

# Reversible metal-ligand coordination for photocontrolled metallopolymer adhesives

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A recent breakthrough reported in *Nature Chemistry* has introduced hydrogel assemblies enabled by a photocontrolled adhesive by combining ruthenium-containing and thioether polymers. This innovation leverages reversible Ru–S bonds responsive to heat and light to enable dynamic structural reconfiguration of hydrogels, showcasing the adhesive's adaptability and environmental resilience and the importance of coordination chemistry in developing reprogrammable hydrogels.

Hydrogels are renowned for their exceptional water absorption and responsiveness to environmental stimuli, positioning them at the forefront of smart-material applications, ranging from soft robotics to biomedicine.<sup>1</sup> However, their development was historically hindered by the static nature of covalent bonds, which restricted their post-synthesis adaptability. The employment of coordination chemistry has shown promise in overcoming this limitation by enabling the design of smart materials that can undergo reversible transformations, paving the way for their applications with customizable adhesion properties and responsiveness to light.

Metal-ligand interactions play a pivotal role in shaping the reversible or irreversible nature of complexes and their applications in catalysis and material processing,<sup>2</sup> typically exemplified by specific metal-ligand coordination, such as zinc with imidazole and pyridine, aluminum and titanium with alkoxides or acetylacetonates, iron with bipyridine or phenanthroline, and copper with amines or phosphines.<sup>3</sup> However, the application of these conventional metal-ligand coordination systems to developing smart responsive materials often faces obstacles because of their sensitivity to environmental conditions such as pH levels and the presence of competing ligands.

For instance, zinc-ligand coordination's dependency on pH makes it less effective in variable environments, whereas the efficacy of copper and iron complexes is diminished by competing ligands, requiring stringent chemical conditions. Furthermore, the dependence of iron-ligand systems on specific redox states for reversibility limits their practical application.<sup>3</sup> Thus, it is imperative to develop reversible and robust metal-ligand coordination that can navigate these challenges to pave the way for smart materials with enhanced responsiveness.

Typical mussel-inspired adhesives, which use catecholamines to mimic the properties of natural proteins, excel in achieving strong adhesion under wet conditions through a mix of covalent and noncovalent bonds.<sup>4</sup> However, they do not possess reversible or stimulus-responsive characteristics. In comparison, supramolecular adhesives utilize reversible noncovalent interactions, such as hydrogen bonding and  $\pi$ - $\pi$  stacking,<sup>5</sup> for dynamic assembly but fall short of specific triggerable reversibility and adhesive strength.

A recent breakthrough reported in *Nature Chemistry* introduces a photocontrolled metallopolymer adhesive that employs dynamic, reversible Ru–S coordination bonds<sup>6</sup> that are sensitive to thermal and photochemical stimuli (Fig-



ure 1A), setting it apart from both traditional mussel-inspired and supramolecular adhesives. This adhesive, featuring photocontrolled Ru-ligand coordination, enables cohesive adhesion and precise separation of hydrogel units, offering unparalleled reconfigurability and environmental resilience free from the limitations of pH, ligands, or redox conditions. This represents a significant evolution from the conditional reversibility in copper, iron, and zinc systems. The adhesive proves crucial in the development of responsive hydrogel actuators that incorporate P1, P2, and P3 gel units capable of reversible transformations (Figure 1B). The non-responsive P1 hydrogel is synthesized from N-hydroxyethyl acrylamide (HEA) polymerized and cross-linked with N,N'-methylenebisacrylamide (Bis). The P2 hydrogel preserves the HEA backbone of P1 while introducing temperature sensitivity through the addition of thermoresponsive 3-dimethyl(methacryloyloxyethyl)ammonium propane sulfonate (DMAPS), endowing it with a low critical solution temperature (LCST) property. This allows the hydrogel to undergo reversible phase transitions in response to temperature variations. The P3 hydrogel, built on the P1 framework and incorporating pH-sensitive groups, such as acrylic acid, dynamically swells or de-swells in response to environmental pH changes. UV-absorption investigations into the adhesive's bonding dynamics confirm the reversible interaction between the thioether ligand and the Ru center (Figure 1C). A scanning electron microscopy (SEM) image illustrating the connection between two P1 gels bonded by this adhesive shows interpenetrated networks with diverse pore sizes, indicating adhesion strong suitable for

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#### Figure 1. Reversible responsiveness of hydrogel assemblies with Ru–S adhesives

(A) Reversible Ru–S bonding enables a transition that responds to heating and UV light exposure.

