REVIEW

Supramolecular adhesive materials from small-molecule self-assembly

Chen-Yu Shi | Qi Zhang | He Tian | Da-Hui Qu

Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai, China

Correspondence
Da-Hui Qu, Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 200237 Shanghai, China. Email: dahui_qu@ecust.edu.cn

Abstract
Developing high-performance adhesive materials not only aims at industrial and social requirements but also bears the fundamental importance of understanding the chemical factors of biological adhesion to develop biomimetic adhesive materials. Owing to the wide development of supramolecular chemistry, numerous supramolecular tools are exploited and proved to be reliable in the replacement of traditional covalent materials by reversible noncovalent or dynamic covalent materials. Taking advantage of these ready-to-use supramolecular toolboxes, supramolecular adhesive materials are rising and promising toward “smart” adhesives, that is, enabling responsiveness, reversibility, and recyclability. Compared with polymeric adhesive materials, low-molecular-weight adhesives feature chemically precise structure, easier engineering by molecular design, and hence higher reproducibility. However, it remains highly challenging to make high-performance adhesive materials by low-molecular-weight feedstocks. This review will focus on the recent advancement in the construction of supramolecular adhesive materials by small-molecule self-assembly. The design guidelines and consideration on the molecular scale will be discussed and summarized on how to enhance the strength of adhesives. Meanwhile, owing to the dynamic nature of supramolecular self-assembly, several “smart” functions of such materials will be presented, such as stimuli–responsiveness and adaptiveness. Finally, current challenges and future perspectives of this emerging field will be proposed.

KEYWORDS
adaptiveness, responsiveness, small-molecule self-assembly, supramolecular adhesive materials
1 | INTRODUCTION

Self-assembly generally exists in life and nature, from the base pairing, protein folding to Rayleigh-Bernard convection, atmospheric storms. The process from disorder to order, along with the diversity and complexity of the functions produced from biologic self-assembly, has promoted the design of nonliving systems, thus a series of artificial molecular aggregates with impressive properties (such as micelles, vesicles, films, fibers, etc.) have been developed by the self-assembly of building blocks. Diverse noncovalent interactions include hydrogen-bonding, π–π stacking, van der Waals interactions, electrostatic interactions, hydrophobic effects, host–guest interactions and dynamic covalent bonds. Precisely tuned precursor molecules organize into desired ensembles with distinct physicochemical properties via the “bottom-up” approaches. Moreover, the dynamics and reversibility of supramolecular architectures have led to new developments of various functional materials with fascinating stimulus-response behaviors, for example, self-healing, self-adjustment, adaptivity, shape memory, and mechanochromic properties.

Adhesion widely exists in nature, such as the mussels attaching on the reef surfaces, and the geckoes crawling freely on the wall. Interfacial adhesion has inspired scientists to create various adhesives with biomimetic structures and functions. These adhesives are in high demand with the increasing growth of smart composite materials. Compared with conventional adhesives consisting of covalent polymeric networks, supramolecular adhesives exhibit unique advantages for their reversible interactions in response to external stimuli. Manifold advantages, including responsiveness, reversibility, and recyclability, endow supramolecular adhesives with a wide scope of applications covering the fields of biomedical materials, for example, wound dressing, tissue repair, and drug delivery; high-performance electronics, for example, flexible electronic screens, wearable devices, and soft actuators; and transportation and aerospace systems. In 1997, the exploration of supramolecular polymer adhesive was pioneered by Stupp et al., after which a series of fundamental research and functional applications of supramolecular adhesive materials have evolved. In 2007, the introduction of polydopamine adhesives was emerging as a landmark to arouse an extensive interest to study polydopamine surface chemistry. Generally, there has been a family of supramolecular toolboxes whose fundamentals have been well established, such as hydrogen bonds, metal coordination, hydrophilic/hydrophobic, and Columbic force. The reversibility of noncovalent interactions enables the dynamic modulation of intermolecular interactions by external stimuli, including light, temperature, pH, chemical redox, and micro-environments. The related studies about macromolecular adhesives and coatings have emerged over the past two decades, which have been well summarized in several outstanding reviews. Thus, the topic of macromolecular adhesives will not be involved in this review.

Herein, we focus on the recent progress on the construction of small-molecule supramolecular adhesives (SSSAs). Compared with those polymer adhesives with high-molecular-weight covalent backbones, SSSAs feature many unique advantages: (i) The adhesive layers of SSSAs are usually formed in situ, allowing more molecule–interface interactions, as well as higher absolute adhesion area on nonideal surfaces, and thus facilitating the strong interfacial adhesion; (ii) The modularity and tunability of small molecules significantly expand the practicability of adhesive materials toward on-demand applications with different substrates; (iii) The dynamic nature of supramolecular interactions endows the adhesive materials with responsiveness, recyclability, and adaptability. These above advantages make SSSAs highly attractive and promising for fundamental research and industrial invention. The aim of this review is to summarize the state-of-the-art performance and functions in this field, meanwhile providing several general guidelines for designing these supramolecular materials from the molecular level. The content of this review is categorized by the different macroscopic properties of adhesion behaviors, including high strength, water-resistance, and stimuli response (Figure 1). At the end of this review, current challenges and prospects are also discussed as a perspective.

