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Supramolecular adhesive materials based on urea assembly

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Abstract:

Supramolecular adhesive materials (SAMs) have garnered significant research interest owing to the outstanding attributes offered by dynamic bonds, including self-healability, stimulus responsiveness, and reversible adhesion. Urea groups with adjustable hydrogen bond strength, directional assembly ability, readily synthesized and amenable to scale-up, represent crucial dynamic bond constituents; this review provides a comprehensive summary of SAMs based on urea assembly. Meanwhile, a comprehensive overview of SAMs' structures, properties, and applications is also provided. SAMs are categorized into four distinct types following the quantity of urea-based assembly sites: one assembly site, two assembly sites, three assembly sites, and multi-assembly sites. Deduced out urea-based assembly promotes molecular weight and cross-linking points increase, which are the main factors for improving the performance of SAMs. The SAMs' limitations, challenges, and prospective directions are also briefly outlined.

Keywords: Supramolecular adhesive materials; urea; self-assembly; hydrogen bond; ureidopyrimidinone

1 **1 Introduction**

2 Adhesive materials (AMs) form bonds between materials of the same or different
3 properties through adhesion on the object's surface. In the past decades, AMs have been
4 utilized in a progressively broader scope of uses, ranging from everyday life to
5 sensors[1-3], electronic skin[4, 5], and medical fields[6, 7]. In response to the
6 increasingly complex and diverse application scenarios, researchers have commenced
7 investigations into novel multifunctional AMs. Supramolecular adhesive materials
8 (SAMs), one kind of AMs, which contain numerous non-covalent interactions[8], have
9 attracted widespread attention among various adhesives due to their reversible
10 bonding[9], self-healing ability[10], strong adhesion[11], and other characteristics[12].
11 These unique and excellent properties are due to the non-covalent interactions in
12 supramolecular materials[13].

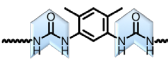

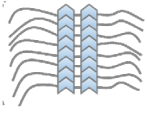
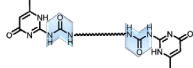


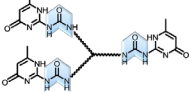


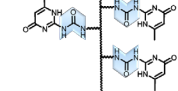


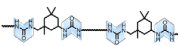



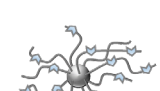
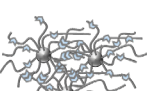

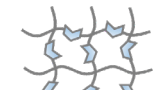

13 Typically, the non-covalent interaction in SAMs can enhance their performance.
14 These non-covalent interactions include hydrogen bonding[14], host-guest
15 interaction[15], metal coordination interaction[16], and so on[17]. Among them, SAMs
16 featuring hydrogen bonds have garnered substantial attention due to their versatile
17 bonding mechanisms and robust dynamic reversibility. Typically, hydrogen bond
18 interactions play a crucial role in SAMs' thermal and mechanical properties, enabling
19 effective control over their adhesive performance[18]. Introducing a solid but reversible
20 non-covalent hydrogen bond component into the structure can lead to SAMs with
21 improved performance, such as adhesion. For example, Qu et al. achieved robust
22 adhesive properties by introducing distinct hydrogen bond networks (carboxylic acid
23 or hydrazide) in dynamic covalent polymers, demonstrating significant influences of
24 different forms of hydrogen bonds on adhesion efficacy, with respective strengths of
25 2.5 MPa and 18.0 MPa[19, 20]. As a crucial form of hydrogen bonding, urea-based
26 hydrogen bonds distinguish themselves from traditional hydrogen bonds (carboxylic,
27 hydroxyl, amino, etc.), exhibiting more robust and unique directionality and
28 complementarity. Simultaneously, the binding energy associated with most hydrogen
29 bonds typically falls within the range of -11.20 to -43.05 kJ·mol⁻¹[21, 22]. In contrast,
30 urea derivatives, such as ureido-pyrimidinone (UPy), exhibit considerably higher

1 binding energies, registering at $-161 \text{ kJ}\cdot\text{mol}^{-1}$ in a vacuum and $-69 \text{ kJ}\cdot\text{mol}^{-1}$ in aqueous
2 environments[23]. This disparity underscores the superior strength of the urea hydrogen
3 bond compared to most conventional hydrogen bonds. Moreover, the hydrogen bonding
4 exhibited by urea derivatives imparts a notably greater enhancement to surface energy
5 compared to straightforward polar functional groups, such as the carboxyl group[24].
6 Concurrently, urea hydrogen bonds offer the added benefits of facile synthesis and
7 tunable strength[25], affording the ability to control shear strength within SAMs within
8 the range of 5.20 kPa to 30 MPa[26, 27]. UPy, the typical self-complementary
9 hydrogen-bonded urea derivative with a strong association constant ($6\times 10^7 \text{ M}^{-1}$ in
10 chloroform)[28], originally discovered by Meijer, Sijbesma, and colleagues[29] as a
11 well-known self-complementary quadruple hydrogen bond group and has shown
12 remarkable thermal responsiveness in SAMs[30]. UPy can be decorated onto both sides
13 of the oligomer and lead end-to-end assemble to stable long supramolecular polymer
14 chain[29]. Combined with suitable oligomers, such supramolecular polymers can be
15 used as SAMs[31]. Urea hydrogen, connected to highly electronegative nitrogen,
16 readily forms stable hydrogen bonds with other carbonyl oxygen atoms. Owing to its
17 advantages, such as easy of synthesis, controllable hydrogen bond numbers, and
18 adjustable building blocks, urea-based hydrogen bonding has been widely applied in
19 polymer self-assembly[32], self-repairing glass[13], self-healing elastomers[33], and
20 other related fields[34]. Furthermore, urea hydrogen bonding has gradually emerged in
21 adhesive development, serving as a significant non-covalent interaction in the context
22 of SAMs[35]. The orientation of two urea groups, parallel or antiparallel, can be
23 reinforced by the spacer connecting them, resulting in the formation of elongated one-
24 dimensional supramolecular assemblies. This assembly process allows for a controlled
25 increase in molecular weight and the modulation of mechanical properties[36]. Urea
26 groups facilitate the self-assembly of small molecules or oligomers into larger
27 structures, thereby increasing cohesive forces and enhancing the adhesion properties of
28 SAMs[37]. In addition, urea groups serve as robust cross-linking points, further
29 enhancing SAMs adhesion by enabling the cross-linking of macromolecules or

1 oligomers into intricate three-dimensional structures[38]. Furthermore, adhesion
2 constitutes a multifaceted process contingent upon numerous factors, including
3 interfacial adhesion, polymer strength, viscosity, surface tension, and other related
4 parameters. As an exemplar urea derivative, UPy has been empirically validated to
5 augment the internal stress and polymer viscosity of viscous materials through its
6 characteristic hydrogen bonding[39, 40]. Additionally, UPy has demonstrated the
7 capacity to substantially elevate surface energy[24], thereby amplifying interfacial
8 adhesion and reinforcing adhesive strength.

9 Here in this review, we present a comprehensive overview of the state-of-the-art
10 progress in urea-based SAMs, categorized into two principal types: the molecular
11 weight growth type and the dynamic cross-linking increase type, based on the
12 functional role of urea within SAMs (Table 1). The molecular weight-increasing type
13 can be further subcategorized into two subtypes: the one assembly site type, where urea
14 groups are located within the cores of the oligomer, and the two assembly sites type,
15 where urea groups exist at both ends. Meanwhile, based on the number of assembly
16 sites in the SAMs, the dynamic cross-linking increase type can be divided into three
17 assembly sites and multi assembly sites. Based on this classification, the molecular
18 design of urea-based SAMs is described, laying the foundation for further research on
19 urea assembly-based SAMs.

1 Table 1. Classification and schematic diagram of urea-based SAMs.

Enhancement mechanism	Number of assembly sites	Decorations of urea	Molecular structure	Cartoon sketch	Schematic diagram after self-assembly
Increase the molecular weight	One assembly site	Urea decorated oligomers in the middle			
	Two assembly sites	Urea decorated oligomers at both ends			
	Three assembly sites	Urea decorated three-armed oligomer on the end groups			
Increase the dynamic cross-linking	Multi-assembly sites	Urea decorated on the side-chain			
		Urea decorated in the backbone			
		Urea decorated on nano-particles			
		Urea decorated on three-dimensional network polymers			

2

3 2 SAMs based on urea assembly

4 2.1 Enhancing cohesion through urea self-assembly to molecular weight increase

5 For SAMs with linear assembly, the aggregates' molecular weight significantly
6 influences the adhesive strength. Studies have demonstrated that the adhesive strength
7 increases with the molecular weight of the adhesive when the adhesive force exceeds
8 the cohesive force[41]. Taking advantage of the excellent directionality of urea
9 hydrogen bonding, oligomers decorated with urea can self-assemble into one-
10 dimensional supramolecular polymers (Fig. 1a), thereby significantly changing the
11 molecular weight and rheology of the supramolecular polymer and obtaining higher

1 and tunable adhesive strengths, which is classified as ‘one assembly site’ type.
2 Costantino Creton and colleagues observed that the elevation in the viscosity of self-
3 assembled urea-based molecules correlates with prolonged relaxation times.
4 Meanwhile, they identified an associated increase in energy dissipation corresponding
5 to the heightened viscosity, thereby suggesting the potential utility of biurea-
6 functionalized molecules as pressure-sensitive adhesives[37]. Furthermore, oligomers
7 furnished with bifunctional ends can interconnect, forming larger polymers through the
8 paired assembly of urea derivatives, particularly those involving Upy. This assembly
9 significantly enhances the molecular weight and bestows the resulting structure with
10 exceptional adhesive strength, categorized as the ‘two assembly sites’ type. These
11 oligomers, through hydrogen bonding interactions between urea moieties or
12 coordination between bis-urea ligands and phosphate ions, are designed and
13 synthesized for multi-functional adhesives, such as pressure-sensitive adhesives
14 (PSAs)[42], self-healing materials[43], photo-responsive reversible adhesives[44],
15 adhesive biomaterials, ion-coordination-driven gels, and other applications[45].

16 **2.1.1 one-assembly site**

17 The urea group, serving as the fundamental structural unit in urea-induced SAMs,
18 plays a decisive role in shaping the adhesive strength of one-assembly site SAMs. One
19 assembly site means that multiple urea groups can be contained at the same site.
20 Research indicates that the number of urea groups in the assembly core significantly
21 influences the molecular weight and dynamics of the resulting supramolecular
22 polymer[25]. In non-aqueous systems, dual or ternary urea groups exhibit an optimal
23 balance between strength and dynamics, providing the linear assemblies with the
24 necessary mechanical robustness while ensuring sufficient flexibility and
25 responsiveness[46].

26 In a significant contribution by Costantino Creton et al., they successfully
27 synthesized a low molecular weight polyisobutylene (PIB) decorated bis-urea in the
28 middle by reacting toluene diisocyanate with PIB amine (Fig. 1b)[37]. Through urea-
29 induced self-assembly, high molecular weight supramolecular polymers were obtained.

