

Cucurbituril Based Supramolecular Polymer Gels: From Macrocycle Synthesis to Functional Composite Networks

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Abstract

Cucurbiturils (CB[n]) are rigid glycoluril-based macrocycles possessing well-defined hydrophobic cavities capable of forming stable host–guest complexes in water. Owing to these properties, CB[n]-containing supramolecular polymer gels have attracted increasing attention as functional composite materials in modern materials science. This review summarizes recent progress in the development of cucurbituril-based supramolecular gels, with particular attention to synthetic approaches, network design, and emerging applications. Both conventional acid-catalyzed methods and more sustainable synthetic strategies for cucurbituril preparation and functionalization are discussed. We further consider the role of CB[n] macrocycles as reversible crosslinking units in polymer networks and analyze how host–guest interactions influence the mechanical properties, self-healing behavior, and stimuli responsiveness of the resulting materials. Recent applications in biomedical engineering, soft electronics, and environmental remediation are also highlighted, demonstrating how molecular-level supramolecular interactions can determine the macroscopic performance of these composite systems. The review concludes with perspectives on scalable synthesis, processing integration, and future directions in supramolecular composite materials.

Keywords: cucurbituril; supramolecular polymer gel; host–guest crosslinking; self-healing composite; dynamic network; functional material

1. Introduction

Polymer gels are three-dimensional networks of crosslinked polymer chains swollen with solvent, and they play a central role in soft-matter science because they combine solid-like integrity with liquid-like transport and deformability. In biomedical and functional materials research, hydrogels are especially important because their water-rich structure can resemble soft biological tissues and support delivery, sensing, and actuation [1–3]. However, conventional covalently crosslinked gels are often brittle, difficult to re-process, and limited in self-healing, which has led to growing interest in supramolecular networks based on reversible noncovalent interactions [4–7].

Within this context, cucurbiturils have attracted considerable attention as supramolecular host molecules due to their rigid glycoluril-based macrocyclic structure, carbonyl-fringed portals, and cavity-size-dependent host–guest selectivity in aqueous media [8,9]. The cucurbituril family comprises several homologues with different cavity volumes, and

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these structural differences strongly affect guest recognition, binding affinity, and the ability to form supramolecular polymer networks [6,10–16].

Smaller homologues such as CB[6] and CB[7] generally form stable 1:1 inclusion complexes, whereas CB[8] is capable of forming ternary host–guest complexes. This property makes CB[8] particularly suitable for the construction of multicomponent and dynamic polymer networks with reversible supramolecular crosslinking [17].

The remarkable host–guest binding properties of cucurbiturils have led to extensive studies in molecular recognition, supramolecular chemistry, medicinal chemistry, and stimuli-responsive materials. The development of functionalized cucurbiturils has further expanded the possibilities for incorporating CB[n] macrocycles into polymeric systems through covalent attachment and selective structural modification, while also improving compatibility with polymer matrices and composite components [17].

Such advances are particularly important for supramolecular hydrogels, where cucurbiturils can serve as reversible crosslinking units that influence stiffness, toughness, injectability, self-healing ability, and responsiveness to external stimuli [8,16].

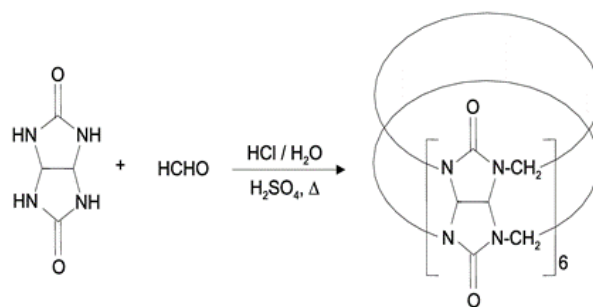
Despite the rapid growth of research in this field, many published studies remain focused on specific hydrogel systems or isolated applications. Existing reviews have discussed cucurbiturils in medicinal chemistry, chemical biology, and biomedical hydrogels; however, less attention has been given to the broader relationships between molecular host–guest interactions and the macroscopic behavior of cucurbituril-based polymer composites. In particular, clearer differentiation is needed between native cucurbituril host systems, functionalized CB[n] derivatives, and polymer gel composites containing cucurbituril motifs. The influence of host structure, guest selection, polymer architecture, and filler incorporation on network properties also remains insufficiently systematized.

This review therefore examines cucurbituril-based supramolecular polymer gels from a structure–property–function perspective. Particular attention is given to cucurbituril synthesis and functionalization, supramolecular network design, structure–property relationships, and recent applications in biomedical engineering, soft electronics, and environmental remediation [4,5,8–10,17,18]. By organizing the field around these design rules rather than isolated case studies, the review aims to highlight both the current state of the art and the unresolved challenges that will shape future progress [1–3,19,20].

2. Synthesis and Functionalization of CB[n]

2.1. Classical Acid-Catalyzed Synthesis

Cucurbituril synthesis is typically based on the acid-catalyzed condensation of glycoluril with formaldehyde under strongly acidic conditions [21]. The product distribution is governed by reaction variables such as acid type and concentration, reactant stoichiometry, temperature, and reaction time, and the reaction usually affords mixtures of cucurbit[n]urils ($n = 5–10$), with CB[9] and CB[10] often predominating [14,21]. Isolation of individual homologues is commonly achieved by exploiting differences in solubility through fractional crystallization or precipitation, sometimes supplemented by chromatographic separation [13,22]. The synthetic route is presented in Scheme 1.



Scheme 1. Classical acid-catalyzed synthesis of cucurbit[n]urils.

2.2. Green and Improved Synthetic Routes

Because conventional cucurbituril synthesis often requires strongly acidic and relatively harsh reaction conditions, alternative synthetic strategies have been explored to improve reaction control and reduce environmental impact. One example is the use of ethan-1,2-diyl bis(hydrogen sulfate) (EDSA), which enables cucurbituril formation under milder and less corrosive conditions while maintaining comparable, and in some cases higher, product yields [14,17,23].

Hydrothermal synthesis performed in sealed reactors at elevated temperature and pressure provides improved control over solubility and intermediate concentrations and may promote the selective formation of homologues such as CB[7] and CB[8]. Mixed-solvent systems and ionic liquids have also been investigated as tools for improving homologue selectivity and reaction reproducibility [24,25].

Such methods are important for the preparation of supramolecular gel composites, where the availability of high-purity CB[n] homologues strongly influences the reproducibility and performance of the resulting materials [15,26].

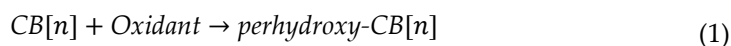
2.3. Functionalization Strategies

Functionalized cucurbiturils play an important role in the incorporation of CB[n] units into polymer networks, extending their application beyond molecular recognition toward structurally integrated supramolecular materials [24].

Several synthetic approaches have been reported for the preparation of functionalized cucurbituril derivatives. One strategy involves the use of substituted glycoluril precursors prior to macrocyclization. After condensation with formaldehyde, the substituents remain incorporated into the final cucurbituril framework, allowing the introduction of reactive groups, hydrophobic fragments, or ionic functionalities directly into the macrocycle [25,26].

