for the photocontrolling of the stiffness of polymer materials by utilizing self-assembled complexes as crosslinking points [42]. A diarylethene derivative bearing two pyridyl groups (L') could be photoisomerized between closed- and opening states [43], thereby altering the angle between the two pyridyl groups through photoirradiation. In the open-ring state under UV irradiation, the angle between the pyridyl groups on diarylethene was 62° , which allowed the molecules to self-assemble with three circularly connected Pd(II) ions to form a ring structure ($\text{Pd}_3L'_6$) (Fig. 4a). This ring structure was reversibly rearranged under visible-light irradiation through ring closure of diarylethene, thereby widening the angle between the pyridyl groups to 138° and generating a rhombicuboctahedral capsule ($\text{Pd}_{24}L'_{48}$) with 24 palladium ions at its vertices [44]. Consequently, poly(ethylene glycol)s bearing two diarylethene derivatives formed polymer networks with palladium ions, where the self-assembled structures served as crosslinking points linking multiple poly(ethylene glycol) chains (Fig. 4b). Among these materials, icosahedral capsules ($\text{Pd}_{24}L'_{48}$) formed crosslinking points with more poly(ethylene glycol) chains than ring structures ($\text{Pd}_3L'_6$). Thus, the $\text{Pd}_{24}L'_{48}$ -crosslinked network exhibited greater elasticity than the $\text{Pd}_3L'_6$ network. In other words, the elastic modulus of materials can be controlled through photoirradiation, enabling alteration of the number of polymer chains accumulated at crosslinking points. These findings present a new methodology for controlling the elasticity of polymer materials through reversible photoswitching of the polymer network topology.

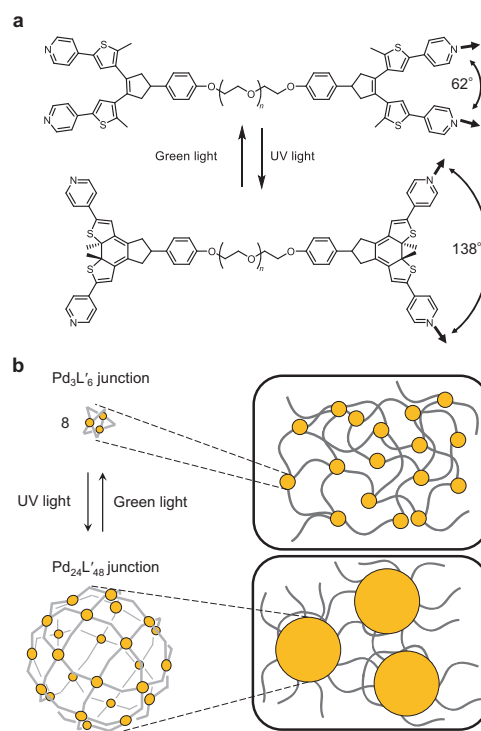


Fig. 4 **a** Photoresponsive polymer ligand composed of diarylethene and pyridyl moieties (L'). **b** Schematics of the photoconversion between $\text{Pd}_3L'_6$ and $\text{Pd}_{24}L'_{48}$ triggered by UV and green light irradiation, respectively, which afford two different network topologies [42]

Photocontrollable materials utilizing the sequential treatment of multiple stimuli

Crosslinking with multiple stimuli-responsive moieties

The abovementioned photoresponsiveness of the materials was attributable to the chemical reactions induced by photoexcitation. These materials can deteriorate or decompose under ambient light, limiting their long-term utility in ambient-lit environments. In other words, highly photoresponsive materials easily deteriorate even under weak irradiation, strictly limiting their applications to environments devoid of light. Recently, the previous focus on the design of photoreactive materials has shifted to a focus on utilizing multiple stimuli, including light, to enable new degradation control mechanisms instead of solely relying on light as the responsive stimulus [45–47]. For example, Sato and Matsumoto developed a debondable adhesive material using a linear block copolymer composed of two types of polyacrylic esters that respond to two sequential stimuli: light irradiation and heat [48]. Moreover, sequential material degradation has been achieved via the photolysis of polymer side chains at physical crosslinking points, followed by the cleavage of other chemical crosslinking points

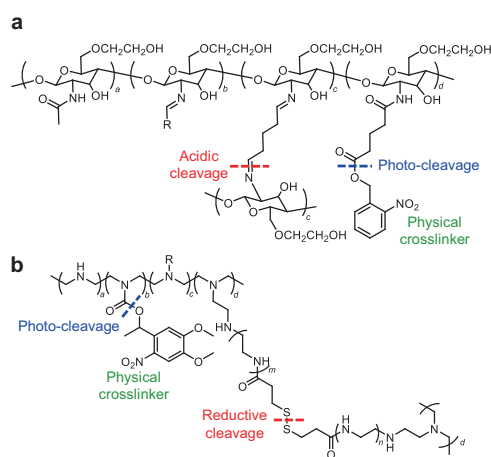


Fig. 5 Chemical structures of polymer networks based on **a** chitosan chains bearing *o*-nitrobenzyl succinate crosslinked with glutaraldehyde [49] and **b** polyetherimide chains containing *o*-nitrobenzyl derivatives and disulfide moieties [50]

with chemical reagents. Huang and Yan et al. investigated the pH- and light-responsive crosslinking points in chitosan-based polymeric micelles (Fig. 5a) [49]. Chitosan polymer chains bearing *o*-nitrobenzyl succinate side chains were crosslinked with glutaraldehyde to form polymeric micelles via self-assembly. The micelles were applied to drug delivery systems of camptothecin (an anticancer drug), which was quickly released at a low pH with 365 nm UV irradiation. Zhu et al. reported a polyetherimide-based micelle-like assembly containing *o*-nitrobenzyl derivatives and disulfide moieties as physical and chemical crosslinking points, respectively (Fig. 5b) [50]. The nanoparticles were degraded after exposure to 365 nm UV light and treatment with glutathione as a reducing agent, which was subsequently applied to the release system of doxorubicin (an anticancer drug).