1

2 Although SAMs based on urea-directed one-dimensional assemblies exhibit good
3 dynamic properties, their cohesive forces are insufficiently robust. The cohesive forces
4 of linear supramolecular polymers can be significantly enhanced, and supramolecular
5 adhesives' (SAs) performance can be improved by introducing cross-linking into the
6 building blocks. Callies et al. accomplished this by introducing epoxy groups into the
7 building blocks for chemical cross-linking and exploring new PSAs[53]. Double-end
8 atom transfer radical polymerization (ATRP) initiator decorated bis-urea was used to
9 initiate the copolymerization of butyl acrylate (BA) and glycidyl methacrylate (GMA),
10 resulting in building blocks capable of one-dimensional assembly induced by urea
11 hydrogen bonding while simultaneously being cross-linked by 1,5-diamino-2-
12 methylpentane. The effect of the proportion of cross-linking points (epoxy groups) in
13 the building blocks on the adhesive was systematically studied, and the results showed
14 that chemical cross-linking could increase the debonding energy threefold (30 J/m^2 to
15 90 J/m^2) while increasing the fibril stability in extension (Table 2).

16 Table 2. Overview of the performance and applications of 'one assembly site' type SAMs.
17 Experiments were performed using various test layouts and substrates.

Name	Applications	Method	Substrate	Strength	Ref.
PIBUT	Soft viscoelastic adhesive	Probe tack test	Glass/stainless steel	1.0 MPa	[37]
PIB XYL	N/A	Probe tack test	Glass/stainless steel	$70 \text{ J}\cdot\text{m}^{-2}$	[47]
PBA 3U	N/A	Probe tack test	Glass/stainless steel	$35 \text{ J}\cdot\text{m}^{-2}$	[52]
PBA 2U	PSAs	Probe tack test	Glass/stainless steel	$90 \text{ J}\cdot\text{m}^{-2}$	[53]

18 PIBUT: bis-urea poly(isobutene ureido toluene); PIB XYL: xylyl bis-urea modified PIB; PBA 3U:
19 PBA decorating three urea; PBA 2U: PBA decorating two urea and cross-linking group.

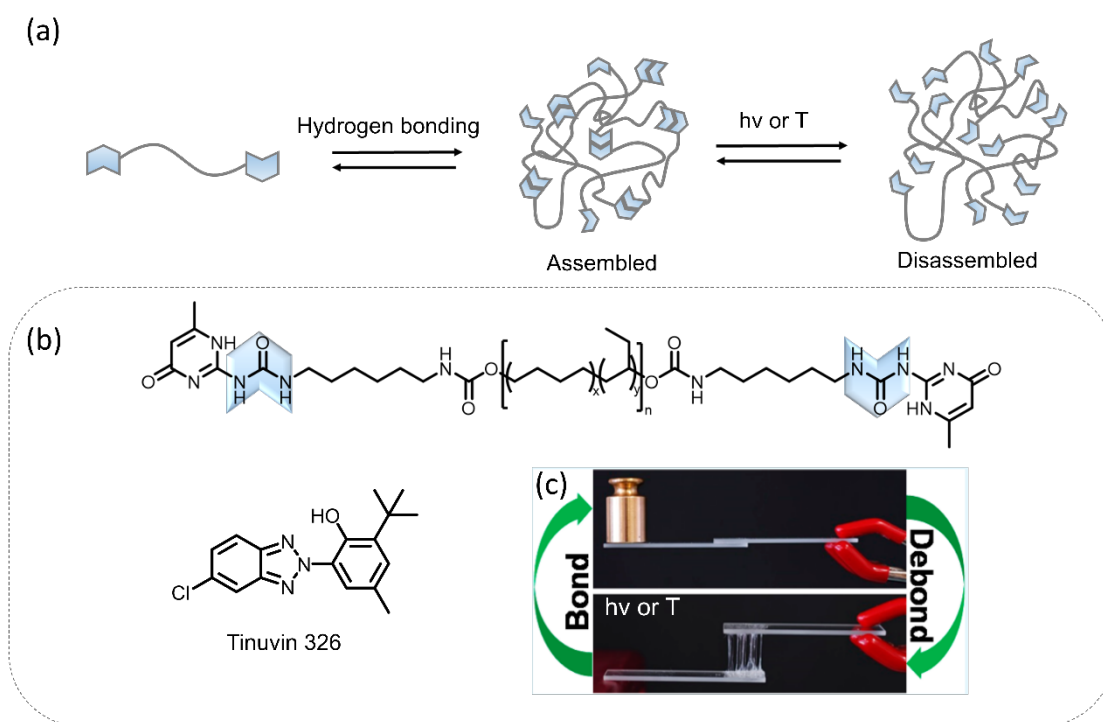
20

21 2.1.2 Two assembly sites

22 Usually, urea derivatives can be assembled into pairs through weak interactions,
23 such as hydrogen bonding[54] or anion coordination, where the urea ligand self-
24 assembles through coordination with the phosphate anion, and the assembles are then
25 assembled into supramolecules by intermolecular hydrogen bonding[55]. By
26 decorating these urea derivatives to both ends of small molecules or oligomers, SAMs
27 can be achieved via end-to-end association, termed two assembly sites SAMs.

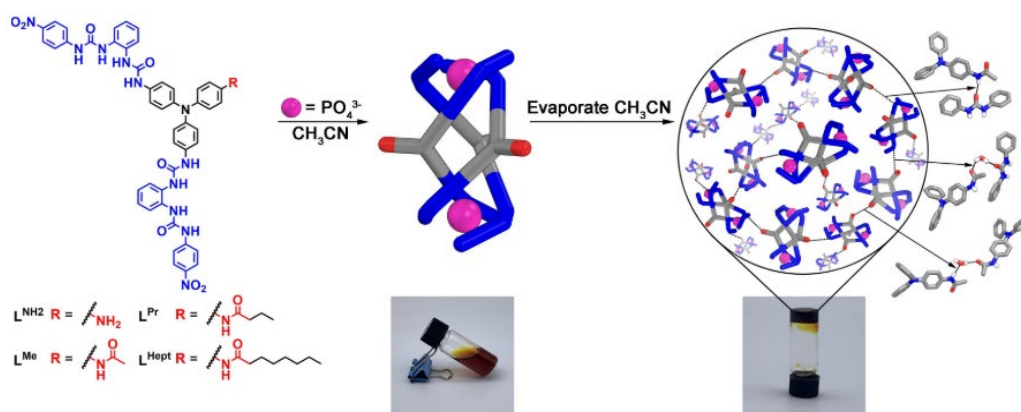
28 The most appealing aspect of SAMs is their dynamic nature. Therefore, in addition

1 to their application as bio-adhesive materials, dual-end modified UPy SAMs can also
 2 be utilized as stimuli-responsive adhesives, achieving on-demand bonding or
 3 debonding. Heinzmann et al. exploited the stimulus-responsive behavior of urea
 4 hydrogen bonds to develop photo-responsive adhesives. They synthesized UPy-PEB-
 5 UPy oligomers (PEB is the abbreviation of poly(ethylene-co-butene), but the quadruple
 6 hydrogen bonds of UPy do not exhibit significant photo-responsiveness since pure UPy
 7 does not absorb light beyond 320 nm. However, the binding between UPy units can be
 8 weakened through heating. Therefore, the authors introduced a photosensitizer (Tinuvin
 9 326) during the assembly of UPy-PEB-UPy oligomers, facilitating the conversion of
 10 UV light into heat and achieving light-triggered adhesion adhesives (Fig. 2a, b).
 11 Ultimately, their adhesive demonstrated a shear modulus of 0.9-1.2 MPa on quartz,
 12 glass, and stainless steel. The samples debonded within seconds when the overlapped
 13 joints were subjected to a load and exposed to light or heat (Fig. 2c). They could be re-
 14 adhered by exposure to light or heat and regain their original adhesive performance[44].



15
 16 Figure 2. (a) Urea self-assembly diagram of ‘two assembly sites’ type SMAs, assembly and
 17 decomposition diagram under light or heat response. (b) The chemical structures of UPy-PEB-UPy
 18 polymers and photosensitizers. (c) Photographs of lap joints bonding and debonding under light or
 19 thermal conditions[44].
 20

1 Although we categorize all SAMs assembled with both end-urea modifications as
 2 two assembly sites type SAMs, it is difficult to confirm the end-to-end assembly.
 3 Specifically, the rigid *ortho*-phenylene-bridged bis-urea and the phosphate group can
 4 be coordinated through twelve N(H)-O hydrogen bonds to form a triple helix assembly
 5 structure, as exemplified by Gao et al.'s supramolecular adhesive conductive gel
 6 preparation, where the end-urea-modified compounds exist in trimeric form after
 7 coordination[55]. A hierarchical self-assembly strategy has been developed to develop
 8 a novel approach for designing and manufacturing ion-coordination-driven gels with a
 9 wide range of mechanical strengths and tenability. In their study, a series of C_2 -
 10 symmetric urea ligands were designed and synthesized, self-assembling them into
 11 helical trimers through coordination with phosphate anions. The resulting trimers can
 12 form gels through multiple intermolecular hydrogen bonds, exhibiting effective and
 13 stable adhesive performance, selective wetting properties, and conductivity (Fig. 3).



14
 15 Figure 3. Scheme of the hierarchical self-assembly of anion-coordinated helicates and subsequent
 16 gelation from hydrogen bonding[55].
 17

18 Besides assembling into trimers or long-chain supramolecular polymers, end-urea-
 19 decorated molecules can also assemble into three-dimensional network structures. Urea
 20 groups without complementary hydrogen bonds tend to assemble with multiple groups,
 21 and bis-end-urea-decorated oligomers will assemble into spatially interconnected
 22 structures. Wayne Hayes's group incorporated 4-(2-aminoethyl)morpholine into
 23 isocyanate-terminated pre-polymers for introducing urea linkages to provide strong
 24 hydrogen-bonding motifs, successfully got supramolecular polyurethane (SPU) as

1 SAMs for hydrogen-bond-driven self-assembly, and exhibiting a storage modulus of 3
 2 MPa at room temperature[54]. When it increases to 50 °C, the physical cross-links
 3 disassemble rapidly, resulting in a significant decrease in the storage modulus by
 4 several orders of magnitude. The material fully recovers its mechanical properties
 5 within 60 minutes at body temperature (37 °C).

6 Moreover, human fibroblast experiments demonstrate excellent biocompatibility
 7 of the material, highlighting its significant potential for essential applications in self-
 8 adhesive biomedical materials. Following this, Hayes et al. incorporated trioxide
 9 tetraoxide into the SAMs and employed an oscillating magnetic field for controlled
 10 heating, enabling the dynamic adhesive to achieve on-demand debonding[56].
 11 Meanwhile, they also utilized self-assembling of both end-urea-decorated
 12 polyurethanes with bulky groups, resulting in SAMs whose performance can be
 13 controlled through processing. The pairing of urea groups via hydrogen bonding
 14 increased the molecular weight, and the benzene groups supplied further
 15 supramolecular cross-linking through π - π stacking, enhancing the cohesion and making
 16 the material a promising candidate for adhesive applications[57]. They also investigated
 17 the structural attributes of the urea group employed for end-capping and assembly
 18 purposes. It was elucidated that the nitro group within the terminal moiety can
 19 effectively engage in hydrogen bonding competition with the urea group. This
 20 phenomenon finely modulates assembly strength and crystallinity, ultimately obtaining
 21 reversible adhesives characterized by a shear strength of up to 5.70 MPa[58]. Zhao et
 22 al. adopted a comparable approach to fabricate low-temperature responsive SAMs.
 23 Diverging from above, they utilized UPy for end-capping and incorporated carbonate
 24 and urethane bonds into the polymer matrix. These additional groups exhibited the
 25 ability to vie with UPy for hydrogen bonding, resulting in an adhesive material that
 26 demonstrated a remarkable shear strength of 7.23 MPa (Table 3) and facilitated
 27 controlled debonding at low temperatures (60°C)[34].