Alternatively, preformed CB[n] homologues can be modified after macrocyclization. A well-known example is the oxidation of cucurbiturils to perhydroxy-CB[n], which provides versatile intermediates for subsequent derivatization reactions. In addition, template-assisted and host–guest-directed modification methods have been developed to improve reaction selectivity and facilitate integration into polymer systems through the use of auxiliary guests, linkers, or reactive templates [25,27].

These complementary approaches (1) provide access to CB[n] derivatives with diverse structures and tunable reactivity, which are important for constructing responsive supramolecular polymer networks with improved mechanical stability and dynamic behavior.



The resulting hydroxyl-functionalized macrocycles can undergo further derivatization, for example, through conversion into azide-containing derivatives for click reactions

or into amino-functionalized analogues suitable for polymer conjugation [26]. Although the cucurbituril framework is chemically relatively inert and therefore difficult to modify directly, successful post-functionalization reactions are typically highly selective, allowing controlled introduction of substituents without substantial disruption of the macrocyclic structure [27,28].

Another useful synthetic strategy is the “X + 1” approach, which is frequently combined with acyclic cucurbituril-type oligomer precursors. In this method, acyclic CB-like oligomers, including glycoluril hexamers or nonamers, are prepared first and subsequently coupled with functionalized monomeric units to complete macrocycle formation while simultaneously introducing specific substituents [28].

Compared with conventional condensation methods, this approach allows better control over substitution patterns and facilitates the synthesis of mono- and hetero-functionalized CB[n] derivatives that are otherwise difficult to access [29].

3. Design Principles of CB Gels

3.1. Specific Network Architectures

A central strategy in the design of cucurbituril-based supramolecular gels is the use of CB[n] hosts as reversible molecular crosslinkers between polymer chains. Variations in macrocycle size and guest identity strongly influence the resulting network topology and mechanical behavior [2,16].

Smaller homologues such as CB[6] and CB[7] generally form stable and well-defined 1:1 inclusion complexes with cationic guests, including ammonium salts and viologen derivatives, as well as with aromatic groups such as adamantyl and naphthyl moieties attached to polymer backbones. Each CB–guest pair functions as a discrete dynamic cross-link with high binding affinity ($K_a \approx 10^3\text{--}10^8\text{ M}^{-1}$, depending on the guest and solvent), producing gels with relatively high elastic moduli and slower stress relaxation [16,30].

In contrast, CB[8] can simultaneously accommodate two different guest molecules within a ternary complex, most commonly pairing complementary aromatic moieties, such as an electron-rich component like pyrene or 1,5-dimethoxynaphthalene with an electron-deficient partner such as 4,4'-bipyridine or paraquat [11,31,32]. A single CB [8] can bridge two polymer chains through this ternary linkage (Figure 1):

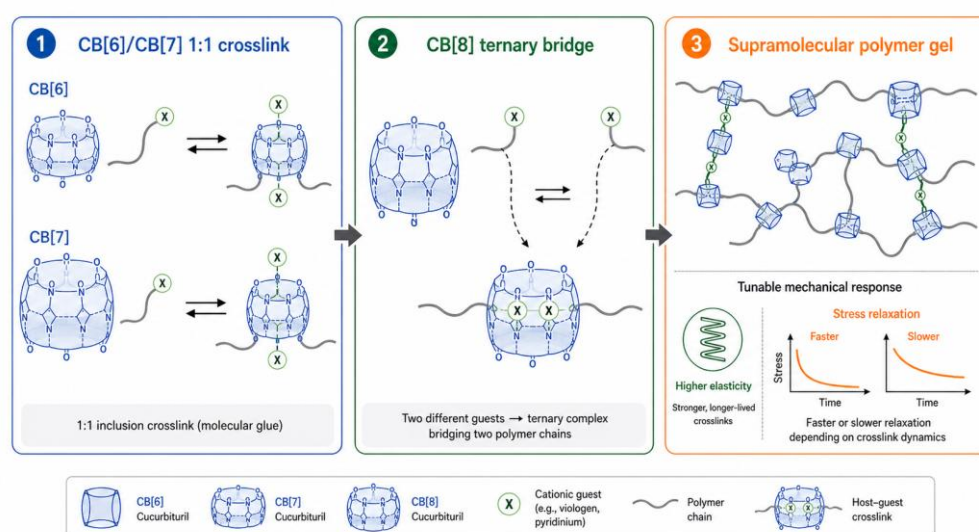


Figure 1. Cucurbituril-Mediated Supramolecular Crosslinking in Polymer Gels.

This ternary mode allows construction of dense, well-connected networks with tunable stiffness based on guest stoichiometry and CB [8] concentration [32–34].

The fundamental supramolecular crosslinking mechanisms used in cucurbituril-based composites are summarized in Figure 2 and Table 1.

Table 1. Cucurbituril-Based Supramolecular Crosslinking Systems and Resulting Composite Properties.

CB[n]	Host–Guest Binding Mode	Typical Guest Units	Polymer Matrix	Mechanical Properties (G'/E)	Key Composite Features	Ref.
CB [6]	1:1 inclusion complex	Alkylammonium, diammonium	PEG, polyacrylamide	$G' \approx 10\text{--}10^3$ Pa	Stable but relatively slow relaxation; good dimensional stability	[10,16]
CB [7]	1:1 inclusion complex	Adamantyl, ammonium, aromatic cations	PEG, gelatin, hyaluronic acid	$G' \approx 10^2\text{--}10^4$ Pa	High binding affinity, enhanced toughness, moderate self-healing	[11,13,30]
CB [8]	Ternary complex (1:2)	Donor–acceptor aromatic pairs	PEG, chitosan, hybrid matrices	$G' \approx 10^3\text{--}10^5$ Pa	Dense reversible crosslinking; excellent self-healing and energy dissipation	[31,35,36]
CB [8] + fillers	Host–guest + physical filler interaction	Aromatic-functional fillers	Nanocomposites (NFC, CNTs, graphene)	$E \approx 10\text{--}500$ kPa	Improved load transfer, crack resistance, multifunctionality	[36,37]

As shown in Figure 2, cucurbiturils can function as reversible molecular crosslinkers through 1:1 inclusion binding, ternary host–guest complexation, and interfacial bridging in composite networks.