Crosslinking with orthogonal stimuli-responsive units connected in parallel

In 2018, DeForest et al. reported the design of multiple stimuli-responsive crosslinkers in hydrogels, where the stimuli-responsive moieties were configured in both parallel and series arrangements [51, 52]. This configuration enables programmed degradation of hydrogels by combining multiple stimuli. A series of crosslinkers were synthesized by utilizing three types of orthogonal stimuli-responsive moieties: *o*-nitrobenzyl ester derivatives cleaved by 365 nm light irradiation, disulfide bonds cleaved by reducing reagents, and peptide sequences cleaved by matrix metalloprotease-8 as an enzyme (Fig. 6a) [53]. For example, a crosslinked network comprising photocleavable *o*-nitrobenzyl ester derivatives and reductively cleavable disulfide bonds cleavable units connected in series (linear) degraded

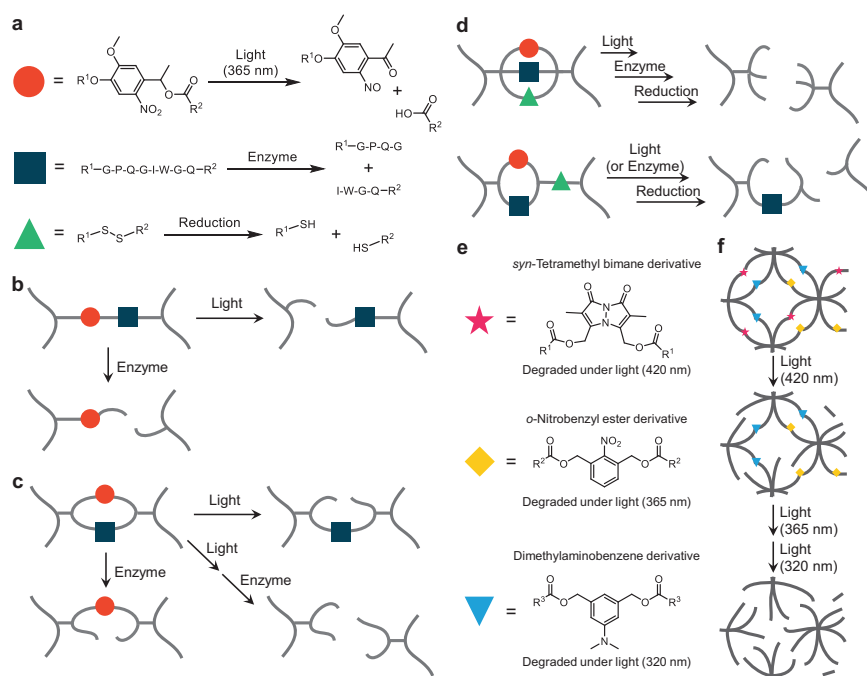
when exposed to light or reductive stimuli (Fig. 6b). In contrast, a crosslinker with photocleavable and reductively cleavable units arranged in parallel (cyclic) resulted in polymer network degradation only under both light and reducing stimuli (Fig. 6c). Conversely, the network remained intact under either light or reducing stimuli. This strategic arrangement of connections among multiple stimuli-responsive units allows for the precise control of material degradation under specific combinations of stimuli. Consequently, 17 distinct types of gel materials with various stimuli responsiveness were successfully synthesized, as exemplified in Fig. 6d. Moreover, this unique responsiveness was employed in drug delivery technology, wherein a drug connected to gel materials was released in the presence of a specific combination of stimuli through the decomposition of the gel. This approach demonstrates the advantages of materials that respond to combined stimuli, enabling the expansion of the usability of photo-reactive materials to broader targets.

Photocontrollable materials bearing multiple photoresponsive units to different wavelengths

In 2021, Truong and Barner-Kowollik demonstrated that the elasticity of hydrogels could be photomanipulated by incorporating three types of photodegradation moieties, each of which respond to different wavelengths [54]. These three units consisted of *syn*-tetramethylbimane, *o*-nitrobenzyl ester, and dimethylaniline derivatives. These products were employed as crosslinkers and degraded under 420, 365, and 325 nm light irradiation (Fig. 6e). The photodegradable crosslinkers in the hydrogels were selectively cleaved by irradiation with individual wavelengths of light. For example, a hydrogel containing dimethylaniline-based crosslinkers was efficiently degraded under 325 nm light irradiation but remained primarily intact under 360 or 380 nm light irradiation [55]. Conversely, a hydrogel with *o*-nitrobenzyl ester-based crosslinkers decomposed under 325 and 360 nm light irradiation but was stable at 420 nm. Additionally, a hydrogel with *syn*-tetramethylbimane-based crosslinkers exhibited efficient photodegradation under 420 nm light irradiation but remained relatively stable under 325 or 360 nm light irradiation [56, 57].