28 Table 3. Overview of the performance and applications of ‘two assembly sites’ type SAMs.
 29 Experiments were performed using various test layouts and substrates.

Name	Applications	Method	Substrate	Strength	Ref.
UPy-PEB-UPy	Light- and heat-responsive	Lap joints	Stainless	1.2 MPa	[44]

	adhesives		steel		
Phosphate assemblies	Viscous conductive gel	Lap joints	PMMA	0.275 MPa	[55]
SPU-M	Biomedical adhesive	Peel test	Porcine skin	0.02 MPa	[54]
SPU-M	Magnetic response adhesive	Lap joints	Glass	1.43 MPa	[56]
SPU-bB	Heat reversible adhesive	Peel test	Metal	740 J·m ⁻²	[57]
SPU-tMN	Self-healing elastomer adhesive	Lap joints	Glass	5.70 MPa	[58]
OU	Temperature activating skin dressing	Lap joints	Stainless steel	7.23 MPa	[34]

1 SPU-M: SPU capped with morpholine. SPU-bB: SPU capped with bis-Benzyl; SPU-tMN: SPU
2 capped with 2,4,6-trimethyl-3-nitroaniline; OU: oligo urethane.

3

4 **2.2 Increasing cohesion by urea self-assembly leading cross-linking**

5 Increasing the cross-linking density is an effective method for improving the
6 properties of traditional AMs. Drawing inspiration from this approach, scholars adjust
7 the adhesive strength of SAMs by varying the number of non-covalent cross-linking.
8 Multi-urea (≥ 3) decorated small molecules or oligomers self-assemble through
9 hydrogen bonding to form dynamic, non-covalent, cross-linked networks. The increase
10 of dynamic cross-linking enhances the cohesive forces, improving adhesion
11 performance. These urea-based SAMs can be categorized into three assemble sites style
12 and multi-assemble sites type. Typically, these SAMs exhibit excellent self-healing,
13 reprocessability, and responsiveness to stimuli. They have been utilized for designing
14 and fabricating multifunctional adhesives, including adhesives[59], hot-melt adhesives
15 (HMA)[60], viscoelastic adhesives[61], self-healing adhesives[62], responsive
16 reversible adhesives[44], adhesive electrode protection films[63], tissue adhesives[64],
17 supramolecular HMA[65], flame-retardant adhesives[66], fluorescent adhesive
18 gels[67], and other adhesive-related applications.

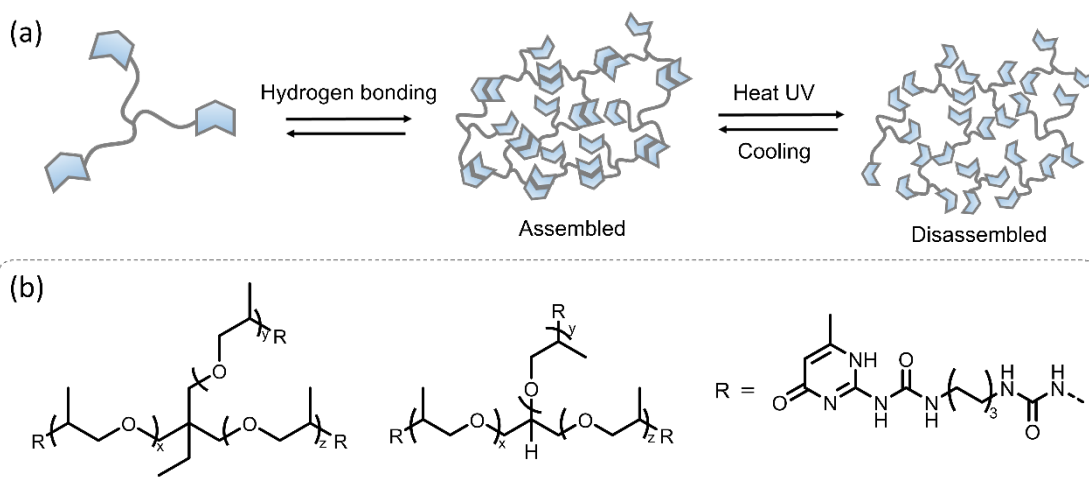
19 **2.2.1 Three assembly sites**

20 Trifunctionality molecular assembly can lead to cross-linking exponentially, and
21 the oligomer can be designed with tri-arms and decorated urea derivatives at the end to
22 obtain dynamic SAMs with increased cross-linking points efficiently. Three-
23 dimensional supramolecules are assembled through the interaction of urea hydrogen
24 bonds in the tri-arms oligomers, which can exhibit excellent cohesion in SAMs. Urea
25 is linked via short alkane chains to form tri-arms molecules and assembled to obtain a

1 UV-responsive hard vitrimer. Balkenende et al. synthesized a low-molecular-weight tri-
2 UPy decorated tri-arms unimer and obtained a UV-responsive transparent vitrimer
3 through self-assembly of this unimer (Fig. 4a), which can serve as an adhesive for
4 achieving light-stimulated reversible adhesion[68]. In order to obtain room-temperature
5 solid adhesion, Zhang et al. tried to introduce ionic liquids (IL) into urea-decorated tri-
6 arms molecules, and they pointed out that this modification significantly increased the
7 adhesive strength to 12.20 MPa. Meanwhile, they incorporated carbon nanotubes,
8 resulting in electrical-responsive detachment of the adhesive[69].

9 Introducing polydimethylsiloxane (PDMS) into the middle of UPy and cross point,
10 the final material exhibits some properties of PDMS except dynamic. Liu et al.
11 synthesized PDMS tri-arms oligomers and modified the end of each arm with urea or
12 urea derivative groups, UPy. Using the self-assembly of end-group multiple hydrogen
13 bonding, they obtained silicone elastomer thin films with adhesiveness and self-
14 repairing properties[70]. They pointed out that UPy first assembled into dimers and
15 then further crystallized with the assistance of other hydrogen bonds, enhancing the
16 material's mechanical properties. In the presence of water, the crystallization involving
17 dimers can be disrupted, leading to improved self-repairing ability of the material.
18 Atomic Force Microscope (AFM) results showed an increased adhesive force of the
19 material from 3 nN under dry to 4.6 nN in the presence of water. The researchers
20 developed this material into a damage-healable, oil-repellent supramolecular silicone
21 (DOSS) coating with good substrate adhesion[27]. Due to the higher content of free
22 UPy and lower content of PDMS chains in the bottom layers, the surface layer of UPy
23 exhibited relatively lower content and tended to form dimers, while the PDMS main
24 chain content was higher. As a result, the surface and bottom layers showed different
25 adhesive strengths (adhesion force of 8.3 nN for the bottom layer and 0.31 nN for the
26 surface layer). This property allows the coating to maintain its oil repellency while
27 retaining the ability to adhere to various surfaces. Furthermore, as an adhesive, this
28 material demonstrated a shear strength exceeding 20 MPa on all metal surfaces and
29 even 10 MPa on polytetrafluoroethylene (PTFE) surfaces.

1 In addition to the self-assembly of tri-arms PDMS oligomers for adhesive material
2 preparation, tri-arms polycarbonate, polyether copolymers, poly(propylene oxide)
3 (PPO), and polyurethanes can also serve as oligomeric scaffolds to fabricate high-
4 performance SAMs. Li et al. functionalized the end of tri-arms polycarbonate and
5 polyether copolymers with UPy to obtain SAMs[59]. They prepared tri-arms
6 copolymers and dimeric and tetrameric oligomers to regulate the adhesion strength.
7 They emphasized that the number of oligomer arms and the proportion of polycarbonate
8 significantly influenced the adhesive strength. The surface energy was negatively
9 correlated with the proportion of polycarbonate and the number of oligomer arms, while
10 the cohesive force positively correlated with these factors. Considering all aspects, the
11 tri-arms oligomer with a polycarbonate content of 44% (termed as 3UPy-CO₂-44%)
12 exhibited the optimal adhesive strength (with shear strengths reaching 7.5 MPa and 9.7
13 MPa on stainless steel and wood substrates, respectively). Diana et al. designed and
14 synthesized two kinds of tri-arms molecules with PPO (440 g/mol or 3000 g/mol)
15 (termed as M1 and M2) in the middle and UPy at the end (Fig. 4b); the mixture of them
16 with different ratios showed tailoring mechanical properties and afforded materials with
17 storage moduli of 37-609 MPa. The materials are suitable for reversible adhesives, for
18 their melt viscosities are 11 Pa·s at 140 °C[71]. Yuan et al. utilized UPy end-capped tri-
19 arms polyurethane (TPU) and conducted a comparative study with tri-arms
20 polyurethanes end-capped with fluoropyridine (FPy), chloropyridine (CPy), and
21 methylpyridine (MPy). They confirmed that UPy, characterized by its quadruple
22 hydrogen bonding capability, is the most suitable candidate for fabricating HMA, with
23 a shear strength of up to 6.8 MPa. Remarkably, even after undergoing five repetitions,
24 the shear strength was still maintained at 70%[72].



1
2 Figure 4. (a) Urea self-assembly diagram of ‘three assembly sites’ type SMAs, assembly and
3 decomposition diagram under light or heat response. (b) Chemical structures of two tri-arms
4 molecules modified by UPy with PPO (440 g/mol or 3000 g/mol) in the middle and UPy at the
5 end[71].
6

7 Introducing additional hydrogen bonds in UPy-decorated tri-arms oligomers
8 enhance SAMs’ performance. Chen et al. designed and synthesized a series of UPy-
9 decorated tri-arms polyether oligomers for this purpose[60]. As an improvement, they
10 incorporated varying quantities of ureas in the polyether segments. These ureas and
11 terminal UPy units formed a hierarchical hydrogen-bonded assembly system, imparting
12 high stiffness to the elastomer due to the abundance of hydrogen bonds. This elastomer
13 exhibited a significantly higher Young’s modulus (148.8 MPa) than other
14 supramolecular polymers and fracture energy comparable to alloys (187 kJ/m²). The
15 multitude of reversible hydrogen bonds endows this elastomer with adhesive
16 capabilities suitable for diverse substrates, offering exceptionally high strength,
17 excellent reusability, and remarkable environmental adaptability. As a HMA for
18 bonding metal sheets, the lap shear strength of the elastomer reached 20.7 MPa (Table
19 4).

20 Table 4. Overview of the performance and applications of ‘three assembly sites’ type SAMs.
21 Experiments were performed using various test layouts and substrates.

Name	Applications	Method	Substrate	Strength	Ref.
(UPyU) ₃ TMP	Photo-responsive polymer glass	Lap joints	Glass	1.2 MPa	[68]
Tri-HT	Electrically conductive ionic liquid adhesive	Lap joints	Ceramics	12.2 MPa	[69]
(UP) ₃ T	Self-healing elastomer	AFM	N/A	4.6 nN	[70]
DOSS	Self-healing oleophobic coating	Lap joints	Glass	>30 MPa	[27]
3UPy-CO ₂ -	Light and heat-responsive	Lap joints	Wood	9.7 MPa	[59]

44%	adhesive					
M1/M2	Reversible supramolecular glass	Lap joints	Stainless steel	5 MPa	[71]	
TPU	HMA	Lap joints	Stainless steel	6.8 MPa	[72]	
TP3	HMA	Lap joints	Iron	20.7 MPa	[60]	

(UPyU)₃TMP: UPy functionalized 1,1,1-tris (hydroxymethyl) propane; Tri-HT: IL in urea-decorated tri-arms molecules; (UP)₃T: UPy terminated tri-arms PDMS; TP3: UPy-decorated tri-arms polyether oligomers, 3 refers to the different numbers of D400 on each of the arms.

