Metallopolymers Organohydrogels with Photo-Controlled Coordination Crosslinks Work Properly Below 0 °C

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Controlled the structures and functions of gels is important for both fundamental research and technological applications. Introducing photoresponsive units into gels enables remote control of their properties with light. However, existing gels show photoresponsiveness only at room temperature or elevated temperatures. The development of photoresponsive gels that work below 0 °C can expand their usage in cold environments. Here, photoresponsive metallopolymer organohydrogels that function even at −20 °C are reported. The organohydrogels are prepared using photoresponsive Ru–thioether coordination bonds as reversible crosslinks to form polymer networks. A water/glycerol mixture is used as an anti-freezing solvent. At −20 °C, the Ru–thioether coordination bonds are dissociated under light irradiation and reformed reversibly in the dark, which result in alternating crosslinking densities in the polymer networks. This process enables inducing reversible gel-to-sol transitions, healing damaged gels, controlling the mechanical properties and volumes of the gels, and rewriting microstructures on the gels below 0 °C.

A hydrogel is a jelly-like soft matter that consists of 3D networks swollen by a large amount of water. Hydrogels, which are responsive to external stimuli (e.g., pH, temperature, redox, light), have many applications in science and technology, ranging from regenerative medicine to soft robotics. Photoresponsive hydrogels are a kind of stimuli-responsive hydrogels that are under intense investigation. [1-6] The photoresponsive-ness of gels is mainly based on photoreactions that change the crosslinking density,[1,6] topology,[7] and other physiochemical properties of hydrogels.[8-10] Their structures and functions can be controlled with light. Compared to other stimuli, light has high spatiotemporal resolution, enables remote control of hydrogels, and can be obtained from the sun. Therefore, light has been used to fabricate 3D extracellular matrices in hydrogels,[1,3,4] induce cargo release from hydrogels,[6,11] regulate adhesion,[12] and control the motion of actuators.[13,14]

Although photoresponsive hydrogels function normally at room temperature, they lose photoresponsiveness below the freezing temperature of water because the frozen matrix hinders photoreactions and structural changes in the hydrogels. A binary solvent system such as water/organic solvent or water/oil can be used to prepare organohydrogels that are non-freezing at subzero temperatures.[15-17]

However, simply replacing water in a photoresponsive hydrogel with a binary solvent usually does not result in a photoresponsive organohydrogel. Gelation and light-triggered structural changes are influenced by solvent-gelator interactions. Replacing water with another solvent may lead to no gelation or cause gels to lose their photo-controlled properties. Furthermore, many photoresponsive hydrogels are based on supramolecular interactions that occur only in water.[18,19] For example, the well-known host–guest complex of cyclodextrin and azobenzene, which has frequently been used as a photoresponsive crosslink for hydrogels, does not form in organic solvents.[20] The host–guest complexes form crosslinks only upon substituting the organic solvent with water.[20] It is essential to design gelators with suitable chemical structures so that photoresponsive gels can work in antifreezing solvents below 0 °C. Previously reported gels showed photoresponsiveness only at room temperature or elevated temperatures. The development of photoresponsive gels that function at subzero temperatures poses a challenge.

Here, we report metallopolymers organohydrogels that are photoresponsive even at −20 °C. The organohydrogels consist of a water/glycerol mixture as an antifreezing solvent, poly(N-hydroxyethyl acrylamide) as a gel-forming polymer, and Ru–thioether coordination bonds as photoresponsive crosslinks (Figure 1). The photoresponsiveness is attributed to ligand photosubstitution of the Ru complex moieties. Ligand photosubstitution means that a coordinated ligand in a metal...
complex is replaced by another ligand upon light irradiation.\textsuperscript{21–28} Although some Ru complexes exhibit reversible ligand substitution,\textsuperscript{21–24} their reactivity at subzero temperatures has not been explored. In our organogel systems (Figure 1), the coordinated thioether ligands in the Ru complex moieties can be substituted by solvent molecules upon light irradiation at $-20$ °C; when the light is turned off, thioether moieties in the polymer network substitute for the coordinated solvent molecules spontaneously. Such reversible ligand substitution can control the crosslinking densities in the organogel, resulting in significant changes in the network structures and properties. We demonstrate that light can induce reversible gel-to-sol transitions, heal damaged organogels, control the mechanical properties and volumes of organogels, and fabricate dynamic microstructures on organogels at $-20$ °C.