Hydrogels with the abovementioned multiple crosslinkers exhibited tunable elasticity upon exposure to stepwise irradiation at multiple wavelengths. For example, the elasticity of a hydrogel bearing *syn*-tetramethylbimane and *o*-nitrobenzyl ester derivatives as crosslinkers in a 1:1 ratio was reduced by 50% with 420 nm light irradiation. Subsequently, the hydrogel was completely decomposed by 365 nm light irradiation. Furthermore, a hydrogel containing a *syn*-tetramethylbimane derivative, *o*-nitrobenzyl ester, and dimethylaniline at a 1:1:1 ratio was exposed to 420, 365, and 325 nm light in sequence to decrease its elasticity by approximately 30% each time (Fig. 6f). These

Fig. 6 **a** Orthogonal stimuli-labile moieties and their cleavage reactions via light, reduction, and enzymes. **b** Schematics of (b) linear and (c) cyclic crosslinkers in network materials, which are cleavable via either light or an enzyme or a combination of light and an enzyme, respectively [51]. **d** Representative crosslinkers bearing three types of stimuli-labile moieties and their cleavage reactions. **e** Chemical structures of photocleavable moieties under three irradiation wavelengths. **f** Schematic of the subsequent degradation of a network material with three photocleavable crosslinkers [54]



results demonstrate the stepwise tunability of the material elasticity by combining multiple photoresponsive crosslinkers that react with the corresponding wavelength of light irradiation.

Degradable materials in response to sequential stimuli with light and acid

An approach to achieve higher-order control of photodegradation involves altering the chemical reactivity of the crosslinker through photoreactions. A novel photoresponsive unit, the *o*-nitrophenylethanol derivative, was incorporated into polymer network materials by Wang et al. in 2019 [58]. This derivative induced photocyclization to initiate degradability under acidic conditions (Fig. 7a). Specifically, the electron-withdrawing nitro group on the aromatic ring stabilized the acetal group at the *para* position. However, this nitro group was converted to an oxindole moiety via intramolecular photocyclization upon irradiation with 300 nm light [59, 60]. The resulting electron-rich oxindole moiety facilitated the hydrolysis of the acetal group on the aromatic ring under acidic conditions. Therefore, the *o*-nitrophenylethanol unit demonstrated unique degradability through sequential stimulation with 300 nm light irradiation followed by the application of acidic conditions. A hydrogel formulated with polyacrylic acid ester crosslinked with this *o*-nitrophenylethanol derivative remained stable under light irradiation but rapidly degraded under acidic conditions at pH 5 following irradiation (Fig. 7b, c). Even at pH 7.4, a level of acidity that is comparable to the skin surface, the hydrogels degraded, albeit at a lower reaction rate than at pH 5. Thus, precise control of hydrogel degradability was achieved through the sequential use of photoreactions and chemical reactions.

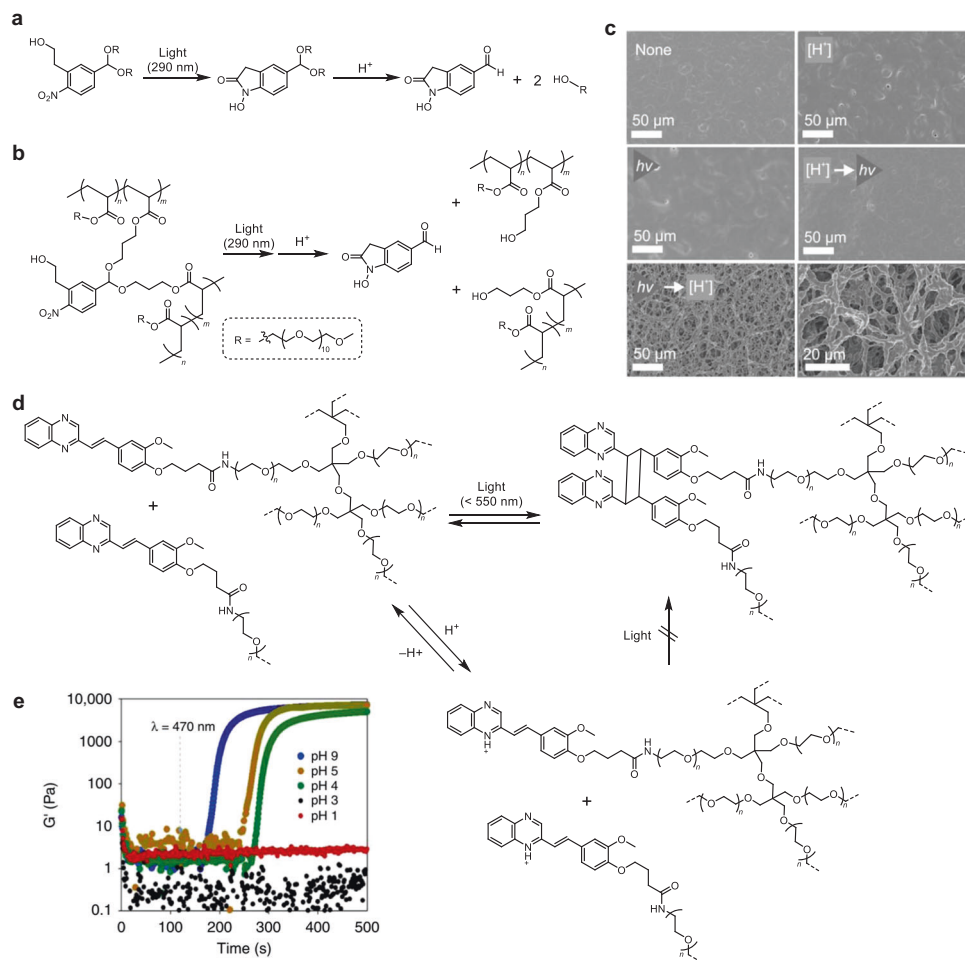
Another approach to controlling the photodegradation of polymer network materials was reported by Truong and Barner-Kowollik in 2020 [61]. These authors altered the photoreactivity of crosslinkers through chemical reactions with acids, specifically using the styrylquinoxaline moiety (Fig. 7d). This vinyl moiety underwent a [2 + 2] photocycloaddition reaction, resulting in cyclobutane derivatives [62, 63]. The styrylquinoxalines were dimerized with green light irradiation under low-pH conditions. In contrast, the reaction was inhibited under high-pH conditions via protonation of the aromatic nitrogen atom within the styrylquinoxaline structure. Another hydrogel composed of polymer networks incorporating styrylquinoxaline moieties exhibited an increased crosslinking density and storage modulus through [2 + 2] photocycloaddition under irradiation (Fig. 7e). Conversely, under acidic conditions, the elastic modulus remained constant even after light exposure. Thus, the photoreactivity of the crosslinker and the elasticity of the hydrogels could be controlled by varying the pH of the external environment.

