Reconfigurable Surfaces Based on Photocontrolled Dynamic Bonds

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Photocontrolled surfaces have attracted increasing interest because of their potential applications in lithography, photopatterning, biointerfaces, and microfluidics. Light provides high spatiotemporal resolution to control functions of such surfaces without getting into direct contact. However, conventional photocontrolled surfaces can only be switched between two states (on and off). The development of photocontrolled reconfigurable surfaces that can be switched among multiple states is highly desirable because these surfaces can adapt to rapid environmental changes or different applications. Herein, recent developments of photocontrolled reconfigurable surfaces are reviewed. Specially, reconfigurable surfaces based on photocontrolled reversible reactions including thiol-quinone methide, disulfide exchange, thiol-disulfide interconversion, diselenide exchange, and photosubstitution of Ru complexes are highlighted. As a perspective, other photocontrolled dynamic bonds that can be used to construct reconfigurable surfaces are summarized. Remaining challenges in this field are discussed.

1. Introduction

Manipulating surface functions plays a significant role in various applications in both academia and industry. For example, surfaces with tunable wettability have been widely studied for the development of adaptive surfaces, biointerfaces, microfluidic devices, and sensors.[1–14] In addition, surfaces that can regulate biological functions have been investigated for controlling protein absorption, manipulating cell adhesion, and sensing.[15–30]

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Stimuli-responsive surfaces have been developed for many years.[31,32] Such surfaces are usually fabricated by surface modification with stimuli-responsive compounds.[14,18,31–36] Physicochemical properties of these surfaces can be irreversibly or reversibly tuned under the stimulation of a stimulus such as light, temperature, chemicals, electric field, or pH.[35,37–45]

Light, an noninvasive stimulus, is particularly attractive due to its remote-control manner and high spatiotemporal resolution.[46] Photoreactions such as photocleavage, photocoupling, and photoisomerization have been utilized to control surface properties and functions.[5,47,48] Photolysis (e.g., using *o*-nitrobenzyl-based photocages) has been widely used for light-controlled adsorption or desorption of biologically active molecules.[29,49–52] Photocoupling reactions including photoinduced Diels–Alder reactions, photoinduced 1,3-dipolar cycloaddition of nitrile imines with alkenes, and photoinduced esterification of benzodioxinones and alcohols, have been used for surface functionalization.[23,29,46,53–58] However, these photolysis and photocoupling reactions are irreversible, resulting in static surfaces because of irreversible formation or breakage of bonds.

Reversible control of surface functions with light was achieved via the modification of surfaces with photoswitchable molecules such as azobenzene,[2,59–66] spiropyran,[16,45,67–69] dithienylethene,[70,71] and molecular shuttles[59,72–74] (**Figure 1**a). We take azobenzene-functionalized surfaces as an example. Azobenzene exhibits reversible trans–cis photoisomerization; trans and cis isomers have different diople moments and other properties. It was demonstrated that photoisomerization of azobenzene on surfaces resulted in changes of wettability, surface area, and surface stress.[63,75] Photoisomerization of azobenzene can also regulate supramolecular interactions.[76] For example, trans azobenzenes can form host–guest complexes with cyclodextrins (CDs), while the cis azobenzenes have weak interaction with CDs, leading to dissociation of the host–guest complexes. The switchable host–guest interaction between azobenzenes and CDs affords a method to control surface wettability and adhesion.[77–80] However, such photoswitchable surfaces can be only switched between two functional states (on and off).

Recently, surfaces that can be interconverted into multiple states under light irradiation have been fabricated using light-controlled dynamic bonds (Figure 1b). These dynamic bonds discussed in this Progress Report include covalent and coordination bonds that undergo exchange, metathesis, and ligand

substitution under light irradiation. Light induces reversible reactions, which result in reversible breakage and formation of the bonds and endow the bonds with dynamic nature. These reactions, including thiol-quinone methide,[81] disulfide exchange,[82,83] thiol-disulfide interconversion,[84] diselenide exchange,[85] and photosubstitution of Ru complexes,[86] enable fabrication of reconfigurable surfaces on demand (**Table 1**).

In this Progress Report, we focus on recent developments of reconfigurable surfaces based on photocontrolled dynamic bonds. We give an overview of photocontrolled dynamic bonds that have been used to construct reconfigurable surfaces. We highlight the potential applications of such surfaces. Alternative ways to construct photocontrolled reconfigurable surfaces and the challenges of this field are discussed.

2. Reconfigurable Surfaces Based on Photocontrolled Dynamic Bonds

2.1. An Overview of Photocontrolled Dynamic Bonds for Reconfigurable Surfaces

The exchange, metathesis, and ligand substitution of dynamic bonds can reach a thermodynamic minimum at equilibrium (Table 1).[87–92] This equilibrium is shifted under external stimuli. Photoreactions of dynamic bonds can be spatially and temporally controlled at a specific area in a reversible way, meanwhile they can be tuned by the wavelength, light intensity, and irradiation time. These features provide a tremendous opportunity to develop photocontrolled reconfigurable surfaces.[88] Surfaces functionalized with photoresponsive compounds that undergo reversible photoreactions such as photoinduced disulfide exchange,[82,83] thiol-quinone methide,[81] thiol-disulfide interconversion,[84] diselenide exchange,[85] and ligand substitution of Ru complexes,[86] are reconfigurable (Figure 1b and Table 1). Next, we will focus on reconfigurable surfaces based on these photoreactions. We will show the mechanisms of these reactions and potential applications of reconfigurable surfaces.

2.2. Reconfigurable Surfaces Based on Thiol-Quinone Methide Photoclick Reaction

Photoclick reactions of thiol-ene/yne in surface modification have been studied extensively.[55,54,87,93–97] However, these reactions cannot switch surface properties reversibly because of irreversible formation of covalent bonds. Arumugam and Popik reported a novel surface photochemistry that allowed immobilization of various substances on surfaces and reversible replacement of immobilized substances under light irradiation (**Figure 2**a,b).[81] The method is based on a reversible photoclick reaction. They used compound **1**, which was converted into compound **2** (2-naphthoquinone-2-methides) under UV irradiation. Compound **2** then reacted with thiols **3** to yield thioethers **4**. The obtained thioether **4** was hydrolytically stable under ambient conditions. Upon UV irradiation, **4** was cleaved to regenerate reactive compound **2** and free thiol groups on the surface (Figure 2a). This reaction has two significant features to endow reusability to surface modification: 1) The unreacted **2**

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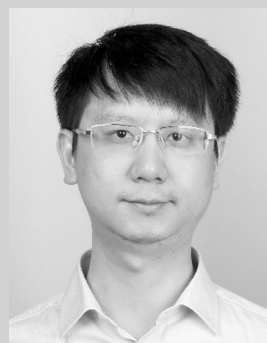
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can be quenched by H_2O, regenerating the initial compound **1**; the prepared solution in the system can be reused for many times depending on the reagent consumption. 2) In addition, the active compound **2** has a short lifetime in aqueous solutions, which cannot migrate from the irradiation sites. Therefore, this approach allows a precise spatiotemporal control.

