

Reconfigurable Materials Based on Photocontrolled Metal–Ligand Coordination

Jianxiong Han, Yun-shuai Huang, Ni Yang, and Si Wu*

Photoresponsive materials have attracted growing interest because of their potential applications in materials science, such as photoswitches, photopatterning, information storage, and so on. However, there are some challenges for photoresponsive materials for certain applications: 1) Only a few photoresponsive surfaces are transformed into multiple states after photoreactions to adapt to changing environmental conditions; 2) Photoresponsive materials may not function properly in cold environments, especially for gels. To address these problems, we have recently developed photoresponsive materials based on ruthenium (Ru) complexes. Such Ru complexes showed a photoinduced ligand substitution under visible light irradiation. Reconfigurable surfaces that can adapt to environmental changes and photoresponsive organohydrogels that function effectively at sub-zero temperatures have been fabricated using photoresponsive Ru complexes. Herein, it is demonstrated that based on photocontrolled Ru–ligand coordination, reconfigurable surfaces can be modified for user-defined functions via visible light irradiation and that photoresponsive gels can function even at $-20\text{ }^{\circ}\text{C}$. As a perspective, Ru-containing photoresponsive complexes could open up pathways for a variety of applications.

compared with other stimuli. Specific photoreactions of photoresponsive materials can be triggered by light irradiation, which results in changes in their physical or chemical properties^[3,8–10] such as polarity, orientation, or wettability.

To date, several photoresponsive compounds have been developed and used in materials science,^[11,12] nanotechnology,^[13–16] and biomedicine.^[17–20] For example, *cis–trans* isomerization of azobenzenes is used for information storage, lithography, and photopharmacology;^[10,21–23] alkenes or overcrowded alkenes have been developed for self-locking and photoinduced surface functionalization;^[24,25] the cleavage of coordination bonds or linkage of transition metal complexes can be used for drug delivery.^[18,19,26] Among these photoresponsive compounds, ruthenium (Ru) complexes are a class of photoresponsive metal complexes. Ru complexes show the ability of ligands to be selectively photosubstituted by solvent molecules under light irradiation.

The photoreactions of Ru complexes can even be induced by long-wavelength light, which is attributed to their metal-to-ligand charge-transfer (MLCT) bands in the visible or near infrared region, which is promising for biological applications compared with other responsive compounds.^[18,27] More importantly, unlike most of the reported photoreactions of photoresponsive compounds that exhibit static and irreversible weakness, the photoreactions of some Ru complexes have reversible and dynamic properties that have already been used in supramolecular chemistry.^[16,28] For instance, some photosubstitutions of Ru complexes with 2,2':6',2''-terpyridine (tpy) and 2,2'-biquinoline (biq) ligands are shown (**Figure 1**).


A number of ligand bonds coordinated to Ru, such as amine, thioether, pyridine, nitrile, or some other more complicated ligands can be photocleaved and further photosubstituted by H₂O upon visible light irradiation. In addition, coordination processes can occur again in aqueous Ru compounds with free ligands in the dark under heat or at room temperature. For example, it has been demonstrated that [Ru(tpy)(biq)(CH₃CN)] can be successfully photocleaved by red light irradiation (671 nm, 110 mW cm⁻²). When the aqueous Ru complex was further refluxed in CH₃CN/H₂O in the dark, [Ru(tpy)(biq)(CH₃CN)] was obtained again.^[29] When thioethers act as photosubstituted ligands, Ru–thioether photocleavage occurs via green (520 nm) or red light irradiation (671 nm). If the mixture remains in the dark at room temperature,

1. Introduction

Stimuli–responsive materials have potential applications in drug delivery,^[1,2] manipulation of macroscopic devices,^[3] information storage,^[4] molecular switches,^[5] lithography,^[6] etc.^[7] These materials can respond to external stimuli, such as heat, light, electric or magnetic field, carbon dioxide, and pH. Among them, light, a noninvasive stimulus, has a high spatiotemporal resolution