2 | HIGH-STRENGTH SUPRAMOLECULAR ADHESIVES

Supramolecular adhesives driven by noncovalent interactions have attracted great attention as a promising bonding strategy due to their reversibility and stimulus–response. Tough adhesion is a prominent feature of the functional adhesives. Their practical applications are limited as the weak bond characteristic weakens their bonding strength relative to traditional polymer binders. To improve their adhesion strength, a number of typical strategies have been employed, such as the branched polymer chain design, the introduction of UPy hydrogen-bonding motifs and the metal–ligand complex. In general, strong adhesion behavior mainly depends on the polymeric structure. In recent years, with the advances
of self-assembly system, SSSA has been increasingly demanded due to their apparent advantages, including simple precursor synthesis and flexible functional group design.

Several efforts have been made in the field of SSSA through hydrogen bonds, host–guest interactions, anion coordination, and dynamic covalent bonds. An overview of typical examples with adhesion strength over 1 MPa on diverse substrates is shown in Table 1. Typical molecular weights of these monomers are below 2,000 g/mol, with a minimum of 186 g/mol, whereas the binding strength values are comparable with those of commercial superglues, allowing SSSA to be worth investigated further as macroscopic adhesion materials.

Polymer networks based on noncovalent bonding tend to exhibit weak mechanical properties owing to weak intermolecular interactions, and the inherent intermolecular property makes the design of high-strength supramolecular adhesives remain a challenge. Many efforts have been made to resolve this issue. For instance, the introduction of metal ions could significantly toughen the supramolecular networks due to their multivalent metallic coordination, resulting in a decreased transparency and thus hindering the potential applications of these adhesives, such as coatings and electronic skin. Introducing covalent crosslinking into the reversible network is also a common method to improve the mechanical strength of a polymeric network, yet the immiscibility, owing to the polarity differences between covalent and noncovalent bonding, suppresses the integration of covalent/noncovalent interactions in the solvent-free network. Besides, using branched building blocks to dense the supramolecular structure for a more robust polymer network frequently results in a brittle material. Recently, Liu et al. designed a trifunctional molecule 1 based on low-molecular-weight building blocks with terminal UPy motifs and a siloxane backbone on each arm, which could offer high cross-linking density when self-assembled into large-scale networks (Figure 2). The high cross-linking density combined with complementary hydrogen bonding provided by the UPy motifs enhanced its mechanical properties, and the
TABLE 1 Overview of the adhesion performances of small-molecule supramolecular adhesives

| Motif                                                                 | Monomer molecular weight (g/mol) | Substrate | Method      | Maximum strength (MPa) | Reference |
|----------------------------------------------------------------------|----------------------------------|-----------|-------------|------------------------|-----------|
| Siloxane oligomer with multivalent H-bonding                        | ~870                             | Glass     | Lap-shear   | 30                     | [53]      |
| βCD-Ad host–guest interactions                                      | 1,188; 206.3                     | Xerogel   | Self-joints | 5.1                    | [55]      |
| Cyanostar-stabilized anion-anion linkages                            | 1,636                            | Glass     | Lap-shear   | 4.2                    | [56]      |
| Four-armed DB24C8                                                   | 2,033.7                          | Steel     | Lap-shear   | 4.174                  | [57]      |
| TC7-water H-bonding                                                 | 1,311.6                          | Glass     | Lap-shear   | 4.15                   | [58]      |
| Thiocyst acid copolymer with triple dynamic bonds                    | 206                              | Glass     | Lap-shear   | 2.5                    | [23]      |
| AESOIPA with H-bonding and π–π stacking                            | ~1,500                           | Steel     | Lap-shear   | 1.7                    | [59]      |
| Azobenzene derivatives                                              | 856.4                            | Glass     | Lap-shear   | 1.34                   | [60]      |
| (UPyU)3TMP with multivalent H-bonding                               | 1,014.1                          | Glass     | Lap-shear   | 1.2                    | [61]      |
| CB[7]-Fc host–guest interactions                                     | 1,178; 186                       | Silicon   | Lap-shear   | 1.12                   | [62]      |

Note: Experiments were performed using various test layouts and substrates.
Abbreviations: CB[7]-Fc, cucurbit[7]uril-aminomethylferrocene; DB24C8, dibenzo-24-Crown-8; TC7, A triply benzo-21-crown-7 (B21C7)–substituted 1,3,5-benzenetricarboxamide (BTA) derivative; AESOIPA, isophthalic acid-functionalized soybean oil; βCD-Ad, β-cyclodextrin and adamantane; (UPyU)3TMP, UPy-functionalized 1,1,1-Tris(hydroxymethyl)propane.

FIGURE 2 Molecular structure of the trifunctional molecule 1 and the proposed adhesion mechanism
proper length of siloxane backbones toughened the network. Interestingly, the attenuated total reflectance infrared spectra revealed there were more dissociated UPy motifs and fewer siloxane backbones in the bottom layer, which was favorable to the strong bonding capability at the coating/substrate interface. The adhesives showed excellent binding strength on various substrates and the highest shear strength can exceed 30 MPa for glass and copper—far higher than the current commercial glues and supramolecular adhesives. The highly ordered assembly of trifunctional molecule 1, as well as the configuration of the small molecular network on various substrates, provides a simple strategy for the fast fabrication of robust SSSA. Moreover, the assembly of these supramolecular polymers can be easily designed due to the special oligomeric units, which provide a powerful way to fabricate a wide range of SSSA with desired multifunctionalities.