Reconfiguring surface properties were demonstrated by preparing of a positive or negative pattern (Figure 2c–e). A **1a**-modified surface was obtained by irradiation of a thiol-coated glass slide in an aqueous solution of **1a**. A pattern with biotins on it was created by irradiation of the **1a**-modified surface in an aqueous solution of **1b** through a shadow mask. Because avidin had specific interaction with biotin, a fluorescent pattern was obtained by treating the surface with fluorescently labeled avidin (FITC-avidin) (Figure 2c). The high contrast of the image indicated that **1a** was efficiently replaced by **1b** in the exposed regions. Then, flood irradiation of this surface in an aqueous solution of **1b** generated a surface modified with **1b**. Photopatterning the surface in an aqueous solution of **1a** resulted in a negative image (Figure 2d). After flood irradiation in an aqueous solution of **1b** and stain with FITC-avidin, a surface
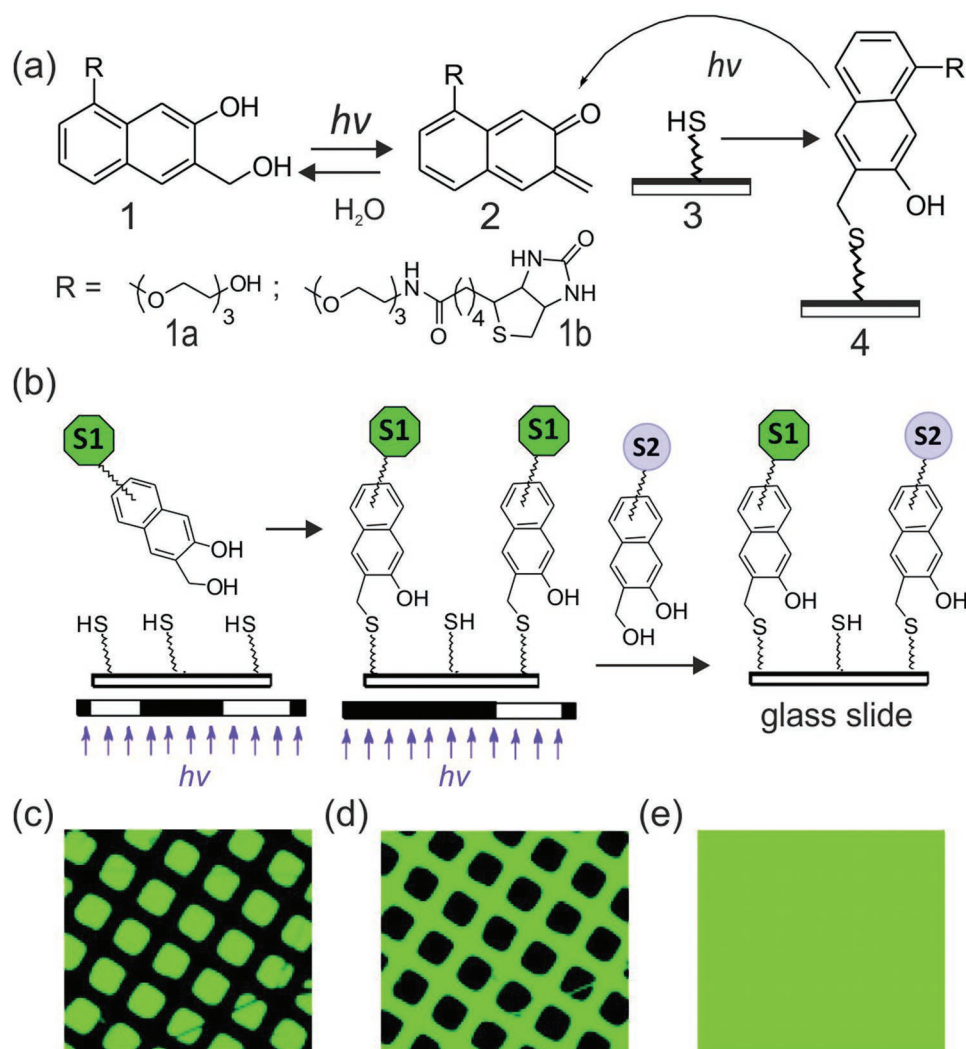
(a) A conventional photoswitchable surface

(b) A photo-controlled reconfigurable surface
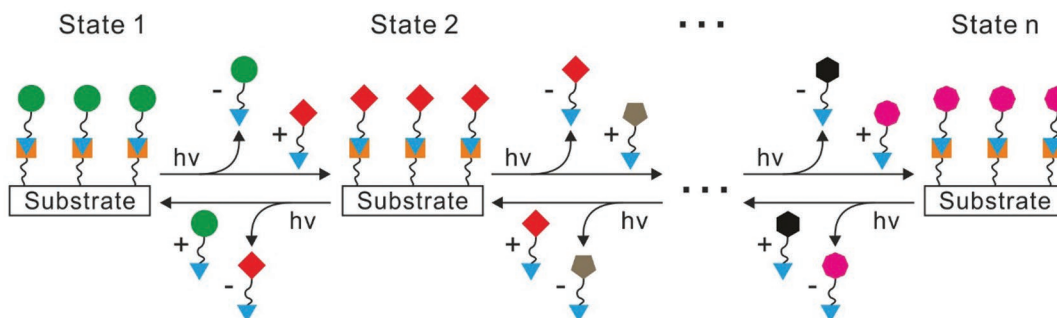
Figure 1. Comparison of a conventional photoswitchable surface with a photocontrolled reconfigurable surface. a) Schematic illustration of a conventional photo photoswitchable surface and two typical photoswitchable compounds (azobenzene and spiropyran). b) A photocontrolled reconfigurable surface that can be interconverted into multiple states reversibly.

Table 1. Photoreactions utilized for the design of reconfigurable surfaces.

Reaction type	Reaction	Refs.
Thiol-quinone methide photoclick reaction		[81]
Disulfide exchange		[82,83]
Thiol-disulfide interconversion		[84]
Diselenide exchange		[85]
Ligand photosubstitution		[86]

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Figure 2. a) Reversible and dynamic surface derivatization based on thiol-quinone methide photoclick chemistry. b) Immobilization and replacement of derivatives of **1** on a thiol-functionalized surface. c–e) Fluorescence microscopy images of surfaces: c) Patterned surface was created after irradiation in a solution of **1a**, and then masked irradiation in a solution of **1b**; d) Patterned surface was created after irradiation in **1b** solution, and then masked irradiation in **1a** solution; e) Surface was created after irradiation in a solution of **1b**. Reproduced with permission.[81] Copyright 2012, American Chemical Society.