Ru complex 1 and thioether ligand 2 (Figure 2a) are model compounds for the designed reversible crosslinks (Figure 1). We synthesized and characterized 1 and 2 (Figures S1–S11, Supporting Information). Their reversible coordination was studied using UV–vis absorption spectroscopy (Figure 2b). The absorption maximum of the mixture of 1 (0.68 $\times$ 10$^{-3}$ M) and 2 (3.4 $\times$ 10$^{-3}$ M) in H$_2$O occurred at 553 nm and is attributed to the metal-to-ligand charge transfer (MLCT) band of 1. When the mixture was kept in the dark for 180 min, the absorption band shifted to 543 nm. The spectral change is identical to the reports in the literature regarding the formation of Ru–thioether coordination bonds,\textsuperscript{21,24} which suggested that thioether-coordinated Ru complex 3 was formed. Subsequently, the absorption spectrum returned to the initial state when the solution was irradiated with light (530 nm, 10 mW cm$^{-2}$, 5 min). This result demonstrated that the coordination was reversible (Figure 2a).

The reversible Ru–thioether coordination was confirmed using $^1$H NMR spectroscopy (Figure S31, Supporting Information), which showed that 2 coordinated with the Ru center in the dark and was substituted by a H$_2$O molecule upon light irradiation. The reversible coordination of 1 and 2 in H$_2$O at 25 °C resulted in reversible color changes (Figure 2e). However, since H$_2$O was frozen at $-20$ °C, 1, 2, and H$_2$O did not have sufficient mobility. Therefore, the reversible Ru–thioether coordination did not work at $-20$ °C (Figure 2f). To overcome this problem, we used a H$_2$O/glycerol (v/v, 1/1) mixture as the solvent, which freezes at $-38$ °C. We studied the Ru–thioether coordination in the H$_2$O/glycerol mixture using UV–vis absorption spectroscopy, which showed that a Ru–thioether coordination bond was formed by mixing 1 and 2 in the H$_2$O/glycerol mixture at 25 °C (Figure 2c). The Ru–thioether bond was cleaved reversibly upon light irradiation (Figure 2c). The reversible Ru–thioether coordination in the H$_2$O/glycerol mixture also induced reversible color changes (Figure 2g). The formation and cleavage of the Ru–thioether bond can be cycled at least five times under dark/light irradiation conditions (Figure 2d). Importantly, this reversible Ru–thioether coordination functions properly in the H$_2$O/glycerol mixture at $-20$ °C (Figure 2h and Figure S32, Supporting Information).

We further synthesized and characterized 1a and 2a (Figure 3a and Figures S12–S30, Supporting Information), which are analogues of 1 and 2 with a polymerizable double bond. The gels were prepared by polymerization of 1a, 2a, and N-hydroxymethyl acrylamide 4 in a H$_2$O/glycerol (v/v, 1/1) mixture (Figure 3a, left and Figure S33, Supporting Information). 4 constitutes the majority of the repeat units in the polymer network, so the network swells in H$_2$O/glycerol mixtures. Because the gels contain H$_2$O and glycerol as the binary solvent and Ru complex moieties as crosslinks, we call them metallopolymers organogels. The Ru complex and thioether moieties spontaneously form coordination bonds in the organogels, which act as photosensitive crosslinks (Figure 3a, right). We studied the gelation of the samples with the same total monomer concentration (0.9 M) and different molar ratios of 1a, 2a, and 4 (Figure 3b). These samples are denoted 1a$_x$2a$_y$4, where $x$ and $y$ are the percentages of 1a and 2a, respectively, and $100 - x - y$ is the percentage of 4. Inverted-vial tests showed that 1a$_2$2a$_3$ and 1a$_2$2a$_3$ formed gels, and the other samples with fewer crosslinks formed viscous solutions (Figure 3b). This result suggested that gelation needs a sufficient amount of...
Ru–thioether coordination bonds as crosslinks. Furthermore, we prepared samples with total monomer concentrations from 0.7 to 2 m and studied the effect of monomer concentration on gelation (Table S1, Supporting Information). As the monomer concentration increased, the samples gelated at a relatively low amount of crosslink. Gelation can occur in samples with suitable monomer concentrations and ratios.