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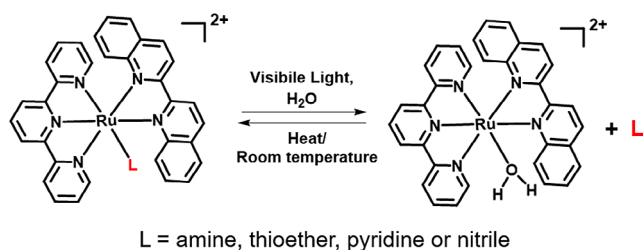


Figure 1. Schematic representation of photoinduced ligand substitution based on ruthenium (Ru) complexes. When irradiated with visible light, a ligand (L) can be substituted by a solvent molecule such as water. For example, a Ru–thioether coordination can form in the dark at room temperature and the ligand can be replaced by water under light irradiation. The formation of other Ru ligand coordinations usually requires heating.

the dynamic bond between Ru and the thioether reforms spontaneously.^[16,28,30,31]

Among these photoreactions based on Ru–ligands, the photo-substitution of Ru–thioether attracts much more attention due to its dynamic and reversible properties. In these research news, we present two applications of reconfigurable materials based on a visible light-controlled Ru–thioether coordination reported by our group.^[30,31]

2. Reconfigurable Materials Based on Photocontrolled Ru–Thioether Coordination

2.1. Reconfigurable Multifunctional Surfaces Based on Ru–Thioether Photosubstitution

As already introduced, Ru–thioether complexes are capable of reversible ligand photosubstitution between two states by visible light irradiation or in dark conditions. In aqueous solution, visible light irradiation breaks the bond between thioether and the Ru backbone and the ligand is replaced by H₂O. If the solution is placed in the dark with free thioethers, the thioethers spontaneously coordinate with the Ru backbone. More importantly, reversible and dynamic photoreactions on the surface allow multiple states in the photosubstitution process.

In 2018, our group reported on a reconfigurable surface modified with Ru–thioether, which is controlled by visible light.^[30] Compared with the conventional reported photoreactions on surfaces, the Ru–thioether-modified reconfigurable surfaces show reversible and dynamic properties under light control. Inspired by the replacement of different bits by a screwdriver, the aqueous Ru compound [Ru(tpy-COOH)(biq)(H₂O)](PF₆)₂ (Ru–H₂O) was first grafted onto a substrate that can be defined as a “multibit screwdriver.” Different functional thioethers acting as “bits” can be coordinated with Ru–H₂O. These “bits” could be dynamically controlled with visible light to modify the reconfigurable surface with several functional states. The bits are removed from the screwdriver by photosubstitution using visible light. In the dark, another set of bits is automatically attached to the screwdriver by a thermal substitution process (Figure 2a,b). In this way, a number of surface applications such as surface pattern rewriting, protein adsorption control, and reversible

surface wettability have been achieved based on visible light-controlled Ru–thioether coordination.

To illustrate the concept of reconfigurable properties of Ru–H₂O-modified surfaces, fluorescein isothiocyanate (MeSC₂H₄-FITC) and rhodamine B isothiocyanate (MeSC₂H₄-RhB), both containing thioether groups, were synthesized to provide the ability to rewrite the surface patterns. MeSC₂H₄-FITC and MeSC₂H₄-RhB are fluorescent under different irradiation wavelengths. First, the Ru–H₂O-modified surface was immersed in the aqueous solution of MeSC₂H₄-FITC in the dark, whereby the color of the surface was transferred from black to green under the fluorescence microscope, demonstrating a fluorescent surface (Figure 2c,d). When the surface under a photomask was irradiated with green light, the exposed area changed back to the original Ru–H₂O (black) due to photocleavage (Figure 2e). Finally, when the substrate was immersed in the aqueous solution of MeSC₂H₄-RhB in the dark, the red area appeared under the fluorescence microscope (Figure 2f). The whole process successfully demonstrates the rewriting property of the Ru complex-modified surface.