with uniform fluorescence was generated. The uniform fluorescence of the resulting surface demonstrated the replacement of **1a** with **1b**, which further proves the reconfigurable feature of the surface (Figure 2e). This thiol-quinone methide photoclick chemistry can be used to develop a sequential click strategy. It might provide benefits in immobilizing light-sensitive molecules on multifunctional surfaces.
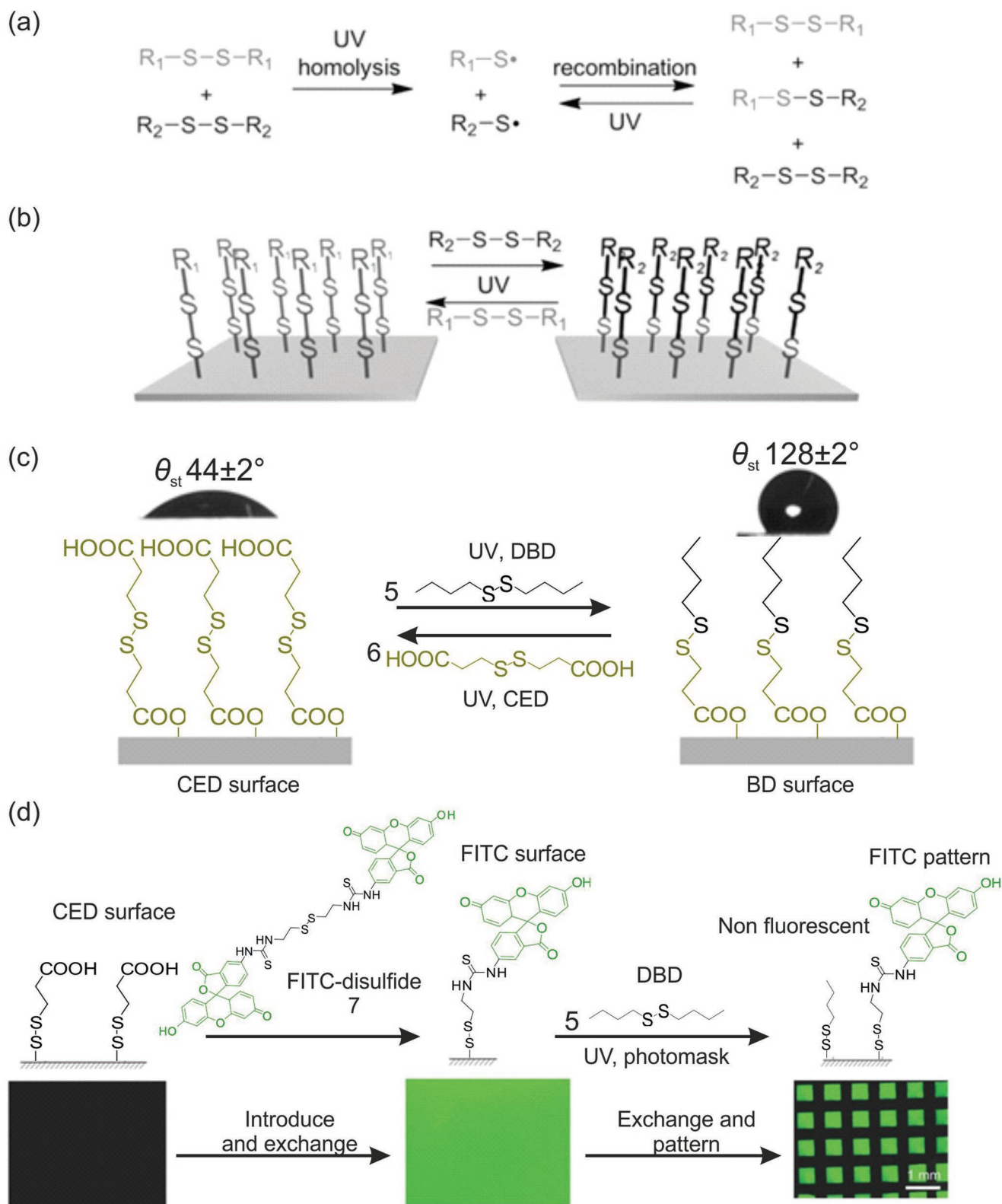
2.3. Reconfigurable Surfaces Based on Photoinduced Disulfide Exchange

The previous example is related to photochemistry that involves C−S bonds. Disulfide bonds can also act as dynamic bonds for surface reconfiguration.[98,99] The mechanism of disulfide exchange follows either anionic or radical pathways. Disulfide bonds cannot only undergo a reversible cleavage through thiol-disulfide exchange, they can also be homolytically cleaved

by light to generate sulfenyl radicals (**Figure 3**a). Due to the controllability of this reaction and easy functionalization with diverse thiol-bearing building blocks, disulfide exchange is popular in construction of reconfigurable materials.[82,95,100]

Levkin and co-workers fabricated a disulfide-modified surface which showed reversible and rewritable functionalities under UV irradiation (Figure 3b).[82] First, they demonstrated that photoinduced switchable wettability on the disulfide-modified surface. The surface was functionalized via esterificating of compound **6** with a polyporous poly(hydroxyethyl methacrylate-*co*-ethylene dimethacrylate) surface. The water contact angle (CA) of the resulting surface was $44 \pm 2°$ that increased to $128 \pm 2°$ after UV light irradiation in the presence of compound **5**. The result demonstrated that the surface was successfully modified with the hydrophobic butyl sulfide units. After wetting the hydrophobic surface with a DMF solution of **6** and UV irradiation, the surface changed back to the original hydrophilic state (Figure 3c). This process can be repeated for 20 times.

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(a)

(b)

(c)

θ_{st} 44±2° θ_{st} 128±2°

CED surface   BD surface

(d)

**Figure 3.** a) Schematic representation of photoinduced disulfide exchange. b) Scheme of dynamic surface modification via photoinduced disulfide exchange. c) Schematic showing the change of wettability using photoinduced disulfide exchange. d) The surface modification using photoinduced disulfide exchange and corresponding fluorescence microscopy images. Reproduced with permission.[82] Copyright 2015, Wiley-VCH.

The surface reconfiguration was further demonstrated by time-of-flight secondary ion mass spectrometry.

Second, surface patterns were created and erased by light irradiation (Figure 3d). A uniform fluorescent surface was created by replacing compound 6 with fluorescent FITC-disulfide 7. Photopatterning was demonstrated by masked irradiation. This method is versatile and fast. Various functional groups were able to be introduced onto a disulfide-functionalized surface and removed reversibly via photoinduced disulfide exchange.

Inspired by the development of disulfide exchange for photo-controlled reconfigurable surfaces, Yang and co-workers fabricated a molecular-motor-modified surface, which showed a reprogrammable assembly on surface (**Figure 4**).[83] Molecular
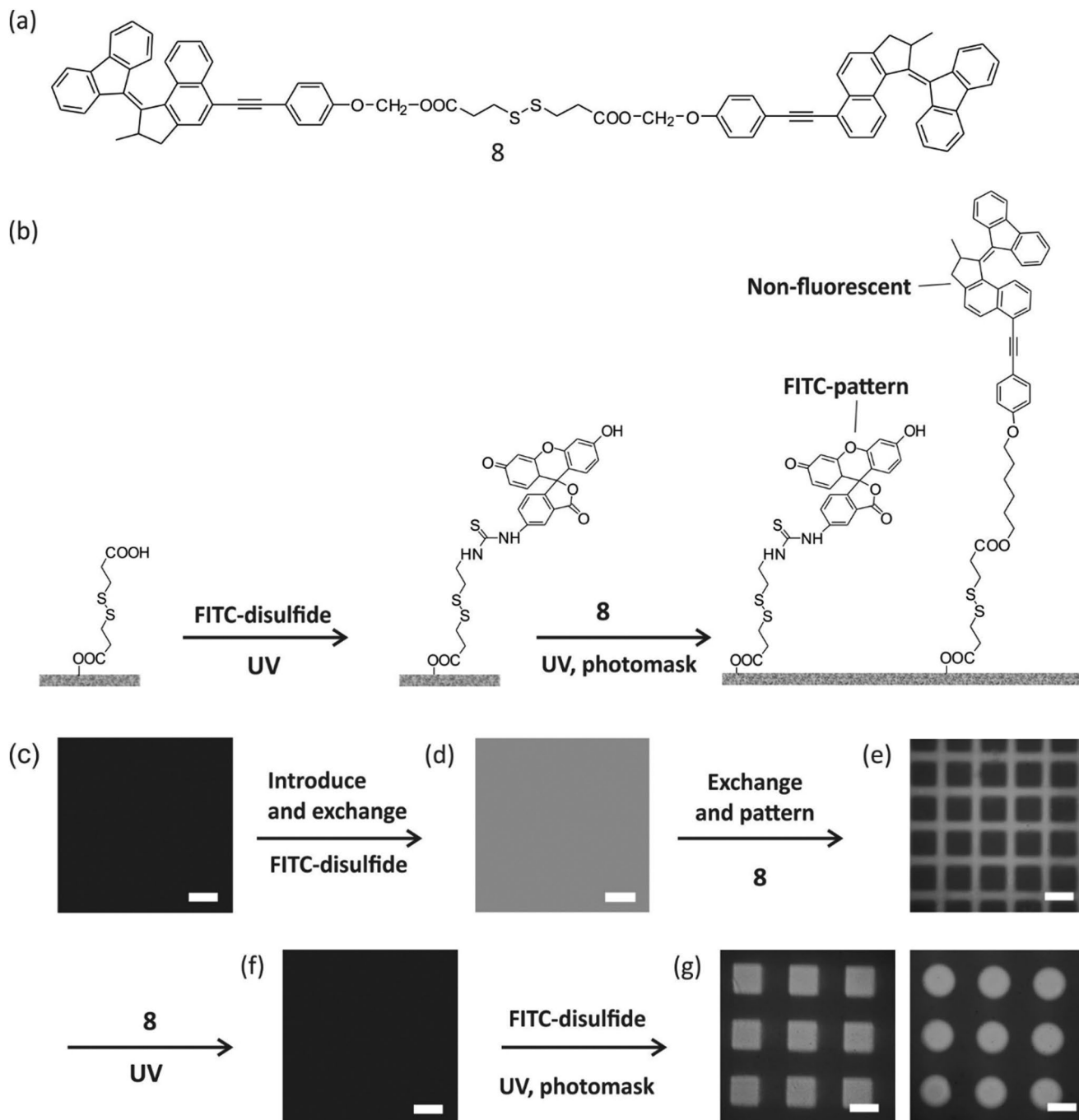
Figure 4. a) Chemical structure of the molecular motor **8**. b) Schematic illustration of photopatterning of molecular motors on a disulfide-modified poly(hydroxyethyl methacrylate-*co*-ethylene dimethacrylate) surface. Fluorescence microscopy images of c) bis(2-carboxyethyl) disulfide-modified surface, d) FITC-modified surface, e) **8**-patterned surface, and f) **8**-modified surface. g) Two different FITC-patterned surfaces. The scale bars are 200 µm. Reproduced with permission.[83] Copyright 2017, Wiley-VCH.