Photocontrollable materials utilizing simultaneous treatment with multiple stimuli

Material degradation under simultaneous light and acid stimuli

The aforementioned stimuli-responsive materials degrade sequentially under various conditions. However, light irradiation without other stimuli triggers localized chemical

Fig. 7 Cleavage reactions of **a** an *o*-nitrophenylethanol derivative, **b** the crosslinked network material via sequential stimuli with light and acid, and **c** SEM images of the network material treated under different conditions. Adapted with permission from ref. [58]. Copyright 2019 Wiley-VCH Verlag GmbH & KaA, Weinheim. **d** [2 + 2] Photocycloaddition of a styrylquinoxaline derivative and inhibition of the reaction under acidic conditions. **e** Time evolution of the storage modulus under 470 nm irradiation at different pH levels. The images were reused under a CC BY license from ref. [61]



reactions within the material. Thus, these materials are not completely stable for long-term use under light irradiation. To address this problem, new materials have been designed that are degradable under simultaneous treatment with multiple stimuli. These materials possess enhanced stability in light-irradiated environments because chemical degradation reactions are initiated only in the presence of light and an additional stimulus.

In 2022, the present authors developed cooperatively degradable materials in the presence of two stimuli, namely, acid and light. In a platinum acetylide complex covered by two permethylated α -cyclodextrins (PM α -CDs) [64–66], the Pt–C bond was cleaved under 365 nm UV irradiation in the presence of HCl, generating a chloroplatinum complex and chloroalkyne derivative (Fig. 8a) [67]. In contrast, the platinum complex was stable when exposed to either 365 nm UV light or HCl, demonstrating specific responsiveness to simultaneous light and acid stimuli [68]. The covering structure of the PM α -CDs contributed to the improvement in the acidic tolerance of the platinum

complex due to steric hindrance [69, 70]. Thus, a new reactivity was determined for the platinum acetylide complex under light and acidic conditions. Next, the incorporation of the unique reactivity of the covered platinum acetylide complexes into poly(methyl methacrylate) as crosslinkers yielded a degradable polymer network material under simultaneous stimulation with 365 nm UV light and HCl, whereas the material was not reactive under either stimulus (light or acidic conditions). Interestingly, the cleavage reaction was attributed to the singlet oxygen species generated via energy transfer from the excited platinum acetylide complex. Therefore, instead of degradation in response to 365 nm UV light irradiation, 470 nm visible-light irradiation also induced material degradation under acidic stimuli in the presence of an iridium photosensitizer, which generated singlet oxygen via energy transfer from excited iridium to oxygen molecules [71]. These results demonstrated that simultaneous stimuli-degradable materials under light and acidic conditions could be obtained by utilizing the covered platinum complex as a crosslinker.