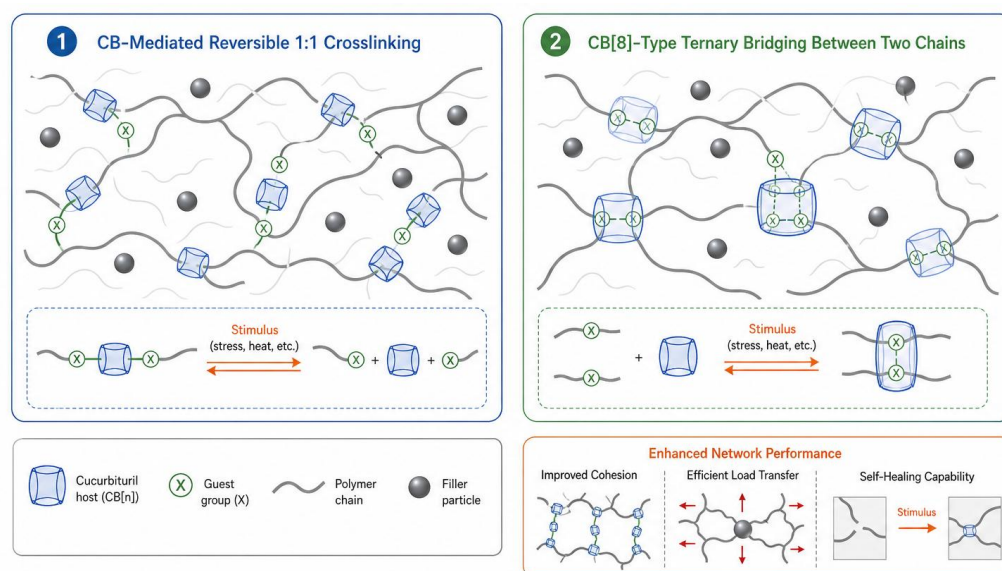


Figure 2. Cucurbituril-mediated supramolecular crosslinking mechanisms in polymer composite networks.

Figure 2 summarizes the main supramolecular crosslinking modes used in cucurbituril-based polymer gel composites.

- (1) CB[6]- and CB[7]-based 1:1 host–guest crosslinking, where a cucurbituril host interacts reversibly with a single guest-functionalized polymer segment to form discrete dynamic junctions.

- (2) CB[8]-mediated ternary complex formation, in which one CB[8] cavity simultaneously binds two complementary aromatic guests, commonly electron-donor and electron-acceptor moieties located on different polymer chains. Such interactions generate highly dynamic supramolecular crosslinks while maintaining good mechanical stability.
- (3) CB-mediated composite supramolecular networks, where cucurbiturils additionally function as reversible interfacial connectors between polymer matrices and secondary fillers, including nanoparticles or nanofibers. These interactions can improve stress transfer, toughness, and self-healing behavior within the material.

3.2. Dynamic Bonding and Self-Healing

A key feature of supramolecular gels is the reversibility of their host–guest crosslinks, which enables efficient dissipation of mechanical energy and is directly responsible for their self-healing properties [38]. Under applied stress, these dynamic junctions can temporarily dissociate, allowing the network to deform without permanent damage. Once the stress is removed, or when an external stimulus such as heat, light, or a chemical signal is applied, the noncovalent interactions reform and the original network structure is gradually restored [39]. Figure 3 illustrates this behavior in cucurbituril-based supramolecular polymer gels. The reversible host–guest interactions break and reform under mechanical loading, enabling energy dissipation and preventing fracture. After unloading or stimulation, the network reorganizes, leading to recovery of the gel’s mechanical integrity.

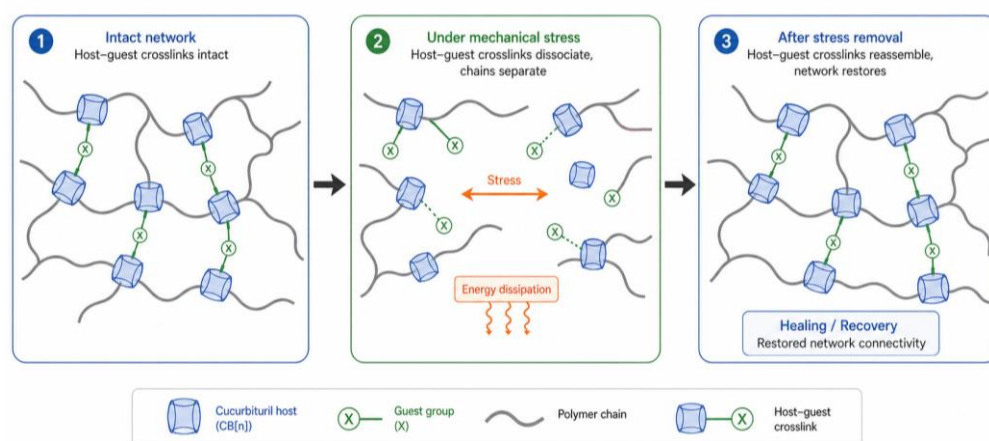


Figure 3. Schematic illustration of the self-healing mechanism in cucurbituril-based supramolecular polymer gels.

The healing rate and degree of structural recovery are largely controlled by the lifetime of the reversible crosslinks, which depends on both the dissociation kinetics and the binding strength of the host–guest pair. Stronger complexes tend to exhibit slower relaxation and thus maintain mechanical integrity over longer timescales, whereas interactions of intermediate strength can promote faster network rearrangement, shear-thinning behavior, and improved injectability. In addition, the spatial distribution and density of dynamic junctions within the polymer network play an important role in determining the overall healing efficiency [19,40,41].

Cucurbituril-based gels are effective self-healing systems because CB[n] host–guest interactions combine relatively high binding affinity with reversibility in aqueous media. In representative examples, CB-crosslinked hydrogels formed from aromatic guest pairs recover around 80–95% of their initial elastic modulus within 24 h after damage [36]. Such performance is comparable to, and in some cases higher than, that of many covalent and

other supramolecular hydrogel systems, reflecting the balance between strong complexation and rapid reassociation characteristic of CB–guest chemistry [42].

3.3. Multistimuli Responsiveness

By incorporating stimuli-responsive functional groups either into the guest molecules or into the polymer backbone, cucurbituril-based gels can be engineered to respond reversibly to external triggers through changes in crosslink density and network mechanics [30,43].

pH-responsive behavior is commonly achieved through protonation–deprotonation equilibria involving amine-, imidazole-, or carboxylic acid-containing guests. For instance, CB[7] shows significantly stronger binding toward protonated ammonium species compared with neutral amines, which can be used to induce pH-dependent softening or controlled release in hydrogel systems [30,34,44].

Redox-responsive systems typically rely on viologen derivatives and related motifs, where electrochemical switching modulates CB[8]-mediated ternary complexes between more and less crosslinked states [33,45]. In a similar manner, photoresponsive units such as azobenzene introduce light-driven control over host–guest interactions via reversible trans–cis isomerization, enabling sol–gel transitions or spatially localized changes in mechanical properties [32,46,47].

Figure 4 summarizes these three classes of stimuli-responsive CB-based gels: (1) pH-induced protonation and deprotonation of amine-functionalized guests affecting CB[7] binding affinity; (2) redox-controlled switching of viologen–CB[8] ternary complexes between crosslinked and decrosslinked states; and (3) light-triggered azobenzene isomerization leading to reversible modulation of host–guest interactions and gel mechanics.