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motor **8** was attached to solid surfaces via disulfide exchange (Figure 4a,b). They modified a quartz surface with molecular motor **8**. Photocleaving and recombining disulfide bonds enabled the reversible assembly and release of molecular motor **8** on the surface. Besides quartz, disulfide exchange also can be used to modify other substrates such as stainless steel, aluminum, and gold.

Patterned surfaces were created via photoinduced disulfide exchange and was verified by fluorescence microscopy (Figure 4c–g). The 2-carboxyethyl groups on disulfide-modified surface were replaced by fluorescent groups to generate a fluorescent surface (Figure 4d). After wetting the fluorescent surface with a DMF solution of the molecular motor **8** and masked irradiation, a micropattern was generated (Figure 4e). The micropattern can be erased by the irradiating the whole surface with UV in a DMF solution of the molecular motor **8** (Figure 4f). Upon UV irradiation in the presence of FITC-disulfide, different micropatterns of molecular motors were generated using other photomasks (Figure 4g). This method endows the storage of geometric information as surface patterns and enables erasing and rewriting of geometric information based on reversible photocontrolled disulfide exchange.

2.4. Reconfigurable Surfaces Based on Photoinduced Thiol-Disulfide Exchange

Photoinduced thiol-disulfide exchange was also used for surface reconfiguration.[84] The thiol-disulfide exchange is through the thiolate-centered mechanism. A disulfide bond is attacked by a thiolate group under basic conditions, causing the cleavage of the original disulfide bond and the formation of a renewed disulfide bond. Meanwhile, a new thiol is generated from a sulfur atom of the original disulfide bond, carrying away the negative charge.[101,102] However, it lacked the spatial control required for surface patterning. Levkin's group designed a light-induced thiol-disulfide exchange reaction that exhibited spatiotemporally controlled thiol-disulfide interconversions.[84] The thiol-disulfide exchange enable reversible transition between thiol-modified surface and disulfide-modified surfaces by combining UV-induced disulfide formation (UV-DF) and UV-induced disulfide reduction (UV-DR) reactions (**Figure 5**a). The formed disulfide-modified surface was reconfigurable. Moieties can be controlled by light to attach on, exchange and detach from the surface (Figure 5b,c).

As one example, dansyl disulfide (DDS) was attached onto the thiol surface through the UV-DF (Figure 5d). After light irradiation in the present of dibutyl disulfide (BDS) with a photomask, the dansyl fluorescence from DDS in the exposed regions disappeared, which indicated the spatial control of disulfide exchange between BDS and immobilized DDS (Figure 5e). After UV-DR reaction in the present of 1,4-dithiothreitol (DTT), the fluorescent dansyl pattern disappeared and a new thiol surface was regenerated (Figure 5f). Furthermore, the process can be recycled (Figure 5g–i).

Based on their previous work, Levkin and co-workers fabricated a new reactive surface, on which the disulfide units were hidden by hydrophobic chains (**Figure 6**).[103] The superhydrophobic surface with hidden reactive disulfide bonds (SuSHiR) enabled photoinduced disulfide exchange. The obtained SuSHiR can be postmodified by replacing the hydrophobic chains with other functional groups via disulfide exchange. In comparison to conventional reactive superhydrophobic surfaces, the SuSHiR was more stable. Upon light irradiation, reactive thiyl radical intermediates were generated on the surfaces. They can react with different molecules such as disulfides, alkenes, thiols and epoxides. This design provides a facile way to postmodify diverse functional groups on the surface (Figure 6).
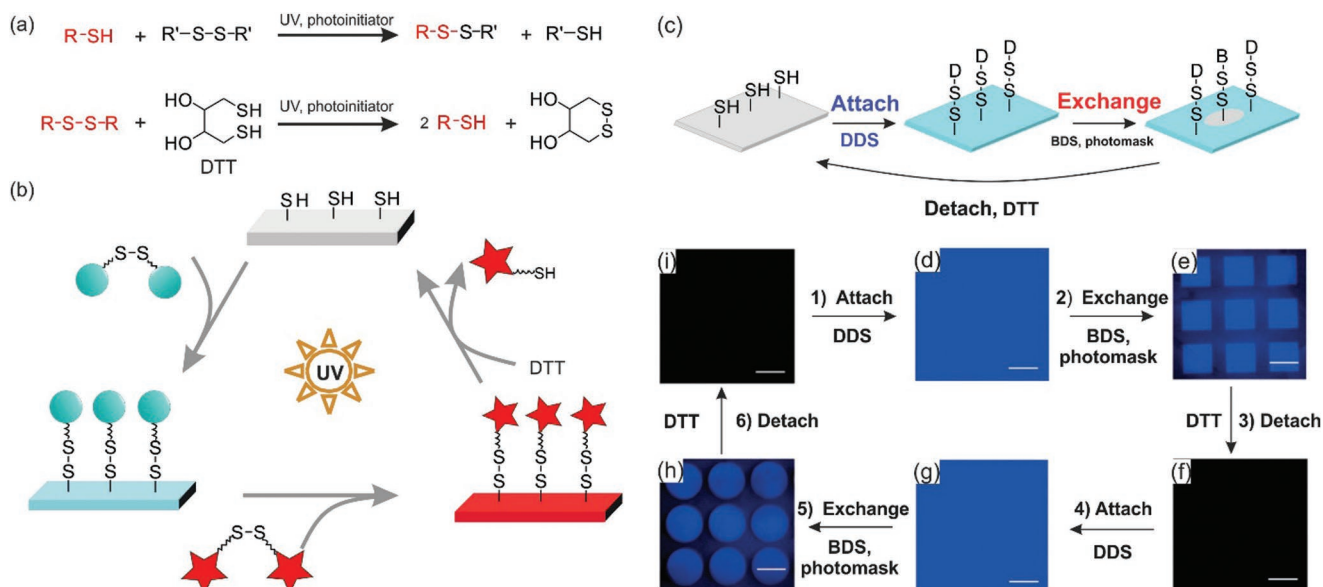
Figure 5. a) Schemes of the UV-induced disulfide formation (top) and disulfide reduction reactions (bottom). b) Scheme of UV-induced thiol-disulfide exchange reaction on the surface. c) Scheme of photoinduced reversible surface modification on a thiol-modified surface. Fluorescence microscopy images of a surface modified by d) DDS, e) DDS (blue) and BDS (dark), f) DTT, g) DDS, h) BDS (dark) and DDS (blue), and i) DTT. Scale bar is 500 mm. Reproduced with permission.[84] Copyright 2016, Wiley-VCH.
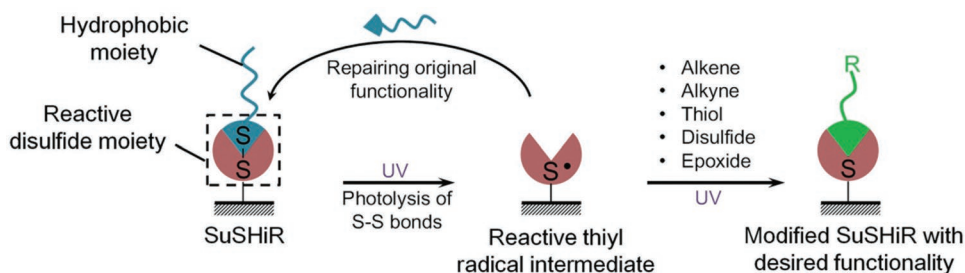
Figure 6. Scheme of possible chemical transformations using the surfaces with hidden reactivity (SuSHiR) concept. After UV light irradiation, thiyl radicals were generated on the surface. Different hydrophobic moieties and various molecules can be used to modify the reactive surfaces. Reproduced with permission.[103] Copyright 2018, Wiley-VCH.

