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# Engineering nanostructured materials using polyphenol-functionalized polymers

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ABSTRACT

The assembly of nanostructured materials with tunable properties is of growing interest across fundamental research and industrial applications. Polyphenol-functionalized polymers, which integrate phenolic moieties within polymer backbones, have emerged as versatile building blocks for engineering nanostructured materials with controlled size, morphology, composition, and functionality. Owing to the chemistry of polyphenols, polyphenol-functionalized polymers enable diverse assembly pathways through covalent and noncovalent interactions with metal ions, small molecules, macromolecules, and nano/microstructures, allowing fine control over the physicochemical properties of the resulting materials. In this review, we provide an overview of polyphenol-functionalized polymers, beginning with key synthetic strategies, including ring-opening polymerization, radical polymerization, controlled/living radical polymerization, and post-modification of preformed polymers. We then discuss the assembly behaviors of these polymers, driven by synergistic interactions between the polyphenol groups and polymer chains, highlighting metal coordination, molecular complexation, and integration with nano/microstructures. These interactions result in assembled materials with tunable physicochemical properties, including surface charge, hydrophobicity–hydrophilicity balance, biocompatibility, stealth and targeting, stimuli-responsiveness, and bioactivity. Finally, we highlight emerging applications of polyphenol-functionalized polymers in multifunctional interfaces, responsive and adaptive materials, energy and electronic devices, and biomedicine. Overall, this review provides a concise and up-to-date overview of the synthesis, self-assembly mechanisms, and physicochemical tunability of polyphenol-functionalized polymers, and their wide application.



*Abbreviations:* 3D, three-dimensional; ADT, alkanedithiol; AEMA, aminoethylmethacrylamide; AgNP, silver nanoparticle; AROP, anionic ring-opening polymerization; ATRP, atom transfer radical polymerization; AuNP, gold nanoparticle; BA, n–butyl acrylate; BCMT, bis-(carboxymethyl)trithiocarbonate; CAF, caffeamide; CAG, catechol-acetonide glycidyl ether; CNT, carbon nanotube; CROP, cationic ring-opening polymerization; CS–C, cross-linked catechol–chitosan; CTA, chain transfer agent; DA, dopamine acrylamide; DBC, DNA block copolymer; DHCA, dihydrocaffeic acid; DHCAF, 2-methacryloylethyl dihydrocaffeate; DMA, dopamine methacrylamide; DMSO, dimethyl sulfoxide; DNA, deoxyribonucleic acid; DOMA, N-(3,4-dihydroxyphenethyl)methacrylamide; DOPA, 3,4-dihydroxyphenylalanine; DOX, doxorubicin; E. coli, Escherichia coli; EDC, N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimide; HA, hyaluronic acid; HAGA, gallic acid-functionalized hyaluronic acid; HAMA, hyaluronic acid methacrylate; HRP, horseradish peroxidase; iBoc, isobutyl carbonate; IONC, iron oxide nanocube; MA, methyl acrylate; MD, molecular dynamics; MMA, methyl methacrylate; MOF, metal–organic framework; MPN, metal–phenolic network; $MPP5_{cone}$, catechol-functionalized calix[4]resorcinarenes; NaOH, sodium hydroxide; NCA, N-carboxyanhydride; NHS, N-hydroxysuccinimide; NIR, near-infrared; P2VP, poly(2-vinylpyridine); PAA, polyallylamine; PAAcat, catechol-functionalized poly(acrylic acid); PBA, poly(butyl acrylate); PBAA, phenylboronic acid acrylate; PDA, polydopamine; PDHS, poly(3,4-dihydroxystyrene); PDMS, polydimethylsiloxane; PEG, polyethylene glycol; PEGp, PEG–phenol; PEI, polyethylenimine; PG, pyrogallol; PMA, poly(methyl acrylate); PMAA, poly(methacrylic acid); PMMA, poly(methyl methacrylate); PNIPAM, poly(N-isopropylacrylamide); POxaD, poly(oxanorbornene dopamine); PS, polystyrene; PTHS, polytrihydroxystyrene; PTMOS, polytrimethoxystyrene; PTMSS, poly(4-trimethylsilylstyrene); PVA, poly(vinyl alcohol); PVA-CA, catechol-functionalized poly(vinyl alcohol); QCS-$Tf_2N$, quaternized chitosan ion-paired with bis(trifluoromethane-sulphonyl)imide; RAFT, reversible addition–fragmentation chain transfer; ROMP, ring-opening metathesis polymerization; ROS, reactive oxygen species; SEM, scanning electron microscopy; SHP, self-healing hydrophobic polymer; TEG, triethylene glycol glycidyl ether; TEM, transmission electron microscopy; TFME, 2,2,2-trifluoroethyl methacrylate; TMOS, trimethoxystyrene; TPT, topotecan; UV, ultraviolet; WCA, water contact angle.

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## 1. Introduction

Nanostructured materials with tunable size, shape, charge, stiffness, stability, bio–nano interactions, and stimuli-responsiveness underpin emerging advances in chemistry, materials science, and biomedical applications [1,2]. The physicochemical properties of these materials are determined by the functions of building blocks and the type of assembly networks [2]. For example, the sequence-defined structure of DNA has enabled the fabrication of dynamic materials that are responsive to different chemical and physical stimuli such as temperature, pH, and complementary strands [3]. In addition, the type of covalent and noncovalent chemistry between building blocks influences the crystallinity, morphology, and stimuli-responsiveness of the assembled constructs [4]. Therefore, it is essential to exploit versatile functional building blocks capable of forming diverse interactions during the assembly process.

Polyphenols, which contain at least one aromatic ring with one or more hydroxyl groups, represent a naturally abundant class of molecules whose redox activity, hydrogen-bonding capability, and metal-chelating behavior endow them with broad functional utility [5,6]. For example, flavonoids, an important group of dietary polyphenolic compounds that occur naturally as pigments in fruits, flowers, and vegetables, have antioxidant properties and protect plants against ultraviolet (UV) radiation from the sun [7–10]. Gram-negative bacteria use phenolic molecules such as the siderophore enterobactin to aggressively acquire iron with high affinity [11]. The plant-derived polyphenol tannic acid, which has a dendrimer-like structure with five inner catechol groups and five outer gallol groups, exhibits antioxidant properties [12]. Polyphenols that contain catechol or gallol groups have been identified as powerful building blocks for nanostructured materials. For instance, tannic acid has been widely employed to fabricate wet-tissue adhesives through a simple mixing process with polymer solutions [13]. Upon mixing, tannic acid forms noncovalent interactions (e.g., hydrogen bonding and hydrophobic interactions) with polymer chains, driving spontaneous self-assembly into aggregated structures. Subsequent stirring or centrifugation yields adhesive materials that strongly adhere to wet tissues such as skin, bone, and stomach. In addition, coordination networks formed between metal ions and phenolic molecules have enabled the preparation of versatile supramolecular coatings [14]. Robust and modular coatings have been deposited on a broad range of substrates, from organic/inorganic materials to biological cells. Polyphenols are known to also form covalent and noncovalent interactions with small molecules, polymers, and biomacromolecules [2]. Collectively, these seminal pioneering studies demonstrate the breadth of polyphenol-based chemistries, thereby positioning polyphenol moieties as versatile building blocks for diverse applications, including catalysis, therapeutic delivery, biological imaging, energy storage, and separation.

Despite the structural diversity of polyphenols in nature—encompassing over 8000 known compounds [15]—polyphenol-based research is largely constrained to commercially available phenolic compounds, such as tannic acid, gallic acid, epigallocatechin gallate, and dopamine [16]. These small molecules share similar catechol or gallol motifs and have limited molecular weight ranges, constraining the tunability of assembly and the resulting material properties. Therefore, there is a need and interest to broaden the range of building blocks in terms of chemical diversity and functionality to fabricate assembled structures with the desired physicochemical properties. In this regard, polyphenol-functionalized polymers, consisting of phenolic groups and well-defined polymer chains with controllable molecular weights, architectures, and functionalities, have emerged as powerful building blocks for designing nanostructured materials with controllable size, morphology, composition, and functional properties. These polymers enable programmable assembly and functionalization via redox-mediated reactions, hydrogen-bonding, and metal-coordination with diverse molecules and substrates. Moreover, their polymer-derived functionalities, ranging from hydrophobicity–hydrophilicity balance to biocompatibility and stimuli-responsiveness, provide additional levers to tailor the behavior of assembled materials.

In this review, we define the scope of polyphenol-functionalized polymers to encompass synthetic macromolecular architectures integrated with either natural polyphenols or polyphenol-related moieties (i.e., catecholamines). Previous reviews have provided valuable overviews of related areas, including natural or dietary polyphenols and their biological activities [17], polyphenol–macromolecule systems and polyphenol-based nanoparticles for drug delivery and bioimaging [18,19], metal–polyphenol self-assembled nanoparticles for inflammatory diseases [20], polyphenol-based functional materials and biomedical composites [21], and plant polyphenols as sustainable raw materials for polymer synthesis [22]. However, these reviews have generally focused on natural polyphenol bioactivity, selected material platforms, specific biomedical applications, or sustainable feedstock chemistry. In contrast, the present Review highlights polyphenol-functionalized polymers as modular macromolecular building blocks for engineering nanostructured materials. Rather than focusing on individual material systems or application areas, this Review integrates polymer synthesis, assembly interactions, physicochemical and biological property engineering, and emerging applications. By emphasizing the relationships among polymer structure, phenolic chemistry, assembly behavior, and material function, our objective is to provide a unified framework for understanding and designing polyphenol-functionalized polymers as an emerging class of programmable building blocks for nanomaterials engineering. Section 2 introduces key synthetic strategies i.e., ring-opening polymerization, radical polymerization, controlled/living radical polymerization, and post-modification of preformed polymers. Section 3 focuses on assembly pathways driven by covalent and noncovalent interactions of polyphenol-functionalized polymers with diverse molecules and substrates, highlighting coordination with metal ions, complexation with small molecules and macromolecules, and integration with nano/microstructures. These interactions are essential for tuning the physicochemical properties of the resulting materials such as biocompatibility, stealth and targeting, surface charge, hydrophobicity and hydrophilicity, and stimuli-responsiveness and bioactivity, as discussed in Section 4. Finally, Section 5 explores emerging applications of polyphenol-functionalized polymers in multifunctional interfaces, responsive and adaptive materials, energy/electronic devices, and biomedicine. Section 6 concludes with a forward-looking discussion on opportunities for molecular design and translational research of polyphenol-functionalized polymers. This review provides a comprehensive overview of the synthesis, self-assembly mechanisms, physicochemical tunability, and broad applications of polyphenol-functionalized polymers in materials engineering, aiming to serve as a valuable, up-to-date resource for both new and established researchers in the field.

## 2. Synthesis of polyphenol-functionalized polymers

Polyphenols are abundant organic compounds that are widely present in natural plants [23]. The catechol or gallol groups in polyphenols can form diverse covalent and noncovalent interactions, which make polyphenols a versatile building block for the design of assembled materials. Commercially available polyphenols, including gallic acid, caffeic acid, pyrocatechol, ellagic acid, quercetin, epigallocatechin gallate, and tannic acid, are shown in Fig. 1. Advances in polymerization techniques have enabled a wide

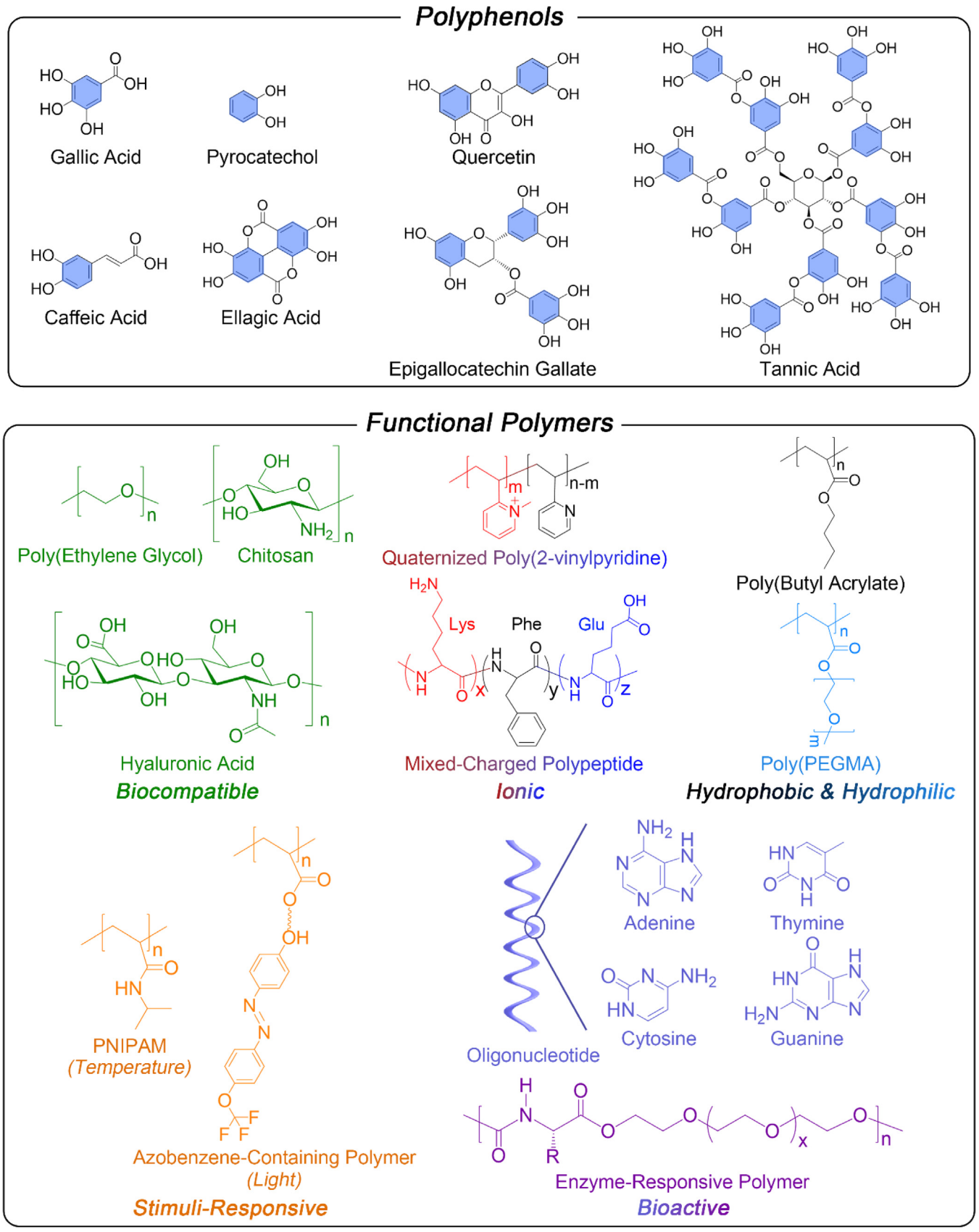


**Fig. 1.** Representative examples of polyphenols and functional polymers. PEGMA, poly(ethylene glycol) methyl ether methacrylate.