Different from monomers encoded with well-defined orthogonal supramolecular linkages (such as hydrogen bonds, metal–ligand coordination and host–guest interactions), most linear polymer chains present irregular bending. In addition, the lack of interchain interaction enhances the fluidity of the polymeric chain, limiting the further secondary self-assembly into ordered polymer building systems. Zhao et al. first reported the stoichiometry-controlled monomer sequence in a linear supramolecular polymer, self-assembled by anion coordination, and realized the adhesion regulation (Figure 3A,B). A 2:1 stoichiometry between glycol-substituted cyanostar macrocycles and phenylene-linked diphosphate monomers produced a homopolymer $2_h$ consisting of cyanostar-stabilized phosphate anion dimers, which can strongly bond with glass similar to commercial superglues (up to 4.2 MPa) due to the dense hydrogen bonding between $\pi$-stacked macrocycles and hydrophilic glass (Figure 3C). Though a 1:1 stoichiometry led to an alternating copolymer $2_c$ with cyanostar-stabilized and cation-stabilized phosphate dimer mixtures, in which the cation-stabilized phosphate dimers significantly reduced the adhesion (0.9 MPa). The crystal-packing structure of $2_c$ proved the supramolecular polymer sequence in the solid state (Figure 3D). The key to the formation of alternating configuration is hierarchical self-assembly in which the formation of cyanostar-stabilized dimmers could release extra cations to be assembled with free phosphate dimers. This study demonstrates the role of anion coordination and hierarchical self-assembly in SSSA and promotes the application of anion-anion linkages in supramolecular systems.

3 UNDERWATER SUPRAMOLECULAR ADHESIVES

Since the first report of polydopamine in 2007, which was inspired by the marine mussels’ foot protein-based adhesion on wet mineral surfaces, dopamine analogs have

![Figure 3](image-url)
emerged as a material-independent surface modification strategy on account of their high bidentate metal ion chelation ability, redox activity, and water resistance. This mussel-mimetic adhesion unfolds its charm in a broad range of applications, including biocompatible surface modifications, in vivo toxicity attenuation, nanomaterial functionalization, and Li-ion batteries. In view of underwater adhesion, the performance is the multiphase interactions of dopamine with the environment on multiscale, instead of catechol moieties alone. The polydopamine cohesive interactions play a crucial role in adhesion in most of the studies at this stage; the investigation of supramolecular assembly of small molecules based on catechol derivative is still in its infancy.

With respect to underwater adhesion, catechol moieties alone are insufficient on account of high salt concentrations, the limited pH range, and substrate hydration layers, which is a strong molecular barrier to adhesives on wet surfaces, whereas the mussels firmly attach to the rocks even in complex water environments. Thus, high levels of lysine and arginine contained in mussel proteins have caught researchers’ attention. The hydrophobic interactions between lysine (Lys) and wet surfaces were reported by Maier et al. The small molecule 3 that possesses adjacent lysine and catechol can form strong adhesion between micas by substituting the hydrated salt ions from the mica surface (Figure 4A), whereas the hydrolysis under acidic conditions limits adhesion over a wide range of pH. Analog molecule 4 was synthesized with pH-resistant tris(2-aminooethyl) amine (Tren) scaffold (Figure 4B), which exhibited a stable high adhesion ranging from pH 3.3 to 7.5. Five additional Tren-based homologs were synthesized to explore the impacts of catechol and Lys on adhesion properties (Figure 4C). Group I with different Lys chain lengths exhibited a similar adhesion behavior. Group II without catechol exhibited only 15% adhesion compared with that of 3 and 4 due to the decrease of hydrogen bonding with mica surfaces. Group III, with impaired amine functionalities, provided no adhesion to the mica surfaces. This series of comparative experiments showed that the amines may take the lead to displace hydrated salt ions and ready the surface for bidentate catechol binding, and the cooperation of amine and catechol moieties was the key to form robust adhesion between wet mineral surfaces.

Rapp et al. subsequently reported the synergy between catechol and arginine (Arg) groups in molecule 5 promoted adhesion between mineral surfaces (Figure 4D) in a similar way, proving the synergy not unique to amine cations. The guanidinium cation in Arg can also displace the surface hydrated salt, yet the adhesion is only 50%–60% relative to the degree of adhesion for molecule 4, because the bulkier structure and delocalized charge of guanidinium decreased the magnitude of the cation’s electrostatic interactions with the negatively charged sites on mica, indicating the contribution of amine cations to adhesion. Furthermore, decorating the catechols with

![Molecular structures](image-url)
duplex lysine cations, molecule 6, could decrease the density of robust bidentate interactions across the surface and showed lower adhesion (Figure 4E), further proving the importance of catechol in robust adhesion. The mixtures of individual amine and catechol functional molecules failed to synergistically mediate mica surface adhesion, indicating the same molecule catechol–cation synergy exhibited the greatest adhesion. Moreover, the small-molecule-assembled dense films have more bonding sites with the substrates compared with random-coil polymers, leading to an enhanced adhesion behavior. All the work from Rapp et al. has carried out thorough research for the catechol adhesion mechanism, and promoted the further development of the biomimetic underwater adhesion. Nevertheless, we still lack a genuine breakthrough, especially for the practical load-bearing applications ever since the initial report of mussel-mimetic adhesion.