Irradiating the 1a,2a organohydrogel with light (530 nm, 10 mW cm$^{-2}$, 5 min) at 25 °C induced a gel-to-sol transition (Figure 3c). Keeping the irradiated sample in the dark at 25 °C for 15 min resulted in regelation. This observation showed that the organohydrogel exhibited reversible photoinduced gel-to-sol transitions. We interpret that the reversible transitions are attributed to the reversible Ru–thioether crosslinks (Figure 3a, right). Importantly, reversible photoinduced gel-to-sol transitions also occurred at −20 °C: light irradiation (530 nm, 10 mW cm$^{-2}$, 15 min) induced the gel-to-sol transition, and the gel reformed when the irradiated sample was kept in the dark for 30 min (Figure 3c).

The 1a,2a organohydrogel is healable at both room temperature and low temperatures based on the reversible gel-to-sol transitions (Figure 3d). When the organohydrogel was damaged (Figure 3d, i and ii), the damaged part was locally irradiated with light (530 nm, 10 mW cm$^{-2}$, 5 min) to induce a gel-to-sol transition (Figure 3d, iii). The irradiated sample flowed across the damaged part. Healing was achieved by keeping the sample in the dark for 15 min to allow a sol-to-gel transition to occur (Figure 3d, iv). Furthermore, we studied photoinduced healing at −20 °C (Figure 3d, v–vii). The damaged organohydrogel was healed by light irradiation (530 nm, 10 mW cm$^{-2}$, 15 min) and then being kept in the dark (30 min). Improved fluidity in the sol state provided sufficient polymer chain mobility for healing (Figure S34, Supporting Information). Dissociation and re-formation of the Ru–thioether coordination bonds were involved in the healing process (Figures S35 and S36, Supporting Information).

The reversible Ru–thioether coordination is also suitable for preparing organohydrogels with photoswitchable mechanical properties. For this purpose, we prepared organohydrogels with both coordination and covalent crosslinks by copolymerization of 1a, 2a, 4, and 4a in a H$_2$O/glycerol (v/v, 1/1) mixture.

**Figure 2.** Photo-controlled reversible coordination of Ru complex 1 and thioether ligand 2 under different conditions. a) Schematic of the reversible coordination in aqueous solutions. b) UV–vis absorption spectra of 1 (0.68 × 10$^{-3}$ m) and 2 (3.4 × 10$^{-3}$ m) in H$_2$O just after mixing (0 min), after mixing for 180 min, and after subsequent light irradiation (530 nm, 10 mW cm$^{-2}$, 5 min). c) UV–vis absorption spectra of 1 (0.68 × 10$^{-3}$ m) and 2 (3.4 × 10$^{-3}$ m) in a H$_2$O/glycerol mixture (v/v, 1/1) after mixing for different times and after subsequent light irradiation (530 nm, 10 mW cm$^{-2}$, 5 min). d) Absorption changes of 1 (0.68 × 10$^{-3}$ m) and 2 (3.4 × 10$^{-3}$ m) in a H$_2$O/glycerol mixture under alternating dark/light irradiation cycles. e–h) Photographs of 1 and 2 in H$_2$O at 25 °C (e) and −20 °C (f) and in a H$_2$O/glycerol mixture at 25 °C (g) and −20 °C (h) in the dark and after light irradiation.
The Ru moieties and thioether moieties spontaneously formed coordination crosslinks in the organohydrogels. 4a is the covalent crosslinker that maintains the network structure when the Ru–thioether coordination crosslinks are cleaved upon light irradiation.