selection of polymer chains with diverse physicochemical properties such as compositions (e.g., hydrophilic, hydrophobic), molecular weights, chemical structures (e.g., linear, branched, bottlebrush), and functionalities (e.g., biocompatibility, ionic, stimuli-responsiveness, bioactivity) [24]. In addition, naturally derived polymers, such as polysaccharides and oligonucleotides, expand the pool of available polymers (Fig. 1). To combine the advantages of polyphenols and polymers as building blocks for nanomaterial assembly, advanced synthesis methods have been developed to synthesize polyphenol-functionalized polymers bearing phenolic groups in main chain, side chain, or end group of the polymer backbone. In this section, we introduce the synthesis protocols of these versatile polymers using various polymerization techniques, including ring-opening polymerization, radical polymerization, controlled/living radical polymerization, and post-modification chemistry.

### 2.1. Ring-opening polymerization

Ring-opening polymerization is a chain-growth method in which strained cyclic monomers are converted into well-defined linear or network polymers. To synthesize polyphenol-functionalized polymers, the design and synthesis of cyclic monomers bearing phenolic groups is required. A series of polymers with varying functionalities and phenolic contents have been synthesized through ring-opening polymerization. The polymerization of *N*-carboxyanhydride (NCA) monomers enables large-scale access to polypeptides. Moreover, the copolymerization of structurally and functionally diverse monomers has emerged as a versatile method for preparing a wide array of functional polymeric materials with tunable properties [25]. Yu and Deming synthesized a water soluble co-polypeptide incorporating both L-dihydroxyphenylalanine and L-lysine units by ring-opening polymerization of functional $\alpha$-amino acid NCA monomers [26]. The hydroxyls of the L-dihydroxyphenylalanine NCA monomer and the amine of the L-lysine NCA monomer are protected with a *N*-carboxybenzyl group to avoid disrupting the ring opening polymerization. Subsequent deprotection of the copolypeptides is accomplished using HBr in acetic acid, yielding polymers that display adhesive properties on diverse substrates under oxidative conditions, comparable to natural marine adhesive proteins. More complex cationic polypeptides incorporating L-dihydroxyphenylalanine groups have also been synthesized via NCA ring-opening polymerization, which can be used in antibacterial and antifouling coatings [27]. In these structures, the L-dihydroxyphenylalanine catechol units impart anchoring ability, L-lysine provides a cationic charge, and the phenylalanine units impart hydrophobicity; a mixed charge can be achieved through the incorporation of specific monomers, such as negatively charged glutamic acid.

Multiloop polymers have been synthesized through anionic ring-opening polymerization (AROP) by using triethylene glycol glycidyl ether (TEG) and catechol-acetonide glycidyl ether (CAG) monomers (Fig. 2a) [28]. The catechol-based epoxide monomer CAG is prepared in a protected form using an acetonide group to prevent unwanted reactions. A series of random copolymers, poly(TEG-*co*-CAG), have been prepared via AROP, followed by deprotection of the protecting groups. By varying the CAG content from 4 to 50%, the adhesive properties and loop dimensions of the resulting copolymers are systematically modulated. Mussel-inspired poly(2-ethyl-2-oxazoline)-based copolymers have been synthesized via microwave-assisted cationic ring-opening polymerization (CROP) (Fig. 2b) [29]. Specifically, copolymerization of 2-ethyl-2-oxazoline and 2-(3,4-dimethoxyphenyl)-2-oxazoline is initiated using different catechol content ratios (2.5–10%). The hindered catechol groups (35%) are exposed through the deprotection process and the positively charged moieties are obtained through hydrolysis reaction using hydrochloric acid with microwave irradiation. The ring-opening metathesis polymerization (ROMP) of norbornene monomers has been employed to prepare gallol-functionalized polymers (Fig. 2c) [30]. Polymerizations are performed using either protected or unprotected gallol-containing monomers. Reactions with unprotected monomers result in slow kinetics and incomplete polymerization, likely due to moderate coordination of phenolic hydroxyl groups to the ruthenium (Ru) atom of the catalyst. These observations underscore the importance of phenolic group protection in metal-mediated polymerization to ensure efficient polymerization.

### 2.2. Radical polymerization

A range of vinyl monomers bearing catechol and gallol groups have been synthesized and used to prepare polyphenol-functionalized polymers using radical polymerization techniques [31]. Phenolic derivatives are regarded as polymerization inhibitors due to their radical scavenging behavior and tendency to generate aryloxy radicals [32,33]. Thus, the radical polymerization of vinyl monomers with unprotected phenolics may seem unexpected. Nonetheless, the radical polymerization of unprotected phenolic-containing monomers has been demonstrated, underscoring the potential of this approach for synthesizing polyphenol-functionalized polymers. Methacrylate copolymers bearing catechol and fluorine groups have been synthesized by radical polymerization of dopamine methacrylamide (DMA) and 2,2,2-trifluoroethyl methacrylate (TFME) (Fig. 3a) [34]. Varying the DMA-to-TFME molar ratio from 25:1 to 1:25 yields copolymers with TFME contents ranging from 3 to 95%. These polymeric materials exhibit composition-dependent physicochemical properties: increasing the DMA content enhances adhesive strength, whereas a higher TFME content improves strain resistance and solvophobic properties. Catechol-functionalized polymers have been prepared through the radical polymerization of *n*–butyl acrylate (BA) and dopamine acrylamide (DA) (Fig. 3b) [35]. The resulting polymer (i.e., poly(DA-*co*-BA)) exhibits self-healing properties that are governed by catechol-driven hydrogen bonding and metal coordination. Notably, high-purity polymers have been obtained in the absence of protection/deprotection steps [36] or restricted polymerization times [37], underscoring the efficiency and simplicity of the method.

Although polyphenol-functionalized polymers can be synthesized in the absence of protection/deprotection chemistry, side reactions such as branching or cross-linking between phenolic groups and propagating radicals remain a concern during radical polymerization [31,38,39]. To circumvent these side reactions, benzyl-protected 3-(3,4-dihydroxyphenyl)propyl acrylate is synthesized by protecting catechol groups with benzyl bromide, followed by acryloylation using acryloyl chloride. Upon copolymerization with BA and subsequent deprotection using iodotrimethylsilane, a series of copolymers poly(3-(3,4-dihydroxyphenyl)propyl acrylate-*co*-butyl acrylate) are obtained (Fig. 3c) [39].

### 2.3. Controlled/living radical polymerization

Controlled/living radical polymerization techniques—such as reversible addition-fragmentation chain transfer (RAFT) and atom transfer radical polymerization (ATRP)—have had a significant impact in polymer science, as these advanced methods have enabled the preparation of polymers with predictable and controlled molecular weights ($M_n$), low dispersity ($M_w/M_n < 1.1$), controlled polymer architecture, consistent compositions, and high end-group functionality/fidelity [40,41]. These techniques allow the rational design and synthesis of polyphenol-functionalized polymers with defined properties for various applications.

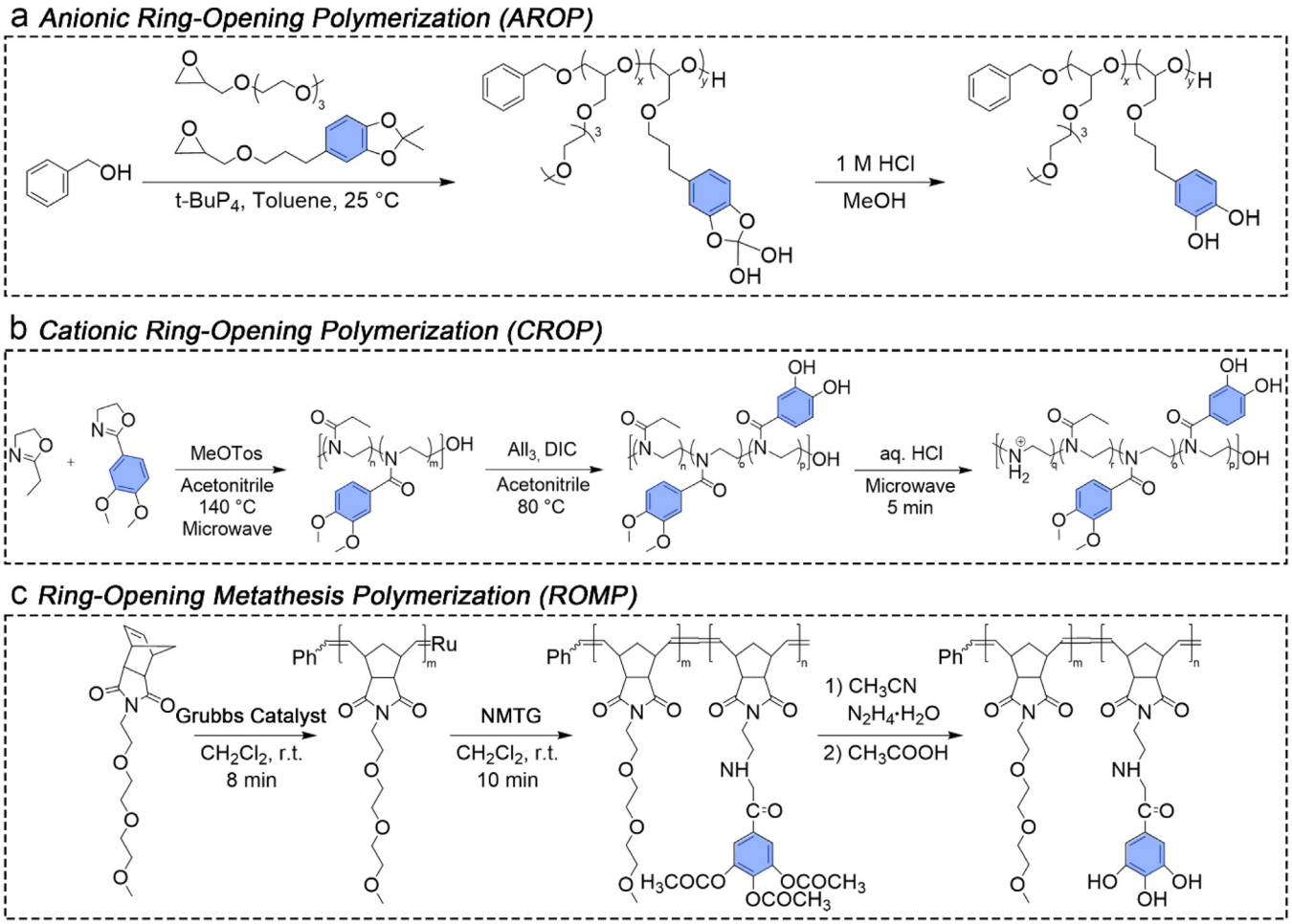


**Fig. 2.** Ring-opening polymerization reactions to prepare polyphenol-functionalized polymers. (a) Synthesis of random copolyethers (i.e., poly(TEG-*co*-CAG)) through AROP [28], Copyright 2020. Adapted with permission from the American Chemical Society. (b) Synthesis of catechol-bearing cationic copolymers inspired by mussel adhesion, prepared through CROP [29], Copyright 2023. Adapted with permission from the American Chemical Society. (c) ROMP synthetic route for fabricating gallol-containing block copolymers [30], Copyright 2018. Adapted with permission from Elsevier Ltd. MeOH, methanol; MeOTos, methyl tosylate; DIC, *N,N*-diisopropylcarbodiimide; NMTG, norbornene monomer containing 3,4,5-triacetoxylphenyl groups; r.t., room temperature.