The intolerance of dopamine to oxygen and pH limits its wide application. On the contrary, the biocompatibility and dense polar groups of amino acids enable their application prospect as wet adhesives in hemostasis, repair of living tissue, and bone fixation. Xu et al. reported an adhesive coacervate based on the self-assembly of polyoxometalates (PMs) and basic amino acids. Due to the unique nanocluster structures, H₄SiW₁₂O₄₀ was used to drive the noncovalent crosslinking of natural amino acids L-histidine (His) in an aqueous solution (Figure 5B). His maintained the structure of H–His⁺ at pH 3 to obtain soft and cross-linked network superstructures (Figure 5A), so we performed the aqueous self-assembly of His and H₄SiW₁₂O₄₀ at pH 3. The obtained coacervate 7 exhibited wet adhesion properties on different solid surfaces (Figures 5C and 5E). The chemical shifts in ¹³C-NMR (nuclear magnetic resonance) spectroscopy and the continuously connected hollow spheres inspected by SEM revealed the self-assembly mechanism that the coacervation results from both the salt-bridged hydrogen bonds of the main chains of basic amino acids and the electrostatic attractions between PMs and the protonated side chains of basic amino acids (Figure 5C,D). The synergy of high-strength cross-linked networks and highly concentrated side chains with polar or charged groups was the key to the excellent bionic adhesion. Liu et al. further utilized arginine (Arg) and K₆[α-SiW₁₁O₃₉] to prepare a coacervate, which was stable in a wide pH range and explored its application as an anticorrosive coating.

The key to underwater adhesion is to overcome the barrier of hydration layers. Besides mussel-mimetic adhesives, in which the required curing agents irreversibly remain on the surface, the host molecular assembly with a hydrophobic cavity and a guest molecule in aqueous media enable the supramolecular host–guest interactions, which can be seen as an ideal strategy for achieving underwater adhesion. Macrocycle-based host–guest interactions are of particular interest due to their unique advantages, such as multiple noncovalent interactions (e.g., hydrogen bonding, π–π stacking, charge transfer, electrostatic, and hydrophobic interactions) and diverse stimuli-response. Cyclodextrins (CDs) and cucurbiturils (CBs) macrocyclic hosts in aqueous media have been explored the most. CDs are known for exhibiting weak bonding in water (association constant, Kₐ ≈ 10⁶), whereas the other class of hosts with better performance, CBs have been extensively studied in recent years. Liu and coworkers introduced CB[8] into the polyacrylic networks to form tough and healable hydrogel adhesives, and azobenzene (AZO) was also combined for dynamic interfacial adhesion. But the substrate-binding was dependent on physical adsorption.
of polymer chains through van der Waals interactions. Ahn et al.\textsuperscript{62} reported a small-molecule recognition based on supramolecular velcro in which cucurbit[7]uril (CB [7]) decorated “loop” silicon surfaces \(8_c\) and amino-methylferrocene (Fc) functionalized “hook” silicon surfaces \(8_f\) bonded together through host–guest recognitions to realize a stronger underwater adhesion compared with commercial adhesives (Figure 6A).\textsuperscript{62} The adhesions of \(8_c\) and \(8_f\) needed to be immersed in an aqueous condition as the water expulsion induced Fc molecules into CB[7] cavities. The dried lap shear adhesion strength was proportional to the amount of Fc, and the maximum strength was 1.12 ± 0.06 MPa. The supramolecular velcro exhibited satisfying mechanical reversibility for several fastening–unfastening cycles, and the adhesion strength of the refastened velcro was approximately 70% relative to the original velcro (Figure 6B,C). Moreover, the redox-active behavior of Fc led to the introduction of chemical switchable supramolecular velcro, although its recovered strength was only 44% of the original sample. It was predicted that the electrooxidation/reduction might be more efficient due to the absence of chemical contaminants. This study offers a new strategy for producing reversible underwater adhesion. Curing-agent-free, as well as the noncytotoxic nature of CB[7] and Fc, allows the development of potential biological applications.

However, this supramolecular velcro currently is not ready for industrialization due to complicated substrate premodification, unsatisfying scale-up potential, and limited host/guest choice. Generally, it is on demand to obtain immediate, long-lasting adhesion based on small molecules, which is independent of the substrate types and shapes, and substrate per-modification is not needed in this case. Li et al.\textsuperscript{57} incorporated dibenzo-24-crown-8 (DB24C8) into a four-armed pentaerythritol to obtain a supramolecular adhesive \(9\) with a low molecular weight of 2033.7 g/mol (Figure 6D). By using a simple hot deposition method, \(9\) exhibited an excellent adhesion (up to 3.237 MPa) on various substrates, including glass, wood, steel, polytetrafluoroethylene, and poly(methyl methacrylate), on account of its extended molecular geometry. This extended geometry was resolved from both the closed ring-type crown ether structures of \(9\) and multiple supramolecular interactions with surfaces (Figure 6E). Moreover, a tiny amount of \(9\) was uniformly coated on the substrate to achieve tough adhesion by electrospinning. Notably, its hydrophobic properties allowed the realization of long-term adhesion in both water and seawater (>12 months). The shear strength of anhydrously prepared adhesives was placed in water and tested; the numerical data indicated that the strength decreased by less than 10% in 24 h compared with that of

\[\text{FIGURE 6} \quad \text{(A)} \quad \text{Graphic descriptions of supramolecular velcro obtained via hook-and-loop strategies for underwater adhesion based on CB[7]/Fc-modified surfaces. (B)} \quad \text{Underwater adhesive properties of the supramolecular velcro. (C)} \quad \text{The detachability of supramolecular velcro with an oxidizing reagent. (D)} \quad \text{A proposed molecular structure of} \quad 9. \quad \text{(E)} \quad \text{Interaction mode of} \quad 9 \quad \text{and glass. (F)} \quad \text{Adhesion strengths of} \quad 9 \quad \text{on different substrates at different humidity or underwater. (G)} \quad \text{Underwater adhesion of} \quad 9\text{.}\]
water-free samples, and the shear strength of 9 prepared in water was still high compared with the relevant data of underwater adhesives reported in the previous literature (Figure 6F). As the underwater and water-resistant adhesion performances were satisfying (Figure 6G), 9 was successfully used to repair broken flasks and leaky water pipes. Therefore, this method is believed to further promote the development of the applications for host–guest assembly in underwater adhesion and offers great potential in biodegradable adhesives, tissue repair, and surface adhesion because of the facile and economically viable methods as well as the constantly stable adhesion properties.