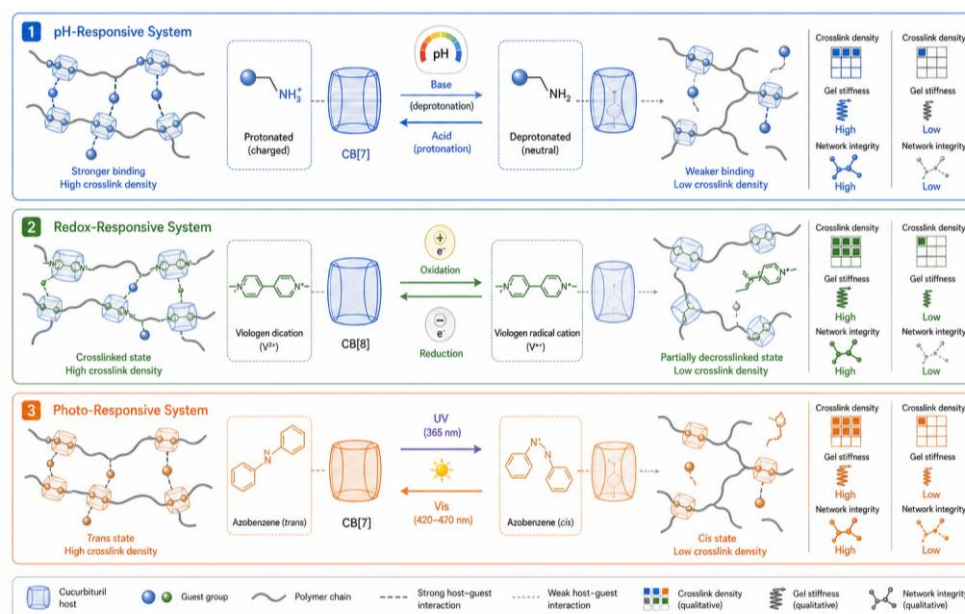


Figure 4. Multistimuli responsiveness of cucurbituril-based supramolecular gels.

3.4. Polymer Backbone Selection and Topology

The polymer backbone plays an important role in determining the gelation behavior and mechanical properties of cucurbituril-based supramolecular networks [6,12,48]. Backbone flexibility, branching, and chain topology influence not only the formation of host–guest junctions but also their ability to reorganize under stress, which ultimately affects the structure, dynamics, and mechanical response of the network [49].

Flexible linear polymers such as poly(ethylene glycol) (PEG) can form dense and mechanically stable networks when functionalized with a sufficiently high density of guest groups. These systems typically show storage moduli on the order of ~ 100 – 1000 Pa or higher, depending on composition and crosslink density [11,36]. At the same time, increased chain mobility can lead to faster stress relaxation compared with more rigid polymer architectures [31,48].

In contrast, semi-rigid and branched polymers, including dendrimers, star-shaped polymers, and bottlebrush structures, introduce additional topological constraints that influence network connectivity and stress distribution [50,51]. As a result, these architectures often improve toughness and failure strain by providing multiple stress-transfer pathways and enabling more efficient dissipation of applied force [40,52].

Biopolymers such as gelatine and hyaluronic acid are particularly attractive for biomedical applications due to their intrinsic biocompatibility and cell-instructive properties. When functionalized with CB[n] guest groups, they can form injectable supramolecular hydrogels with mechanical properties that more closely resemble native soft tissues, making them especially promising for tissue engineering and regenerative medicine [7]. To highlight how backbone architecture governs network formation, crosslink density, and macroscopic mechanics, the principal topology effects are schematically illustrated in Figure 5.

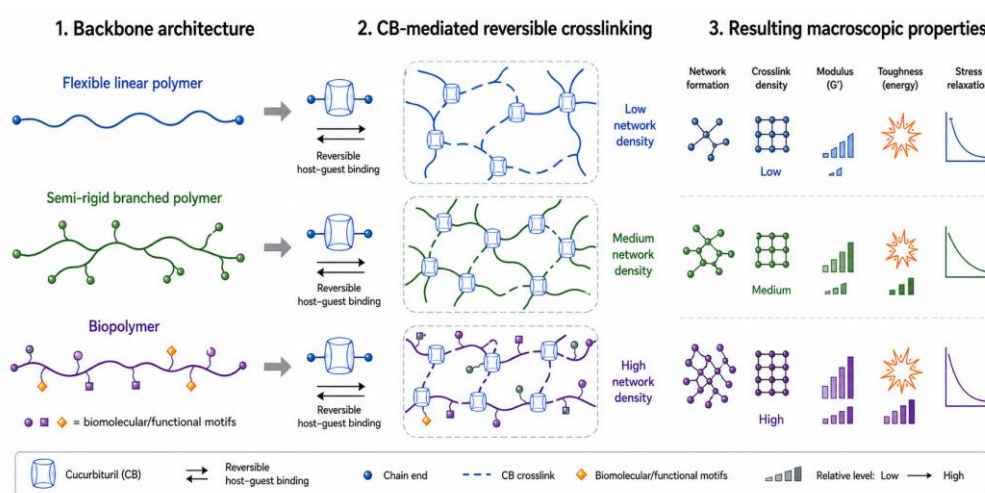


Figure 5. Schematic illustration of the effect of polymer backbone topology on cucurbituril-based supramolecular gel networks. Flexible linear, semi-rigid branched, and biopolymer backbones generate distinct crosslinking patterns, which in turn govern network formation, crosslink density, modulus, toughness and stress relaxation.

3.5. Composite Design: Integration with Secondary Fillers

Many modern CB-based hydrogels are prepared as hybrid composites through the incorporation of secondary fillers such as nanoparticles, nanofibres, clays, or conductive additives, extending their functionality beyond simple gel formation [6,37,53]. In these systems, cucurbituril host–guest interactions function not only as dynamic crosslinks within the polymer network but also as interfacial bridges between the polymer matrix and filler surfaces. This can improve filler dispersion, enhance interfacial adhesion, and contribute to more efficient stress transfer across the composite [7,54,55].

In CB[8]-based systems in particular, such interactions can make the filler phase an active component of the network, contributing to mechanical reinforcement, self-healing behavior, and stimulus responsiveness. A representative example is nanofibrillated cellulose (NFC), which can be embedded within a CB-crosslinked polymer matrix to yield com-

posites with improved mechanical properties and better recovery after damage. Compared with the corresponding gelatin–NFC composite lacking cucurbituril crosslinks, the CB [8]-containing system benefits from an additional reversible bonding mechanism that reinforces the network while preserving dynamic rearrangement under stress [56,57]. This combination of filler reinforcement and supramolecular crosslinking is particularly attractive for designing robust yet adaptive hydrogel composites for biomedical and soft-material applications [10,36,58]. The influence of secondary fillers on network reinforcement, interfacial adhesion, and self-healing is schematically shown in Figure 6.