2.2.2 Multi-assembly sites

Multi-assembly sites SAMs often require the incorporation of urea-derived onto polymers, employing four modification strategies: 1. attaching urea-derived to polymer side-chains, 2. introducing urea into the polymer backbone, 3. decorating urea group onto nanoparticles, 4. introducing urea into the chemical cross-linked network polymers. While these four methods differ significantly in the synthetic approach, they share the same underlying principle for enhancing the properties of SAMs. Four methods aim to provide abundant dynamic cross-linking points through numerous hydrogen bonds, thereby improving the performance of AMs.

Urea decorated on the side-chain

Compared to incorporating urea groups into the polymer backbone, modifying urea to polymer side-chain is more prevalent in academic research. To provide a more straightforward description of these side-chain urea-decorated SAMs, we have categorized them in the order of urea introduction methods, strategies for enhancing SAMs' performance, and approaches for introducing functional groups into SAMs.

1) Introduction of urea

Copolymerization of urea modified acrylate or methacrylate

Better than the UPy decorated oligomers, the exploration of polymer side-chain-branched UPy, which facilitates multiple hydrogen bonding self-assembly, has witnessed substantial advancement since its initial report by Meijer in 1997[29]. Among these developments, the copolymerization of acrylate or methacrylate functionalized UPy stands out, particularly in SAMs. As early as 2003, researchers introduced UPy into polymers to create supramolecular PSAs. Koji et al. copolymerized methacrylate-functionalized UPy with BA, resulting in a thermos-responsive supramolecular

1 polymer[73]. They demonstrated its potential as PSAs and emphasized that the content
2 of UPy in the polymer significantly influences the adhesive's properties (with
3 polyethylene terephthalate (PET) as the membrane and glass as the substrate, the 90-
4 degree peel strength was 1.0, 2.0, and 3.0 J/m² for UPy contents of 0%, 2.5%, and 3.3%,
5 respectively). Faghihnejad et al. synthesized adhesive supramolecular polymers by
6 copolymerizing BA and UPy derivatives; acrylic acid esters base UPy derivatives were
7 used, wherein the connecting chains for UPy were modified to hexyl groups[24]. These
8 modifications increased chain flexibility, facilitating UPy moieties' assembly.
9 Employing a surface forces apparatus, they conducted a more comprehensive analysis
10 of the SAs' surface properties and adhesion mechanism. They highlighted the robust
11 intermolecular interactions of UPy, leading to a significant enhancement in the surface
12 energy of dry, smooth PBA, elevating it from 31-34 mJ/m² to 45-56 mJ/m². Furthermore,
13 the adhesion strength of butyl acrylate and UPy-acrylate copolymer (PBA-UPyA) was
14 influenced not only by the UPy content but also by factors such as contact time,
15 temperature, and humidity levels. Remarkably, the adhesion strength of PBA-UPyA
16 exhibited a recovery of 40%, 81%, and 100% within 10 seconds, 3 hours, and 50 hours,
17 respectively. Except for UPy, copolymers composed of PBA and other tetrahydroxyurea
18 derivatives can also exhibit significant cohesive strength. Zhang et al. introduced
19 ureido-cytosine (UCy) into PBA polymers to create PBA-UCy with quantitatively
20 controlled UCy content. Systematic studies demonstrated that introducing quadruple
21 hydrogen bonding can significantly enhance material cohesion and thermal stability,
22 making it more suitable for use as adhesives and thermoplastic elastomers[74].

23 Beyond BA, other monomers can be copolymerized with UPy monomers to
24 synthesize SAMs. Heinzmann et al. achieved the preparation of reversible SAMs by
25 copolymerizing either butyl methacrylate (BMA) or hexyl methacrylate with UPy-
26 functionalized hydroxyethyl methacrylate (HEMA) through hexamethylene
27 diisocyanate (HDI) linkage[75]. They emphasized that the supramolecular cross-
28 linking resulting from UPy dimeric assembly significantly enhanced the adhesive
29 strength of the rubbery state of the adhesive. In contrast to homopolymers lacking

1 dynamic cross-linking, which rapidly deteriorate above their glass transition
2 temperature (T_g), UPy-cross-linked poly-alkyl-methacrylates exhibited sustained
3 adhesion strength over a wide temperature range. Moreover, benefiting from the
4 temperature-responsive quadruple hydrogen bonding of UPy, the resultant SAs
5 demonstrated temperature and UV-triggered debonding. Addressing the challenge of
6 incorporating UPy monomers, which are typically solids, into efficient
7 copolymerization with other monomers, Heinzmann introduced a solution by linking
8 methyl methacrylate and UPy with amine-terminated oligo(propylene glycol) (OPG),
9 yielding liquid UPy-modified methyl methacrylate monomers. These liquid monomers
10 were subsequently copolymerized with benzyl methacrylate (BnMA), BMA, hexyl
11 methacrylate, and HEMA in bulk, developing photo-thermally responsive SAMs[76].
12 Mechanical and bonding tests demonstrated that an increased UPy content significantly
13 elevated the system's mechanical performance. Additionally, adhesive experiments
14 indicated that when the UPy content reached 5 mol%, the system displayed complete
15 reversibility under heating or UV light exposure.

16 *Ring-opening polymerization of urea modified monomers*

17 Besides copolymerizing urea-functionalized acrylate, urea groups can be
18 introduced into polymer side-chains through other polymerization methods, such as
19 epoxy ring-opening or grafted onto natural macromolecules. Sun et al. achieved the
20 ring-opening polymerization of epoxy resin using amine-modified UPy and
21 polyethylene glycol (PEG)amine, resulting in a robust and reusable supramolecular
22 epoxy adhesive (SEA) with remarkable properties (Fig. 6b)[77]. The adhesives
23 exhibited an exceptionally high bonding strength of 10.2 MPa, retaining 80%
24 reusability after six cycles and demonstrating 5-minute rapid adhesion. Building upon
25 this work, Han et al. modified the adhesive by introducing UPy and enhancing chemical
26 cross-linking by incorporating hyperbranched epoxy resin (MHER), increasing
27 adhesive strength[65]. Their research demonstrated that with increasing content of
28 MHER, the tensile strength, fracture elongation, and toughness of hyperbranched epoxy
29 hot melt adhesive (HEA) thin films initially increased and then decreased. The optimal

1 performance was achieved at an MHER content of 8 wt%, resulting in a tensile strength
2 of 10.7 MPa. Polyamide, polyurethane, and other polymers containing numerous amide
3 groups can be used as adhesives. Introducing urea into polyamides for strong hydrogen
4 bonding assembly, instead of conventional chemical cross-linking, can lead to
5 developing SAMs (Fig. 6a). Tan et al. devised a strategy by incorporating UPy and
6 carboxyl groups into polyurethane, resulting in an elastomeric adhesive with
7 hierarchical dynamic hydrogen bonding. This adhesive exhibits toughness, extensibility,
8 and repairability[61]. The rich hydrogen bonding increases adhesive strength without
9 additional curing or heating steps. These functional groups' presence enables bonding
10 with various materials, including glass, wood, steel, and polymer substrates, making
11 this material a potential candidate for surface adhesive applications. Eisenreich et al.
12 utilized a small quantity of azobenzene-modified UPy (Azo-UPy) molecules grafted
13 onto the side-chains of flexible polysiloxanes. Intramolecular hydrogen bonding within
14 the UPy molecules was converted through photo-induced conformational changes in
15 the azobenzene, enabling the fabrication of light-controllable liquid-to-solid transition
16 elastomers. Upon exposure to 365 nm UV light, the adhesive achieved an adhesive
17 strength of approximately 0.1 MPa, representing a fivefold increase compared to the
18 0.02 MPa observed under dark conditions[78].

19 *Urea-modified natural macromolecules*

20 For natural macromolecules, polymer modification is more effective for grafting
21 urea on polymer. Nishiguchi et al. grafted UPy onto porcine tendon collagen (TG)
22 molecules to create an injectable thermo-sensitive tissue adhesive[79]. In their research,
23 a tissue adhesive was obtained with a debonding temperature slightly above body
24 temperature by adjusting the grafting concentration of UPy and the length of the
25 molecular chain connecting UPy to TG. This adhesive could debond at 40 °C and adhere
26 at 37 °C. Furthermore, this tissue adhesive exhibited excellent biocompatibility and
27 remained stable under physiological conditions for extended periods. It also effectively
28 prevented postoperative adhesions between rats' cecum and abdominal wall. They
29 proceeded to prepare tissue-adhesive decellularized extracellular matrix (dECM)-based
30 biological patches by further mixing the SAs UPy functionalized TG (TGUPy) with

1 urinary bladder matrix (UBM) powder in dimethyl sulfoxide (DMSO)[80]. These
 2 patches demonstrated exceptional mechanical properties similar to the SAs and
 3 exhibited the degradability of the biomaterial. Zhao et al. prepared dual physically
 4 cross-linked hydrogel adhesives by complexing UPy-grafted gelatin (GTU) and
 5 dopamine-grafted polyethylene glycol (PEGSD)[26]. These hydrogel adhesives
 6 exhibited excellent self-healing, shape-adaptive, injectable, and near-infrared (NIR) or
 7 pH-responsive properties. When the ratio of PEGSD to GTU was 2:5, the material
 8 exhibited a maximum adhesive strength of 5.20 kPa on porcine skin (Table 5), and NIR
 9 irradiation or acidic solution assistance facilitated easy removal of the adhesive from
 10 the substrate.

11 Table 5. Overview of the performance and applications of ‘multi assembly sites/ introduction of
 12 urea’ type SAMs. Experiments were performed using various test layouts and substrates.

Name	Applications	Method	Substrate	Strength	Ref.
PBA-UPyMA	Heat sensitive adhesive, PSA	Peel test	Glass	3 J·m ⁻²	[73]
PBA-UPyA	Self-healing adhesive	Tensile testing	N/A	11 MPa	[24]
PBA-UCy	Thermoplastic elastomer adhesive	N/A	N/A	N/A	[74]
UPy-HDI-HEMA	Photothermal response adhesive	Lap joints	Stainless steel	4.1 MPa	[75]
UPy-OPG-MAA	Photothermal response adhesive	Lap joints	Glass	2.86 MPa	[76]
SEA	HMA	Lap joints	Stainless steel	10.2 MPa	[77]
HEA	HMA	Lap joints	Stainless steel	10.7 MPa	[65]
UPy-CPU	Self-healing elastomer adhesive	Lap joints	Wood	1 MPa	[61]
Azo-UPy-PDMS	Photo-responsive adhesive	Lap joints	Glass	0.1 MPa	[78]
TGUPy	Tissue adhesive	Tensile testing	Tissue	4-5 kPa	[79]
UBM-TGUPy	Tissue adhesive	Tensile testing	Tissue	6 MPa	[80]
PEGSD/GTU hydrogel	Removable wound dressings	Lap joints	Tissue	5.20 kPa	[26]

13 PBA-UPyMA: copolymer of butyl acrylate and Upy-methacrylate; UPy-HDI-HEMA: UPy-
 14 functionalized HEMA through HDI linkage; UPy-OPG-MAA: UPy modified methacrylamide
 15 through OPG linker; UPy-CPU: UPy modified carboxylated polyurethane; Azo-UPy-PDMS: Azo-
 16 UPy functionalized PDMS; UBM-TGUPy: mixture of UBM and TGUPy.