4 | STIMULI-RESPONSIVE SUPRAMOLECULAR ADHESIVES

4.1 | Temperature-responsive supramolecular adhesives

Since 1950s, hot melt adhesives have been widely applied in packaging, product assembly, and envelope encapsulation due to their excellent mechanical properties and debonding on demand. The high melting viscosity resulted from the high-molecular-weight polymer backbones has limited their application as reversible adhesives. Recently, it is suggested to replace hot-melt adhesives with supramolecular polymeric materials for temperature-responsive adhesion due to the dynamic and reversible nature of noncovalent bonding within the polymeric structure. Courtois et al. investigated the rheological and adhesive properties of bis-urea functionalized low-molecular-weight polyisobutylenes, self-organized into a comb-shaped polymer structure through hydrogen bonding. They further realized the temperature-controlled disassembly and re-assembly. Heinzmann et al. investigated a new type of temperature-responsive reversible adhesives, UPy hydrogen-bonded, side-chain-functionalized poly(alkyl methacrylate)s, which are useful for (de)bonding on-demand applications.

In fact, high temperature can usually lead to undesired side reactions, such as an irreversible fracture of covalent interactions and unfavorable accelerated oxidation metamorphism. The challenge lies in achieving an intact performance of the temperature-responsive adhesion. It is an ingenious strategy to self-assemble monomers into polymer networks through supramolecular interactions solely. Simple precursor synthesis, as well as the temperature-sensitive of the supramolecular bonding, enables the SSSA to demonstrate significant advantages in (de)bonding on demand and exhibit great potential for industrialization.

Thiolic acid (TA) is an ideal supramolecular building block as a natural small molecule, thanks to the simultaneous existence of dynamic disulfide bonding and noncovalent sites within this single molecule. A pioneering work conducted by Zhang et al. developed a supramolecular adhesive assembled from TA, polymer 10. 1,3-disopropenylbenzene (DIB) was used to quench the terminal diradicals of poly(TA) by inverse vulcanization, thus strengthening the network by covalent cross-linking. Iron(III) ions were also introduced into the network to form a strong metal-organic complex with the carboxylic groups. The low melt temperature (70°C) of TA enabled the supramolecular polymer networks with three different types of dynamic chemical bonds (dynamic covalent disulfide bonds, noncovalent H-bonds, and iron (III)-carboxylate coordinative bonds) through simple heating and cooling (Figure 7A). The synergy of the triple dynamic bonding endowed the polymer machinability, high ductility, self-healing, and reversible adhesion, extending its application into supramolecular adhesives. Polymeric films prepared via the hot-pressing method exhibited excellent adhesion due to the hydrogen bonds formed between the abundant carboxyl groups in the copolymer and the polyhydric surfaces (Figure 7B). The shear strength of copolymer enhanced with the iron (III) content, up to 2.5 MPa (Figure 7C). Notably, the copolymer also exhibited decent adhesion of 1 MPa to hydrophobic Teflon surfaces due to the dense hydrogen interactions between the hydroxy groups and the fluorine groups of Teflon substrates. The copolymer adhesion on various surfaces was higher than that of commercial glues (Figure 7D). Moreover, the adhesion decreased with the temperature due to the existence of heat-labile hydrogen interactions (Figure 7E). The adhesion remained stable after 30 times temperature cycling tests, thus reviewing excellent reversibility (Figure 7F). Given the strong mechanical properties of the dry network and the synthesis that is free from a complex precursor, this study achieved a unique combination of simple design and impressive performance, beneficial for industrialization.

Except for the CDs and CBs mentioned above, crown ethers have played a seminal role in supramolecular chemistry as the first generation of macrocyclic hosts and have been widely applied in various fields, such as ion transport, artificial molecular muscles, and stimuli-responsive gels. However, the application in interface adhesion has been rarely developed. Although structural water is well known as an essential constituent in protein folding, water is commonly used as a solvent in supramolecular polymerization to disperse and solvate the monomers rather than a comonomer. A typical example of the incorporation of structural water (as a comonomer) into supramolecular polymers was reported by Dong et al. The triply crown ether-substituted 1,3,5-benzenetricarboxamide (BTA) derivative 11 was a fragile amorphous glass (Figure 8A). The addition of a minimum
**FIGURE 7** A schematic representation of (A) the synthesis route of the copolymer network and (B) the adhesion procedure. (C) Shear strength of the copolymers with different thioctic acid (TA)-to-iron (III) molar ratios. (D) Comparison of shear strength between polymer 10 and commercial adhesives on nine different types of surfaces. (E) Shear strength versus temperature curves of the copolymer for glass and Teflon surfaces. (F) Shear strength of the copolymer after 30 times cycling experiments.