In addition, surface wettability could be reversibly controlled by photosubstitution. By preparing a Ru–H₂O-modified surface on a porous silica coating, two functional thioether ligands could be coordinated onto the substrate. 2-(Methylthio)ethanol (MTE) could modify the substrate to become hydrophilic. (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)(methyl)sulfane (HFDMS) was thus able to make the surface hydrophobic by photosubstitution. Figure 1g shows the changes in surface wettability by measuring the contact angle. A Ru–MTE-modified substrate had a water contact angle of 27 ± 2°. After green light irradiation, the hydrophilic MTE was cleaved off, and HFDMS was able to coordinate to the Ru–H₂O-modified surface in the dark. We could observe that the water contact angle increased dramatically to 154 ± 2°. Thus, we can tune the reconfigurable surface wettability with photosubstitutions of dynamic Ru–thioether bonds.

Not only organic small molecules but also polymers are suitable ligands for the fabrication of reconfigurable surfaces. Manipulable protein adsorption surfaces can be modified by Ru complexes controlled by visible light. By addition of poly(ethylene glycol)-modified thioether (MeSC₂H₄-PEG) to the Ru–H₂O-modified surface a protein-resistant surface was produced because PEGylation has a high resistance to protein adsorption. When the surface is immersed for 2 h in the solution of fluorescence-labeled bovine serum albumin (BSA), it still shows no fluorescence, which is a strong evidence for a protein adsorption-resistant surface. When exposed to visible light through a photomask, exposed parts of the surface coordinated with MeSC₂H₄-PEG were cleaved. In addition, the surface was immersed again in BSA solution, whereby the exposed Ru–H₂O (black) regions captured the fluorescence-labeled BSA via electrostatic interactions (Figure 2h). The Ru–H₂O-modified surface was converted from protein resistant to protein adsorptive. In addition, a number of photoresponsive biomaterials require a deep penetration of light into the tissue. We were able to show that red light successfully penetrated a 4 mm piece of pork tissue and photoactivated the Ru–MeSC₂H₄-PEG-modified surface, thereby converting it into protein adsorptive. Thus, a functional manipulating protein adsorption surface with Ru–thioether complexes was created.