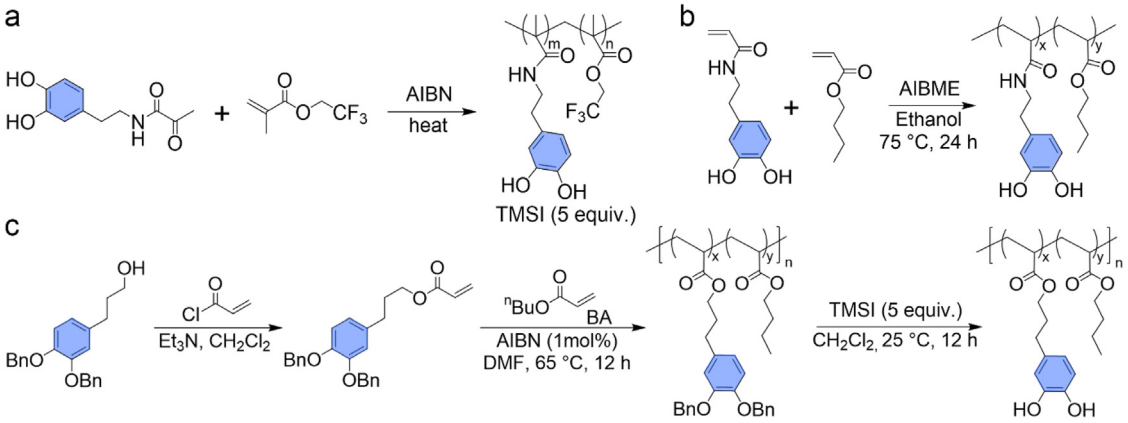


**Fig. 3.** Radical polymerization reactions to prepare polyphenol-functionalized polymers. (a) Synthesis of poly(DMA-*co*-TFME) via free-radical copolymerization of DMA and TFME [34], Copyright 2015. Adapted with permission from Elsevier B. V. (b) Preparation of poly(DA-*co*-BA) through radical copolymerization of DA and BA [35], Copyright 2016. Adapted with permission from the American Chemical Society. (c) Synthesis of catechol-based copolymers employing protected 4-propanol catechol derivatives [39], Copyright 2024. Adapted with permission from Elsevier B. V. AIBN, 2,2′-azobis(2-methylpropionitrile); AIBME, 2,2′-azobis(2-methylpropionate); DMF, dimethylformamide; TMSI, iodotrimethylsilane.

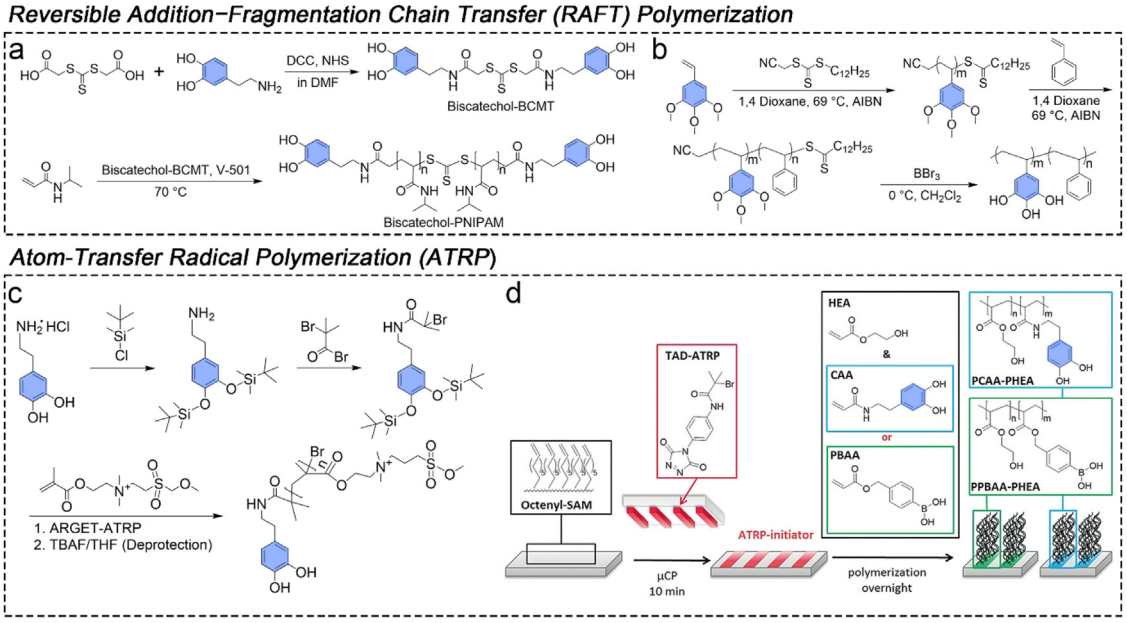


**Fig. 4.** Controlled/living radical polymerization for the preparation of polyphenol-functionalized polymers. (a) Synthesis of biscatechol-functionalized PNIPAM via RAFT polymerization of NIPAM using a biscatechol-functionalized CTA (biscatechol-BCMT) [45], Copyright 2022. Adapted with permission from the American Chemical Society. (b) Synthesis of PTHS-*b*-PS via RAFT polymerization followed by hydrolysis [48], Copyright 2022. Adapted with permission from the American Chemical Society. (c) Synthesis of a catechol-terminated zwitterionic polymer using a catechol-containing initiator [50], Copyright 2019. Adapted with permission from Elsevier B. V. (d) Surface patterning via microcontact printing of a triazinedione (TAD)-based ATRP initiator on an octenyltrichlorosilane self-assembled monolayer (SAM), followed by surface-initiated ATRP of catechol-functionalized (PCAA-*co*-PHEA) or phenylboronic acid-functionalized (PPBAA-*co*-PHEA) copolymer brushes [51], Copyright 2018. Adapted with permission from Wiley-VCH GmbH & Co. KGaA, Weinheim. DCC, *N,N′*-dicyclohexylcarbodiimide; ARGET, activators regenerated by electron transfer for ATRP; TBAF, tetrabutylammonium fluoride; THF, tetrahydrofuran; HEA, hydroxyethyl acrylate; CAA, catechol acrylamide; PBAA, phenylboronic acid acrylate.

RAFT polymerization has demonstrated excellent tolerance to phenolic groups. Therefore, this technique has enabled the synthesis of various well-defined polymers in the absence of protection strategies [42,43]. Polyphenol-functionalized polymers based on styrene [42], oligo(ethylene glycol) methyl ether methacrylate [44], and *tert*–butyl acrylate [43] have been synthesized with relatively narrow molecular weight distributions ($M_w/M_n < 1.20$) using unprotected phenolic-functionalized chain transfer agents (CTAs). To synthesize biscatechol-functionalized polymers, a biscatechol-functionalized RAFT agent, bis-(carboxymethyl)trithiocarbonate (biscatechol-BCMT), is first obtained via amide coupling of BCMT with dopamine using *N,N′*-dicyclohexylcarbodiimide and *N*-hydroxysuccinimide (NHS). *α,ω*-Biscatechol-functionalized poly(*N*-isopropylacrylamide)s (PNIPAMs) are then obtained via RAFT polymerization using a symmetrical CTA with two catechol groups (Fig. 4a) [45]. Protection strategies for the phenolic moieties have been employed to prevent side reactions of aromatic hydroxyls, including radical scavenging, polymerization inhibition, and self-condensation with carboxylic acid groups [16,46]. For example, the hydroxyl groups in catechol-containing dihydrocaffeic acid (DHCA) are protected using isobutyl carbonate (iBoc) to afford DHCA carbonic anhydride (iBocDHCA). Coupling iBocDHCA with 2-hydroxyethyl methacrylate yields a catechol-functionalized monomer. RAFT copolymerization of iBocDHCA methacrylate and methyl methacrylate with a carboxylic acid-terminated CTA (4-cyano-4-(thiobenzoylthio)pentanoic acid) affords the catechol-functionalized copolymer poly($MMA_{40}$-*co*-$iBocDHCA_{23}$) with a terminal carboxylic acid group [47]. A well-defined gallol-containing block copolymer, polytrihydroxystyrene-*b*-polystyrene (PTHS-*b*-PS), has been prepared using a combination of RAFT polymerization and subsequent deprotection (Fig. 4b) [48]. In another example, trimethoxystyrene (TMOS) is first polymerized to polytrimethoxystyrene (PTMOS) using RAFT techniques, and the resulting PTMOS serves as a macro-CTA for the preparation of PTMOS-*b*-PS. Subsequent demethylation of the methoxy groups in PTMOS using boron tribromide yields PTMOS-*b*-PS, efficiently converting the protected methoxyl groups to hydroxyl groups.

The application of ATRP to synthesize phenolic-containing polymers can be challenging because phenolic groups readily coordinate with the transition metal in the catalysts, thereby disrupting controlled polymerization [49]. To prevent this interference, phenolic protection strategies have been employed to suppress possible catalyst–substrate interactions and enable efficient ATRP. For example, a zwitterionic polymer bearing adhesive catechol units has been synthesized through ATRP of a zwitterionic monomer using dopamine-functionalized initiators with protected catechol groups, followed by post-polymerization deprotection (Fig. 4c) [50]. The catechol hydroxyls are first protected with *t*-butylchlorodimethylsilane and subsequently coupled with bromoisobutyryl bromide to yield the ATRP initiator. Then, zwitterionic monomers (i.e., sulfobetaine methacrylate) are polymerized via ATRP, and the *t*-butylchlorodimethylsilane groups in the resulting polymers are removed by hydrolysis to recover the adhesive properties of the catechol groups. Despite the concern about the retardation effect of phenolic groups on ATRP via radical scavenging and aryloxy radical generation [32,33], a range of acrylamides and acrylates have been homo-polymerized or block copolymerized directly from an unprotected dopamine-functionalized initiator using copper-mediated radical polymerization, thus producing polymers with narrower molecular weight distributions ($M_w/M_n < 1.2$) at high or full conversion rates [31]. Surface-initiated ATRP has enabled the preparation of well-defined polyphenol-functionalized polymers without phenolic protection (Fig. 4d) [51]. An ATRP initiator is first immobilized on glass and silicon substrates using microcontact printing through a triazolinedione click reaction [52]. Copolymerization of phenylboronic acid acrylate or catechol acrylamide with hydroxyethyl acrylate results in two different polymer brushes on the surfaces. Leveraging the dynamic covalent interactions between phenylboronic acid and catechol, these brushes have

been used to fabricate a reversible, water-resistant supramolecular adhesive. Catechol-terminated copolymers of di(ethylene glycol) methyl ether methacrylate and poly(ethylene glycol) methyl ether methacrylate have been synthesized via ATRP using an unprotected catechol-functionalized initiator [53]. These polymers are then anchored to magnetic nanoparticles via ligand exchange, effectively mimicking a "grafting-to" approach.

### 2.4. Post-modification of preformed polymers

Chemical conjugation of phenolics onto preformed polymers is a widely used strategy for preparing polyphenol-functionalized polymers [2,31]. Synthetic polymers and naturally occurring biopolymers possess functionalities, such as amine ($-NH_2$), carboxylic acid (–COOH), aldehyde (–CHO), and hydroxyl (–OH) groups, which are readily introduced into polymer chains using well-established synthetic protocols.

Phenolic moieties have been conjugated to the terminal or repeating groups of synthetic polymers with controllable properties, such as architecture, charge, molecular weight, and diverse functionalities. For example, the hydrophilic, biocompatible, and low-fouling polyethylene glycol (PEG) with linear or branched structures has been conjugated to dopamine into the end-functional groups of polymer chains through amide formation [54,55]. Phenolic carboxylic acid small molecules are known to form through self-condensation between phenol hydroxyl and carboxylic acid groups, which can reduce coupling efficiency between phenolics and polymers [56–58]. To circumvent potential side reactions, successive steps containing protection and conjugation methods have been employed to generate caffeic acid-functionalized PEG building blocks with different architectures and molecular weights (Fig. 5a-i) [16]. Alkyl chloroformates provide a versatile route to both protect the hydroxyl groups and activate the carboxylic acid of caffeic acid, yielding a caffeic acid–carbonic anhydride. The resulting activated derivative (i.e., caffeic acid–carbonic anhydride) is conjugated to end-functional PEG-amines of varying architectures (i.e., 2-, 4-, 8-arm) and molecular weights (2.5–20 kDa) to produce a series of protected PEG-caffeamide building blocks. In the subsequent step, carbonate-protected hydroxyl groups are deprotected by a low molecular weight amine isopropyl amine, thereby yielding PEG–caffeamide conjugates. In addition to amide bond formation, esterification reactions between hydroxyl and carboxylic acid groups have been used to synthesize catechol-functionalized ethoxylated polyethylenimine [59]. Functionalization with phenolic moieties has been extended to a variety of functional polymer systems, broadening the scope of polyphenol-functionalized polymers. A range of biscatechol-functionalized polymers (biscatechol-polymers) with tunable hydrophobicity and charge have been synthesized via RAFT polymerization, followed by amide bond coupling [60,61]. To achieve this, a biscarboxylic acid-terminated trithiocarbonate CTA, bis($\alpha$,$\alpha'$-dimethyl-$\alpha''$-acetic acid)-trithiocarbonate, is synthesized [62]. Hydrophobic monomers (i.e., BA and methyl acrylate (MA)), exhibiting different hydrophobicity BA > MA, are polymerized through RAFT using bis($\alpha$,$\alpha'$-dimethyl-$\alpha''$-acetic acid)-trithiocarbonate to yield $\alpha$,$\omega$-biscarboxylic acid-functionalized polymers. The resulting polymers are then transformed to biscatechol-polymers through amide coupling with dopamine (Fig. 5a-ii) [60]. The hexafluorophosphate azabenzotriazole tetramethyl uronium-mediated coupling is performed at a high polymer-to-dopamine molar ratio (i.e., 1:10) to achieve a 100% coupling efficiency. The synthesized biscatechol-functionalized hydrophobic polymers are purified by repeated precipitation (three cycles), followed by dialysis for 2 days. It is worth noting that the dialysis process should be performed in acidic water (adjusted to pH 4) to prevent undesirable self-polymerization of residual dopamine [63]. Biscatechol-functionalized pyridine-based polymer chains (e.g., poly(2-vinylpyridine) (P2VP)) have been prepared using similar synthetic methods [61]. The prepared polymers display tunable charge properties owing to the basicity of the pyridine ring ($pK_a$ of pyridinium ion = 5.23) [64] and transformation to permanent polycations through quaternization with alky halides (e.g., methyl iodide) [64].