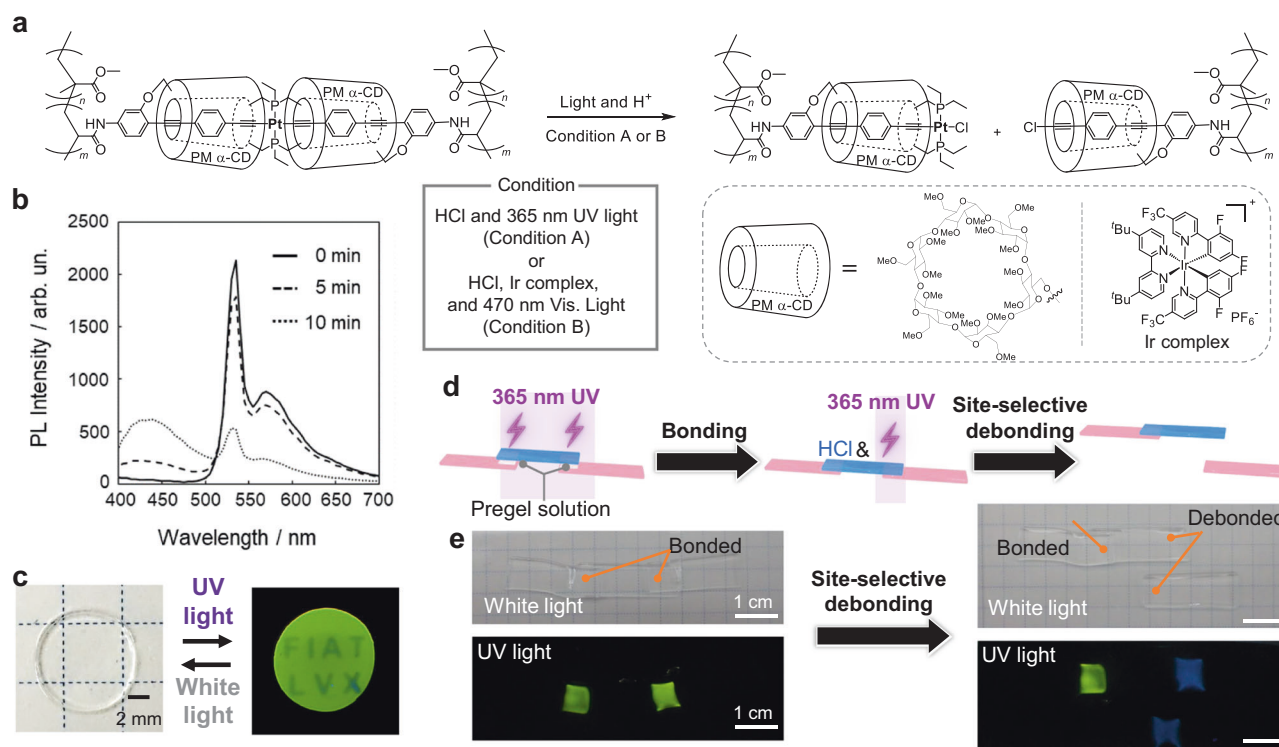


Fig. 8 **a** Cooperative cleavage reaction of a polymer network cross-linked with platinum complexes under light and acidic conditions. **b** Photoluminescence spectra of the crosslinked gel before and after the cooperative reaction with light and acid. **c** Photographs of the polymer network observed under white light (left) and 365 nm UV light (right) irradiation, revealing the microscale letters obtained by processing

with 365 nm UV light and acid. **d** Schematic and **e** photographs of photoadhesive and site-selective debonding of polymer films with 365 nm UV light and acid observed under white light (top) and 365 nm UV light (bottom) irradiation. Adapted with permission from ref. [67] and [72]. Copyright 2022 and 2023 Wiley-VCH Verlag GmbH & KaA, Weinheim

Functionalities of acid-induced photocontrollable materials

Polymer network materials crosslinked with a covered platinum complex could be exploited for the photocontrol of various functionalized materials utilized under light irradiation owing to their unique reactivity under simultaneous treatment with light and acid. After photoreaction with acid for processing, the photostability of the resultant materials was restored by removing the acidic reagents. In other words, network materials crosslinked by covered platinum acetylide complexes could be utilized as photocontrollable materials under acidic conditions as well as optically functional materials without acidic reagents. The platinum acetylide complex in the materials exhibited yellow phosphorescence at 535 nm under 365 nm UV light excitation, with a vibration band at ~570 nm (Fig. 8b). In contrast, the photocleaved products with acid on the platinum-carbon bond, including the chloroalkyne derivatives, emitted blue fluorescence at 430 nm under 365 nm excitation. As a result, the photoreaction of gels with 365 nm UV light under acidic conditions afforded luminescent colors that differed from those in the initial states. In other words, the micropatterning of luminescent colors,

such as microscale letters described with a photomask, was achieved using an acid-induced photoreaction followed by the removal of the acid (Fig. 8c). The luminescent letters were readable under 365 nm UV irradiation and transparent under ambient light, which could be applied to encryption and information-hiding technologies.

The degradation phenomenon under simultaneous light and acidic stimuli can be applied to photopolymerized materials [72]. *N*-(2-hydroxyethyl)acrylamide (HEAA) was photopolymerized under 365 nm UV light in the presence of covered platinum acetylide complexes as crosslinkers. The platinum acetylide crosslinkers remained intact during photopolymerization because of the high photostability of the platinum complex without acids. However, the photopolymerized gels could be degraded under 365 nm photoirradiation with acid, demonstrating the acid-induced photodegradation of the photofabricated materials under the same wavelength of light irradiation. Thus, the compatibility of the two photoprocesses, that is, fabrication and degradation, could be applied to photoadhesive materials [73–75]. A solution of the HEAA monomer and platinum complex crosslinker was coated between multiple polymer films and irradiated with 365 nm UV light to bond the films (Fig. 8d). Subsequently, after the bonded sample was immersed in an

acidic solution, 365 nm UV light irradiation was used to debond the polymer films on the irradiated area. After removing the acid, the photoluminescence of the bonded region under 365 nm excitation exhibited yellow phosphorescence. In contrast, the debonded area showed blue fluorescence (Fig. 8e). The results demonstrated macroscopic debonding of the polymer films attributable to the microscopic cleavage of the covered platinum acetylide complexes under light and acidic stimuli. Accordingly, acid-induced photoreactivity can be exploited for photoadhesives that can be debonded with the same wavelength of light irradiation.

Photodegradation under acidic conditions can be extended to occur under 470 nm blue light by utilizing a photosensitizer. The bonded samples were stable under 470 nm light exposure; however, they rapidly debonded under irradiation at 470 nm in the presence of an iridium complex due to the energy transfer from the excited photosensitizer. Conventionally, photochemically adaptable materials are unstable under light irradiation, which hinders their long-term use or limits the environment of the irradiated light wavelengths. In contrast, acid-induced photocontrollable materials, which are derived from reactivity under simultaneous treatment with light and acidic stimuli, are photostable under irradiation at various wavelengths without acidic reagents. This unique reactivity enables materials with diverse photofunctionalities, including photoluminescence and photoadhesion, to be controlled by photoirradiation with an acid, regardless of the irradiation wavelength. Accordingly, the acid-induced photoreactivity of materials can lead to a new class of intelligent materials by combining their photocontrollability and photofunctionalities.

Conclusion

This Focus Review discusses recent advancements in photochemically adaptable polymer network materials on the basis of their reaction systems. These advancements include cleavage reactions at the crosslinking points triggered by standalone photoirradiation, sequential treatment with light and other stimuli, and simultaneous treatment with light and other stimuli. In conventional systems activated solely by photoirradiation, novel photoreactive moieties have been engineered and integrated into materials as crosslinkers. This approach facilitates rapid responsiveness, broadens the range of effective irradiation wavelengths, and enables reversible reactivity. Additionally, polymer network materials incorporating multiple stimuli-responsive crosslinkers undergo sequential degradation in response to specific combinations of stimuli. Such sequential reactivity offers new avenues for fine-tuning material properties, such as elasticity, and enables stepwise photodegradation. Moreover, a new class of photoreactive crosslinkers that can be cleaved under the

simultaneous influence of light and acidic conditions was prepared. This cooperative reactivity allows for the development of photochemically adaptable materials that are stable in the absence of acidic agents, effectively enabling an on/off switch for photodegradation. These unique properties have led to the development of new and unprecedented phototechnologies, such as photocontrollable luminescent materials and photoadhesives, that can be debonded using light. As described above, advancements in photocontrollability are attributed to the precise molecular design of photocleavable units incorporated into polymer networks. The preparation of a new class of photocleavable moieties could open new avenues for more sophisticated methods for photocontrolling polymer network materials, paving the way for a wide array of functional applications. The integration of sophisticated photoresponsive designs with diverse polymer network materials is expected to drive the development of a new generation of photocontrollable materials.