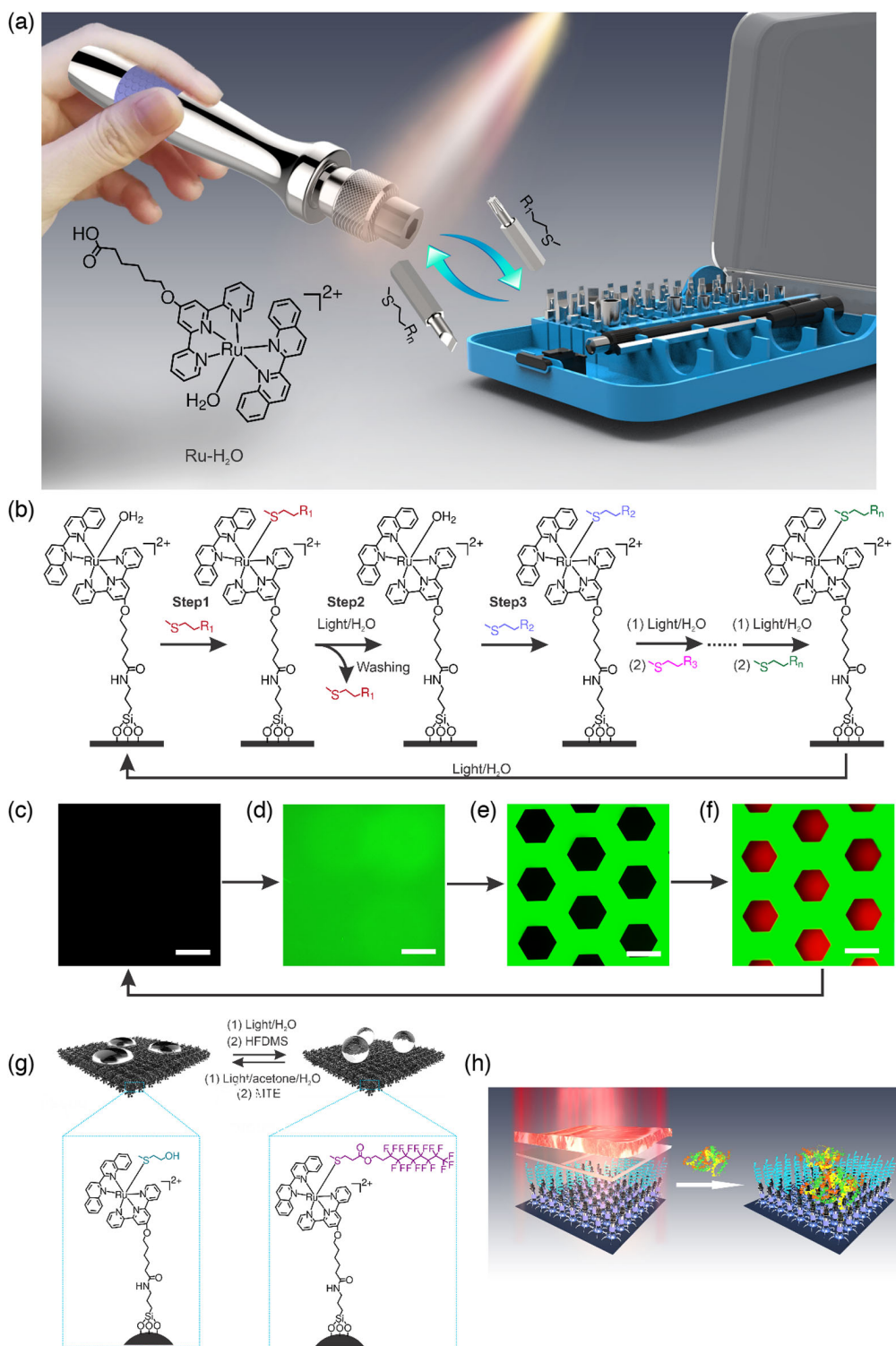


Figure 2. a) Scheme of reconfigurable surfaces based on light-controlled Ru–thioether complexes. b) Schematic illustration of photosubstitutions for Ru–H₂O and different functional thioether ligands. The fluorescence microscopy images of c) Ru–H₂O coated substrate, d) Ru–MeSC₂H₄–FITC-coated substrate, e) patterned substrate with Ru–MeSC₂H₄–FITC-modified (green) and Ru–H₂O-modified (black), and f) patterned substrate with Ru–MeSC₂H₄–FITC-modified (green) and Ru–MeSC₂H₄–RhB-modified (red). (Scale bars: 300 μm.) g) Schematic illustration of reversible surface transitions between hydrophilic and hydrophobic properties based on a Ru backbone and functional thioethers controlled by visible light. h) Schematic of a light-controlled Ru–H₂O-modified surface for protein resistance and adsorption. Reproduced under the terms and conditions of the CC-BY 4.0 License.^[30] Copyright 2018, The Author(s), published by Springer Nature.

2.2. Photocontrolled Organohydrogels Based on Ru–Thioether Work Properly Below 0 °C

Photoresponsive hydrogels based on polymer networks are well known and appealing for their tremendous applications in science and technology, such as 3D extracellular matrices fabrication,^[32] cell adhesive regulation,^[33] cargo release,^[34] and actuator controlling.^[35] However, most photoresponsive gels cannot operate below freezing temperature, because the frozen matrix inhibits photoreactions and structural changes in the gel. Furthermore, it is known that most photoresponsive hydrogels with their supramolecular interactions are only obtained in water. It is desirable to design and synthesize a hydrogel that can work in antifreeze solvents below the freezing point.