Naturally occurring polymers, such as chitosan, alginate, hyaluronic acid (HA), collagen, and gelatin, have been coupled with phenolic molecules to yield biocompatible polyphenol-functionalized polymers. To synthesize catechol-functionalized chitosan, highly deacetylated chitosan (>90%) is conjugated with 3,4-dihydroxyhydrocinnamic acid via *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide (EDC)-mediated activation of the phenolic carboxyl groups, followed by coupling to the amine groups of chitosan under acidic conditions (Fig. 5b-i) [65]. This standard EDC coupling has been widely applied to synthesize phenolic-conjugated chitosan, enabling the preparation of functional hydrogels [66] and thin films [67] with adhesive and biocompatible properties. Schiff base reaction between chitosan and 3,4-dihydroxybenzaladehyde has been employed to synthesize catechol-grafted chitosan [68]. Carboxylic acid-functionalized polysaccharides, such as HA and alginate, have been conjugated with amine-functionalized phenolic molecules (e.g., dopamine, 5-hydroxydopamine, gallic acid hydrazide) via amide bond formation [69–74]. For example, the carboxylic acid groups of HA are coupled to the amine groups of the phenolic moiety through carbodiimide coupling reaction with EDC and NHS chemistry in an aqueous buffer at pH 6 (Fig. 5b-ii). Likewise, collagen and gelatin, which intrinsically contain both amine and carboxylic acid groups, have been modified by analogous EDC/NHS and Schiff base strategies to synthesize polyphenol-functionalized derivatives [75–77].

The synthesis of polyphenol-functionalized polymers has advanced considerably through the development of ring-opening polymerization, radical polymerization, controlled/living radical polymerization, and post-polymerization modification strategies. However, the chemical diversity of both polyphenol and polymer building blocks remain limited. Most reported systems rely on a small number of commercially available phenolic molecules, such as dopamine, gallic acid, and caffeic acid, despite the structural diversity of naturally occurring polyphenols. Likewise, the polymer components are largely restricted to a relatively small library of synthetic and naturally derived polymers with well-established chemistries. Expanding the diversity of both polyphenol moieties and functional polymer architectures will provide new opportunities to tailor intermolecular interactions, assembly behaviors, and physicochemical properties, thereby significantly broadening the design space of polyphenol-functionalized polymers.

## 3. Engineering nanostructured materials through assembly interactions of polyphenol-functionalized polymers

Polyphenols exhibit diverse and robust interaction properties that are conferred by the catechol and gallol moieties [78]. These phenolic groups enable a range of covalent processes, including oxidation-mediated reactions, cross-linking reactions, and dynamic boronate–phenolic complexations. Additionally, these moieties display multiple noncovalent interactions such as hydrogen bonding, metal coordination, hydrophobic interactions, ionic interactions, and $\pi$ interactions. Synthetic and natural polymers possess diverse functionalities such as carboxyl (–COOH), amine ($-NH_2$), alkyl ($-C_nH_{2n+2}$), aromatic ($-C_nH_n$), and ether (–O–) groups, facilitating noncovalent interactions during the assembly process. Consequently, polyphenol-functionalized polymers, integrating the dynamic chemistries of polyphenols and the structural diversity of polymer chains, are versatile building blocks for engineering assembled structures with desired physicochemical proper-

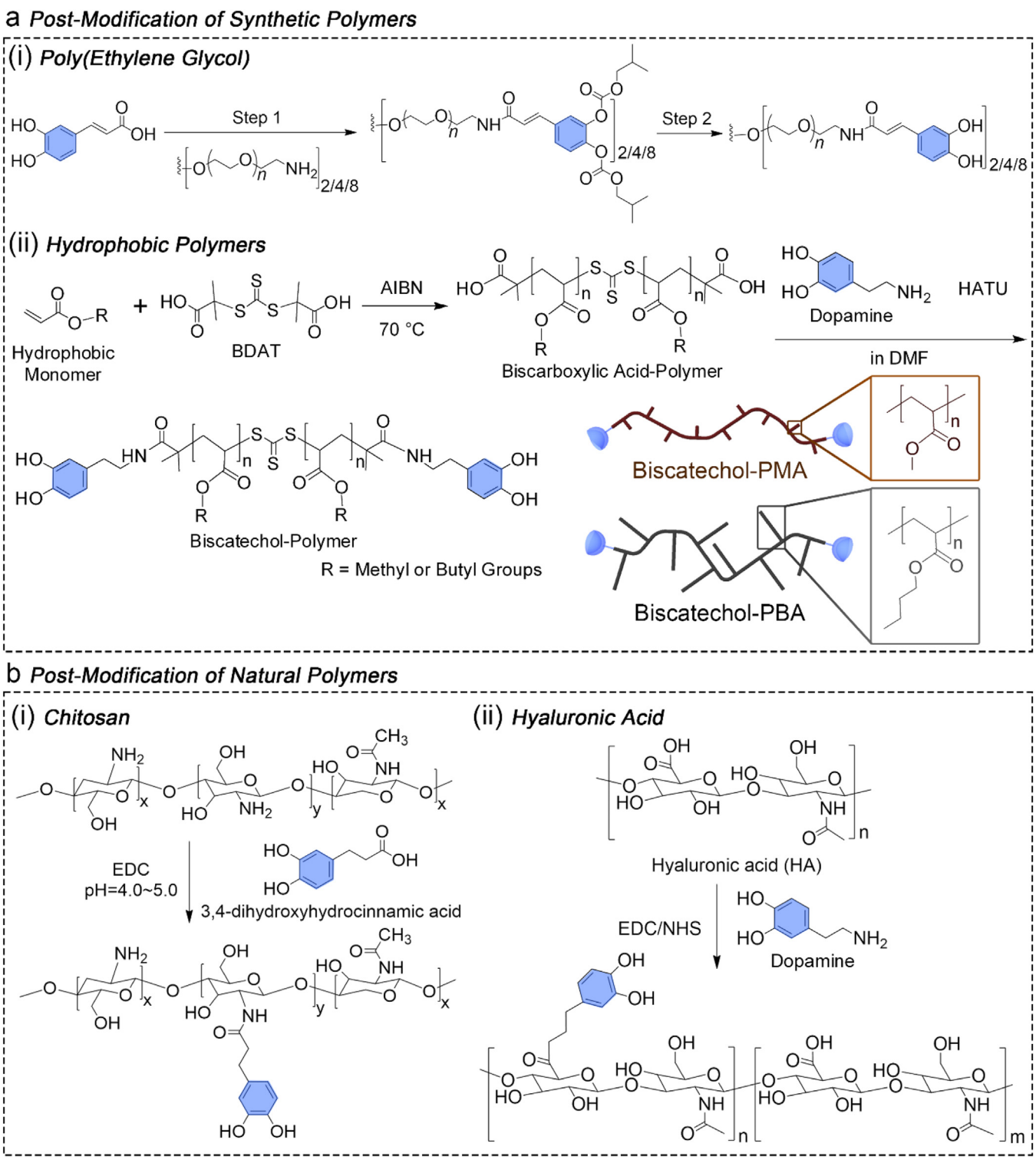


**Fig. 5.** Post-modification of preformed polymers for the preparation of polyphenol-functionalized polymers. (a-i) Synthesis of 2-, 4-, and 8-arm catechol-functionalized PEG derivatives (PEG–caffeamides) via the caffeic acid carbonic anhydride coupling method [16], Copyright 2021. Adapted with permission from the American Chemical Society. (a-ii) Synthetic routes for preparing biscatechol-functionalized hydrophobic polymers (i.e., biscatechol-poly(methyl acrylate) (biscatechol-PMA) and biscatechol-poly(butyl acrylate) (biscatechol-PBA)) [60], Copyright 2023 Kim *et al*. Adapted with permission from Wiley-VCH GmbH. (b) Synthesis of catechol-functionalized chitosan (i) and HA (ii) [65], Copyright 2022. Adapted with permission from The Royal Society of Chemistry [70], Copyright 2013. Adapted with permission from Wiley-VCH GmbH & Co. KGaA, Weinheim. BDAT, bis($\alpha$,$\alpha'$-dimethyl-$\alpha''$-acetic acid)-trithiocarbonate; HATU, hexafluorophosphate azabenzotriazole tetramethyl uronium.

ties. In this section, we focus on the hierarchical assembly behaviors driven by covalent and noncovalent interactions of polyphenol groups and polymer chains (Fig. 6), highlighting coordination with metal ions, complexation with small molecules and macromolecules, and integration with nano/microstructures.

### 3.1. Covalent interactions

Oxidative coupling among phenolic groups (i.e., catechol, gallol) can be initiated by oxidizing agents, elevated pH or temperature, or enzymatic catalysis, resulting in the formation of covalent linkages

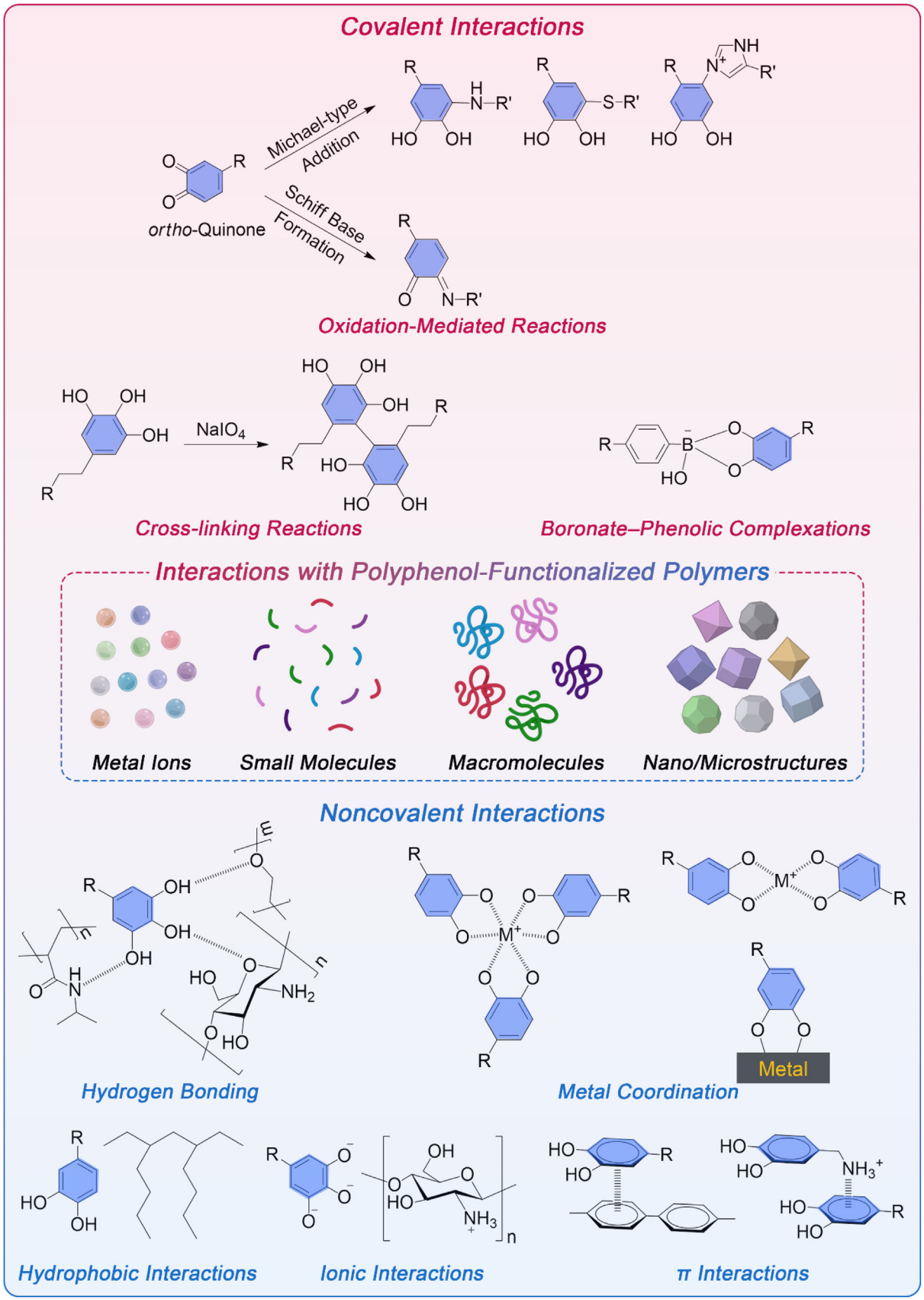


**Fig. 6.** Covalent and noncovalent interactions governing the assembly of polyphenol-functionalized polymers into nanostructured materials.