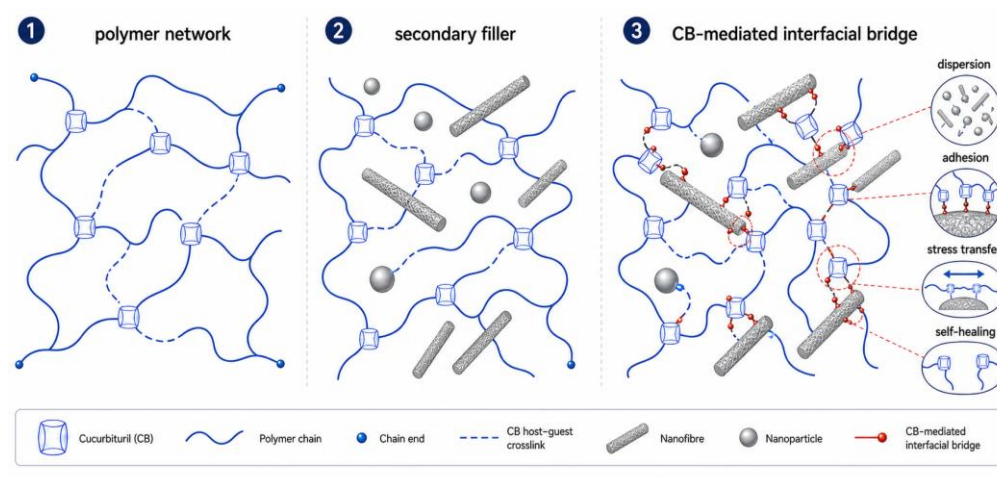


Figure 6. Schematic illustration of composite design in cucurbituril-based hydrogels.

4. Structure–Property Relationships

4.1. Rheological Characterization

Viscoelastic characterization is central to understanding the structure–property relationships of CB-based supramolecular gels, because rheology directly probes the lifetime, strength, and reversibility of host–guest crosslinks. Frequency-sweep oscillatory measurements provide the storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$), which together quantify the balance between elastic energy storage and viscous dissipation within the network [36,59].

In well-formed CB-based gels, G' typically exceeds G'' at low frequencies, confirming a predominantly solid-like response; as the frequency increases, the dynamic junctions have less time to reorganize, leading to reduced G' and altered viscoelastic behaviour [52,59]. The crossover frequency (ω^* , where $G' = G''$) is especially informative because it reflects crosslink lifetime: stronger host–guest interactions or higher CB content generally shift the crossover to lower frequencies, whereas weaker or more labile networks relax more rapidly and cross over at higher frequencies [11].

Temperature-dependent rheology further reveals the kinetics of network rearrangement. As temperature increases, host–guest dissociation accelerates, typically causing G' to decrease and G'' to rise, consistent with faster bond exchange and reduced elastic persistence [52].

Together, these measurements provide a quantitative framework for linking molecular binding strength, dynamic relaxation, and macroscopic gel mechanics, making rheology an essential tool for evaluating CB-based supramolecular networks [52,59,60]. The viscoelastic response of CB-based gels is schematically summarized in Figure 7.

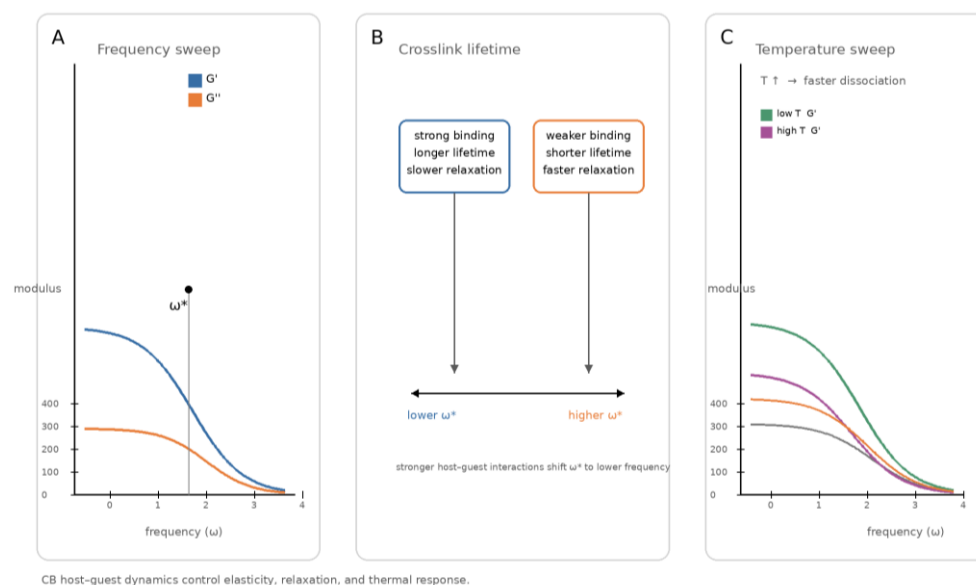


Figure 7. Schematic representation of rheological characterization of cucurbituril-based supramolecular gels. Frequency-sweep measurements provide the storage modulus (G'), loss modulus (G''), and crossover frequency (ω^*), which reflect the lifetime and reversibility of host–guest crosslinks. Temperature increase accelerates bond dissociation and network rearrangement, leading to reduced elasticity and enhanced viscous response.

4.2. Mechanical Properties and Failure Behavior

Compression and tensile testing are essential for evaluating gel stiffness, toughness, and failure behavior. In CB [6]-based supramolecular gels, elastic moduli typically span the kilopascal range, with CB [6]- and CB [7]-crosslinked systems often falling around 1–100 kPa, while CB-based gels can reach substantially higher values, frequently in the 10–500 kPa range, owing to the formation of denser and more effective crosslinks through ternary host–guest complexes [35,36].

Beyond stiffness, these materials are distinguished by their ability to dissipate mechanical energy efficiently. Because reversible crosslinks can rupture under load and subsequently reform, supramolecular gels often exhibit markedly enhanced toughness relative to covalently crosslinked analogues, with fracture toughness and strain energy density at break commonly exceeding those of chemically permanent networks by one to two orders of magnitude for comparable modulus values [39,41]. This behavior reflects the well-known “property-to-property synergy,” in which dynamic bonding allows a material to combine high extensibility with efficient energy dissipation [38–40].

In some CB-functionalized gel systems, large-strain deformation also induces strain hardening, where the stress required for further extension increases sharply at high strain. This effect may arise from backbone alignment and partial crystallization, or from deformation-driven network reorganization that effectively increases crosslink density during stretching [40,42]. Figure 8 summarizes how cucurbituril-mediated dynamic crosslinks govern stiffness, toughness, and strain hardening in supramolecular gels under compressive and tensile loading.

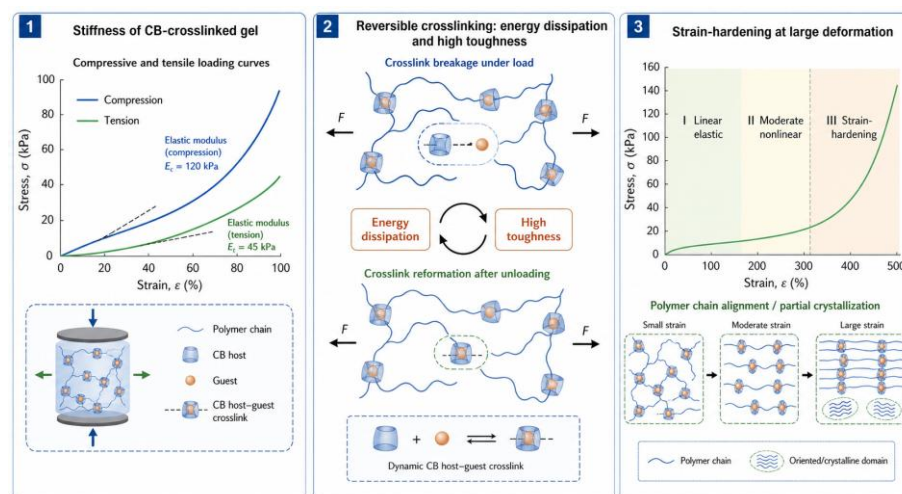


Figure 8. Schematic illustration of the mechanical response of cucurbituril-based supramolecular gels under compression and tension.