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Compliance with ethical standards

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References

1. Kaur G, Johnston P, Saito K. Photo-reversible dimerisation reactions and their applications in polymeric systems. *Polym Chem.* 2014;5:2171–86.
2. Ruskowitz ER, Deforest CA. Photoresponsive biomaterials for targeted drug delivery and 4D cell culture. *Nat Rev Mater.* 2018;3:17087.

- Schumers JM, Fustin CA, Gohy JF. Light-responsive block copolymers. *Macromol Rapid Commun.* 2010;31:1588–607.
- Jiang ZC, Xiao YY, Tong X, Zhao Y. Selective decrosslinking in liquid crystal polymer actuators for optical reconfiguration of origami and light-fueled locomotion. *Angew Chem Int Ed.* 2019;58:5332–7.
- Huang B, Wei M, Vargo E, Qian Y, Xu T, Toste FD. Backbone-photodegradable polymers by incorporating acylsilane monomers via ring-opening metathesis polymerization. *J Am Chem Soc.* 2021;143:17920–5.
- Lipinski BM, Morris LS, Silberstein MN, Coates GW. Isotactic poly(propylene oxide): a photodegradable polymer with strain hardening properties. *J Am Chem Soc.* 2020;142:6800–6.
- Wong DY, Griffin DR, Reed J, Kasko AM. Photodegradable hydrogels to generate positive and negative features over multiple length scales. *Macromolecules.* 2010;43:2824–31.
- Scheiger JM, Li S, Brehm M, Bartschat A, Theato P, Levkin PA. Inherently UV photodegradable poly(methacrylate) gels. *Adv Funct Mater.* 2021;31:2105681.
- Kloxin AM, Tibbitt MW, Kasko AM, Fairbairn JA, Anseth KS. Tunable hydrogels for external manipulation of cellular micro-environments through controlled photodegradation. *Adv Mater.* 2010;22:61–66.
- Yang C, DelRio FW, Ma H, Killaars AR, Basta LP, Kyburz KA, et al. Spatially patterned matrix elasticity directs stem cell fate. *Proc Natl Acad Sci USA.* 2016;113:E4439–E4445.
- Zhao D, Tang Q, Zhou Q, Peng K, Yang H, Zhang X. A photodegradable injectable self-healing hydrogel based on star poly(ethylene glycol)-b-polypeptide as a potential pharmaceuticals delivery carrier. *Soft Matter.* 2018;14:7420–8.
- Wang R, Yang Z, Luo J, Hsing IM, Sun F. B12-dependent photoresponsive protein hydrogels for controlled stem cell/protein release. *Proc Natl Acad Sci USA.* 2017;114:5912–7.
- Sasaki S, Sugita Y, Tokita M, Suenobu T, Ishitani O, Konishi G-i. Smart network polymers with bis(piperidyl)naphthalene cross-linkers: selective fluorescence quenching and photodegradation in the presence of trichloromethyl-containing chloroalkanes. *Macromolecules.* 2017;50:3544–56.
- Lunzer M, Shi L, Andriotis OG, Gruber P, Markovic M, Thumer PJ, et al. A modular approach to sensitized two-photon patterning of photodegradable hydrogels. *Angew Chem Int Ed.* 2018;57:15122–7.
- Strasser P, Russo M, Stadler P, Breiteneder P, Redhammer G, Himmelsbach M, et al. Green-light photocleavable meso-methyl BODIPY building blocks for macromolecular chemistry. *Polym Chem.* 2021;12:6927–36.
- Zhu H, Yang H, Ma Y, Lu TJ, Xu F, Genin GM, et al. Spatio-temporally controlled photoresponsive hydrogels: design and predictive modeling from processing through application. *Adv Funct Mater.* 2020;30:2000639.
- Jung K, Corrigan N, Ciftci M, Xu J, Seo SE, Hawker CJ, et al. Designing with light: advanced 2D, 3D, and 4D materials. *Adv Mater.* 2020;32:1903850.
- Nishida H. Development of materials and technologies for control of polymer recycling. *Polym J.* 2011;43:435–47.
- Brevé TG, Filius M, Weerdenburg S, van der Griend SJ, Groeneveld TP, Denkova AG, et al. Light-sensitive phenacyl cross-linked dextran hydrogels for controlled delivery. *Chem Eur J.* 2022;28:e202103523.
- Takashima Y, Hatanaka S, Otsubo M, Nakahata M, Kakuta T, Hashidzume A, et al. Expansion-contraction of photoresponsive artificial muscle regulated by host-guest interactions. *Nat Commun.* 2012;3:1270.