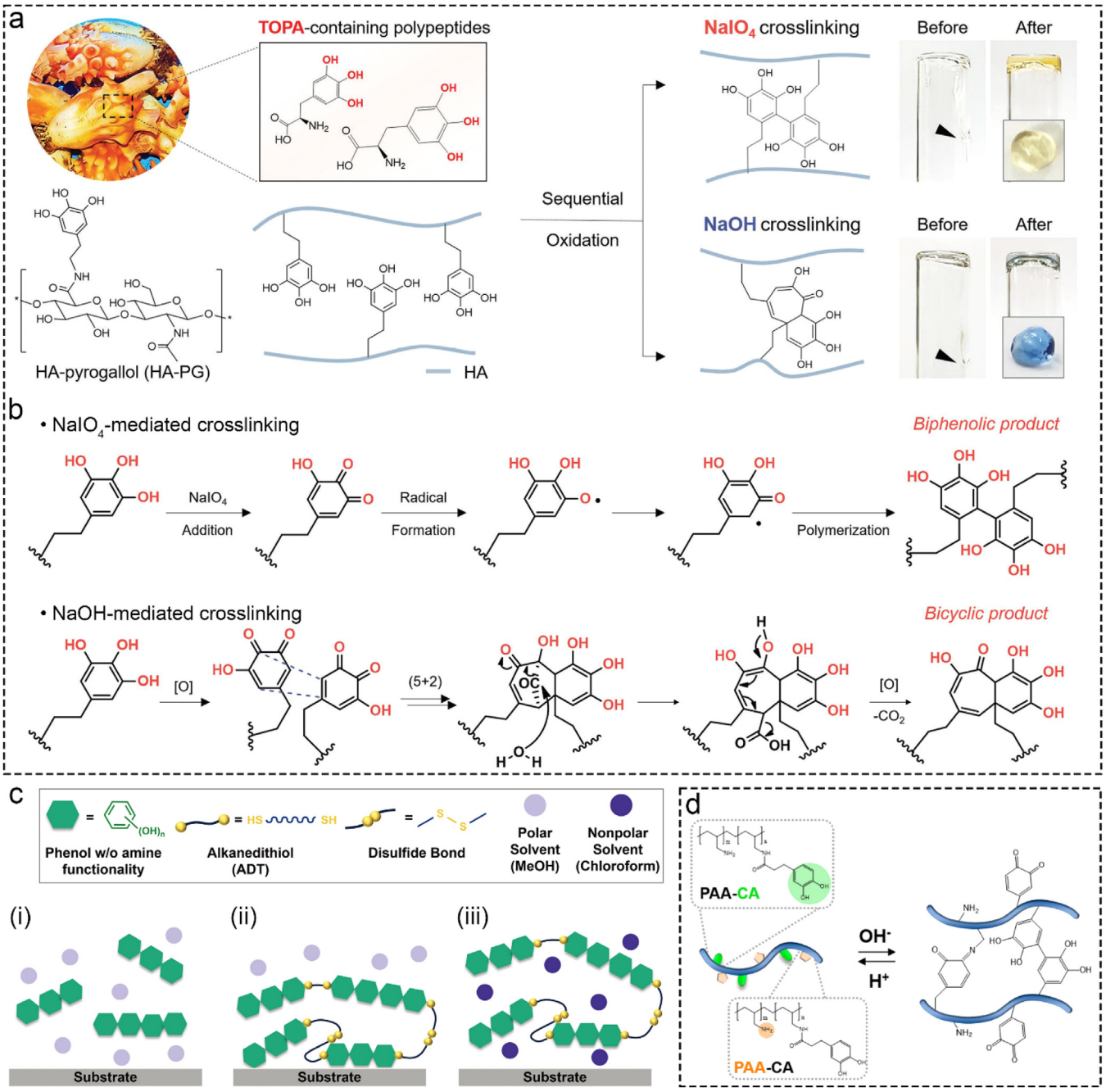


**Fig. 7.** Covalent interactions derived from polyphenol-functionalized polymers. (a) Synthesis of HA–PG conjugates and hydrogel formation via $NaIO_4$- or NaOH-induced crosslinking, yielding yellowish and blue constructs, respectively. (b) Proposed oxidative coupling mechanisms for HA–PG hydrogel formation under $NaIO_4$ or NaOH conditions [74], Copyright 2017. Adapted with permission from Wiley-VCH GmbH & Co. KGaA, Weinheim. (c) Illustration of binding mechanism of polyphenol-alkanedithiol (ADT) copolymers: (i) solubilized phenolic oligomer in polar solvents, (ii) hydrophobic nature of the ADT linker causes the copolymer to reach its solubility limit in polar solvent, and (iii) solubilized copolymer films in nonpolar solvent [79], Copyright 2024 Lim *et al.* Adapted with permission from Wiley-VCH GmbH. (d) Preparation of polyallylamine–hydrocaffeic acid (PAA–CA) hydrogels through dynamic imine bond formation via Schiff base reaction [80], Copyright 2021. Adapted with permission from the American Chemical Society. TOPA, 3,4,5-trihydroxyphenylalanine.

that stabilize polymeric polyphenolic assemblies [7]. Polyphenol-functionalized polymers have similarly been employed to generate robust assembled structures via oxidative coupling reactions. For example, HA-conjugated pyrogallol (HA–PG) building blocks have been exploited to develop bioinspired hydrogel systems (Fig. 7a) [74]. The HA–PG conjugates are cross-linked through two distinct oxidative pathways employing either sodium periodate ($NaIO_4$) or sodium hydroxide (NaOH). These oxidation routes promote covalent coupling among phenolic groups, leading to the formation of robust hydrogel networks with distinct molecular architectures. The $NaIO_4$-mediated oxidation results in a yellowish hydrogel that is obtained via the generation of biphenolic coupling products. In contrast, oxidation under alkaline conditions with NaOH results in the formation of blue hydrogels, attributed to the development of bicyclic oxidation products (Fig. 7b). The contrasting coloration and network structures reflect the mechanistic divergence between periodate-mediated and base-induced oxidation of phenolic moieties.

The phenolic groups in polyphenols can react with nucleophilic functional groups (e.g., –SH, $-NH_2$) through Michael ad-

dition and/or Schiff base reaction, thereby introducing additional covalent linkages with functional materials. A sequential self-polymerization approach integrating phenolic compounds with alkanedithiol (ADT) cross-linkers has been established as a robust and generalizable method for surface-independent coating and functionalization (Fig. 7c) [79]. The copolymerization process encompasses three primary reactions: (i) oxidative self-polymerization of the phenolic component, (ii) self-polymerization of the dithiol, and (iii) thiol–phenol Michael addition, all of which occur under similar mildly basic conditions. This strategy has been successfully applied to a range of phenolic monomers, such as dopamine, 3,4-dihydroxybenzylamine, 4-ethylcatechol, levodopa, tannic acid, caffeic acid, and 3,4-dihydroxybenzylaldehyde, demonstrating the versatility of the approach. Catechol-bearing polyallylamine–hydrocaffeic acid conjugates are first synthesized to introduce phenolic functionality along the polyallylamine backbone (Fig. 7d) [80]. Hydrogel formation is then achieved through simple pH modulation, which promotes reversible imine bond formation via a Schiff base reaction between amine and aldehyde groups. In addition to these dominant dynamic covalent interactions, catechol–catechol coupling forms as a secondary cross-linking mechanism, further reinforcing the three-dimensional (3D) polymer network. Boronate–phenolic complexation has also been explored. For example, a catechol-functionalized copolymer was employed to conjugate the chemotherapeutic drug bortezomib into polymeric nanogels through boronate–phenolic complex formation [81]. The resulting nanocomplexes exhibited stability under physiological conditions, effectively suppressing drug leakage, while enabling triggered drug release in response to elevated glutathione level at target sites.

### 3.2. Noncovalent interactions: metal ions

Phenolic groups (i.e., catechol, gallol) in polyphenols readily coordinate with metal ions, forming mono-, bis-, or tris-type complexes [14]. The stoichiometry of these complexes is determined by environmental and chemical factors, including pH, metal valency, and the molar ratio of metal ions to phenolic groups. Polyphenol-functionalized polymers featuring diverse architectures and functional groups have been synthesized to exploit these coordination interactions for a broad range of applications. The mechanical performance of polymeric materials is commonly constrained by an intrinsic trade-off between stiffness and extensibility: increasing cross-linking generally improves strength but reduces ductility [82]. Inspired by polyphenol–metal coordination, this limitation has been addressed by introducing sacrificial and reversible iron–catechol networks into a dry and amorphous epoxy networks (Fig. 8a) [83]. A high-catechol-content network (~14 mol% of starting constitutive units) was synthesized from a short-chain bisepoxide [poly(ethylene glycol) diglycidyl ether], a triethylsilyl-protected catechol monoepoxide, and a tetrafunctional diamine cross-linker (1,4-diaminobutane), followed by iron treatment to establish reversible Fe–catechol linkages. As shown in the stress–strain curves (Fig. 8a-i), deprotection of the catechol groups increases the elastic modulus from 0.24 to 0.45 MPa through catechol-mediated reversible hydrogen bonding, whereas subsequent Fe–catechol coordination further increases the elastic modulus to 184 MPa while preserving the maximum extensibility of the network. The Fe-treated network also exhibits strain–rate-dependent mechanical behavior (Fig. 8a-ii). The resulting Fe-containing network displays enhanced mechanical properties, with increases in stiffness, tensile strength, and toughness compared to the Fe-free precursor, while preserving extensibility and enabling recoverable hysteretic energy dissipation. Inspired by the combination of hardness and extensibility characteristic of mussel byssal thread cuticles [84], 3,4-dihydroxyphenylalanine (DOPA)-modified PEG (PEG-$DOPA_4$) has been used to prepare polymer gels through catechol-$Fe^{III}$ interpolymer cross-linking [85]. In a related approach, biocompatible alginate films have been fabricated through a spin-coating-assisted deposition process, in which catechol-functionalized alginate is coated onto polydopamine (PDA)-modified substrates and subsequently cross-linked via $Fe^{III}$–catechol complexation [86]. Furthermore, the formation of coordination networks between polyphenols and metal ions has enabled the development of a rapid and broadly applicable method for engineering supramolecular assemblies, termed metal–phenolic networks (MPNs) [14]. The use of MPNs has gained prominence as a versatile platform for engineering particle systems through the deposition of metal–phenolic assemblies onto diverse substrates. The physicochemical properties of MPN particles, including permeability [87], endosomal escape [88], and temperature-induced structural rearrangement [89], are influenced by the selection of phenolic ligands (e.g., PG, tannic acid, gallic acid, and quercetin). Expanding the library of synthetic phenolic building blocks, particularly polyphenol-functionalized polymers, beyond commercially available compounds is therefore expected to yield MPN systems with enhanced diversity in structure and function. In this context, MPN capsules with controllable properties—including shell thickness, permeability, and cell association—have been fabricated using catechol-functionalized PEG blocks with varying architectures and molecular weights [16]. Additionally, programmable MPN particle systems capable of complementary DNA hybridization have been prepared using catechol-functionalized DNA block copolymers (DBCs) [47]. Thermoresponsive MPN capsules have been fabricated using $Fe^{III}$ ions and PNIPAM (Fig. 8b) [45]. Phenolic groups are known to coordinate with a wide range of metal ions, and the physicochemical MPN structures can be tuned through the choice of the metal ions used in the assembly [90,91]. To investigate the influence of metal ion on the thermoresponsive properties of PNIPAM–metal ion MPN capsules, biscatechol-PNIPAM was coordinated with 18 different metal ions: $Al^{III}$, $V^{III}$, $Cr^{III}$, $Mn^{II}$, $Fe^{III}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$, $Zn^{II}$, $Zr^{IV}$, $Mo^{II}$, $Rh^{III}$, $Ag^{I}$, $Cd^{II}$, $Ce^{III}$, $Eu^{III}$, $Gd^{III}$, and $Tb^{III}$ (Fig. 8c) [45]. The metal ion type strongly influenced both the mechanical and thermoresponsive properties of the capsules. For example, $Al^{III}$-based capsules, characterized by lower stiffness, underwent substantial temperature-induced size contraction (~63%), whereas $Tb^{III}$-based capsules, possessing higher stiffness, exhibited minimal size reduction (<1%). Catechol-functionalized hydrogels have been prepared through the copolymerization of DMA and *N*-hydroxyethyl acrylamide and subsequently incubated in borate buffer to temporally protect the catechol side chain [92]. Localized incorporation of $Fe^{III}$ ions into the resulting hydrogel is achieved by applying an electric potential using an iron electrode as the anode and an aluminum foil as the cathode (Fig. 8d). Iron is oxidized upon the application of the electric potential and released as $Fe^{III}$ ions, which are subsequently captured by the catechol side chains, generating localized dark-colored regions within the hydrogel network. Exposure of the hydrogel to basic conditions induces bending, as tris-complex formation increases local cross-linking density. Conversely, incubation under acidic conditions restores the hydrogel to its original shape through conversion to mono-complex formation with reduced cross-linking density (Fig. 8d). Polyphenol-functionalized polymers can coordinate metal ions through multiple interaction sites along their functional polymer chains. For example, poly(vinylpyridine)s, including the structural isomers P2VP and poly(4-vinylpyridine), bind metal ions via coordination to the pyridinyl nitrogen atoms [93,94]. Biscatechol-functionalized P2VP (biscatechol-P2VP) chains have been used as MPN building blocks to construct functional assemblies (i.e., P2VP–metal MPN capsules) [61]. Conventional MPN assembly generally affords films with a thickness of approximately 10 nm, irrespective of the type of metal ion or phenolic ligand, as a result of kinetically trapped, symmetry-