(B) Chemical structures of the hydrogels. The non-responsive P1 gel is prepared from UV-cured HEA and Bis, the P2 gel incorporates thermoresponsive DMAPS or poly(N-isopropylacrylamide) (PNIPAAm) into HEA and Bis, and the pH-responsive P3 gel includes acrylic acid with HEA and Bis.

(C) UV spectra of the Ru–S solution's behavior before and after heating and UV light exposure.

(D) SEM image of the interface of two P1 gels reattached at their junction with the Ru–S adhesive.

(E) Scheme of how hydrogel assemblies with the Ru–S adhesive can undergo shape changes when exposed to different temperatures or pH levels. (F) The reversible adhesion of P1 gels using the Ru–S adhesive.

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reconfiguring hydrogel structure (Figure 1D). Responsive hydrogel actuators, assembled with this Ru–S polymer solution at their interfaces, demonstrate the material's programmable responsiveness to both thermal and chemical stimuli (Figure 1E). Additionally, the experimental adhesion of two non-responsive P1 gels with this adhesive upon heating and subsequent light-induced detachment highlights the controllable reversible adhesion (Figure 1F).

The common reversible-bonding methods used for stimulus responsiveness often depend on specific environmental triggers for reversibility, narrowing their application scope. For instance, amide bonds, crucial in biological contexts, typically require enzymatic catalysts for reversibility, restricting their practical use because of stability concerns. Ester bonds need acidic or basic conditions for reversibility, which might not always be feasible. Disulfide bonds, relying on redox reactions for



temperature-controlled reversibility,<sup>7</sup> cannot be controlled as easily as Ru-S coordination. Additionally, although hydrogen bonds are reversible, they lack the necessary strength for use in structural materials because of their non-covalent nature. The development of a metallopolymer adhesive featuring reversible Ru-S bonding represents a significant advancement in smart responsive materials because it enables the construction of hydrogel assemblies that react to a variety of stimuli. This adhesive traditional adhesion outperforms methods, such as mussel-inspired and supramolecular adhesives, by providing dynamic, on-demand actuation capabilities. Its unique attribute of robust responsiveness to light and heat allows for reversible assembly without the need for additional catalysts or stringent conditions. This is a marked improvement over traditional reversible bonds, including amide, ester, disulfide, acetal, ketal, hydrogen, and various metal-ligand and ionic bonds, as well as Diels-Alder adducts.

Moreover, the metallopolymer adhesive with reversible Ru-S bonding stands out by enabling the programming of material functions and dynamic reconfiguration without depending on permanent covalent bonds or physical interlocking, which sets it apart from traditional topological adhesion.<sup>8</sup> This often requires harsh conditions for reversibility despite its strong interfacial adhesion. Unlike methods that rely on auxiliary physical forces, such as ultrasound, to modify adhesive properties,<sup>9</sup> the Ru-S adhesion system, leveraging the photochemical and thermal properties of ruthenium complexes for reversible ligand-exchange reactions, enables precise molecular-level adjustments of adhesion properties through specific stimuli, such as light or temperature, offering unparalleled specificity in initiating or reversing

adhesion. Although mucoadhesive microgels, such as bismuth-pectin hybrids, provide strong mucosal adhesion and high flowability, <sup>10</sup> they are tailored for specific biomedical applications and lack the reversible switching characteristic essential to Ru–S coordination.

Exploring reversible metal-ligand interactions illuminates the transformative potential of hydrogel adhesives, enabling photocontrolled adhesion and programmable material reconfiguration for dynamic assembly and disassembly. These metallopolymer adhesives, resilient across a range of pH and temperature conditions, mark a revolution in smart materials, enabling multi-stimulus-responsive actuation with the capability of state switching, self-healing, and responding to external cues in applications ranging from 4D printing to soft robotics.

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#### **DECLARATION OF INTERESTS**

The authors declare no competing interests.

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