4.3. Swelling and Solvent Uptake

Equilibrium swelling in CB-based hydrogels can be interpreted as the balance between network elasticity and osmotic driving forces, with the latter governed by polymer–solvent interactions (χ), ionic contributions, and the density of effective crosslinks [12,48]. In Flory–Rehner terms, increasing crosslink density reduces the number of elastic chains between junctions, thereby lowering the equilibrium swelling ratio and restricting water uptake [6,7].

In CB-based systems, this relationship remains highly tunable because the number of effective junctions depends not only on total host and guest concentration, but also on the fraction of complexes that are actually engaged in stable crosslinking [52]. As a result, increasing CB[n] or guest loading generally decreases swelling by tightening the network, whereas competitive guests can displace polymer-bound guests, reduce effective crosslink density, and increase swelling. Ionic strength and pH provide additional control by altering electrostatic screening and guest protonation state, which can either strengthen or weaken host–guest association and thereby shift the swelling equilibrium [51,57]. This tunability is particularly useful in controlled-release systems, where swelling-mediated mesh size changes regulate solute diffusion and thus the release kinetics of encapsulated drugs [30,36]. The key factors governing equilibrium swelling in CB-based hydrogels are summarized schematically in Figure 9.

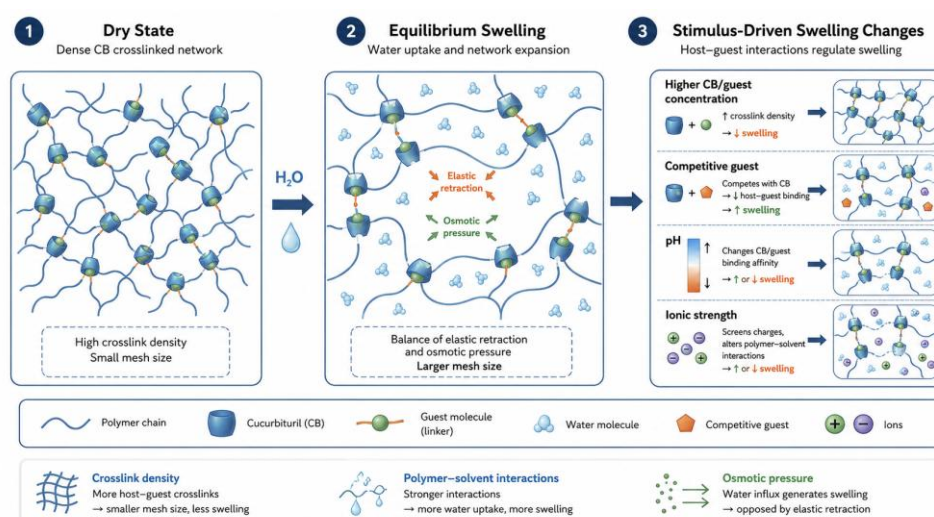


Figure 9. Schematic of swelling regulation in CB-based hydrogels. The equilibrium swelling ratio is controlled by network crosslink density, polymer–solvent interactions, and external stimuli such as pH, ionic strength, and competitive guests, which alter host–guest binding and mesh size.

5. Applications of Cucurbituril-Based Polymer Gel Composites

An overview of representative applications of cucurbituril-based polymer gel composites is provided in Table 2.

Table 2. Cucurbituril-Based Supramolecular Polymer Gel Composites: Applications and Functional Advantages.

Application Area	Composite Components	CB[n] Role	Stimulus/Function	Composite Advantage	Ref.
Biomedical scaffolds	Biopolymer + CB[n]	Dynamic crosslinker	pH, redox	Self-healing, injectability, tissue-matching mechanics	[7]
Injectable drug carriers	PEG/CB [8] networks	Ternary junctions	Shear, pH	Shear-thinning, rapid recovery, controlled release	[30,36]
Soft robotics	Polymer + CB [8] + redox guest	Switchable crosslinks	Electric potential	Reversible stiffness modulation	[33]
Soft electronics	Polymer + CNT/graphene + CB[n]	Interfacial binder	Mechanical damage	Self-healing conductivity	[37]
Environmental remediation	Gel + CB[n]	Selective adsorption sites	pH, competing guests	Regenerable composite sorbents	[4,10]

5.1. Biomedical Engineering and Drug Delivery

CB-based supramolecular hydrogels have attracted considerable interest in therapeutic and regenerative medicine because their dynamic host–guest crosslinks enable injectability, self-healing, and stimuli-responsive drug release [1,7,12]. The key biomedical functions of these systems are summarized in Figure 10.

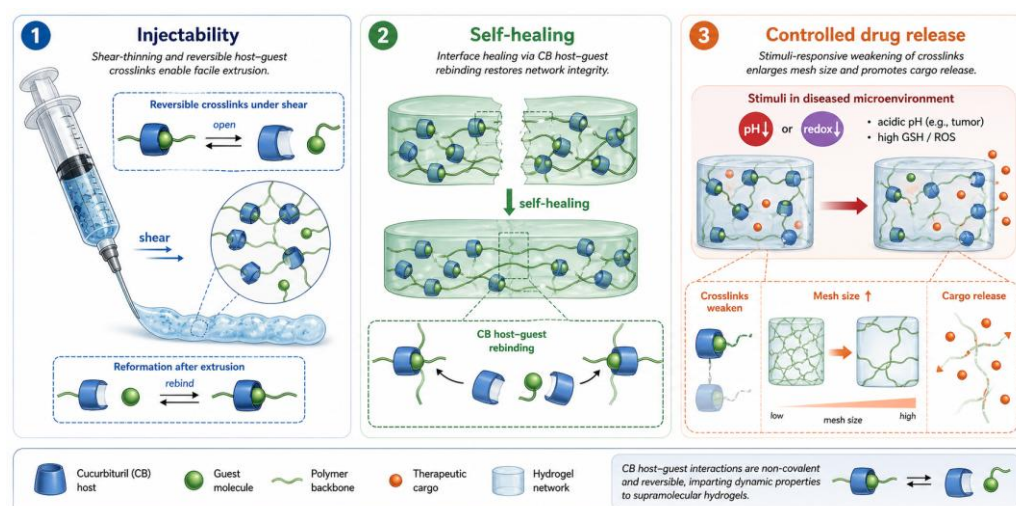


Figure 10. Mechanistic illustration of the biomedical functions of cucurbituril-based supramolecular hydrogels.