17

18 2) Strategies for enhancing SAMs’ performance

19 *Increase polarity and cross-linking density*

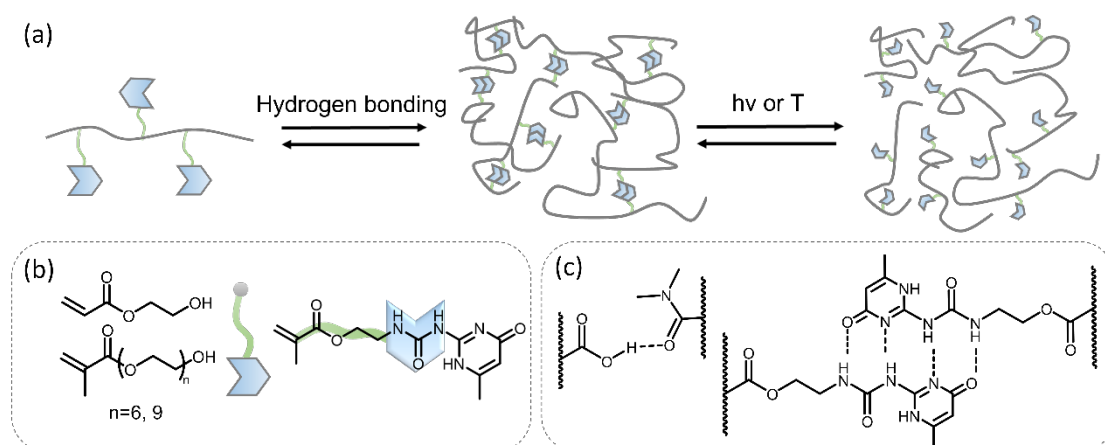
20 Enhancing polymer polarity and increasing chemical cross-linking are effective
 21 strategies for improving the performance of SAMs. Zhu et al. concurrently

1 implemented these two enhancement strategies in their SAs, resulting in a remarkable
2 adhesive with self-healing capability[81]. Through the introduction of UPy units linked
3 with poly(ethylene glycol) methacrylate (PEGMA) of varying molecular weights, they
4 synthesized PEGMA-UPy monomers, which were subsequently copolymerized with
5 PEGMA and *N, N'*-Methylenebis(acrylamide) (MbiA) to obtain a polymer with both
6 adhesive and self-healing properties (Fig. 5b). Their findings revealed that longer PEG
7 side-chains increased molecular polarity and surface energy (from 38 to 81 mJ/m²) yet
8 led to relatively lower cohesive forces, resulting in a reduction in adhesive performance
9 (at room temperature, peel strength decreased from 355 kN/m² to 63 kN/m² upon 180°
10 peeling). In addition to serving as a conventional SAs, Using the UPy reduction by
11 lithium, wang et al. have further developed PEGMA and PEGMA-UPy copolymer
12 adhesives (LiPEO-UPy) for use as a high-rate, high-capacity lithium metal anode
13 protective layer in lithium-ion batteries[63]. Within the protective layer, the UPy
14 hydrogen bonds provide robust cohesion through assembly and react in situ with the
15 lithium anode to form extra adhesive forces, significantly enhancing stability.
16 Ultimately, the electrode protective layer they obtained demonstrates excellent self-
17 stability and strong adhesion.

18 *Synergistic enhancement of multiple weak bonds*

19 Multiple weak bond synergistic effects represent a practical approach for
20 enhancing the mechanical properties of SAMs. Jiang et al. have fabricated a dual-layer
21 hydrogel adhesive, where the base layer's high strength is derived from a dual hydrogen
22 bond cooperative network composed of weak hydrogen bonds between *N, N*-dimethyl
23 acrylamide (DMAA), and acrylic acid (AAc) units, as well as multiple solid hydrogen
24 bonds between UPy units (Fig. 5c)[82]. The orchestrated hydrogen bond network
25 contributes to energy dissipation, resulting in excellent toughness exhibited by the gel.
26 Tensile fracture results indicate that the gel can maintain a fracture elongation of 840%
27 even when cut to one-third of its original size. Additionally, this gel material
28 demonstrates exceptional adhesion, securely binding to various solid surfaces (such as
29 glass, Al₂O₃ ceramics, and stainless steel), and tissues like pig skin and pig kidney,

1 showing promising potential for biomedical applications. Besides the synergistic dual
 2 hydrogen bond network, orthogonal hydrogen bonding coupled with metal coordination
 3 can also bestow AMs with multi-stimuli responsive properties. Han et al. introduced
 4 tridentate pyridine groups (TPy) and UPy into PMMA via free radical polymerization,
 5 achieving tunable interfacial adhesion through orthogonal supramolecular forces
 6 involving TPy coordination with Zn^{2+} and hydrogen bonding between UPy[83]. They
 7 introduced competitive small molecules (cyclen and excess UPy monomers) into the
 8 copolymer to disrupt TPy coordination within the polymer and UPy dimers to achieve
 9 multi-stimuli responsiveness. The interface adhesion was further modulated by
 10 adjusting the ratio of TPy and UPy units within the polymer.



11
 12 Figure 5. (a) The self-assembly diagram of ‘urea decorated on the side-chain’ type SMAs, assembly
 13 and decomposition diagram under light or heat response. (b) The structural formulas of the UPy-
 14 functionalized monomer and PEGMA with different molecular weights[81]. (c) Two kinds of
 15 hydrogen bonds in the double network[82].

16

17 *Multi-network interpenetrating adjustment*

18 Interpenetrating networks can be used to enhance the performance of adhesive
 19 polymer materials. Dominik Konkolewicz’s group introduced a dynamic covalent bond
 20 network based on reversible Diels-Alder (re-DA) covalent bonds into the framework of
 21 a network formed by UPy quadruple hydrogen bonds, thereby enhancing the toughness
 22 of adhesive polymer materials[38]. Their studies underscored the role of the dynamic
 23 covalent bond network in improving material toughness. Additionally, they investigated
 24 the influence of weak hydrogen bond quantity on the overall material performance by
 25 comparing poly(ethyl acrylate) (PEA) and poly(2-hydroxyethyl acrylate) (PHEA) as

1 the base polymer. The results demonstrated that, under similar UPy substitution degrees,
 2 the toughness, fracture energy, and self-healing capacity of the PHEA-based material
 3 were inferior to those of PEA. This observation suggests that the effects derived from
 4 the quality of hydrogen bonds far surpass those derived from quantity. They also
 5 assessed the impact on the thermomechanical properties of the material through
 6 systematic comparisons of network types, chain lengths, dynamic bond compositions,
 7 crosslink densities, and crosslink distributions[84]. They highlighted the significant
 8 role of polymer network architecture in material performance for interpenetrating
 9 network materials. The coordinated and complementary interaction between hydrogen
 10 bonds and thiol-maleimide bonds increased the material's adhesive capabilities, and the
 11 material exhibited adhesive stress of up to 9 MPa on aluminum (Table 6.).

12 Table 6. Overview of the performance and applications of 'multi assembly sites/ strategies for
 13 enhancing SAMs' performance' type SAMs. Experiments were performed using various test layouts
 14 and substrates.

Name	Applications	Method	Substrate	Strength	Ref.
P(PEG-UPy)	Self-healing adhesive	Peel test	Stainless steel	335 kPa	[81]
LiPEO-UPy	High capacity lithium metal anode protective film	N/A	N/A	N/A	[63]
DN hydrogel	Tissue hydrogel adhesives	Peel test	Stainless steel	1290 Pa	[82]
P(TPY-UPy)	Multi-stimulus response adhesive	N/A	N/A	N/A	[83]
PEA, PHEA	Self-healing elastomer	N/A	N/A	N/A	[38]
UPy IPN	Heat response adhesive	Lap joints	Aluminum	9 MPa	[84]

15 P(PEG-UPy): copolymer of PEGMA and UPy-methacrylate; DN hydrogel: double network
 16 hydrogel; P(TPY-UPy): copolymer of terpyridine-acrylate and UPy- methacrylate; UPy IPN:
 17 interpenetrating network contains UPy.

19 3) Introducing designed functions into SAM

20 *Introducing functional networks into the system*

21 The resulting material will exhibit corresponding functionalities if the second
 22 interpenetrating network possesses distinct properties. Chen et al. introduced a
 23 poly(pyrrole) secondary network into a UPy-modified PEGMA network, yielding an
 24 elastomer with rapid self-healing capabilities and inherent adhesiveness, further utilized
 25 in sensor applications for its conductivity[85]. The self-complementary quadruple
 26 hydrogen bonds between UPy units were utilized as cross-linking points for forming a
 27 flexible elastomeric matrix, and the bond's reversibility imparted rapid self-healing

1 properties to the composite material. Additionally, dynamic hydrogen bonding
2 facilitated exceptional and repeatable adhesion to various substrates, including glass.
3 Apart from enhancing mechanical strength, the poly(pyrrole) network also provided
4 electronic conductivity. The coexistence of these two networks endowed the material
5 with remarkable strain propagation capabilities. The introduction of metal ions can also
6 yield adhesive conductive materials in the UPy-modified PEGMA network; Chen et al.
7 incorporated lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) into a network
8 composed of PEG-UPy and polyethylene glycol diacrylate (PEGDA), resulting in a
9 polymer gel electrolyte with excellent mechanical strength, high conductivity,
10 outstanding self-healing capability, and this electrolyte exhibits exceptional lithium
11 metal adhesive ability (Fig. 6c)[86].