In 2020, our group reported for the first time about a reversible photosubstitution process below freezing point based on Ru complexes.^[31] The photoresponsive organohydrogel based on a Ru-containing polymer can operate even at $-20\text{ }^{\circ}\text{C}$. **Figure 3a** shows the schematic concept of photocontrolled organohydrogels based on Ru–thioether crosslinks. We used $\text{H}_2\text{O}/\text{glycerol}$ as a binary solvent for the antifreeze and Ru–thioether complexes as crosslinks, therefore we call the gel a metallopolymer organohydrogel. First, we prepared three different molar ratios of monomer concentrations to check for gelation. The results suggest that a sufficient amount of coordination bond between Ru and thioether is the key factor for gelation. With a suitable concentration ratio of coordination crosslinks, gel-to-sol transitions occurred under light irradiation at room temperature

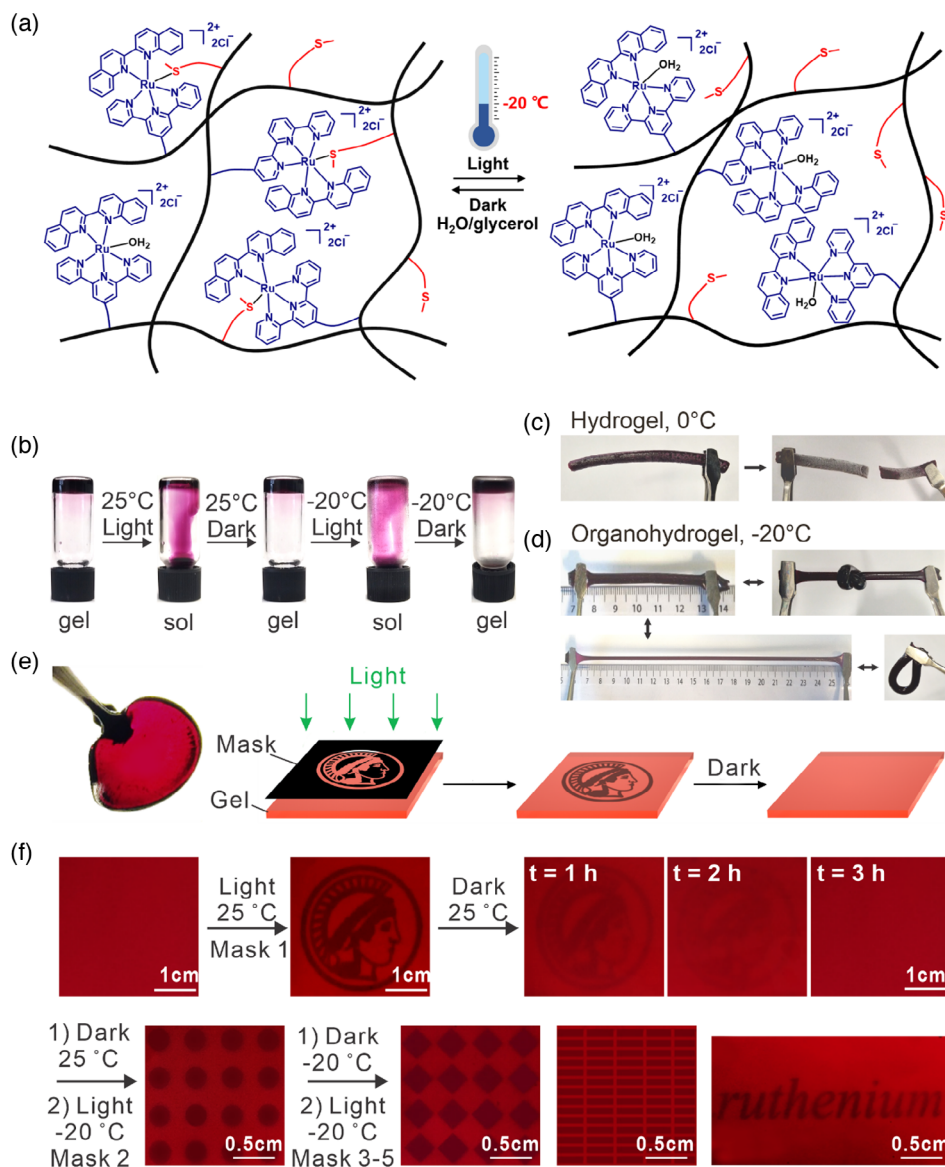


Figure 3. a) Scheme of photocontrolled organohydrogels based on Ru–thioether crosslinks. b) Organohydrogels with photoinduced reversible sol–gel transitions at $25\text{ }^{\circ}\text{C}$ and $-20\text{ }^{\circ}\text{C}$. c) Hydrogel of Ru–thioether at $0\text{ }^{\circ}\text{C}$. d) Organohydrogel of Ru–thioether at $-20\text{ }^{\circ}\text{C}$. e) Free-standing organohydrogel for self-erasing patterns. f) Self-erasing and rewritable patterns fabricated on an organohydrogel with different photomasks processed at $25\text{ }^{\circ}\text{C}$ and $-20\text{ }^{\circ}\text{C}$. Reproduced with permission.^[31] Copyright 2020, Wiley-VCH.

and reversed to the gel state in the dark (Figure 3b). When the temperature dropped to -20°C , the gel-to-sol transitions persisted.

To demonstrate the photoswitchable mechanical properties of the reversible Ru-containing organohydrogels, we prepared control sample hydrogels with the same component ratio in H_2O . Both hydrogel and organohydrogel worked perfectly at room temperature. When the temperature dropped to 0°C , the hydrogel immediately froze and showed no elastic properties. When the hydrogel was stretched, it became weak and brittle (Figure 3c). In contrast, even at -20°C , the organohydrogel still showed the highly elastic properties. When twisted, knotted, and stretched, it did not become brittle (Figure 3d).