In injectable systems, shear disrupts noncovalent CB[8] crosslinks transiently, reducing viscosity and enabling extrusion through fine needles; once the shear field is removed, host–guest reassociation restores the percolated network and recovers gel integrity [36,57,61]. This dynamic bond exchange also underlies self-healing, since broken junctions

can reform at damaged interfaces without permanent network failure, thereby preserving scaffold continuity during implantation and use [7]. Mechanical properties can be tuned by adjusting CB[n] identity, concentration, and guest density, which changes the number of effective junctions and the relaxation dynamics of the network; this makes it possible to match softer or stiffer tissues by design [7,18].

For controlled release, external or local stimuli such as pH or redox conditions can shift host–guest binding equilibria, alter mesh size and diffusional permeability, and thereby trigger cargo release from CB/amine-guest or related systems under diseased microenvironments [7,49].

5.2. Soft Robotics and Actuators

Supramolecular hydrogels are of particular interest for soft actuators and robotic systems because their network mechanics can be reversibly tuned by external stimuli, allowing controlled changes in shape, stiffness, and motion [46].

In electroresponsive CB[8]-based systems, ternary networks incorporating redox-active viologen units respond to applied potential through changes in host–guest complex stability. This can translate into variations in network stiffness and contraction behavior, which has been explored for applications such as artificial muscles and soft grippers in film and fiber geometries [30,33,36].

Photoresponsive systems based on azobenzene guests rely on light-induced trans–cis isomerization to modulate CB[8]-mediated binding. The weaker binding of the cis form reduces crosslink stability, while the reverse isomerization restores the stronger interacting state [32,45]. When incorporated into structured or layered materials, this asymmetry can generate bending, crawling, or other directional shape changes relevant to soft robotic actuation.

Overall, these examples demonstrate how changes in supramolecular binding equilibria can be translated into macroscopic mechanical work [34,43,46]. Figure 11 summarizes how external stimuli regulate CB host–guest interactions and drive reversible deformation in soft robotic systems.

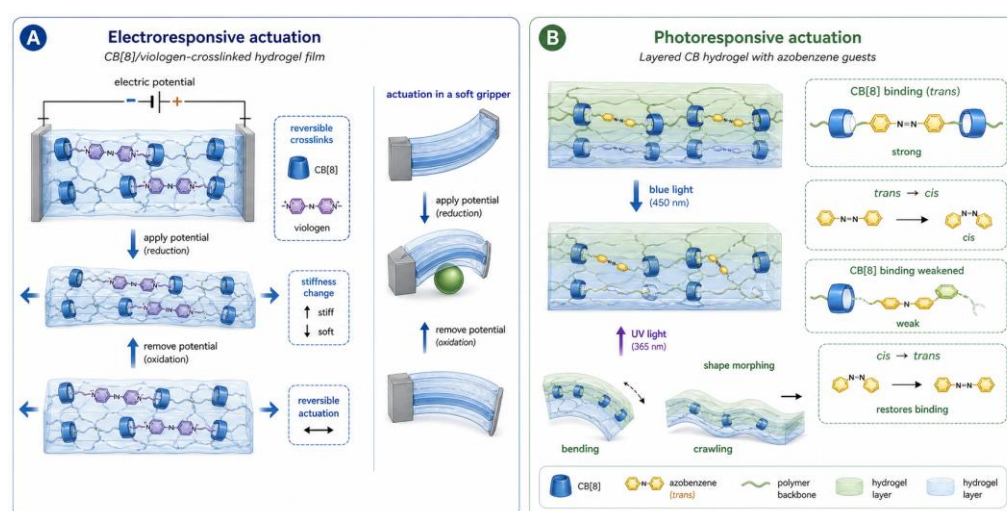


Figure 11. Two-panel schematic of electro- and photoresponsive CB hydrogel actuators.

5.3. Soft Electronics and Sensors

The combination of stretchability, self-healing behavior, and stimulus responsiveness makes CB-based hydrogels well suited for applications in wearable electronics and chemical sensing, where both mechanical compliance and reversible signal transduction

are required [37,62,63]. Figure 12 summarizes the key design principles together with representative sensing mechanisms used in these systems.

In conductive composites, CB-crosslinked networks can be combined with conducting polymers such as polyaniline or PEDOT, as well as carbon-based nanofillers including graphene and carbon nanotubes, to form flexible hydrogel conductors capable of maintaining electrical pathways under mechanical deformation [34,64]. The reversibility of the supramolecular junctions allows the material to tolerate repeated strain, while local damage can be partially repaired through reformation of host–guest interactions, enabling recovery of conductivity after fracture or cutting [37,53,65].

For chemical sensing applications, CB-based hydrogels can be functionalized with molecular receptors, chromophoric dyes, or other recognition motifs to enable selective detection of analytes such as glucose, metal ions, or proteins. In these systems, changes in host–guest interactions or local network structure can be translated into optical or mechanical responses, forming the basis of the sensing signal. The hydrogel matrix provides a hydrated and biocompatible environment, while swelling, affinity competition, or conformational changes can amplify the resulting optical or electrical response. In this way, the supramolecular network serves not only as a passive scaffold but also as an active signal-amplifying component [36,56,66].

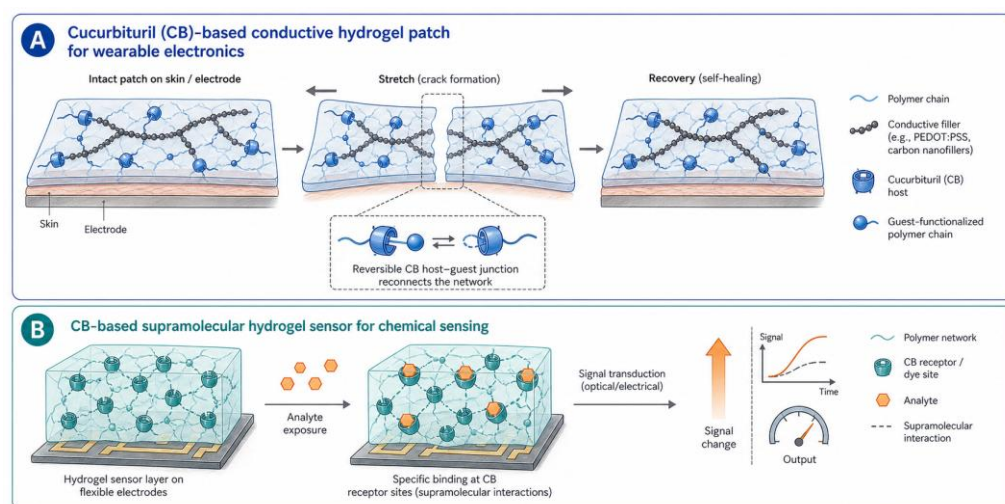


Figure 12. Schematic illustration of CB-based supramolecular hydrogels for wearable electronics and chemical sensing, highlighting stretchability, self-healing conductivity, and analyte-responsive signal transduction.