This approach enables secondary modification and repair of damaged functions.

2.5. Reconfigurable Surfaces Based on Photoinduced Diselenide Exchange

Diselenide bond has a bond energy of 172 kJ mol^{-1}, which is lower than that of disulfide bond (240 kJ mol^{-1}). This energy difference indicates that diselenide bond is more dynamic and diselenide exchange can happen under milder conditions.[104,105] In 2014, Xu and co-workers found that diselenide bond is a visible-light-controlled dynamic covalent bond (**Figure 7**a).[106–108] Diselenide exchange reaction can be triggered by visible light irradiation. It can reach equilibrium in a minute. Xu and co-workers found that diselenide exchange reaction even occurred under the irradiation of long-wavelength light (wavelength

>600 nm). Moreover, the reaction can be proceeded in various solvents. These features of diselenide exchange offer the possibility for surface reconfiguration. In addition, compared to UV light, visible light is noninvasive and can penetrate deeper into tissue. Therefore, diselenide-modified reconfigurable surfaces are more suitable for biomedical applications.

In 2019, a photocontrolled reconfigurable surface based on diselenide bonds was developed by Xu and co-workers (Figure 7b).[85] Diselenide bonds were used for the modification of various solid surfaces, including polydimethylsiloxane, quartz, and indium tin oxide (ITO) glass. Various diselenide compounds with different functions **9–12** were immobilized onto surfaces. Photocontrolled wettability and photopatterning were demonstrated based on diselenide metathesis. The photoreaction on the surface was fast and was finished within 30 s. Based on the fast reaction, they demonstrated light-driven motion of liquid in a capillary (Figure 7c). The inner wall of the
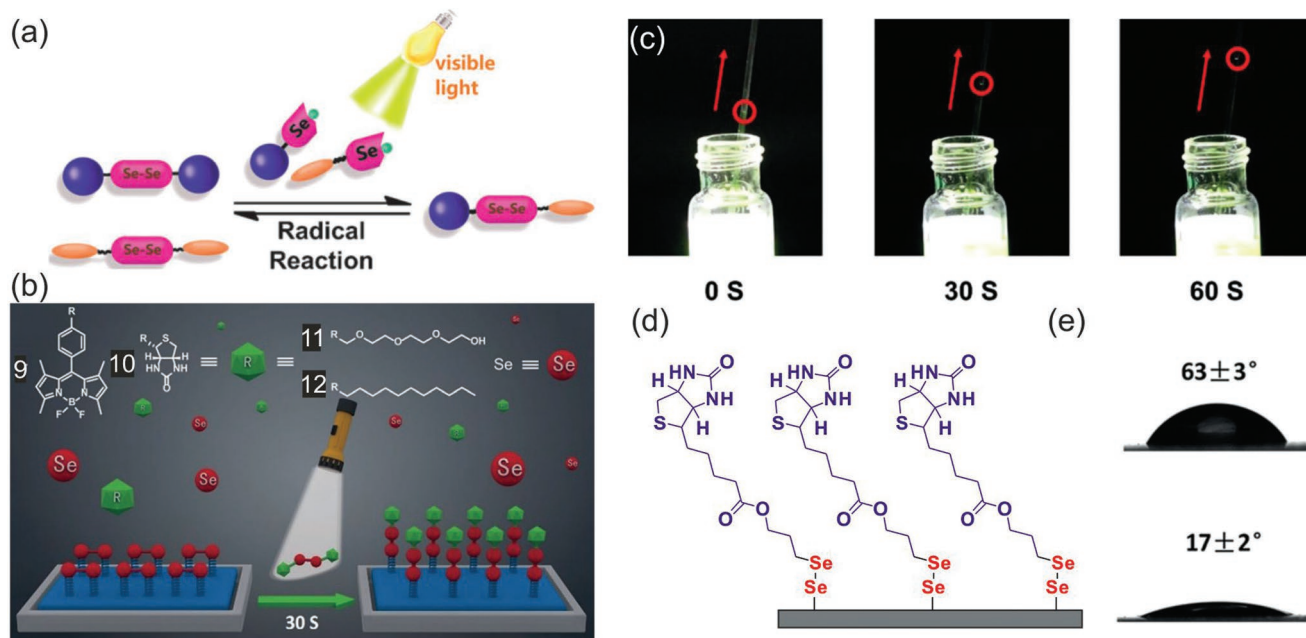
Figure 7. a) Scheme of a visible-light-induced diselenide exchange. b) Scheme of diselenide exchange driven reversible and fast surface modifications. c) Visible-light-triggered liquid motion in a capillary with diselenide-modified inner surface. The solution in the vial was an aqueous solution of **11**-modified diselenide (0.2 M). The liquid level was marked as Red circle in the capillary. d) A surface modified with biotin-functionalized diselenide. e) Static water contact angle of the surface in d) before (top) and after (bottom) the treatment with streptavidin. Reproduced with permission. Panel a) reproduced with permission.[106] Copyright 2014, Wiley-VCH. Panel b–e) reproduced with permission.[85] Copyright 2019, Wiley-VCH.

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capillary was modified with diselenide compounds. The obtained capillary was put into an aqueous solution of **11**-modified diselenide in the dark. The liquid level in this capillary gradually raised with an average speed of 0.2 mm s^{-1} upon visible light irradiation, while the liquid level in an unmodified capillary did not change during the whole irradiation period. The rise of the liquid level was attributed to the increased wettability of the inner surface, which was caused by the diselenide metathesis at the inner surface.