**FIGURE 8** (A) The chemical structure of molecule 11. (B) Images for the synthesized samples of molecule 11 with different water contents. (C) Graphs for the fibers of 11H. (D) Molecular structures of monomer 12 and 12Pt. (E) Water absorption behaviors of monomer 12 and 12Pt. (F) 12Pt-waterfibers with different lengths.
amount of water converted 11 into a highly viscous liquid 11H, which was then easily processed into thin and smooth fibers (Figure 8B,C). Structural water molecules were verified to only form hydrogen bonds with O atoms of the crown ethers rather than amide groups. Moreover, the copolymer viscosity decreased with the increased water content because the excess water was used as free water to increase the flexibility of the polymeric network. The synergy of water-crowned ether-based and BTA core-based hydrogen interactions made 11H a powerful adhesive for hydrophilic surfaces. The adhesive effect of hot-pressed glass was stable for at least 24 months under ambient conditions. The pull-off adhesion strength of 11H coating could reach up to 4.15 MPa at 25°C, and decreased with temperature, yet the adhesion strength at 60°C was still comparable with that of commercial glue at room temperature. The temperature-sensitive viscosity supported its reversible adhesion. The adhesion strength was ideally comparable with the initial strength even after 10 cycles between 25°C and 60°C. This study highlighted the possibility of using water, one of the simplest small molecules, as a building block of supramolecular polymers instead of a traditional solvent, providing a conceptually novel strategy to make supramolecular adhesive materials.

The same group further enriched the supramolecular adhesive family based on structural water hydrogen bonding. In contrast with the previous work, a small monomer 12 failed to interact with water to thicken the adhesive (e.g., increase the adhesion viscosity) due to the strong intermolecular aggregation of 1,4-disubstituted derivatives and the expulsion of the water molecules. Pt-pyridine coordination was thus introduced to prevent the p-diamide-based aggregation, and to allow the formation of water-crowned ether-based hydrogen bonding (Figure 8D–F). The Pt-coordinated monomer 12Pt self-assembled to a cross-linked polymer through bridging of incorporated water hydrogen bonding, which exhibited an adhesion (273 ± 27 psi) superior to commercial glues. The ability to regenerate, thanks to the metal coordination and water-crowned ether hydrogen bonding, endowed the copolymer-precise temperature-dependent behavior and lossless adhesion after eight heating–cooling cycles between 25°C and 50°C. The unique hydrogen bonding of the structural water makes it an important member of SSSA and has widened its range of applications in advanced supramolecular adhesives.

4.2 Chemically stimulated supramolecular adhesives

Life is a natural chemical responsive system. Diverse physical and psychological activities operate orderly under specific chemical stimuli. More specifically, the generation of dopamine in vivo creates the feeling of pleasure. Proteins provide the energy for substrate transport by consuming adenosine triphosphate. Researchers have designed a series of artificial chemical-responsive supramolecular systems, ranging from micro to macro, to simulate living systems to the greatest extent. Chemical stimuli, including pH, metal ions, and redox, have been widely used to regulate the polymeric properties, such as the adhesion switch between interfaces. Guo et al.88 grafted β-cyclodextrin (β-CD) and Fc amino derivatives onto the imidazolium type of poly (ionic liquid) (PIL) membrane surfaces, respectively (Figure 9A). The host–guest recognitions between 13C and 13F constructed a polymer velcro with strong adhesion under both open-air and aqueous conditions. The adhesion reversibility of the polymer velcro could be realized by the oxidoreduction of Fc. Immersing in an aqueous NaCLO solution (5 mmol/L) oxidized Fc to Fc+, which had a much lower binding affinity with β-CD, thus diminishing the binding between PIL surfaces and separating the supramolecular velcro, whereas a Vitamin C solution (15 mmol/L) could reduce Fc+ back to Fc and refasten the supramolecular velcro. After five cycles, the adhesion strength of the polymer velcro could be recovered to a value, which was 35% of that for the original velcro. The reduction of adhesion strength may be attributed to chemical contaminations and the destruction of PIL membranes. Moreover, the intrinsic ionic conductivity of the PIL membranes facilitated electrochemical-stimulated adhesive switch. This electrochemically and (or) chemically controllable adhesion is versatile in both air and aqueous environments.

On the contrary, the majority of the investigation has focused on the bonding between smooth homogeneous interfaces, such as glasses, metal, poly(methyl methacrylate), wood, polytetrafluoroethylene, and the self-adhesion between gel surfaces. In fact, modern society requires increasingly complex substrate mixtures to fulfill the requirements for the applications of high-performance smart materials, such as hydrogel paints, sensors, and soft robotics. Consequently, the on-demand (de)bonding of hydrogels and solid substrates may construct new functional synergistic materials for usage in dynamic and complex conditions. Li et al.91 created a simple approach for instant on-demand (de) bonding of hydrogel to various metal surfaces with arbitrary shapes. They designed a 14-1 molecule, where 14-1 contains a carboxylic acid group binding with the metallic surfaces and a methacrylic group chemically connected with the polymeric hydrogel network. The standard 90° peeling tests demonstrated that the bonding energy between hydrogels and 14-1 modified metallic...
surfaces (including nickel, aluminum, tantalums,argentum, stainless steel, titanium, and some of their alloys)could reach up to 1,000–1,200 J/m², which was comparablewith the interfacial bonding strength of tendon aswell as between cartilage and bone tissues. The toughbonding was attributed to the strong coordination be-tween the dense carboxylate groups, coming from14–1, and the metal ions on the substrates, as well as electro-static and hydrophobic interactions. Notably, an addi-tional dynamic disulfide bonding was introduced into14–1 to obtain 14–2, giving similar adhesion properties to14–1 (Figure 9B). Reductive glutathione (GSH) was wellknown to break disulfide bonds into thiol groups, thus easily removing the hydrogel from the metal surfaces. The residual thiol groups after GSH treatment could further rebond with hydrogen under UV radiation via photoinitiated free-radical polymerization, whose average interfacial toughness was about 800 J/m², only slightly lower than that of the original samples (Figure 9C). This universal and efficient method mightinspire the development of functional hybrid materials, such as detachable tissue adhesives and recyclable softelectronics.