5.4. Separation and Environmental Remediation

CB-based gels have also been explored for the removal of pollutants and toxic species from aqueous media, taking advantage of the strong host–guest affinity of cucurbituril cavities combined with the processability of hydrogel materials in bulk form [4,10,67]. In these systems, contaminant uptake and subsequent regeneration typically proceed through reversible binding and release processes within the polymer network. The main adsorption and regeneration pathways are summarized in Figure 13.

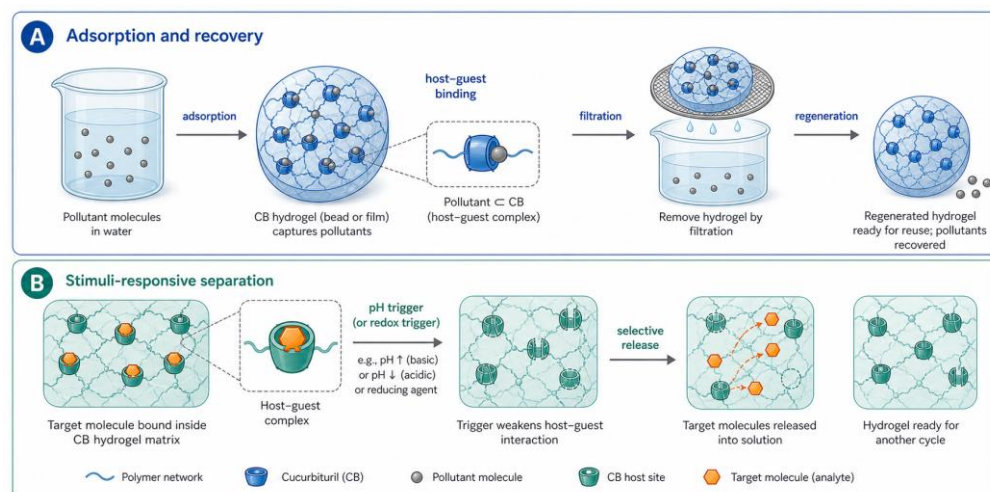


Figure 13. Schematic illustration of cucurbituril-based hydrogels for pollutant adsorption, recovery, regeneration, and stimuli-responsive separation.

In adsorption systems, CB[n] macrocycles can bind cationic, aromatic, and other compatible contaminants through host–guest recognition, while immobilization within a hydrogel matrix helps prevent material loss and allows the adsorbent to be recovered by simple filtration or decantation. These composites can be prepared either by covalent incorporation of CB units into the polymer network or through supramolecular assembly within preformed gels, offering a practical balance between adsorption performance, mechanical stability, and reusability [4,25,30].

Regeneration is typically achieved by changing solution conditions such as pH or ionic strength, or by introducing competitive guests that disrupt the host–guest interactions and release the bound species, enabling repeated use of the material [10,19,20].

Beyond bulk removal, pH- or redox-responsive CB gels can also function as selective separation media, where target molecules are captured under specific conditions and subsequently released upon a change in the external environment. This reversible switching behaviour makes them particularly useful for applications such as protein purification [30,62,63].

6. Outlook and Future Directions

6.1. Scalable Green Synthesis

Although significant progress has been achieved in cucurbit[n]uril synthesis, a truly scalable and sustainable manufacturing route is still lacking, which continues to limit wider practical applications. The main difficulties are largely related to process engineering rather than the underlying chemistry: most current methods rely on strongly acidic conditions, generate corrosive waste, and are not readily compatible with continuous production [22,25,27].

Future development will therefore need to address both efficiency and sustainability, particularly through approaches that reduce acid usage, enable continuous-flow processing, and introduce greener solvent and catalyst systems without compromising synthetic performance [18,61,68]. Until such advances are realized, large-scale implementation of CB[n]-based materials is likely to remain constrained by cost, safety, and environmental considerations [20,69].

6.2. Advanced Fabrication and 4D Printing

The integration of cucurbituril-based supramolecular chemistry with advanced fabrication techniques such as 3D/4D printing, electrospinning, and microfluidic templating

may enable the construction of complex hierarchical architectures and programmable, shape-changing materials [18,50,54]. In particular, the reversibility of CB-based crosslinks makes these systems well suited for 4D printing approaches, where externally applied stimuli induce time-dependent changes in structure or function [3,64].

6.3. Multi-Component Adaptive Composites

Future CB-based composite materials may rely less on static crosslinking and more on dynamic interfacial control, with CB[n] acting as programmable connectors between polymers, nanoparticles, and cells. Such hierarchical architectures could support self-organizing, self-diagnostic materials that continuously adjust to mechanical or chemical perturbations, moving the field closer to truly adaptive supramolecular systems [7,70].

6.4. Mechanistic Understanding and Modeling

The development of quantitative structure–property relationships linking host–guest binding kinetics to macroscopic mechanics and healing remains one of the most important outstanding challenges in CB-based materials. Integrating simulation with real-time mechanical and spectroscopic measurements will be essential for building predictive models that can guide the design of composites with target functionality [23,52,60,71].

7. Conclusions

Cucurbituril-based supramolecular polymer gels constitute a rapidly growing class of composite materials at the intersection of supramolecular chemistry, polymer science, and functional materials engineering. Their significance lies not only in their structural diversity, but more importantly in the ability of the rigid, shape-persistent CB[n] macrocycle to translate molecular recognition into tunable macroscopic properties. By exploiting strong yet reversible host–guest interactions and combining different guest motifs, polymer backbones, and secondary components, CB-based gels offer a highly adaptable platform for tailoring stiffness, self-healing, injectability, adhesion, transport behavior, and stimulus responsiveness across multiple length scales.

At the same time, the field is clearly evolving from empirical material discovery toward a more rational, mechanism-based design framework. Although progress in greener synthesis, post-synthetic functionalization, and composite engineering has substantially broadened the scope of cucurbituril-based materials, an important challenge remains: the absence of a unified structure–interaction–property relationship that directly links CB[n] identity, binding mode, network topology, and final material performance. In particular, simple host–guest crosslinking, ternary CB[8]-mediated junctions, and filler-bridging architectures should not be regarded as interchangeable variants, but rather as distinct design strategies with different kinetic, mechanical, and functional consequences. Establishing a clearer conceptual distinction among these motifs will be essential for interpreting existing results and guiding the design of next-generation materials with predictable behavior.

The present review has therefore sought not only to summarize the literature, but also to define the principles that establish cucurbituril gels as a coherent materials platform. These principles include the way cucurbituril structure governs binding selectivity, the way association and dissociation kinetics shape viscoelastic response, and the way network architecture determines bulk function. Looking forward, further progress will depend on coordinated advances in scalable and greener synthesis of specific CB[n] hosts, quantitative modeling of dynamic network formation and relaxation, and processing strategies that enable practical implementation in formats such as 3D/4D printed structures, injectable systems, and continuously manufactured composites. From this perspective, cucurbituril-based gels should be regarded not only as functional materials in their

own right, but also as a model system for the broader development of adaptive, reversible, and programmable soft matter.

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