Xu et al. also demonstrated the potential of surface bioconjugation based on diselenide bonds. They immobilized biotinylated compound **10** on the surface via diselenide exchange (Figure 7d). The water contact angle of the biotinylated surface was 63 ± 3° (Figure 7e, top). After wetting the biotinylated surface with streptavidin buffer solution and washing away the unbind residue streptavidin, the water contact angle decreased to 17 ± 2° because of the highly hydrophilic structure of streptavidin (Figure 7e, bottom).

2.6. Reconfigurable Surfaces Based on Ru-Thioether Photosubstitution

Some Ru–ligand coordination bonds are photoresponsive.[109–112] A coordinated ligand in a Ru complex can be photosubstituted by a free ligand.[23,56,113–121] Ligand photosubstitution of Ru complexes is a powerful reaction for preparing photocontrolled reconfigurable surfaces. Several years ago, del Campo group and our group have demonstrated the use of photosubstituion to change surface properties irreversibly.[23,121] Some Ru complexes are able to reversibly switch between two states via reversible ligand photosubstitution.[122–124] For example, thioethers coordinated in some Ru complexes can be substituted by H$_2$O upon light irradiation; coordinated H$_2$O in these Ru complexes can be substituted by thioethers spontaneously in the dark (Table 1).[124]

In 2018, our group reported a Ru complex-modified surface that is reconfigurable under visible light irradiation.[86] Compound **13** (Ru-H$_2$O) acted as the "multi-bit screwdriver." We introduced thioethers as "bits" to control surface functions (**Figure 8**a). Photosubstitution of Ru complexes can be controlled by visible light to remove the "bit" from the "screwdriver," while another "bit" can be automatically attached to the "screwdriver" via thermal substitution in the dark. Various functions can be endowed to the reconfigurable surface using this design.

A substrate was modified with Ru-H$_2$O to demonstrate this concept. The R$_1$-thioether substituted the coordinated H$_2$O in Ru-H$_2$O complex so that the surface was endowed with the function of R$_1$ (Step 1 in Figure 8b). Upon light irradiation, R$_1$-thioether can be substituted by H$_2$O (Step 2). After washing away R$_1$-thioether, the coordinated H$_2$O was spontaneously substituted by R$_2$-thioether in the dark (Step 3). So, the surface displayed the function of R$_2$. The surface exhibits user-defined functions using diverse thioether ligands (Figure 8b).

As a proof of concept, we rewrote surface patterns, manipulated protein adsorption, and controlled surface wettability using photosubstitution (**Figure 9**). For rewritable surface patterns, thioether-containing fluorescein isothiocyanate (MeSC$_2$H$_4$-FITC) and thioether-containing rhodamine B isothiocyanate

(MeSC$_2$H$_4$-RhB) were used (Figure 9a). MeSC$_2$H$_4$-FITC and MeSC$_2$H$_4$-RhB can be patterned with a good spatial resolution (Figure 9b–e). Moreover, the rewritable Ru-H$_2$O-modified surface was regenerated by irradiating the surface with visible light in water.

Visible light can also manipulate protein adsorption on Ru-H$_2$O-modified surfaces. A protein-resistant surface was prepared by immobilizing poly(ethylene glycol)-modified thioether (MeSC$_2$H$_4$-PEG) on a Ru-H$_2$O-functionalized surface based on Ru-thioether coordination (Figure 9f left and Figure 9g). The surface resisted protein adsorption because of PEGylation (Figure 9h). Upon light irradiation with a photomask, MeSC$_2$H$_4$-PEG was cleaved from the exposed regions of the surface, meanwhile the fluorescent bovine serum albumin (BSA) was attached on the exposed areas via electrostatic interactions (Figure 9i). Red light was used to pass through a piece of tissue and manipulate protein adsorption underneath the tissue. The result shows the advantages of such a surface for biomedical applications because the surface can be controlled with red light that penetrates deeper into tissue than UV or short-wavelength visible light.

In addition, we switched wettability via photosubstituion (Figure 9j,k). We prepared a Ru-H$_2$O modified porous silica coating. Two thioether ligands, hydrophilic 2-(methylthio)ethanol (MTE) and hydrophobic (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)(methyl) sulfane (HFDMS) can be interconverted on the coating via photosubstitution. The water contact angle of the Ru-MTE-modified coating was 27 ± 2°. Upon green light irradiation, MTE can be cleaved from the coating. Subsequently, hydrophobic HFDMS can be immobilized on the surface, and the water contact angle of the surface increased to 154 ± 2°. The hydrophilic-to-superhydrophobic transitions were reversible and recyclable (Figure 9k).

3. Other Photocontrolled Dynamic Bonds

At present, a few types of photo-controlled dynamic bonds have been applied to construct reconfigurable surfaces (Table 1). However, the potential of photocontrolled dynamic bonds has not been fully explored yet. Some other photocontrolled dynamic bonds have been studied but they have not been used to prepare reconfigurable surfaces yet (**Table 2**).