We studied organohydrogels with the same total monomer concentration (1 mM) and different molar ratios of the monomers at room temperature (Figure 4b and Table S2, Supporting Information). These samples are denoted $1a_x 2a_y 4a_1$, where $x$ and $y$ are the percentages of $1a$ and $2a$, respectively; the molar ratio of $4a$ is always 1%; and $100 - x - y - 1$ is the percentage of $4$. All the studied $1a_x 2a_y 4a_1$ samples were gels, showing that 1% covalent crosslinks resulted in the formation of polymer networks. We studied the mechanical properties of the organohydrogels using oscillatory rheology (Figure 4b and Figure S37, Supporting Information). Storage modulus ($G'$) is a measure of elastic response of a material and loss modulus ($G''$) is a measure of viscous response of a material. Comparing $G'$ of $1a_0 2a_0 4a_1$, $1a_{0.25} 2a_{0.25} 4a_1$, $1a_{0.5} 2a_{0.5} 4a_1$, $1a_1 2a_1 4a_1$, and $1a_1 2a_3 4a_1$ showed that $G'$ increased as the amount of coordination crosslinks increased. Tougher

Figure 3. Preparation of photoresponsive metallopolymer organohydrogels and photoinduced reversible gel-to-sol transitions and healing at 25 °C and −20 °C. a) Chemical structures of the monomers ($1a$, $2a$, and $4$) for the preparation of the organohydrogels and photoinduced reversible gel-to-sol transitions. b) Photographs of the samples (monomer concentration: 0.9 mM) prepared using different molar ratios of $1a$ and $2a$: $1a_0 2a_0 4a_1$ (0% $1a$, 0% $2a$, and 100% $4$), $1a_{0.25} 2a_{0.25} 4a_1$ (0.25% $1a$, 0.25% $2a$, and 99.5% $4$), $1a_{0.5} 2a_{0.5} 4a_1$ (0.5% $1a$, 0.5% $2a$, and 99% $4$), $1a_1 2a_1 4a_1$ (1% $1a$, 1% $2a$, and 98% $4$), $1a_1 2a_3 4a_1$ (1% $1a$, 3% $2a$, and 96% $4$), and $1a_1 2a_5 4a_1$ (1% $1a$, 5% $2a$, and 94% $4$). c) Photographs showing photoinduced reversible gel-to-sol transitions of the $1a_1 2a_5$ organohydrogel at 25 °C and −20 °C. d) Optical microscopy images of photoinduced healing of the $1a_1 2a_5$ organohydrogel at 25 °C and −20 °C.
organohydrogels were obtained by increasing the crosslinking density. \( G'' \) and loss tangent (\( \tan \delta = \frac{G''}{G'} \)) decreased as the amount of the coordination crosslinks increased. These data suggested that the rigidity of the organohydrogels increased as the crosslinking density increased. Comparing \( 1a_02a04a_{1} \), \( 1a_12a_04a_{1} \), and \( 1a_02a_54a_{1} \) showed that adding either the Ru moiety or the thioether moiety alone into the gel network did not improve the mechanical properties. This result confirms that the improved mechanical properties of \( 1a_02a_54a_{1} \) and \( 1a_12a_54a_{1} \) were attributed to the Ru–thioether coordination crosslinks.

As a control sample, hydrogel \( 1a_12a_54a_{1} \) was prepared by polymerization of \( 1a \), \( 2a \), \( 4a \), and \( 4a \) in \( H_2O \). The hydrogel functioned properly at room temperature. However, at \( 0^\circ C \), it was frozen, lost elasticity, and became fragile under stretching (Figure 4c). In contrast, the organohydrogel \( 1a_12a_54a_{1} \) did not freeze even at \( -20^\circ C \) (Figure 4d). It remained highly elastic and was capable of twisting, knotting, and stretching. The deformed organohydrogel also showed resilience for shape recovery.