4.3 | Photoresponsive supramolecularadhesives

The key advantage of dynamic supramolecular adhesivesis the on-demand assembly/disassembly in response toexternal stimuli. The inherent feature of the adhesiveshas offered them attractive applications, such as re-versible wound dressings and semiconductor adhesion. Although many strategies use heat and chemical stimuli to regulate adhesion strength, light is favored as an ideal stimulus on account of its contactless remote stimula-tion, spatial-temporal control, wavelength tunability, andbeing pollutant free. 92,93 These unique advantages have
promoted the research regarding the (de)bonding of photoresponsive adhesive materials. It is a common strategy to introduce the photoswitchable units (such as AZO, stilbene, spiropyran (SP), diarylethene (DAE), and their derivatives) into the molecular frameworks, to drive spatial rearrangements and to construct the optical dynamic systems. A typical example is that doping SP/DAE photochromes into polystyrene networks can induce a UV-induced adhesion enhancement without the facilitation of covalent cross-linking. However, the adhesion reversibility is limited by the permanent changes in the internal polymeric structure. Therefore, high-molecular-weight polymer adhesives often find it difficult to achieve a complete debonding and a full recovery due to their high viscosities, which calls for the development of SSSA.

The isomerization and rearrangement of the photochromic small molecules under the light stimulation effectively control the molecular fluidity, enabling SSSA to have a wide range of regulated viscosity. The photoresponsive solid–liquid phase transition of AZOs is often used in reworkable adhesives, whereas the photoisomerization of AZOs often requires a long time to spontaneously revert back, thereby hindering the immediate response of the adhesives. A recent study by Wu et al. reported a green-light-triggered instant reversible adhesive based on the AZO-phase transition. 15-1 and 15-2, with the corresponding melting points of 44°C and 53°C, exhibited a remarkable solid-to-liquid transition induced by green light (500–550 nm) (Figure 10A). Unlike the phase transition induced by azobenzene photoisomerization in which the spontaneous reduction from cis to trans configuration takes several hours to achieve, the 15-1/15-2 based liquid can spontaneously revert to a solid within 2 min. UV-Vis absorption spectra showed that 15-1 and 15-2 are monomers in a dichloromethane solution and can assemble to form aggregates with an absorption enhancement within the visible region in solid state (Figure 10A).

According to the 1H-NMR spectra (recorded in CDCl3) (Figure 10C), no significant changes were observed after being irradiated with green light, while variations was detected after UV irradiations. The recorded spectra verified that the solid-to-liquid transition of 15-1 induced by green light is driven by photothermal effects resulting from aggregation absorption enhancement instead of trans-to-cis isomerization, and the spontaneous rapid solidification is thought to be a pure physical heat release. The rapid, reversible phase transition enabled

Figure 10 (A) Chemical structures of 15-1 and 15-2. (B) UV-vis absorption spectra of 15-1 and 15-2 in the solid state. (C) 1H-nuclear magnetic resonance spectra of 15-1 in CDCl3: (I) original sample, (II) sample after green light irradiation, and (III) sample after UV light irradiation. (D) A schematic representation of the 15-1 adhesion procedure and the photoinduced separation of two glass plates.
A strong reversible adhesive with the maximum adhesion strength of 1.34 MPa and over 10 cycles (Figure 10D). In addition, the adhesion strength of 15-2 (0.14 MPa) is much lower, as the odd number of carbon atoms on 15-1 alkane chains leads to different assembly states, affecting the macroperformance. The initiation of the green light, instead of high-power and harmful laser source and UV light, is able to expand the scope of this light-induced adhesive’s biological applications. This study affords a novel concept to construct light-triggered reversible adhesives via phase transitions of organic compounds.

Another strategy to accomplish photoadhesive switching is to modify the polymer morphology through light-induced sintering or melting. A series of photo-thermal responsive supramolecular adhesives were explored by Prado et al. and Balkenende et al., based on trifunctional small molecular skeletons and noncovalent crosslinking. They reported an amorphous supramolecular glass with high stiffness (flexural modulus = 3.04 ± 0.26 GPa), assembled by trifunctional low-molecular-weight building blocks through UPy groups. The highly cross-linked nature and a large content of UPy motifs reduced the molecular mobility and hindered the crystallization. The adhesion derived from rose significantly with the increase of temperature, when above Tg, on account of the dynamic equilibrium of UPy–UPy interactions between bound and dissociated states. The equilibrium shifted to the monomer side, thereby reducing the cross-linking density as the temperature was further increased. The high optical absorption resulted from high UPy content also enabled optically (de)bonding of 16 on demand due to the conversion of optical energy into heat by nonradiative relaxation of the excited state, which caused the reversible dissociation of the network and the formation of a low-viscosity melt. The film-coated glass substrates could bond with each other with a shear stress of 1.2 ± 0.2 MPa by heating to 200°C for 10 s and cooling to ambient temperature, and further debonded within 30 s when exposed to ultraviolet light, which was then rebond through exposure to light or heat without the loss of adhesion. However, the current reported limitations are mainly related to the nonideal toughness and the unfavored (high) brittleness, which subsequently impeded the applicability and processability for this particular type of adhesives.