- Kloxin AM, Kasko AM, Salinas CN, Anseth KS. Photodegradable hydrogels for dynamic tuning of physical and chemical properties. *Science.* 2009;324:59–63.
- Zhao H, Sterner ES, Coughlin EB, Theato P. O-Nitrobenzyl alcohol derivatives: opportunities in polymer and materials science. *Macromolecules.* 2012;45:1723–36.
- Romano A, Roppolo I, Rossegger E, Schlögl S, Sangermano M. Recent trends in applying ortho-nitrobenzyl esters for the design of photo-responsive polymer networks. *Materials.* 2020;13:2777.
- Doi N, Yamauchi Y, Ikegami R, Kuzuya M, Sasai Y, Kondo SI. Photo-responsive polymer micelles from o-nitrobenzyl ester-based amphiphilic block copolymers synthesized by mechanochemical solid-state copolymerization. *Polym J.* 2020;52:1375–85.
- Azagarsamy MA, McKinnon DD, Alge DL, Anseth KS. Coumarin-based photodegradable hydrogel: Design, synthesis, gelation, and degradation kinetics. *ACS Macro Lett.* 2014;3:515–9.
- Schmidt R, Geissler D, Hagen V, Bendig J. Kinetics study of the photocleavage of (coumarin-4-yl)methyl esters. *J Phys Chem A.* 2005;109:5000–4.
- Cazin I, Rossegger E, Guedes de la Cruz G, Griesser T, Schlögl S. Recent advances in functional polymers containing coumarin chromophores. *Polymers.* 2021;13:56.
- Muralidhar JR, Kodama K, Hirose T, Ito Y, Kawamoto M. Photocleavage behavior of a polythiophene derivative containing a coumarin unit. *Polym J.* 2022;54:191–8.
- Ayer MA, Schrettl S, Balog S, Simon YC, Weder C. Light-responsive azo-containing organogels. *Soft Matter.* 2017;13:4017–23.
- Ayer MA, Simon YC, Weder C. Azo-containing polymers with degradation on-demand feature. *Macromolecules.* 2016;49:2917–27.
- Weissleder R. News and views: a clearer vision for in vivo imaging. *Nat Biotechnol.* 2001;19:316–7.
- Theis S, Iturmendi A, Gorsche C, Orthofer M, Lunzer M, Baudis S, et al. Metallo-supramolecular gels that are photocleavable with visible and near-infrared irradiation. *Angew Chem Int Ed.* 2017;56:15857–60.
- Teasdale I, Theis S, Iturmendi A, Strobel M, Hild S, Jacak J, et al. Dynamic supramolecular ruthenium-based gels responsive to visible/NIR light and heat. *Chem Eur J.* 2019;25:9851–5.
- Salierno M, Marceca E, Peterka DS, Yuste R, Etchenique R. A fast ruthenium polypyridine cage complex photoreleases glutamate with visible or IR light in one and two photon regimes. *J Inorg Biochem.* 2010;104:418–22.
- Iwamura T, Sakaguchi M. A novel de-cross-linking system from cross-linked polymer to linear polymer utilizing pressure or visible light irradiation. *Macromolecules.* 2008;41:8995–9.
- Riem RH, Maclachlan A, Cobaor GR, Urban EJ. The flash photolysis of a substituted hexaarylbiimidazole and reactions of the imidazolyl radical. *J Org Chem.* 1971;36:2272–5.
- Shima K, Mutoh K, Kobayashi Y, Abe J. Enhancing the versatility and functionality of fast photochromic bridged imidazole dimers by flipping imidazole rings. *J Am Chem Soc.* 2014;136:3796–9.
- Ahn D, Zavada SR, Scott TF. Rapid, photomediated healing of hexaarylbiimidazole-based covalently cross-linked gels. *Chem Mater.* 2017;29:7023–31.
- Honda S, Toyota T. Photo-triggered solvent-free metamorphosis of polymeric materials. *Nat Commun.* 2017;8:502.
- Oka M, Takagi H, Miyazawa T, Waymouth RM, Honda S. Photocleavable regenerative network materials with exceptional and repeatable viscoelastic manipulability. *Adv Sci.* 2021;8:2101143.
- Oldenhuis NJ, Qin KP, Wang S, Ye HZ, Alt EA, Willard AP, et al. Photoswitchable sol-gel transitions and catalysis mediated by polymer networks with coumarin-decorated Cu24L24 metal-organic cages as junctions. *Angew Chem Int Ed.* 2020;59:2784–92.