To understand the mechanical properties of the hydrogel and the organohydrogel at different temperatures, we measured their \( G' \) and \( G'' \) values between \(-20 \) and \( 80^\circ C \) (Figure 4e). For the hydrogel, \( G' \) and \( G'' \) were \( \approx 2.8 \)–\( 5.2 \) kPa and \( 0.4 \)–\( 1.5 \) kPa, respectively, between \( 5 \) and \( 80^\circ C \). For the organohydrogel, \( G' \) and \( G'' \) were \( \approx 2.5 \)–\( 3.0 \) kPa and \( 0.2 \)–\( 0.3 \) kPa, respectively, between \( 5 \) and \( 80^\circ C \). Thus, both the hydrogel and the organohydrogel were elastic in this temperature range. However, the \( G' \) and \( G'' \) values of the hydrogel increased dramatically as the

Figure 4. Organohydrogels with coordination and covalent crosslinks and their photoswitchable mechanical properties at room temperature and \(-20^\circ C \). a) Schematic illustration of organohydrogels with coordination and covalent crosslinks under light irradiation and in the dark. The chemical structure of the covalent crosslinker \( 4a \) is shown. b) Storage moduli (\( G' \)), loss moduli (\( G'' \)), and loss tangent (\( \tan \delta = \frac{G''}{G'} \)) of organohydrogels prepared using \( 1a \), \( 2a \), \( 4a \), and \( 4 \) with different molar ratios. c) Photographs of hydrogel \( 1a_12a_04a_{1} \) at \( 0^\circ C \). d) Photographs of organohydrogel \( 1a_12a_04a_{1} \) at \(-20^\circ C \). e) Temperature dependence of \( G' \) and \( G'' \) of hydrogel \( 1a_12a_04a_{1} \) and organohydrogel \( 1a_12a_54a_{1} \) measured at a constant strain of \( 0.1\% \) and frequency of \( 1 \) rad s\(^{-1} \). f,g) Frequency dependence of \( G' \) and \( G'' \) for organohydrogel \( 1a_12a_54a_{1} \) before irradiation, after light irradiation (\( 530 \) nm, \( 10 \) mW cm\(^{-2} \), \( 20 \) min), and after being kept in the dark for \( 6 \) h at \( 25^\circ C \) (f) and \(-20^\circ C \) (g), respectively.
temperature decreased from 5 to −20 °C. We conclude that the hydrogel lost elasticity and became fragile at ≈0 °C because of the modulus changes induced by frozen water. In contrast, the \( G' \) and \( G'' \) values of the organohydrogel were almost constant between −20 and 80 °C. Thus, the organohydrogel had a wider working temperature than the hydrogel. Organohydrogels with different ratios of \( H_2O/glycerol \) (v/v = 2/1 and 1/2) were studied, which also showed working temperatures below 0 °C (Figure S38, Supporting Information).

We further studied the effects of light irradiation on the mechanical properties of organohydrogel 1a,b,4a1 at 25 and −20 °C (Figure 4f,g). At 25 °C, \( G' \) and \( G'' \) increased from 2.1 to 4.1 kPa and from 0.05 to 0.5 kPa, respectively, when the frequency increased from 0.1 to 100 rad s\(^{-1}\) (Figure 4f). These moduli are typical for elastic gels. Irradiating (530 nm, 10 mW cm\(^{-2}\), 20 min) the organohydrogel resulted in a decrease in \( G' \) and an increase in \( G'' \). The stiffness of the organohydrogel was decreased via light irradiation. Subsequently, the moduli were recovered when the irradiated organohydrogel was kept in the dark for 6 h. The reversible changes in the moduli are in accordance with the reversible cleavage and reformation of the Ru–thioether crosslinks under light irradiation and dark storage (Figure 4a). At −20 °C, the changes in moduli showed the same trend when the organohydrogel was irradiated with light (530 nm, 10 mW cm\(^{-2}\), 20 min) and subsequently kept in the dark (Figure 4g). These results demonstrated that the organohydrogel exhibited photoswitchable mechanical properties at both room temperature and low temperatures.