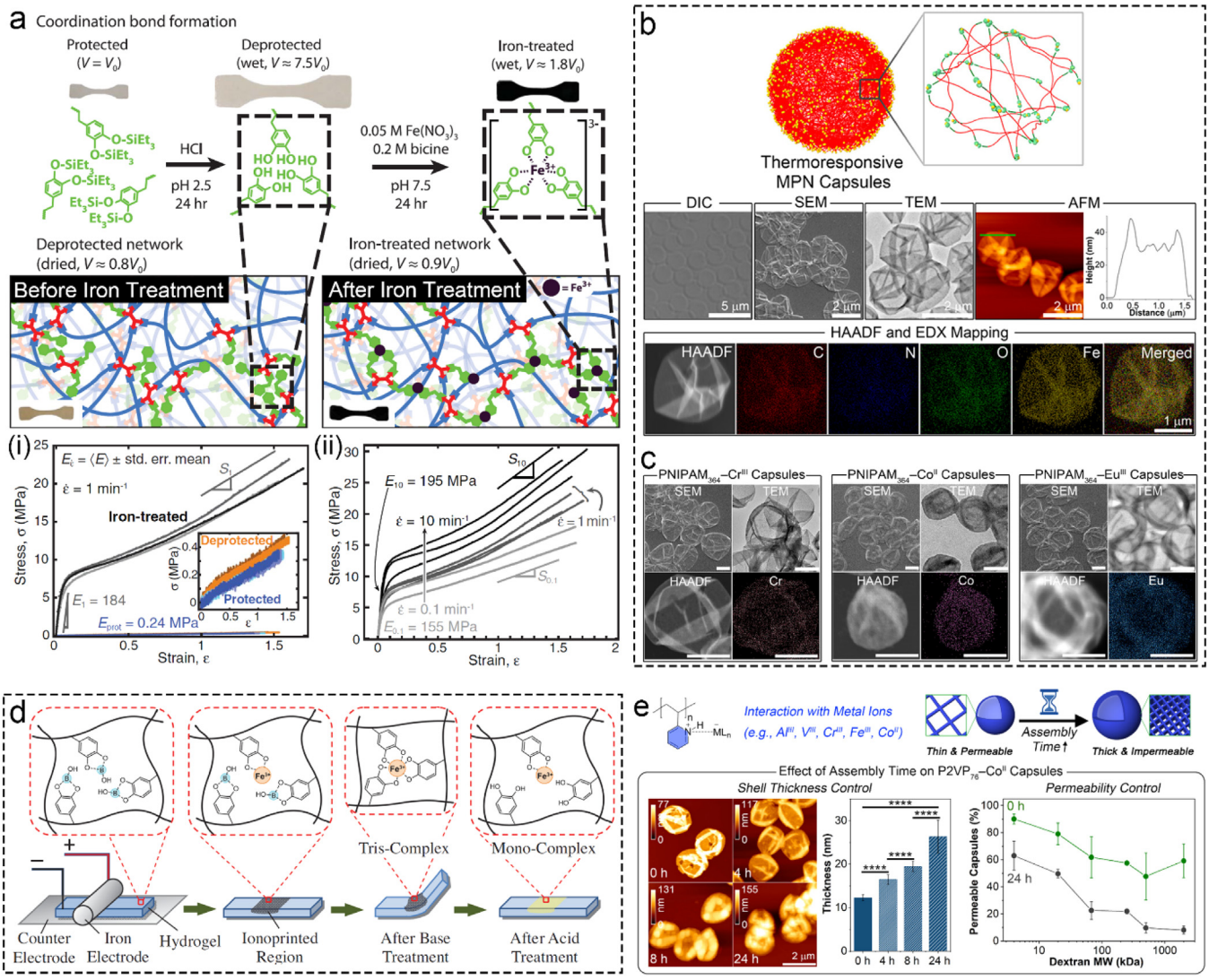


**Fig. 8.** Interactions of polyphenol-functionalized polymers with metal ions. (a) Cleavage of silyl protecting groups followed by $Fe^{III}$ complexation, leading to specimen swelling and evolution from mono- to tris-complexed network structures. (i) Engineering stress–strain relationship of protected (blue), deprotected (orange), and Fe-treated (gray) samples (strain rate, $\dot{\varepsilon} = 1\ min^{-1}$). (ii) Strain-rate dependence ($\dot{\varepsilon} = 0.1$, 1, and 10 $min^{-1}$) of Fe-treated samples [83], Copyright 2017. Adapted with permission from The American Association for the Advancement of Science. (b) Fabrication of thermoresponsive MPN capsules via coordination between $Fe^{III}$ ions and biscatechol–PNIPAM. (c) Coordination of biscatechol–PNIPAM with diverse metal ions. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-angle annular dark-field (HAADF), and energy-dispersive X-ray spectroscopy (EDX) elemental mapping of $PNIPAM_{364}–Cr^{III}$, $PNIPAM_{364}–Co^{II}$, and $PNIPAM_{364}–Eu^{III}$ MPN capsules. Scale bars are 1 $\mu$m [45], Copyright 2022. Adapted with permission from the American Chemical Society. (d) Iron electrode contact with DMA-containing hydrogel enabling electrochemical displacement of borate protecting groups (blue) and ionoprinting of $Fe^{III}$ ions (orange) near the electrode–hydrogel interface [92], Copyright 2014. Adapted with permission from Wiley-VCH GmbH & Co. KGaA, Weinheim. (e) Coordination network between pyridinyl nitrogen sites in polymer chains and metal ions. Modulation of shell thickness and permeability of $P2VP_{76}–Co^{II}$ MPN capsules via assembly time [61], Copyright 2025. Reproduced with permission from the American Chemical Society. DIC, differential interference contrast; AFM, atomic force microscopy.

broken interfacial assembly occurring within a short deposition time (<1 min). In contrast, the dual coordination motifs, catechol–metal and pyridine–metal interactions, in the biscatechol-P2VP–metal ion systems facilitate continuous film growth with assembly time (Fig. 8e). Furthermore, the capsules prepared using longer assembly times are less permeable than those formed over shorter times, reflecting a higher degree of cross-linking in the thicker capsule shells.

### 3.3. Noncovalent interactions: small molecules and macromolecules

The catechol and gallol moieties characteristic of polyphenols facilitate a variety of noncovalent interactions such as hydrogen bonding, hydrophobic interactions, ionic interactions, and $\pi$ interactions. Polyphenols represent broadly compatible structural motifs for the rational design of functional materials across chemistry, materials science, and nanomedicine [78,95]. Similarly, functional groups (e.g., carboxyl (–COOH), amine ($–NH_2$), alkyl ($–C_nH_{2n+2}$), aromatic ($–C_nH_n$), and ether (–O–) groups) in synthetic and natural polymers allow them to engage in diverse types of intermolecular interactions. Consequently, polyphenol-functionalized polymers interact with broad molecules, ranging from small molecules (e.g., aromatic molecules) to macromolecules (e.g., polymers, polysaccharides, proteins, and oligonucleotides). For example, aromatic amino acid-based polymers containing either phenol (tyrosine) or catechol (DOPA) side chains were synthesized to investigate their drug-loading capabilities toward aromatic anticancer agents such as doxorubicin (DOX) and topotecan (TPT) [96]. The DOPA-containing polymers exhibit substantially higher loading efficiencies compared to their tyrosine analogues, which is attributed

to the formation of strong $\pi$-interactions between the catechol groups and the aromatic moieties of the drug molecules (Fig. 9a). These results highlight the essential role of catechol-mediated aromatic interactions in enhancing the molecular affinity and loading capacity of polymer assemblies. In nature, sandcastle worms build robust structures underwater using a combination of polyanionic peptides rich in O-phosphoserine and cationic peptides enriched with lysine and arginine [97]. Inspired by the chemical features of these natural cement proteins, Zhao et al. developed a bioinspired wet-contact adhesive using oppositely charged polyelectrolytes: catechol-functionalized poly(acrylic acid) (PAAcat) and quaternized chitosan ion-paired with bis(trifluoromethanesulphonyl)imide (QCS-Tf2N) (Fig. 9b) [98]. QCS-Tf2N and PAAcat are first dissolved in dimethyl sulfoxide (DMSO), which ensures that most acrylic acid groups (COOH) on PAAcat remain unionized. In organic solvents, which display lower dielectric constants ($\varepsilon$) than that of water, the ionization of weak polyelectrolytes is significantly suppressed, resulting in predominantly neutral PAAcat chains [99]. Subsequent solvent exchange from DMSO to water induces deprotonation of the carboxylic acid groups, generating negatively charged PAAcat chains that spontaneously form electrostatic complexes with the cationic QCS-Tf2N, thereby forming a water-resistant adhesive network (Fig. 9b).

Copolymers incorporating three types of phenolic groups with different numbers of hydroxyl groups—phenol (monodentate), catechol (bidentate), and gallol (tridentate)—were synthesized to systematically investigate their binding interactions [100]. Samples containing phenol exhibited negligible binding strength, reflecting the weak interaction of monohydroxyl phenolic units. The gallol-functionalized copolymers showed approximately 7-fold greater adhesive strength than the catechol-functionalized counterparts, indicating that the tridentate interactions from gallol groups offer a higher binding affinity than the bidentate interactions from catechol groups. In parallel, Shin and Lee explored the multifunctionality of gallol moieties in hydrogel systems and designed gallol-rich hydrogels using gallol-functionalized HA and gallol-rich oligomeric cross-linker (oligo-epigallocatechin gallate) (Fig. 9c) [101]. Upon mixing gallol-functionalized HA and oligo-epigallocatechin gallate, the gallol-rich hydrogels spontaneously form through extensive multivalent hydrogen bonding between gallol-to-gallol units and gallol-to-HA backbones. A DBC featuring hydrophobic and catechol-containing segments with programmable molecular recognition properties, DNA-*b*-poly(methyl methacrylate-*co*-2-methacryloylethyl dihydrocaffeate) (DNA-*b*-poly(MMA-*co*-DHCAF) was synthesized by coupling an amine-terminated DNA strand with a carboxylic acid-terminated catechol-functionalized copolymer [47]. Coordination between the catechol groups in DBC and multivalent metal ions, such as $Fe^{III}$, induces controlled assembly into uniform DBC–$Fe^{III}$ MPN particles and capsules with tunable sizes and a narrow size distribution (Fig. 9d). Beyond coordination networks, hydrogen bonding and hydrophobic interactions contribute to the assembly process, resulting in the structural integrity of the DBC assemblies under acidic, metal-chelating, and surfactant solutions. Collectively, these studies underscore how the integration of phenolic moieties into polymer chains enables precise control of intermolecular networks through the additional noncovalent interactions such as hydrogen bonding, metal coordination, hydrophobic interactions, ionic interactions, and $\pi$ interactions.

### 3.4. Noncovalent interactions: nano/microstructures

Catechol moieties adhere strongly to inorganic surfaces with a higher affinity than carboxylic acid groups via coordination interactions with metal ions [31,102]. Gallol, a trihydroxylated phenolic analogue of catechol, exhibits even stronger binding to inorganic substrates [100,103].