12 *Copolymerizing functionalized monomer in the system*

13 Besides introducing a functional network, incorporating functional monomers into
14 urea-modified polymers can yield self-healing and tailored functionalities SAMs.
15 Dopamine, a crucial catechol donor, is commonly employed to prepare underwater
16 adhesives; Balkenende et al. copolymerized dopamine and UPy into amphiphilic
17 copolymers, creating adhesive patches with a wet tissue bonding strength of 122 kPa
18 by adjusting the proportions of dopamine, UPy, hydrophilic, and hydrophobic
19 monomers (Table 7)[64]. UPy contributed to high-strength cohesion through self-
20 assembly cross-linking, while the catechol structure facilitated mussel-like tissue
21 adhesion. Effective phase separation between hydrophilic (UPy/alkane) and
22 hydrophilic dopamine methacrylamide (DMA)/ oligoethylene glycol (OEG) phases
23 allowed the material to exhibit strong adhesion on high-humidity tissue surfaces.
24 Phosphorus-containing compounds often possess excellent flame-retardant properties;
25 Yu et al. prepared a reversible flame-retardant adhesive by copolymerizing acrylate
26 phosphoric ester monomers with acrylate UPy monomers and BA/MA monomers[66].
27 The UPy-modified flame-retardant adhesive copolymer exhibited a 40% increase in
28 peel strength and a 200% increase in shear strength compared to the unmodified
29 copolymer, and it was suitable for various substrates. Furthermore, flame-retardancy

1 tests indicated that incorporating phosphoric esters led to a 14.6 to 22.4–22.7% increase
 2 in Limiting Oxygen Indices (LOIs) for PET films coated with a thin layer of flame-
 3 resistant adhesives. Incorporating functional groups with aggregation-induced emission
 4 (AIE) properties into UPy-modified polymers can imbue AMs with AIE characteristics.
 5 Zhang et al. introduced poly benzoxazole-based chromophores (PBHZ, traditional AIE
 6 monomer) into UPy-cross-linked polymers through methyl methacrylate free-radical
 7 polymerization, resulting in multi-color fluorescent supramolecular adhesive gels
 8 (MSAG)[87]. Thanks to the aggregation-induced restricted emission (AIRE) effect,
 9 they tuned the fluorescence colors from blue to bright green by adjusting the
 10 concentration of PBHZ groups within the polymer. Simultaneously, the self-healing and
 11 adhesive properties afforded by UPy assembly allowed for the assembly of different gel
 12 blocks, yielding gel blocks with diverse information patterns suitable for encrypted
 13 materials, including information codes, biomimetics, and data patterns. Incorporating
 14 acid-responsive rhodamine derivative, UV-responsive spirobenzopyran derivative, and
 15 Fe³⁺-responsive rhodamine derivative into the UPy modified polymethyl methacrylate
 16 (PMMA)-supramolecular adhesive gel imparts vinegar vapor responsiveness, UV
 17 responsiveness, and Fe³⁺ responsiveness to the gel, respectively. Zhang et al. used these
 18 three types of gels to process three fragments of a quick response (QR) code and used
 19 gel adhesion to bond the fragments into a complete QR code, achieving triple
 20 information encryption[88].

21 Table 7. Overview of the performance and applications of ‘multi assembly sites/ introducing
 22 designed functions into SAMs’ type SAMs. Experiments were performed using various test layouts
 23 and substrates.

Name	Applications	Method	Substrate	Strength	Ref.
PPy/PEG-UPy	Conductive adhesives	Lap joints	Stainless steel	53 kPa	[85]
P(PEG-UPy) and PEGDA	Self-healing adhesive gel electrolyte	N/A	N/A	N/A	[86]
DUOE	Wet tissue adhesive	Lap joints	Tissue	122 kPa	[64]
UFR-PAcr-1	Flame retardant adhesive	Lap joints	PET	1.09 MPa	[66]
PPBHZ- <i>r</i> -PMMA- <i>r</i> -PUPy	Responsive fluorescent gels	N/A	N/A	N/A	[67]
Gel QR code	Information encryption	N/A	N/A	N/A	[88]

24 PPy/PEG-UPy: composite of polypyrrole and P(PEG-UPy); DUOE: copolymer of DMA, UPy-
 25 methacrylate, OEG, and 2-ethylhexyl methacrylate; UFR-PAcr-1: copolymer of UPy-methacrylate,
 26 diethyl(acryloyloxymethyl)phosphonate, 2-ethylhexyl acrylate, BA, methyl acrylate, and AAc;

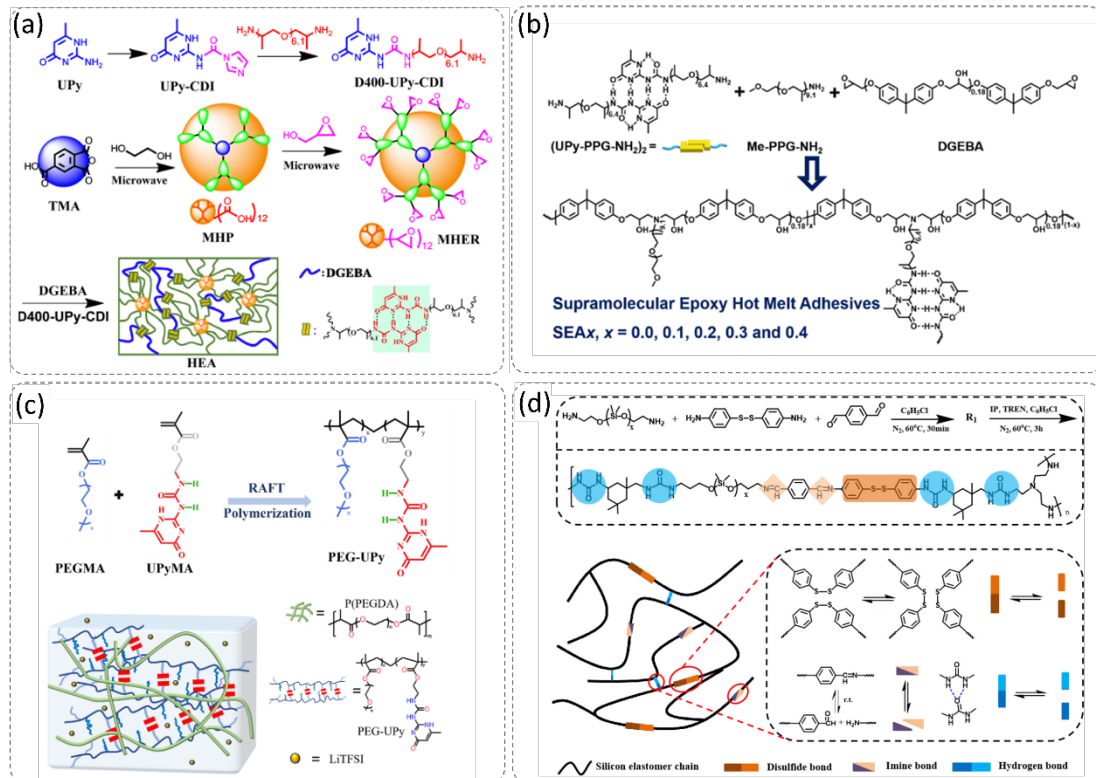
1 PPBHZ-r-PMMA-r-PUPy: copolymer of PBHZ, methyl methacrylate, and Upy-methacrylate; Gel
2 QR code: assembly of three color “turn-on” supramolecular polymer gels.

4 *Urea decorated in the backbone*

5 Compared to branched polymers, linear polymers with the same molecular weight
6 typically exhibit higher crystallinity, greater packing density, increased strength, and
7 higher melting points. Besides side-chain modifications in polymers, Urea groups can
8 also be incorporated into the polymer backbone. This backbone modification can
9 maintain polymer regularity, provide strong hydrogen bonding cross-linking sites, and
10 retain polymer packing density (Fig 8a).

11 Many researchers frequently modify the siloxane backbone with urea groups due
12 to its outstanding stability, flexibility, and biocompatibility, resulting in the preparation
13 of high-performance SAMs. Yan et al. prepared urea-spaced HDI-PDMS by reacting
14 amino-modified PDMS with HDI. HDI-PDMS can rapidly bond to glass, iron, PET,
15 and PTFE underwater due to chemical cross-linking and numerous hydrogen bonds.
16 The adhesive strength on PET reaches up to 2.8 MPa[89]. Lv et al. prepared tunable
17 materials by introducing aromatic thiol-urea and urea into PDMS. A systematic study
18 highlighted the synergistic effect between thiol-urea and urea in maintaining the
19 material’s mechanical and dynamic properties. When used as a recyclable glass
20 adhesive, the adhesive strength of the material reached 7.1 MPa[90]. The synergistic
21 interaction between dynamic covalent bonds and multiple hydrogen bonds can impart
22 materials with enhanced responsiveness to stimuli and more excellent self-healing
23 capabilities. Dai et al. utilized the synergistic multiple dynamic covalent bonds and
24 hydrogen bonds by introducing urea into PDMS, further incorporating dynamic imine
25 and disulfide bonds to create AMs with excellent tensile properties (368%), room
26 temperature (98.1% after 5 hours), and water environment (96.4% after 5 hours) self-
27 healing abilities. This adhesive material maintains good stability in various solvent
28 environments, with a glass adhesive strength of up to 300 kPa in ambient air, and
29 repeated experiments demonstrate its excellent cyclic stability (Fig. 6d)[91]. The
30 presence of aromatic carboxyl groups can significantly influence the adhesives. Xu et

1 al. prepared PSAs based on urea-spaced PDMS and polypropylene glycol (PPG)
 2 copolymers with varying carboxyl group contents. They observed that as the aromatic
 3 carboxyl groups increased, the 180° peel strength and shear strength increased by 180.0%
 4 and 46.2%, respectively[42]. Introducing quadruple hydrogen-bonding UPy into the
 5 backbone can provide stronger hydrogen bonds and modify the mechanical properties
 6 of PDMS. Guo et al. achieved a tensile strength of up to 7.28 MPa in their
 7 supramolecular siloxane elastomer (SPSO) by introducing both urea and UPy into the
 8 PDMS backbone, which induced phase separation and physical cross-linking through
 9 UPy quadruple hydrogen bonding interactions. Numerous hydrogen bonds in SPSO
 10 also resulted in a reversible adhesive strength of up to 4.8 MPa when applied to wood
 11 surfaces (Table 8)[39].

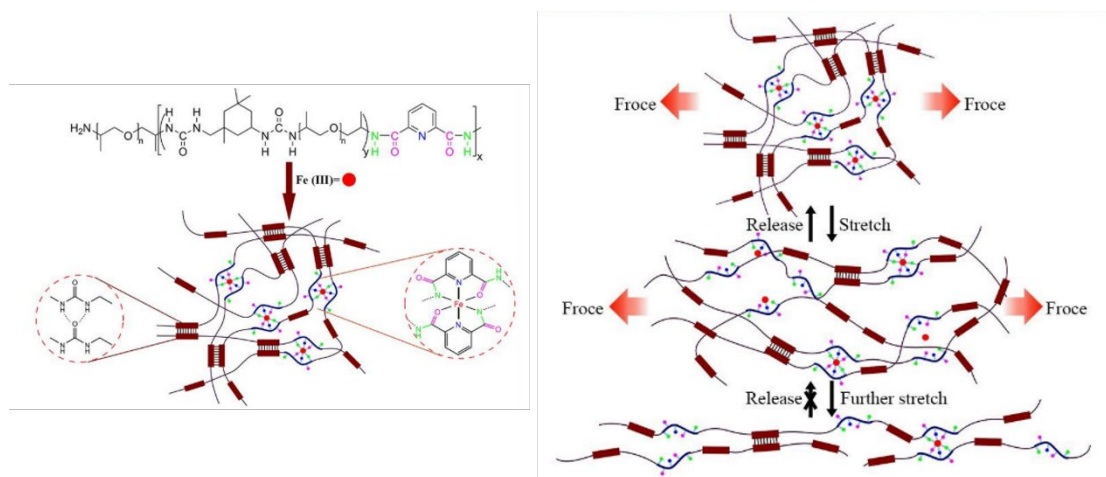


12
 13 Figure 6. (a) Preparation schemes of MHER, UPy modified polyether, and HEA[65]. (b) Chemical
 14 structure and synthesis of SEA[77]. (c) The synthesis process of PEG-UPy, and schematic diagram
 15 of gel electrolyte[86]. (d) Modified PDMS molecular chain structure, and force diagram of self-healing
 16 silicone rubber[91].

17

18 In addition to PDMS, many other polymers can be enhanced by introducing urea
 19 into the backbone to enhance mechanical strength and adhesive properties. He et al.