Recently, they explored a supramolecular polymer (SMP) network self-assembled by soybean oil-derived multifunctional branched monomers, using isophthalic acid (IPA) as H-bonding and π–π stacking motifs (Figure 11B). Given that the polarity differences between the triglyceride backbone and the IPA groups would lead to a microphase separation, MCC was mixed well with 17 polymers to obtain composites with excellent properties due to the favorable interactions between the hydroxyl groups located at the surface of MCC and IPA motifs, as well as the increased domain of the amorphous phase. The crystallization temperatures (Tc) (60°C) and the maximum mechanical stress (1.4 MPa) of 17-MCC composites (when above Tg) were lower than those of the neat 17 (Tc = 80°C, maximum stress = 1.9 MPa), whereas the corresponding elongation at break was significantly increased from 12% to 47%. The adequate mechanical properties at room temperature, low melt viscosity, and improved toughness were beneficial in processing and (de)bonding on-demand applications. As an SMP adhesive, 17-MCC composites revealed high shear strength (2.3 and 2.2 MPa) for stainless steel.
substrates. The adhesives can bridge two pieces of substrates under the stimulus of heat or temporary UV radiation and further debond within 45 s when exposed to UV radiation. Notably, the addition of 0.2 wt% UV light absorber could significantly accelerate the (de)bonding process. Thereby, this study verifies the superiority of MCC composite adhesives both in adhesion strength and toughness.

5 SUMMARY AND PERSPECTIVES

With the development of supramolecular chemistry, assembling small-molecule building blocks into polymeric architectures with unique structures and multiple functions through noncovalent interactions has become a significant topic. Small molecules can self-assemble into vesicles, gels, micelles, nanotubes, spirals, and other ordered structures under certain conditions, leading to attractive applications, such as stimuli-responsive materials, smart drug delivery systems, and tissue engineering. The self-assembly at the microlevel has been widely investigated, but the study about its application at the macrolevel is relatively deficient. More specifically, the transformation of the microscopic assemblies into macroscopic adhesive materials has been preliminarily explored. As described in this review, SSSA exhibits a noticeable superiority compared with widely researched polymeric adhesives, such as simple precursor synthesis, accurate structural design, precise performance regulation, ideal reversibility, and explicit mechanism exploration.

However, a few issues remain unsolved and could potentially block further scientific development and valorization of SSSA: (i) Precisely, controlled ordered assembly is ideal to construct function-editable complex materials. Though the existing examples are almost disordered self-assembly, neither guidelines for their molecular design nor methods for controlling their aggregation morphologies, which are suitable for adhesive application, have been established. This results in the difficulty of further developing these adhesives into high-performance materials, such as soft actuators and wearable devices. (ii) Current SSSA has been developed from limited classes of small-molecule building blocks, such as UPy, host–guest molecules, catechol, and azobenzene derivatives. Thus, more ingeniously designed small molecules are yet to be discovered for strengthening the SSSA family. (iii) Contrary to artificial molecular structures that may require a meticulous structural design and a complex synthesis, natural small molecules, such as amino acids, carbohydrates, and nucleotide bases are more favorable building blocks on account of their unique chiral structures, multiple action sites, and excellent biocompatibilities. It is worth pointing out that their applications in adhesive materials have shown tremendous potential but have been rarely exploited. (iv) The current level of design for SSSA is fairly primitive. Although close-to-ideal synthesis processes have been repeatedly presented in the literature, it is unlikely to use these approaches in industrial scale adhesive productions. The reasons for this are (i) the industrial production environment is rather harsh and complex, relative to the bench scale; (ii) The stimulation source used in scientific studies is fairly singular, but this is not the case for scaled-up processes. Therefore, multimode response adhesion in a more sophisticated environment will be preferred when scaling up. In summary, the opportunities and challenges co-exist in the advancement of SSSA. A better understanding of the explicit mechanisms underlying adhesion behavior will point in the right direction for future development. It is for sure that we will witness a promising prospect once the aforementioned challenges are solved.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

ORCID

Da-Hui Qu http://orcid.org/0000-0002-2039-3564

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**AUTHOR BIOGRAPHIES**

Chen-Yu Shi was born in 1996 in Jiangsu, China. She attended East China University of Science and Technology (ECUST) for her undergraduate studies and obtained her BE degree in applied chemicals in 2018. She is currently a PhD student in the group of Prof. Da-Hui Qu and Prof. He Tian. Her current research focuses on supramolecular self-assembly and smart materials.
Qi Zhang was born in 1993 in Anhui, China. He obtained his BS in 2015 and received his PhD in Applied Chemistry in 2020 in ECUST, under the supervision of Prof. Da-Hui Qu and Prof. He Tian. He currently works with Prof. Ben L. Feringa as a postdoctoral fellow at the University of Groningen. His research interests mainly rest on supramolecular polymers and artificial molecular machines.

He Tian obtained his PhD degree from ECUST in 1989. Since 1999, he is an appointed, Cheung Kong-Distinguished Professor by the Education Ministry of China. He became the academician of the Chinese Academy of Science in 2011 and a Fellow of TWAS—The World Academy of Sciences for the advancement of science in developing countries—in 2013. His current research interests focus on the development of interdisciplinary materials science that determines the electronic and optical properties of materials. He has been listed as a Highly Cited Researcher in Chemistry (2014–2018) by Clarivate.

Da-Hui Qu obtained his BS from Qingdao University in 2000 and received his PhD in Applied Chemistry in 2006 from ECUST, under the supervision of Prof. He Tian. From July 2006 to January 2009, he worked with Prof. Ben L. Feringa as a postdoctoral fellow at the University of Groningen. Since 2009, he has worked at ECUST, and he became a full professor in 2014. His current research focuses on controllable supramolecular systems and molecular level devices and machines with adjustable optical properties.

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