Accordingly, polyphenol-functionalized polymers have been widely used to modify nanoparticle surfaces, connect nanoparticle systems, align nanoparticles within templates, and fabricate hierarchical nanostructures. For instance, gallol-conjugated PEG has been employed to stabilize iron oxide nanoparticles via spontaneous assembly in aqueous media, driven by the high binding affinity of gallol toward iron oxide [104]. The resulting particles could be freeze-dried and redispersed without aggregation or corrosion, and further functionalized with bioactive ligands such as biotin, demonstrating facile secondary surface modification. Na et al. introduced multidentate catechol–PEG oligomers (OligoPEG–DOPA) incorporating two PEG side chains (i.e., PEG-$N_3$ and PEG–$OCH_3$) and dual metal-coordinating groups (i.e., catechol and carboxylic acid) (Fig. 10a-i) [105]. Ligand exchange of hydrophobic iron oxide nanoparticles with OligoPEG–DOPA proceeded efficiently, yielding nanoparticles that maintained excellent dispersibility across a broad pH range and under high ionic strength conditions. In a separate example, a multi-interaction ligand consisting of mPEG-grafted cationic hyperbranched polyethylenimine (PEI) and multivalent polyDOPA peptides was synthesized for surface functionalization of diverse nanoparticles (Fig. 10a-ii) [106]. This polymeric ligand stabilizes diverse metal (oxide) nanoparticles, including $Fe_3O_4$, MnO, and Au, through cooperative binding interactions involving catechol–metal coordination, amine chelation, and electrostatic interactions. The interaction of polyphenol-functionalized polymers with silicon nanoparticles has also been demonstrated for potential energy storage applications. Silicon has emerged as a promising anode material for lithium-ion batteries owing to its high theoretical capacity ($\sim$3580 mAh $g^{-1}$) and natural abundance [107]. However, the practical implementation of silicon-based anodes is limited by substantial volume expansion (>400%) and poor interfacial stability with conductive agents during electrochemical cycling [108]. To overcome these issues, a multifunctional polymeric binder composed of DMA, PEG monomethyl ether acrylate, and poly(ethylene glycol) diacrylate was synthesized to form a 3D cross-linked network (Fig. 10b) [109]. Each component provides a specific structural or functional contribution: (i) poly(ethylene glycol) diacrylate acts as a cross-linker to interconnect the polymer chains, imparting structural integrity and mechanical strength; (ii) DMA introduces catechol moieties that establish strong interfacial adhesion with silicon surfaces through hydrogen bonding or metal coordination with inorganic materials; and (iii) PEG monomethyl ether acrylate enhances the conductivity of $Li^+$ ions by transporting Li-ions along the polymer matrix. This synergistic integration of cross-linking, adhesion, and ionic conductivity yields a binder that effectively mitigates silicon expansion and improves cycling performance, underscoring the potential of polyphenol-functionalized polymers in energy storage systems. In addition to phenolic-mediated coordination, polymers bearing chelating groups such as pyridines can form strong interactions with inorganic nanoparticles [64]. For example, P2VP exhibits affinity toward nanoparticle surfaces through coordination between the pyridinyl nitrogen atoms and metal surfaces. This coordination behavior has been exploited to fabricate hierarchical assemblies, wherein P2VP–metal MPN capsules serve as core templates for assembling secondary superstructures (Fig. 10c) [61]. The exposed pyridinyl nitrogen on the surface of the capsules facilitates coordination with gold nanoparticles, resulting in the formation of hollow superstructures. A higher concentration of gold nanoparticles (AuNPs) yields hollow architectures with denser nanoparticle coatings on the capsule surface. Polymer-derived core–shell nanostructures have attracted considerable attention due to their tunable physicochemical properties (e.g., size, structure, and functionality) which can be tuned by varying the polymeric building blocks [110,111].

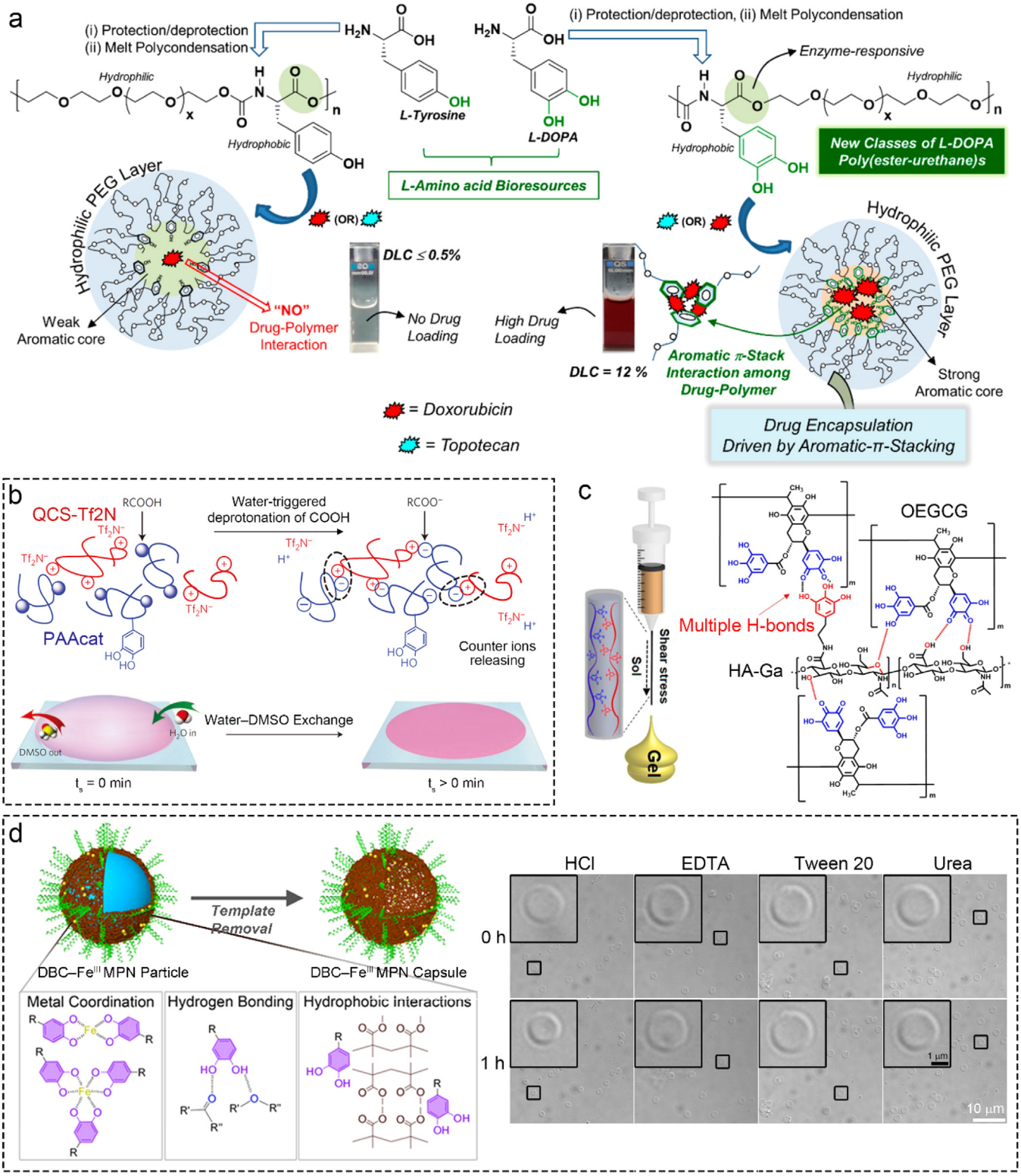


**Fig. 9.** Interactions of polyphenol-functionalized polymers with molecules. (a) Enhanced drug encapsulation through the aromatic $\pi$-stacking interactions of catechol-functionalized poly(ester-urethane)s [96], Copyright 2022. Adapted with permission from the American Chemical Society. (b) Solvent exchange between water and DMSO and subsequent ionic complexation between catechol-functionalized PAAcat and quaternized chitosan paired with QCS-Tf2N [98], Copyright 2016. Adapted with permission from Springer Nature Limited. (c) Fabrication of gallol-rich and shear-thinning hydrogels formed from gallol-tethered HA (HA-Ga) and a gallol-rich oligomeric cross-linker (oligo-epigallocatechin gallate, OEGCG) via multiple hydrogen bonds between gallol–gallol and gallol–HA moieties [101], Copyright 2017. Adapted with permission from the American Chemical Society. (d) Schematic representation of coordination-driven assembly between DBCs and $Fe^{III}$ ions, forming an MPN (Left). Stability investigation of DBC–$Fe^{III}$ MPN capsules in acidic (0.5 M HCl), metal-chelating (100 mM ethylenediaminetetraacetic acid (EDTA)), and surfactant (100 mM Tween 20, 100 mM Urea) environments (Right) [47], Copyright 2022. Adapted with permission from the American Chemical Society. DLC, drug loading content.

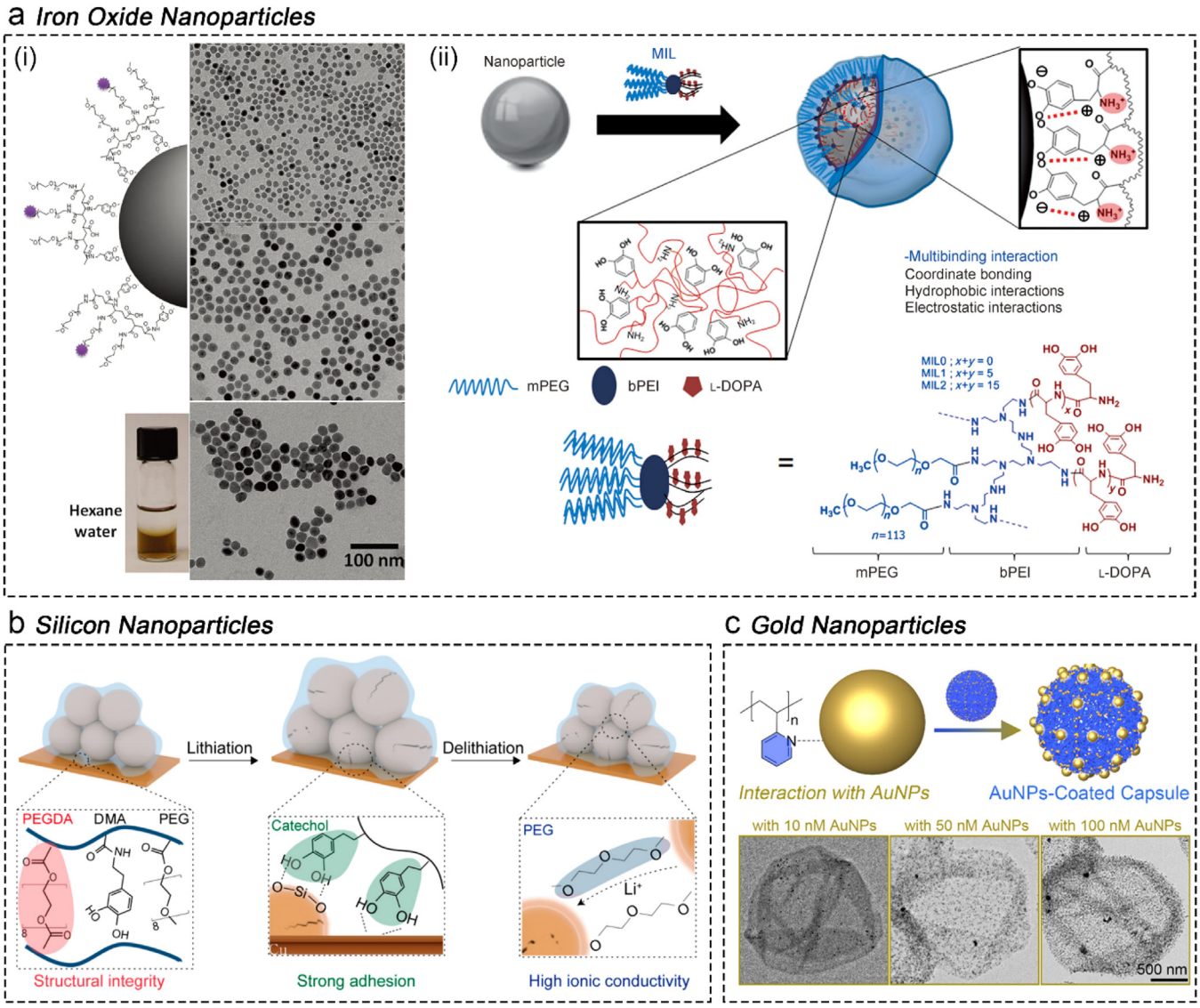


**Fig. 10.** Interactions of polyphenol-functionalized polymers with nanoparticles. (a) Iron oxide nanoparticles. (i) TEM images of OligoPEG-DOPA-functionalized $Fe_3O_4$ nanoparticles with core sizes of 11, 17, and 23 nm, and a photograph of an organic/aqueous dispersion of the particles [105], Copyright 2012. Adapted with permission from the American Chemical Society. (ii) Schematic representation of multi-interaction ligand stabilization leading to water-dispersible nanoparticles [106], Copyright 2011. Adapted with permission from Wiley-VCH GmbH & Co. KGaA, Weinheim. (b) Multifunctional polymeric binder composed of poly(ethylene glycol) diacrylate (PEGDA), DMA, and PEG monomethyl ether acrylate units, providing structural integrity through cross-linking, strong adhesion to silicon nanoparticles and current collectors, and enhanced ionic conductivity, respectively [109], Copyright 2022. Adapted with permission from the American Chemical Society. (c) Coordination-driven assembly of $P2VP_{76}$–$Fe^{III}$ MPN capsules (core) with Au nanoparticles (satellite) via interactions between pyridine moieties in the P2VP chains and AuNP surface, yielding hollow superstructures [61], Copyright 2025. Adapted with permission from the American Chemical Society. MIL, multiple-interaction ligand.