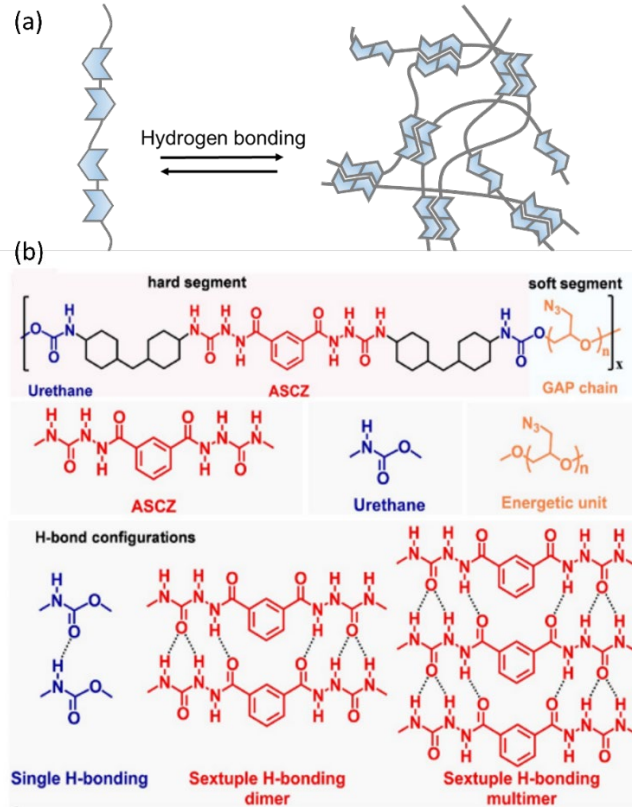
1 synthesized polyurea oligomers using Priamine 1074 and isophorone diisocyanate
 2 (IPDI) and controlled the mechanical properties, processability, and reusability of the
 3 adhesive by competing hydrogen bonding between urea groups through the
 4 incorporation of carvacrol oils. When the urea and carvacrol oils were in a 1:1 ratio, the
 5 PSAs achieved 1.2 MPa adhesive stress on a glass surface, which is six times that of
 6 commercial 3M double-sided tape. Their adhesive also possesses antibacterial
 7 properties due to the incorporation of carvacrol oils, exhibiting rapid contact killing
 8 (99.9% within 15 minutes) and long-term controlled release capabilities (up to 70
 9 days)[92]. IPDI and amine-terminated PPG were used by Zhang et al. to synthesize a
 10 urea-spaced linear polymer, followed by amide linkage of pyridine. They developed a
 11 dual dynamic network adhesive elastomer through metal-ligand interactions with iron
 12 ions and hydrogen bonding interactions of UPy (Fig. 7)[87]. Their material exhibited
 13 elongation up to 40 times without fracture, rapid self-healing capability with 80%
 14 recovery in 5 minutes at room temperature, and remarkable tear resistance, among other
 15 exceptional properties.



16
 17 Figure 7. The structure of the adhesive elastomer and the energy dissipation diagram during
 18 stretching[87].

19
 20 Urea-spaced polyurethane, where urea and urethane synergistically form multiple
 21 hydrogen bonds, can enhance elastomers' strength and adhesive properties. Li et al.
 22 prepared a water-soluble polyurethane (WPU-CHZ-NAGA) containing various forms

1 of hydrogen bonds by incorporating serial tri-urea units through carbonyldihydrazide
2 (CHZ) into polyurethane and introducing side-chain amide bonds using *N, N*-bis(2-
3 hydroxyethyl)-3-aminopropionylglycinamide (HO-NAGA-OH). This polyurethane,
4 owing to the distinct forms of hydrogen bonds, exhibits excellent adhesive capabilities
5 without heating or curing agents, achieving a reversible bonding strength of 1.5 MPa
6 on wood at room temperature[93]. Wei Jiang's group introduced acylthiourea (ASCZ)
7 groups into the polyurethane backbone to enhance the adhesive performance. Unlike
8 UPy, ASCZ tends to form larger hydrogen-bonded aggregates, and tensile strength and
9 toughness were enhanced for the dense hydrogen bonding interactions. However, the
10 closely packed hard segments reduce the dynamics of hydrogen bonds, limiting the self-
11 healing capability. Therefore, they adjusted the hydrogen bond density by introducing
12 an asymmetric structure to improve the self-healing performance (Fig. 8b). The
13 synthesized energetic polymer adhesive (EPA) exhibits outstanding comprehensive
14 performance, achieving reversible bonding strength of up to 3 MPa on steel
15 surfaces[94]. They further prepared a self-healing adhesive to achieve high dynamic
16 properties at room temperature by introducing asymmetric alicyclic structure and
17 multiple urea groups. This adhesive demonstrates excellent room-temperature self-
18 healing capability (no visible scratches after 72 hours of repair) while maintaining a
19 relatively high adhesive strength (adhesion strength on PMMA surface is 1.2 MPa)[62].



1
2 Figure 8. (a) The self-assembly diagram of ‘urea decorated in the backbone’ type SMAs. (b)
3 Schematic illustration showing the aggregation of hard segments of GAP series adhesives[94].
4

5 Table 8. Overview of the performance and applications of ‘multi assembly sites/ heteroatoms in the
6 backbone’ type SAMs. Experiments were performed using various test layouts and substrates.

Name	Applications	Method	Substrate	strength	Ref.
HDI-PDMS	Underwater adhesives	Tensile testing	PET	2.8 MPa	[89]
PDMS-PDITC-IPDI	Self-healing glass adhesive	Lap joints	Glass	7.1 MPa	[90]
PDMS-APD-TPA-IP	Elastomer adhesive	Lap joints	Glass	300 kPa	[91]
PDMS-PPG-MCAP	PSA	Lap joints	Stainless steel	87.2 kPa	[42]
SPSO	Elastomer adhesive	Lap joints	Mood	4.8 MPa	[39]
PU-C	Reusable antibacterial adhesive	Lap joints	Glass	1.2 MPa	[92]
DPPy-Fe	Self-healing elastomer adhesive	Lap joints	Aluminum	0.158 MPa	[87]
WPU-CHZ-NAGA	Self-healing fluorescent adhesive	Lap joints	Mood	1.5 MPa	[93]
GAP-HI-IPDH	Energetic polymer adhesive (EPA)	Lap joints	Stainless steel	3 MPa	[94]
GPU	Energetic polymer adhesive (EPA)	Lap joints	PMMA	1.2 MPa	[62]

7 PDMS-PDITC-IPDI: copolymer of PDMS, *p*-phenylene diisothiocyanate, and IPDI; PDMS-APD-
8 TPA-IP: copolymer of di-amine-PDMS, 4,4'-diamino diphenyl disulfide ether, 1,4-phthalaldehyde,
9 and isophorone diisocyanate; PDMS-PPG-MCAP: copolymer of PDMS, 4-methacrylamidophthalic
10 acid, and PPG; PU-C: polyurea-carvacrol; DPPy-Fe: polyamide-urea elastomer with FeCl₃; GAP-
11 HI-IPDH: copolymer of glycidyl azide, 4,4'-methylenebis (cyclohexyl isocyanate), IPDI, and

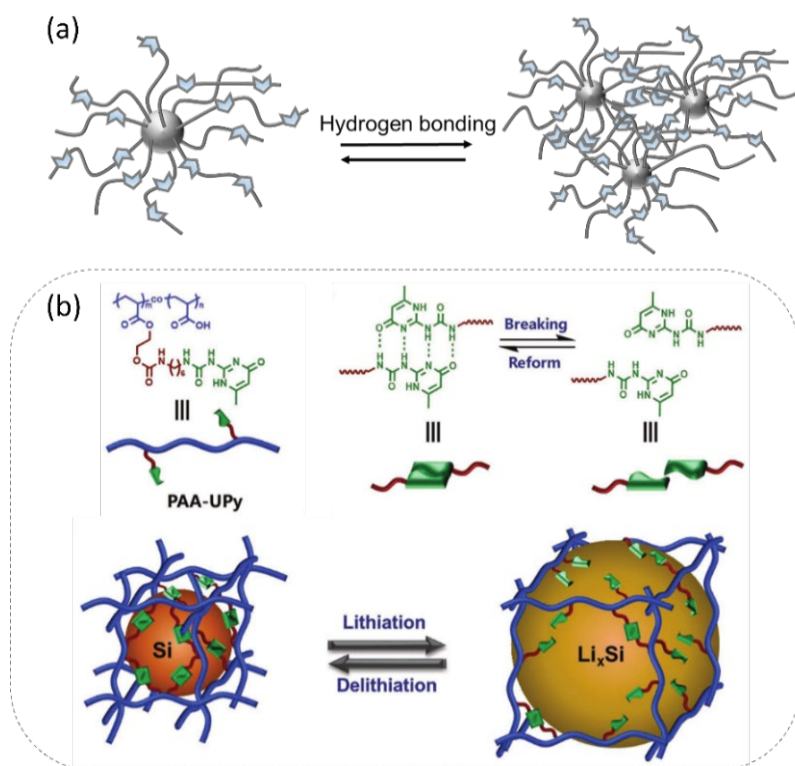
1 isophthalic dihydrazide; GPU: glycidyl azide polymer-based polyurethane.

3 ***Urea decorated on nano-particles***

4 Modifying nano-particles with urea is a strategic approach to overcome some
5 disadvantages associated with nano-particles. It can enhance their stability,
6 biocompatibility, and controlled release capabilities, making them more suitable for
7 various medical and materials science applications. Due to a substantial number of
8 hydrogen bonds in urea-derived derivatives, such modified nano-particles have found
9 application in the research of AMs.

10 Deng et al.'s work convincingly demonstrates stability enhancement through urea
11 modification. In their study, a SAMs UPy modified polyacrylic acid (PAA-UPy)
12 copolymer was employed to encapsulate silicon nano-particles. When used as
13 electrodes, these encapsulated nano-particles exhibited remarkable stability (Fig. 9b),
14 maintaining a high capacity of $2638 \text{ mAh}\cdot\text{g}^{-1}$ even after 110 cycles. As an adhesive
15 agent, the 180° peel strength is 12 N on the surface of the electrode[95]. Wang et al.'s
16 study demonstrates the application of urea-modified nano-particles as SAMs in drug
17 delivery. In-situ prepared a copolymer of poly(*N*-isopropylacrylamide) (PNIPAM) and
18 UPy on oxidized graphene nano-sheets, where UPy provided strong cohesion and
19 adhesion capabilities, while PNIPAM conferred thermal responsiveness to the nano-
20 particles. The SAMs exhibited a shear strength of 2.5 kPa on pigskin, and the stimuli-
21 responsive release of doxorubicin hydrochloride exhibited potent cytotoxicity against
22 tumor cells[96]. Yao's work demonstrates that UPy-modified polyethyleneimine (UPy-
23 PEI) can self-assemble into nanostructures in aqueous solutions and be used as SAMs
24 with sustained antibacterial capabilities. These SAMs exhibit muscular bonding
25 strength (35 kPa on mouse skin), are exudate-sensitive, and can continuously release
26 antimicrobial particles[97]. Their further research indicates that UPy-PEI can co-
27 assemble with oxidized graphene to prepare conductive tape (UPy-PEI-GO). This tape
28 exhibits an adhesion strength of up to 700 kPa on copper surfaces, three times that of
29 3M double-sided tape. Simultaneously, this tape can also be utilized as an on-skin
30 sensor, precisely monitoring various physical and physiological conditions at different

1 body parts[98]. Fu et al.'s work elucidates the application of urea-modified carbon
 2 nanotubes (urea-g-MWCNTs) in conjunction with polyurethane composite materials as
 3 self-healing sealants for electronic devices. In their research, the urea-g-MWCNTs
 4 serve as physical cross-linking points, enhancing the composite material's mechanical
 5 strength and self-healing properties. Additionally, the photothermal effect of MWCNTs
 6 imparts photo-induced healing capability to the material. As an adhesive, the shear
 7 strength remains high at 1.01 MPa (on a glass surface) even after soaking in water for
 8 6 hours (Table 9)[99]. Zhang et al. prepared coatings with strong fouling resistance and
 9 strong adhesion to various substrates by grafting perfluoroalkanes, PEG, and urea onto
 10 siloxane. The coating exhibited muscular adhesion strength (3-15 MPa) on various
 11 substrates, including glass, ceramics, steel, Ti, and epoxy resin[100].