Organohydrogels showed photoinduced volume changes in the \( H_2O/glycerol \) (v/v, 1/1) mixture. When disk-shaped organohydrogel 1a,b,4a1 was irradiated with light (530 nm, 10 mW cm\(^{-2}\), 2 h) at 25 °C in the \( H_2O/glycerol \) (v/v, 1/1) mixture, its diameter increased to ≈118% of the original diameter (Figure 5a). Light irradiation cleaved the Ru–thioether bonds and reduced the crosslinking density in the organohydrogel. Thus, the gel network expanded. The irradiated organohydrogel contracted to the original volume when it was kept in the dark for 6 h (Figure 5a). The volume change was reversible. Some interesting soft actuators,\(^{[20,29,30]}\) which showed photoinduced volume changes at room temperature, have been reported. In contrast, our organohydrogel also showed photoinduced volume changes at −20 °C (Figure 5b). The diameter of the organohydrogel increased to ≈105% of the original diameter after light irradiation (530 nm, 10 mW cm\(^{-2}\), 3 h) and contracted to the original diameter after being kept in the dark for 6 h. The organohydrogel exhibited reversible volume changes even at −20 °C.

The reversible coordination of Ru–thioether not only results in changes in the crosslinking density but also results in color changes (Figure 2g,h). Therefore, the organohydrogel is a suitable material for reversible photo-patterning (Figure 6). We prepared a piece of free-standing organohydrogel 1a,b,4a1 (Figure 6a). The organohydrogel was irradiated with light (530 nm, 10 mW cm\(^{-2}\), 10 min) through a mask (Figure 6b, left). The color of the exposed areas changed, and a pattern was generated (Figure 6c,d). The Ru moieties and thioether moieties coordinated spontaneously when the irradiated organohydrogel was kept in the dark. The color of the irradiated areas

![Figure 5](image-url)

**Figure 5.** Photoinduced reversible volume changes of organohydrogel 1a,b,4a1. Expansion and contraction of the organohydrogel under light irradiation and in the dark in the \( H_2O/glycerol \) (v/v, 1/1) mixture a) at 25 °C and b) at −20 °C.

![Figure 6](image-url)

**Figure 6.** Preparation of self-erasing patterns on organohydrogels with light at 25 and −20 °C. a) Photograph of freestanding organohydrogel 1a,b,4a1. b) Schematic illustration of writing patterns on the organohydrogel and the self-erasing process in the dark. c–i) Self-erasable and rewritable patterns fabricated on an organohydrogel using different photomasks and different temperatures.
changed back, and the pattern was self-erased in the dark at room temperature (Figure 6b, right and Figure 6e).

Self-erasable gels were proposed for storing sensitive or temporary information, anti-counterfeiting, and encryption.[31,32] The reported self-erasable gels work properly at room temperature. We further demonstrated that our self-erasable organohydrogel also worked at −20 °C. Therefore, we fabricated an array on the organohydrogel via light irradiation through Mask 2 at −20 °C (Figure 6f). The array self-erased when the organohydrogel was stored in the dark for 6 h. We rewrote different patterns at −20 °C using different marks (Figure 6g–i). These results showed that our organohydrogel is a rewritable and self-erasable material at both room temperature and low temperatures, which expands the usage temperature of rewritable and self-erasable materials.

In conclusion, we have demonstrated that metallopolymer organohydrogels with photoresponsive Ru–thioether coordination crosslinks function properly even at −20 °C. The Ru–thioether coordination bond forms spontaneously in the dark and can be cleaved by light in H2O/glycerol mixtures at −20 °C. The metallopolymer organohydrogels showed photo-triggered reversible gel-to-sol transitions, photoinduced healing, photo-switchable mechanical properties, and photo-controlled volume changes and were applied for rewritable and self-erasable photopatterning at −20 °C. Photoresponsive metallopolymer organohydrogels are new materials with multiple functions and many potential applications in cold environments. Light can remotely and precisely control the properties of metallopolymer organohydrogels with high spatiotemporal resolution. We anticipate that the design principles can be applied to designing other materials that work in cold environments. Our study opens up an avenue for remote control of soft matter below 0 °C, which is important for both the fundamentals of soft matter and their applications in cold environments.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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