Allyl sulfides are efficient agents for addition fragmentation chain transfer (RAFT) polymerization. Inspired by the regenerative nature of RAFT agent,[56,71,125–130] Anseth and co-workers demonstrated that allyl sulfide was a candidate to precisely control the introduction, exchange, and removal of biochemical ligands in a 3D polymer network. Reversible addition and removal of thiols are possible. The double bond of allyl sulfide was attacked by a thiyl radical, resulting in a symmetric intermediate; then the following β-scission of the intermediate caused an addition reaction of the attacking species and regenerated a new thiyl radical species and a new double bond. Furthermore, the new double bond can be attacked by another thiyl radical, therefore giving the opportunity for the exchange and removal of another thiol-containing bioligands. This reaction was applied to dynamic hydrogel networks and has potential for constructing reconfigurable surfaces.
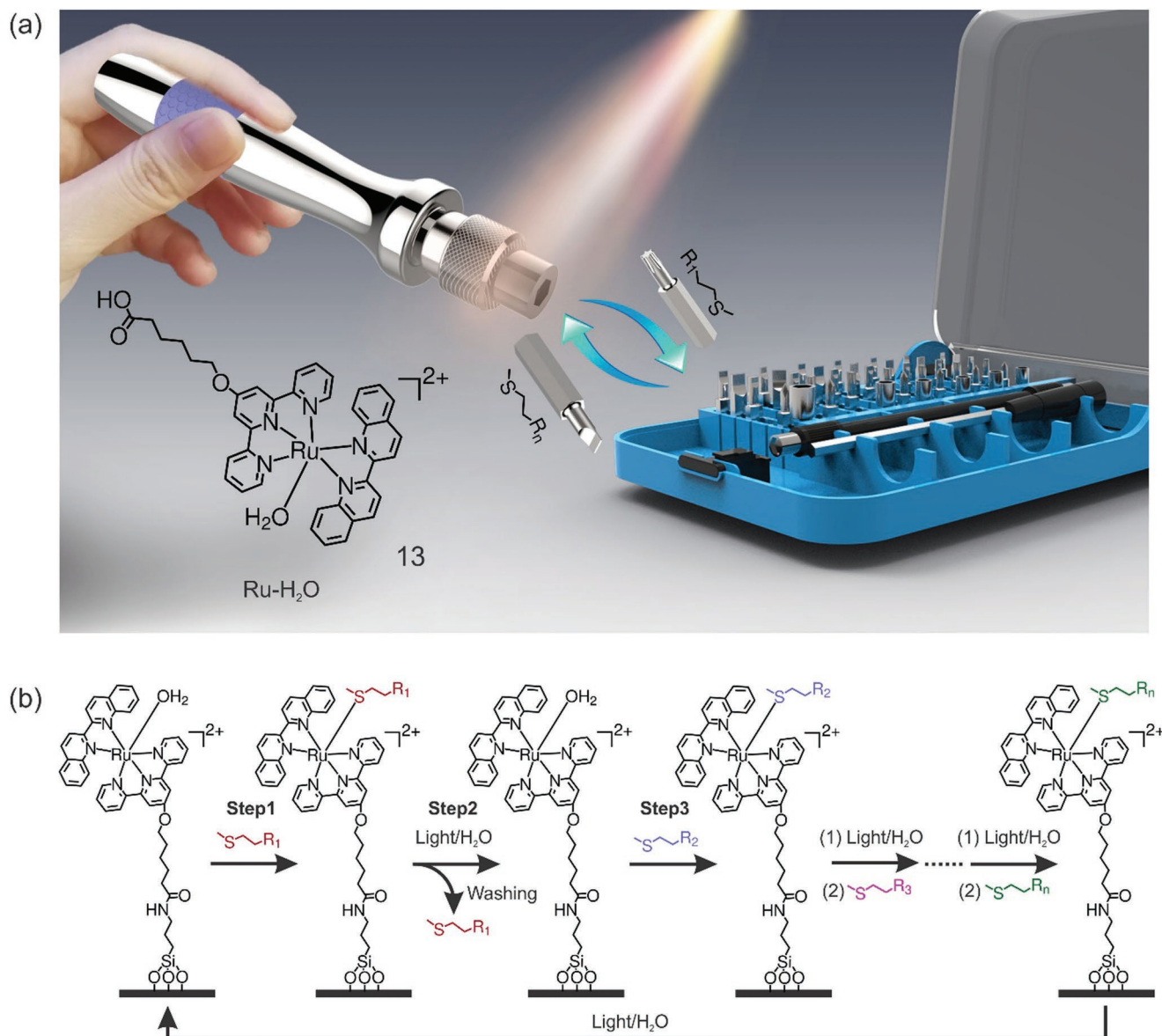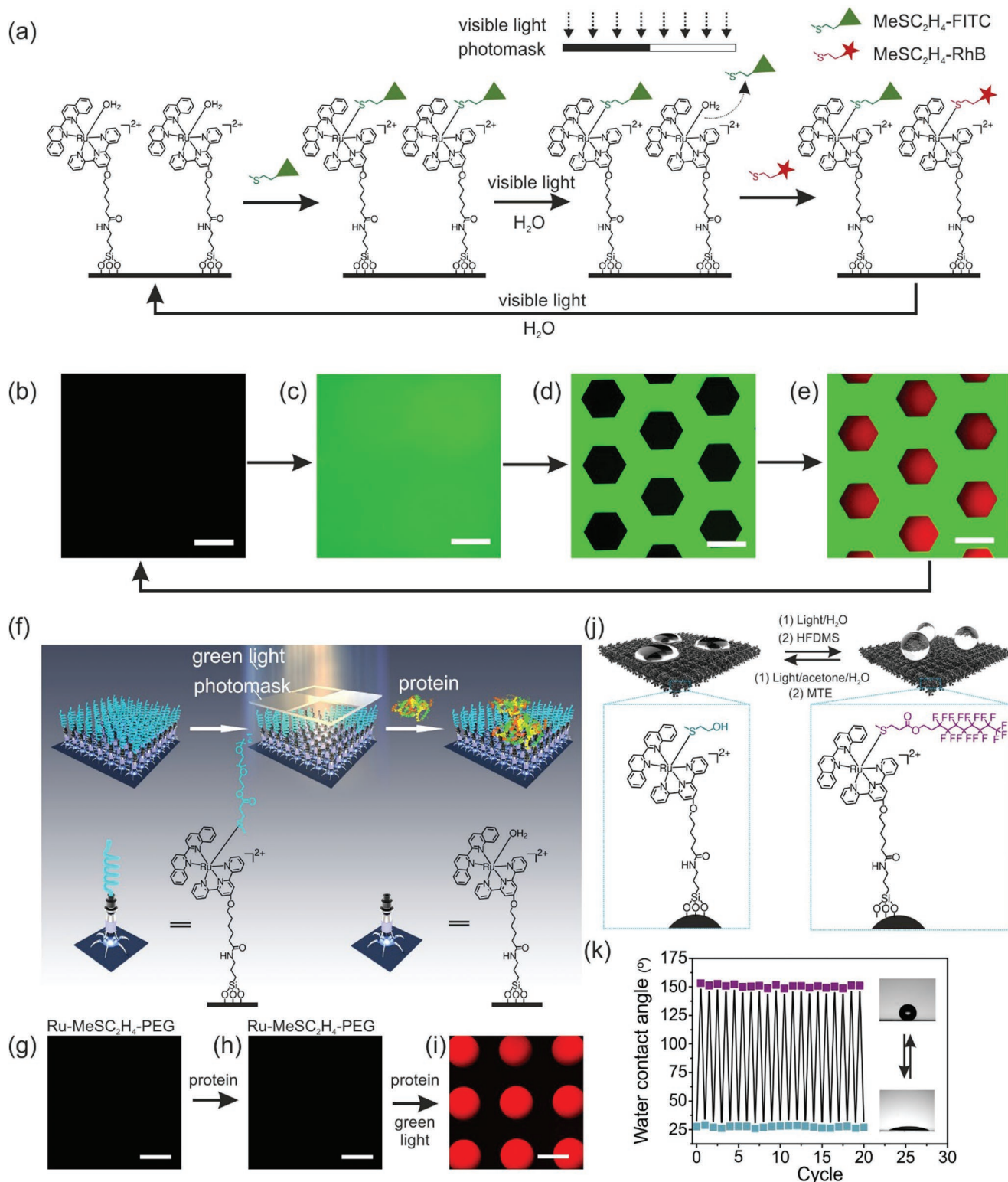
Figure 8. a) Scheme of a visible-light-controlled reconfigurable material. b) Scheme of reconfiguring surfaces based on ligand substitution of Ru-H$_2$O complex and thioethers with different functional units. Adapted under the terms and conditions of the CC-BY Creative Commons Attribution 4.0 International License.[86] Copyright 2018, The Authors, published by Springer Nature.

Dithiocarbamate has the regenerative nature.[131] The carbon–dithiocarbamate bond is labile and can be cleaved under low intensity UV irradiation. The generated radical initiates free radical polymerization. This reaction is promising for surface reconfiguration.[131]
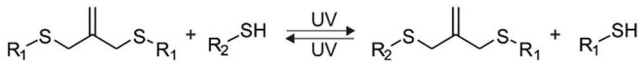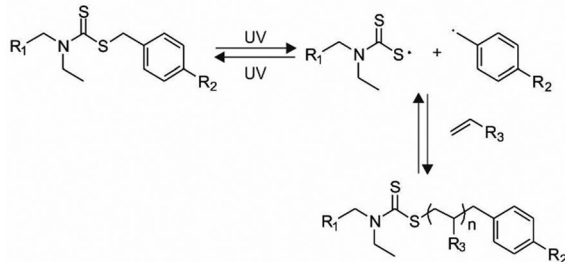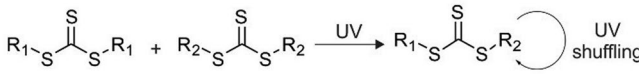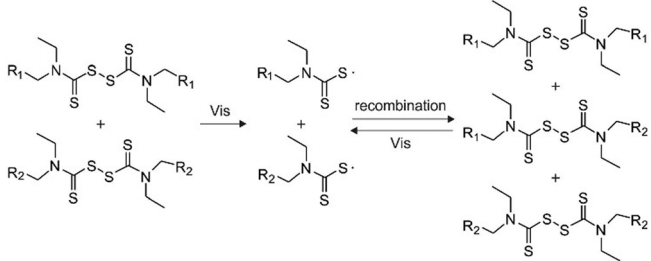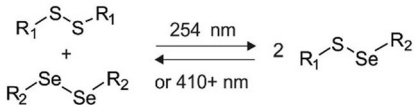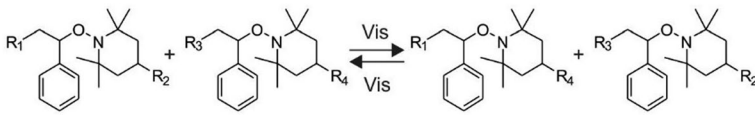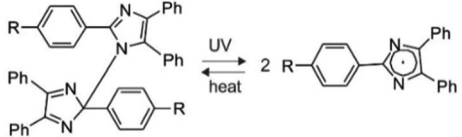
Light can induce exchange of covalent bonds in trithiocarbonates (TTCs). TTCs are RAFT agents.[132,133] Based on the photoresponsive nature of TTC units, Matyjaszewski and co-workers designed a model reaction of two different TTC-containing small molecules.[134] TTC units can undergo photoinduced exchange reactions. They fabricated healable polymers based on photoinduced bond exchange of TTC units. Later, the same group found that thiuram disulfides (TDS) can proceed a solvent-free exchange reaction under visible light