42. Gu Y, Alt EA, Wang H, Li X, Willard AP, Johnson JA. Photo-switching topology in polymer networks with metal–organic cages as crosslinks. *Nature*. 2018;560:65–69.
43. Irie M, Fukaminato T, Matsuda K, Kobatake S. Photochromism of diarylethene molecules and crystals: memories, switches, and actuators. *Chem Rev*. 2014;114:12174–277.
44. Harris K, Fujita D, Fujita M. Giant hollow MnL₂n spherical complexes: structure, functionalisation and applications. *Chem Commun*. 2013;49:6703–12.
45. Badeau BA, Deforest CA. Programming stimuli-responsive behavior into biomaterials. *Annu Rev Biomed Eng*. 2019;21:241–65.
46. Guragain S, Bastakoti BP, Malgras V, Nakashima K, Yamauchi Y. Multi-stimuli-responsive polymeric materials. *Chem Eur J*. 2015;21:13164–74.
47. Fu X, Hosta-Rigau L, Chandrawati R, Cui J. Multi-stimuli-responsive polymer particles, films, and hydrogels for drug delivery. *Chem*. 2018;4:2084–107.
48. Inui T, Sato E, Matsumoto A. Pressure-sensitive adhesion system using acrylate block copolymers in response to photoirradiation and postbaking as the dual external stimuli for on-demand dismantling. *ACS Appl Mater Interfaces*. 2012;4:2124–32.
49. Meng L, Huang W, Wang D, Huang X, Zhu X, Yan D. Chitosan-based nanocarriers with pH and light dual response for anticancer drug delivery. *Biomacromolecules*. 2013;14:2601–10.
50. Huang Q, Liu T, Bao C, Lin Q, Ma M, Zhu L. Light and reductive dual stimuli-responsive PEI nanoparticles: ‘AND’ logic response and controllable release. *J Mater Chem B*. 2014;2:3333–9.
51. Badeau BA, Comerford MP, Arakawa CK, Shadish JA, Deforest CA. Engineered modular biomaterial logic gates for environmentally triggered therapeutic delivery. *Nat Chem*. 2018;10:251–8.
52. Ruskowitz ER, Comerford MP, Badeau BA, Deforest CA. Logical stimuli-triggered delivery of small molecules from hydrogel biomaterials. *Biomater Sci* 2019;7:542–6.
53. Nagase H, Fields GB. Human matrix metalloproteinase specificity studies using collagen sequence-based synthetic peptides. *Biopolymers*. 1996;40:399–416.
54. Pelloth JL, Tran PA, Walther A, Goldmann AS, Frisch H, Truong VX, et al. Wavelength-selective softening of hydrogel networks. *Adv Mater*. 2021;33:2102184.
55. Ding X, Wang P. Photochemical cleavage of benzylic C–O bond facilitated by an ortho or meta amino group. *J Org Chem*. 2017;82:7309–16.
56. Truong VX, Li F, Forsythe JS. Visible light activation of nucleophilic thiol–X addition via thioether bimeane photocleavage for polymer cross-linking. *Biomacromolecules*. 2018;19:4277–85.
57. Chaudhuri A, Venkatesh Y, Behara KK, Singh NDP. Bimeane: a visible light induced fluorescent photoremovable protecting group for the single and dual release of carboxylic and amino acids. *Org Lett*. 2017;19:1598–601.
58. Lai J, Abune L, Zhao N, Wang Y. Programmed degradation of hydrogels with a double-locked domain. *Angew Chem Int Ed*. 2019;58:2820–5.
59. Bakke J, Wiklund E, Wikander G, Karrer P, Shimizu A. The photocyclization of 2-(o-nitrophenyl)-ethanol to N-hydroxyoxindole. *Acta Chem Scand*. 1970;24:2650–1.
60. Lai J, Yu A, Yang L, Zhang Y, Shah BP, Lee KB. Development of photoactivated fluorescent N-hydroxyoxindoles and their application for cell-selective imaging. *Chem Eur J*. 2016;22:6361–7.
61. Kalayci K, Frisch H, Truong VX, Barner-Kowollik C. Green light triggered [2+2] cycloaddition of halochromic styrylquinoxaline—controlling photoreactivity by pH. *Nat Commun*. 2020;11:4193.
62. Frisch H, Marschner DE, Goldmann AS, Barner-Kowollik C. Wavelength-gated dynamic covalent chemistry. *Angew Chem Int Ed*. 2018;57:2036–45.
63. Offenloch JT, Gernhardt M, Blinco JP, Frisch H, Mutlu H, Barner-Kowollik C. Contemporary photoligation chemistry: the visible light challenge. *Chem Eur J*. 2019;25:3700–9.
64. Masai H, Liu M, Tachibana Y, Tsuda S, Terao J. Synthesis of insulated heteroaromatic platinum–acetylide complexes with color-tunable phosphorescence in solution and solid states. *J Org Chem*. 2020;85:3082–91.
65. Russell GM, Inamori D, Masai H, Tamaki T, Terao J. Luminescent and mechanical enhancement of phosphorescent hydrogel through cyclic insulation of platinum–acetylide crosslinker. *Polym Chem*. 2019;10:5280–4.
66. Masai H, Yokoyama T, Miyagishi HV, Liu M, Tachibana Y, Fujihara T, et al. Insulated conjugated bimetallopolymer with sigmoidal response by dual self-controlling system as a biomimetic material. *Nat Commun*. 2020;11:408.
67. Russell GM, Kaneko T, Ishino S, Masai H, Terao J. Transient photodegradability of photostable gel induced by simultaneous treatment with acid and UV–light for phototuning of optically functional materials. *Adv Funct Mater*. 2022;32:202205855.
68. Kaneko S, Masai H, Yokoyama T, Liu M, Tachibana Y, Fujihara T, et al. Complementary color tuning by HCl via phosphorescence-to-fluorescence conversion on insulated metallopolymer film and its light-induced acceleration. *Polymers*. 2020;12:244.
69. Masai H. Controlling excited-state dynamics and chemical reactivities of platinum acetylide complexes via self-threading ligands with permethylated α -cyclodextrin. *Bull Chem Soc Jpn*. 2023;96:1196–205.
70. Hosomi T, Harada R, Masai H, Fujihara T, Tsuji Y, Terao J. Kinetic stabilization of a Ni^{II} bis(dithiobenzoate)-type complex achieved using three-dimensional insulation by a [1]rotaxane structure. *Chem Commun*. 2018;54:2487–90.
71. Takizawa SY, Aboshi R, Murata S. Photooxidation of 1,5-dihydroxynaphthalene with iridium complexes as singlet oxygen sensitizers. *Photochem Photobiol Sci*. 2011;10:895–903.
72. Kaneko T, Russell GM, Kawano Y, Masai H, Terao J. Fabrication of photoprocessable materials via photopolymerization using an acid-induced photocleavable platinum–acetylide crosslinker. *Angew Chem Int Ed*. 2023;62:e202305374.
73. Zhang X, Liu H, Yue L, He J, Bai Y. Mussel-inspired polymer: a photocurable and degradable polymer network for adhesives. *Polym Degrad Stab*. 2019;167:130–8.
74. Jamaludin FH, Mohd Yusoff NIS, Chida H, Yang X, Wong TW, Zhou H, et al. Photo-triggered sustainable adhesive based on itaconic acid. *ACS Sustain Chem Eng*. 2022;10:6389–401.
75. Shirai M. Photocrosslinkable polymers with degradable properties. *Polym J*. 2014;46:859–65.