12
 13 Figure 9. (a) The self-assembly diagram of 'urea decorated on nano-particles' type SMAs. (b)
 14 Chemical structure of PAA-UPy supramolecular polymer and schematic illustration of the charge-
 15 discharge process of silicon anodes using PAA-UPy polymer as binder[95].

16
 17 Table 9. Overview of the performance and applications of 'multi assembly sites/ on nano-particles'
 18 type SAMs. Experiments were performed using various test layouts and substrates.

Name	Applications	Method	Substrate	strength	Ref.
PAA-UPy	Self-healing adhesives	Peel test	Stainless steel	12N	[95]

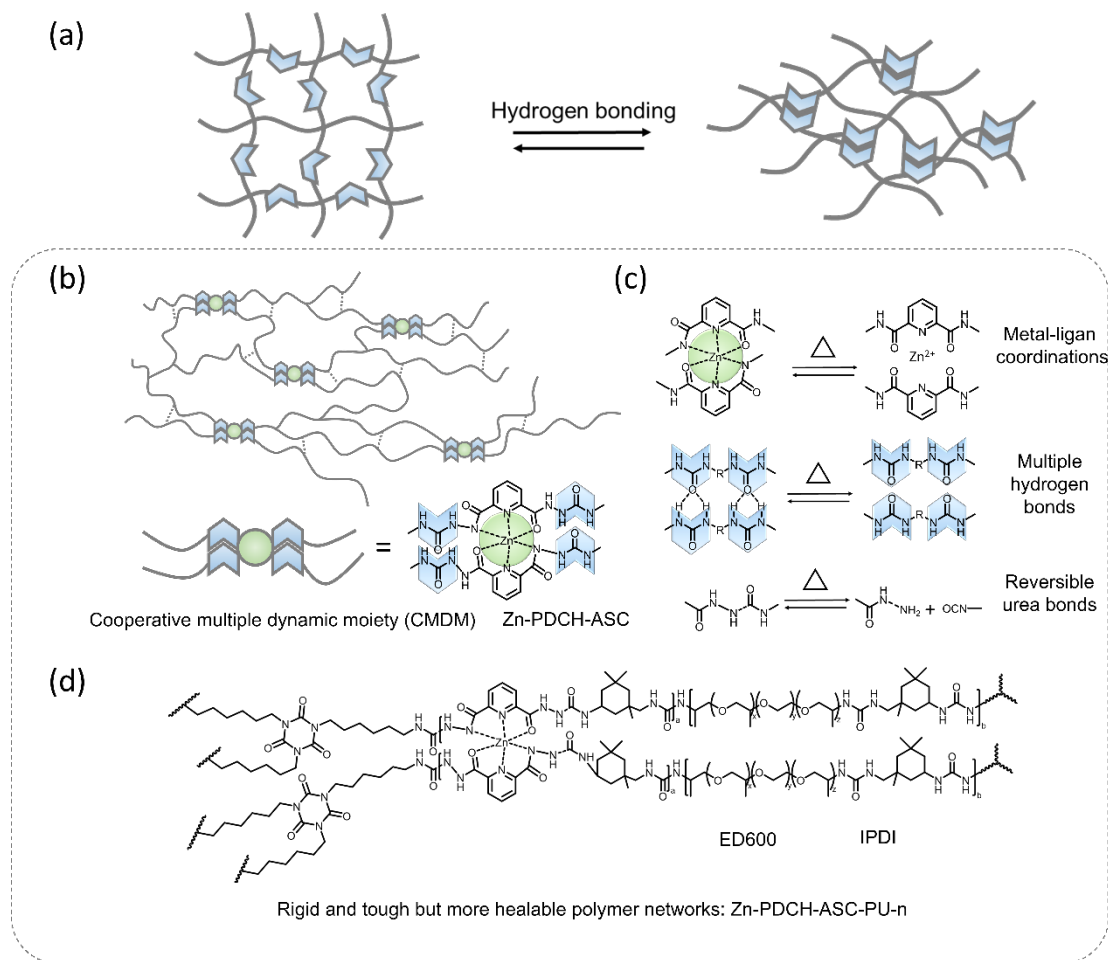
GO-HSH	Heat- and Ph-responsive bio-adhesives for drug delivery	Lap joints	Porcine skin	2.5 kPa	[96]
UPy-PEI	Antibacterial adhesive	Lap joints	Mouse skin	35kPa	[97]
UPy-PEI-GO	Skin sensor tape	Lap joints	Aluminum	816kPa	[98]
U-MWC-PUS	Self-healing sealant for electronic devices	Lap joints	Glass	1.01MPa	[99]
STPU-N ₅₀	Anti-protein and bacterial contamination coatings	Tensile testing	Glass	14.40MPa	[100]

1 GO-HSH: graphene oxide hybrid supramolecular hydrogels; U-MWC-PUS: complex of urea-g-
2 MWCNTs and poly(urethane-sulfide); STPU-N₅₀: bis-silane-terminated polyurea with the weight
3 ratios of methyltriethoxysilane (MTES) and phenyltriethoxysilane (PTS) is 50%.

4

5 ***Urea decorated on three-dimensional network polymers***

6 Three-dimensional network polymers typically exhibit strong mechanical
7 properties, but high cross-linking density often prevents reprocessing, while low cross-
8 linking density results in poor mechanical performance. The introduction of non-
9 covalent bonds in three-dimensional network polymers is an effective improvement
10 strategy. Xia et al. achieved a polymer with both efficient self-healing capabilities and
11 excellent mechanical properties by introducing urea hydrogen bonding and metal
12 coordination interactions in a copolymer of PPG and PEG. They pointed out that the
13 introduction of coordinating metals not only supplied the cross-linking points but also
14 catalyzed the dynamic exchange of urea bonds (Fig. 10), resulting in an increase in the
15 healing efficiency from 48% to 90%. Preliminary lap shear adhesion measurements
16 experiments showed that the adhesive, after cooling, exhibited a shear strength of 3.2
17 MPa on an aluminum substrate, and after 3 cycles, the adhesive strength did not show
18 a significant decrease[101].



1

2 Figure 10. (a) The self-assembly diagram of 'urea decorated on three-dimensional network polymers'
 3 type SMAs. (b) Schematic diagram of polymer containing urea group and metal coordination. (c)
 4 Metal-ligand coordination, multiple hydrogen bonds and reversible urea bonds in the cross-linked
 5 network. (d) Molecular structure of polymer containing urea group and metal coordination[101].
 6

6

7 **3. Conclusion and outlook**

8 This review selects some examples to summarize and demonstrate how urea and
 9 its derivatives function in the self-assembly of SAMs (such as adhesives, adhesive
 10 coatings, self-adhesive sensors, etc.) through hydrogen bonding. In this review, we
 11 categorize these materials into four major classes (one assembly site (section 2.1.1),
 12 two assembly sites (2.1.2), three assembly sites (2.2.1), and multi assembly sites (2.2.2))
 13 based on the form of urea derivative assembly (the number of assembly sites) and
 14 discuss their molecular design, structure, properties and applications accordingly,
 15 highlighting that urea components primarily enhance the adhesive properties by
 16 increasing the molecular weight of the assemblies, introducing additional cross-linking,

1 and providing hydrogen bonds at the adhesive interface. For multi-assembly-sites type,
2 we conducted a more detailed categorization-dividing them into side-chain type,
3 backbone type, nanoparticle type, and three-dimensional polymer type based on the
4 position of the urea groups.

5 Regardless of the specific classifications, the study of urea-based self-assembled
6 SAMs is not only about the internal structure and properties but also the
7 characterization of its adhesion properties. This requires the use of accurate
8 characterization methods. Employing universally applicable and diverse performance
9 characterization methods becomes paramount to advancing the understanding and
10 development of urea-based SAMs. A comprehensive, systematic, and diversified
11 assessment of bonding properties can facilitate a thorough comparison of adhesive
12 materials across various dimensions.

13 Beyond shear strength testing, essential evaluations encompass tensile strength,
14 peel strength, repeated-use assessments, and solvent resistance examinations. The
15 criteria for these diverse assessments should be meticulously selected in alignment with
16 the specific application requirements of adhesive materials, considering factors such as
17 curing methods, operational conditions, and environmental contexts. For example, in
18 the case of hot melt adhesives, a thorough consideration is warranted for the influence
19 of shear strength, reusability, solvent resistance, and temperature on bonding efficacy.
20 Conversely, in the case of light- and thermally-responsive adhesives, special attention
21 should be directed towards assessing the impact of temperature on shear strength and
22 peel strength under conditions of light or thermal exposure.

23 In addition to adhesion properties, majority of urea assembly based SAMs,
24 manifest notable advantages over conventional AMs, such as stimulus responsiveness,
25 self-healing, reversible adhesion, etc. However, we also need to acknowledge the
26 conspicuous limitations of these materials. These limitations encompass diminished
27 long-term adhesion performance, compromised resistance in adverse environmental
28 conditions, imprecise stimulus response, difficult synthetic processes, elevated
29 production costs, challenges pertaining to large-scale manufacturing, and the inherent

1 non-sustainability of their reactant.

2 The cooperative interaction between urea-based hydrogen bond networks and
3 dynamic covalent bond networks holds promise for improving urea-based AMs' poor
4 long-term adhesion performance. The efficient dynamics of urea-based hydrogen bonds
5 endow the materials with excellent self-healing properties, while the covalent bonds
6 ensure the stability of AMs during extended service. Protecting urea-based derivative
7 groups with hydrophobic, aromatic, and other groups enhances their resistance to harsh
8 environments. Introducing various stimulus-responsive functional groups will possibly
9 endow the urea-based AMs with multi-level and multi-stimulus precise-responsive SAs.
10 Developing new synthesis methods to improve the preparation efficiency of urea-based
11 derivatives, reduce their preparation complexity, and minimize the use of toxic
12 compounds like isocyanates, and substitute bio-based compounds for petroleum-based
13 ones holds promise as an effective approach to address the synthesis, promotion, and
14 environmental sustainability problem. In summary, the future research direction for
15 urea-based SAMs should primarily consider aspects such as supramolecular stability,
16 dynamics, precise responsiveness, cost-effectiveness, environmental friendliness,
17 diversification of applications, and so on.

18 **Declaration of Competing Interest**

19 The authors declare that they have no known competing financial interests or
20 personal relationships that could have appeared to influence the work reported in this
21 paper.

22

23 **Data availability**

24 No new data were created in this study. Data sharing is not applicable to this article.

25

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