irradiation. Despite the fact that this reaction has been used to construct self-healing materials,[135] they are not yet used for surface reconfiguration.

Wavelength-controlled dynamic reactions are more desirable because they can use different wavelengths to independently control different reactions. Xu and co-workers designed a wavelength-controlled dynamic exchange based on the different bond energies between the S–S and Se–Se bonds.[136] They found the exchange between S–S and Se–Se bonds occurred and generated Se–S bonds under UV light irradiation (254 nm), and the reverse reactions can be driven by visible light (>410 nm). They further demonstrated that this exchange reaction can be applied to light-triggered self-healing polymer materials. This straightforward chemistry and wavelength-dependence

Figure 9. a) Scheme of rewritable photopatterns via ligand substitution. The fluorescence microscopy images of the surface modified with b) Ru-H$_2$O, c) Ru-MeSC$_2$H$_4$-FITC, d) Ru-MeSC$_2$H$_4$-FITC (green) and Ru-H$_2$O (dark), and e) Ru-MeSC$_2$H$_4$-FITC (green) and Ru-MeSC$_2$H$_4$-RhB (red). (Scale bars: 300 μm). f) Controlling protein adsorption on the Ru-H$_2$O-modified surface. The fluorescent images of the surface modified with g) Ru-MeSC$_2$H$_4$-PEG, h) Ru-MeSC$_2$H$_4$-PEG, after immersing in a solution of fluorescently labeled BSA and washing with an aqueous solution of NaCl (1×10^{-3} M, pH 9), and i) Ru-MeSC$_2$H$_4$-PEG surface (dark) and protein-attached surface (red) created using the method in (f). (Scale bars: 300 μm). j) Switching wettability of the Ru-H$_2$O-modified surface. k) Water contact angles of Ru-MTE-modified surface (blue squares) and Ru-HFDMS-modified surface (purple squares). Adapted under the terms and conditions of the CC-BY Creative Commons Attribution 4.0 International License.[86] Copyright 2018, The Authors, published by Springer Nature.

Table 2. Photoreactions that have potential to construct photocontrolled reconfigurable surfaces.

Reaction type	Reaction	Refs.
Allyl sulfide addition		[71,126–128]
Dithiocarbamate addition		[131]
Trithiocarbonate exchange		[134]
Thiuram disulfide recombination		[135]
Disulfide-diselenide exchange		[136]
Alkoxyamine exchange		[145]
Hexaarylbiimidazole dissociation		[147–151]

will make this dynamic reaction an excellent candidate for surface reconfiguration.

The previous photoreactions are based on the labile C−S bonds, S−S bonds, and S−Se bonds. The following two reactions are based on dynamic C−ON and C−N bonds, respectively, which may be suitable for surface reconfiguration.[137–140] The dynamic nature of alkoxyamines has been used to generate switchable surfaces.[140–144] However, the reversibility of surfaces in all cases was achieved by heating. In 2018, Herder and Lehn found photodynamic bonds of alkoxyamines.[145] Alkoxyamines are stable in the dark at ambient temperatures. Upon light irradiation, they can efficiently dissociate and return to the original structure via thermal recombination.

Hexaarylbiimidazole, a well-known photoinitiator,[146] shows reversible photodissociation. The C−N bond between the imidazole rings of hexaarylbiimidazole can be homolytically and reversibly cleaved, generating two teal-colored 2,4,5-triarylimidazoyl radicals upon light irradiation. These radicals thermally recombine to obtain the original imidazole dimer. Due to the photocontrolled dynamic feature, hexaarylbiimidazole derivatives have been widely employed as dynamic cross-linkers for the preparing of de-crosslinkable polymer networks.[147–151] The use of hexaarylbiimidazole for reconfigurable surfaces has still not been explored.

4. Summary and Outlook

Photocontrolled reconfigurable surfaces that can be switched among multiple states are highly appealing because they are reusable, have multifunction, and can adapt to rapidly changing environments or different applications. The challenges and perspectives are summarized.

First, some compounds with dynamic bonds have been used for photocontrolled reconfigurable surfaces but some others (Table 2) have not been exploited yet. It is possible to fabricate new reconfigurable surfaces using other photoresponsive compounds.

Second, some dynamic bonds have drawbacks. Some reactions based on dynamic bonds have side reactions, leading to the loss of reversibility and function. For example, the radials generated by irradiation are very reactive, which can proceed several reaction paths, resulting in rearrangement reactions and the formation of irreversible bonds or static materials. When radials react with oxygen, oxidized side-products usually terminate the dynamic feature of reconfigurable materials. Thus, they may cause the loss of reconfigure function due to irreversible termination. There are very few photocontrolled dynamic bonds with non-radical intermediate (e.g., Ru complexes). In addition, some dynamic bonds are not stable and may be damaged when the environment changes. For instance, S−S bonds can be damaged under a basic condition. Thus, it is important develop robust dynamic bonds with prolonged lifetime. The stability and dynamics of these bonds are somehow a dilemma.

Third, how to design photocontrolled reconfigurable surfaces for deep-tissue biomedical applications (e.g., implants with reconfigurable surfaces) poses a challenge. The photoreactions in Tables 1 and 2 are induced by UV light or visible light. Although red light in the visible region already makes some biology experiments possible (e.g., red-light induced ligand substitution of Ru complexes for controlled protein adsorption), near-infrared (NIR) light is even better because it can penetrate deeper into the tissue and is invasive to biological components. Although two-photon absorption[56,121,126] and upconverting-nanoparticle (UCNP)-assisted photochemistry[23,152–154] can activate photoresponsive units using NIR light, they still suffer from some problems. Two-photon absorption is induced using lasers with high intensities and only occurs at the focus of pulsed lasers. It has a low efficiency even though femtosecond lasers are used. UCNP-assisted photochemistry is more efficient than two-photon absorption, but still needs high-intensity NIR light, which can cause photothermal overheating. Red-shifting the activation wavelength of photoreaction into the NIR region is a way to control reconfigurable surfaces for deep-tissue biomedical applications. The wavelength red-shifting may be achieved via substituting photoresponsive compounds or design new photoresponsive units.[155,156] NIR light-controlled reconfigurable surfaces is an exciting research topic.

Conflict of Interest

The authors declare no conflict of interest.

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