Due to the reversible coordination of Ru–thioether, which induced color changes, we expected a reversible photopatterning based on the organohydrogel. Covering a piece of free-standing organohydrogel with a photomask could achieve this feature. On irradiation with green light, the exposed area of the organohydrogel cleaved the thioether ligand from the Ru backbone and transformed into Ru– H_2O , which caused a color change and created a pattern. Afterward, the free-standing organohydrogel was placed in the dark at room temperature and the pattern disappeared, which was due to a coordination of the thioether ligand to Ru (Figure 3e,f). In addition, we first reported on a self-erasable organohydrogel that functioned properly at -20°C . An array pattern was produced by green light irradiation through mask 2 at -20°C . Another three masks were also used for photopatterning by alternating light irradiation and dark transitions at the same temperature. In this way, we produced an antifreeze, reversible, and self-erasing photopatterning material by light control of a Ru–thioether–organohydrogel.

3. Conclusions

In summary, some ruthenium (Ru) complexes, especially Ru–thioether complexes, show dynamic and reversible properties during photosubstitution as ideal photoresponsive materials. These excellent advantages based on Ru–thioether complexes for multifunctional reconfigurable surfaces and antifreeze organohydrogels via light control have been developed. Ru-containing photoresponsive complexes could open up avenues for a wide range of applications. We believe that our work is a versatile method for adaptive surface functionalizations and provides fundamental knowledge of soft matter in cold environments.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

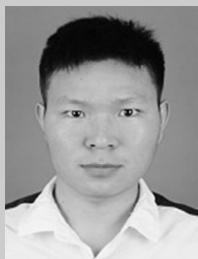
antifreeze gels, photoresponsive materials, reconfigurable surfaces, ruthenium complexes

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