In addition to interacting with nanoparticles, polyphenol-functionalized polymers have been widely applied to modify the surfaces of low-dimensional materials, enabling the design of advanced hybrid materials with tailored properties. MXenes, an emerging class of 2D materials, have attracted attention as electrically conductive fillers that can form efficient charge transport pathways within hydrogel systems [112,113]. However, achieving MXene-based hydrogels with reliable sensing performance and long-term stability is challenging, as MXenes are prone to oxidative degradation in aqueous environments. The suppression of MXene oxidation has been demonstrated through the introduction of a catechol-functionalized poly(vinyl alcohol) (PVA-CA) in a hybrid hydrogel (PVA-CA-MXene hydrogel) (Fig. 11a) [114]. The PVA-CA polymer interacts with MXene nanosheets through noncovalent interactions, wherein the catechol groups form coordination networks with multivalent titanium ions, hydrogen bonding with -O and -F termini, and hydrophobic interactions with nanosheets [115]. These strong interactions effectively reduce oxidation-accessible sites on MXene surfaces, thereby inhibiting the oxidation of MXene in the hydrogel. In another example, the oxidative polymerization of dopamine has been used to deposit a nanoscale, conformal PDA coating on patterned aluminum nanoarrays (Fig. 11b) [116]. The resulting PDA layer provides a corrosion-resistant barrier for aluminum and serves as a matrix to immobilize organic photosensitizers within the localized surface plasmon resonance regions of aluminum nanostructures. This strategy allows the reliable use of aluminum plasmonic resonances in a highly corrosive photocatalytic redox environment and facilitates the nanoscale organization of photosensitizers on aluminum surfaces. Beyond the stabilization and functionalization of 2D and metallic surfaces, the interfacial versatility of polyphenols extends to the modular assembly of complex, 3D porous

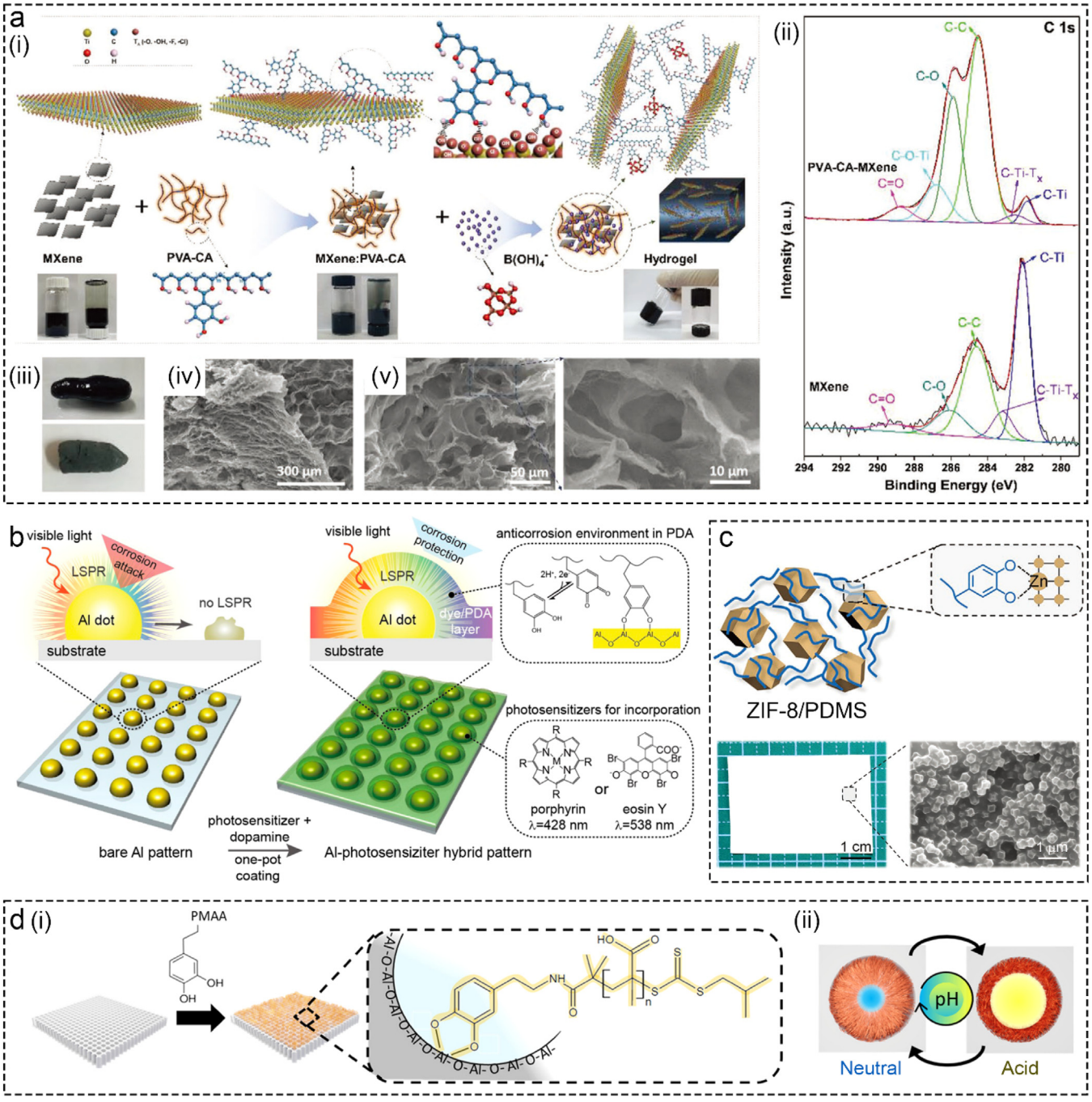


**Fig. 11.** Interactions of polyphenol-functionalized polymers with other nano/microstructured materials. (a) Preparation of PVA–CA–MXene hydrogel: (i) synthetic route; (ii) C1s X-ray photoelectron spectroscopy patterns of pristine MXene and PVA–CA–MXene; (iii) photographs of PVA–CA–MXene hydrogel before (top) and after (bottom) freeze-drying; (iv, v) field-emission SEM images of the freeze-dried network [114], Copyright 2023. Adapted with permission from Wiley-VCH GmbH. (b) Fabrication of aluminum nanoarrays for plasmonic-enhanced light harvesting, where a PDA coating immobilizes photosensitizers within localized plasmonic regions while preventing corrosion, enabling stable localized surface plasmon resonance (LSPR) [116], Copyright 2015. Adapted with permission from the American Chemical Society. (c) Coordination-assisted assembly of ZIF-8 frameworks with catechol-functionalized PDMS, yielding homogeneous and adherent ZIF-8/PDMS hybrid coatings [117], Copyright 2020. Adapted with permission from Wiley-VCH GmbH. (d) Functionalization of an alumina membrane with catechol-terminated PMAA. (i) Illustration of polymer adsorption onto the membrane surface through catechol–alumina coordination. (ii) Schematic representation of pH-responsive pore-size modulation via reversible contraction–extension of the polymer chains (blue and yellow correspond to neutral and acidic pH, respectively) [118], Copyright 2021. Adapted with permission from the American Chemical Society.

architectures. For example, a coordination-driven assembly strategy integrating metal–organic frameworks (MOFs) with catechol-functionalized polydimethylsiloxane (PDMS) polymers was developed to produce superhydrophobic and catalytically active hybrid nanoparticles (Fig. 11c) [117]. In this process, the catechol moieties of catechol-functionalized PDMS serve as versatile interfacial linkers, coordinating directly to the metal sites on the MOF surface while simultaneously engaging in noncovalent interactions with the underlying casting substrate, improving substrate adhesion to the MOF coating. This coordination-mediated assembly provides a generalizable strategy for constructing multifunctional MOF–polymer composites with tailored properties. Such phenolic coordination chemistries can be further leveraged to engineer stimuli-responsive systems through the attachment of responsive

polymer chains onto targeted substrates. For example, the surface of an alumina membrane was functionalized with a catechol-terminated poly(methacrylic acid) (PMAA) through coordination-driven interfacial assembly (Fig. 11d) [118]. The polymer chains at the membrane interface exhibit reversible conformational transitions between extended and globular states in response to environmental pH, thereby regulating the membrane pore size. When the pH exceeds the intrinsic $pK_a$ of PMAA (~5.8), the carboxylic acid groups become protonated, reducing electrostatic repulsion along the polymer backbone and causing the chains to adopt a globular conformation. This structural collapse corresponds to the open-pore state of the membrane, allowing enhanced permeability. In contrast, under acidic conditions, the deprotonated carboxylic acid groups induce electrostatic repulsion along the polymer backbone, extending the chains that reduce pore size.

The studies discussed in this section demonstrate that polyphenol-functionalized polymers provide a highly versatile platform for engineering hierarchical materials through diverse covalent, noncovalent, and coordination interactions. However, these interactions often operate cooperatively rather than independently, making it challenging to predict and precisely control the resulting assembly structures and functions. A deeper understanding of the mechanisms governing these interactions, together with strategies to selectively modulate their relative contributions, will be essential for the rational design of hierarchical materials with tailored physicochemical properties and application-specific functionalities.

## 4. Engineering physicochemical and biological properties of assembled materials through harnessing polymer functionality

Polyphenol-functionalized polymers serve not only as chemical building blocks but also as powerful design tools for tailoring the physicochemical properties of assembled materials. The integration of phenolic motifs into polymer backbones or side chains enables control over the properties of assemblies such as surface charge, hydrophilicity, crystallinity, and cross-linking dynamics, thereby dictating how these materials organize, interact, and perform under different environmental or biological conditions. In this section, we focus on how polymer-derived properties such as tunable charge, hydrophobicity/hydrophilicity balance, biocompatibility, targeting capability, and programmability can be harnessed to engineer the structural, mechanical, and interfacial behaviors of polyphenol-functionalized polymer assemblies. By exploring these structure–property relationships, this section provides a framework for understanding how polymer chemistry guides the transformation of polyphenol–polymer conjugates into functional materials with programmable physicochemical and biological performance.

### 4.1. Surface charge

Polyphenol-functionalized polymers have been engineered to present programmable surface charges—ranging from zwitterionic and pH-switchable to permanently cationic—thereby enabling precise control over antifouling behavior, biomolecular adsorption, and cell association. For example, biscatechol-functionalized P2VP was used to prepare MPN capsules exhibiting pH-dependent charge reversal properties (≈ −10 mV at pH 12 to +20 mV at pH 2) (Fig. 12a). The application of quaternization during assembly resulted in permanently cationic QP2VP/P2VP–$Fe^{III}$ capsules ($\zeta \approx$ 6–53 mV) with bioactive loading and controlled cell association capabilities depending on the surface charge of the capsules [61]. Zwitterionic designs have enabled the integration of catechol-mediated surface adhesion with hydration layer-based antifouling functionality. For instance, catechol-functionalized sulfobetaine coatings, deposited via pH-induced aggregation formation on a substrate, have demonstrated uniform immobilization on nitinol substrates and suppressed *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* attachment by nearly 100%, while maintaining near-neutral $\zeta$-potential [119]. Similarly, catechol/phosphorylcholine copolymers form thin (~10 nm) coatings on hydroxyapatite and significantly reduce adhesion of *E. coli* and *Streptococcus oralis* under oral-mimicked conditions, highlighting catechol anchoring and zwitterionic hydration as a robust charge-balanced antifouling strategy [120].

Positive charge can also be leveraged to enhance redox-active functions and the interfacial adhesion of polyphenol-functionalized polymers. For instance, Kord Forooshani et al. integrated catechol and hematin into microgels that generated •OH via $O_2 \rightarrow H_2O_2 \rightarrow$ •OH cascade, and showed that introducing quaternary ammonium comonomer markedly strengthened antimicrobial/antiviral activity through electrostatic attraction to negatively charged pathogens [121]. In another study, cationic polyallylamine–catechol hydrogels exemplified how amine protonation and catechol chemistry cooperate to deliver strong wet adhesion and self-healing via dynamic imine/ionic cross-links, underscoring the role of positive charge in interfacial mechanics under physiological conditions (Fig. 12b) [80].

The surface charge of polyphenol-functionalized polymer is a multifunctional design element that can be integrated with catechol-mediated adhesion, hydration-layer antifouling, redox activity, and dynamic cross-linking to tailor material performance. However, current strategies largely rely on empirical optimization, and systematic design principles for fine-tuning surface charge to precisely control material performance remain underdeveloped. Future research should focus on establishing quantitative structure–property relationships that correlate charge characteristics, including charge density, distribution, and responsiveness, with biological and interfacial outcomes, thereby enabling the rational design of application-specific polyphenol-functionalized polymer assemblies.

### 4.2. Hydrophilicity and hydrophobicity

Polyphenol-functionalized polymers have also been exploited to tune hydrophobicity and hydrophilicity across molecular, nano-, and supramolecular scales, thereby governing interfacial energy, self-assembly morphology, and material properties. In the context of surface engineering, Kang et al. have demonstrated that spontaneous oxidative deposition of dopamine results in an ultrathin, conformal PDA coating that converts superhydrophobic substrates (contact angle ≈ 158°) into hydrophilic substrates (≈ 37°) while enhancing adhesion [122]. This work established the fundamental concept that catechol-based surface layers can reset surface energy through strong interfacial adhesion and increased surface polarity. Building on this foundation, Hsueh and Chai incorporated 2-bromoisobutyryl-functionalized catechol initiators into PDA films to enable surface-initiated ATRP [123]. Grafting polymer brushes with different chemistries—hydrophilic or hydrophobic—afforded programmable control of surface wettability and interfacial reactivity, advancing catechol chemistry from passive adhesion toward active, tunable interface design.

At the molecular level, hydrophilicity–hydrophobicity balance has been shown to dictate polyphenol aggregation and solvation behavior. Polyphenol-containing fluoropolymers exhibit intermolecular aggregation of phenolic units in water, forming compact, hydrophobic assemblies that exclude solvent molecules [124]. Increasing the polarity of side chains, for example by grafting PEG, disrupts this aggregation and restores hydration, rendering the polymers water-dispersible. Distinct structure–property relationships between catechol exposure and surface wettability have been established using L-amino-acid-based poly(ester-urethane)s bearing either silyl-protected or deprotected DOPA units (PDOPA-Si-12,

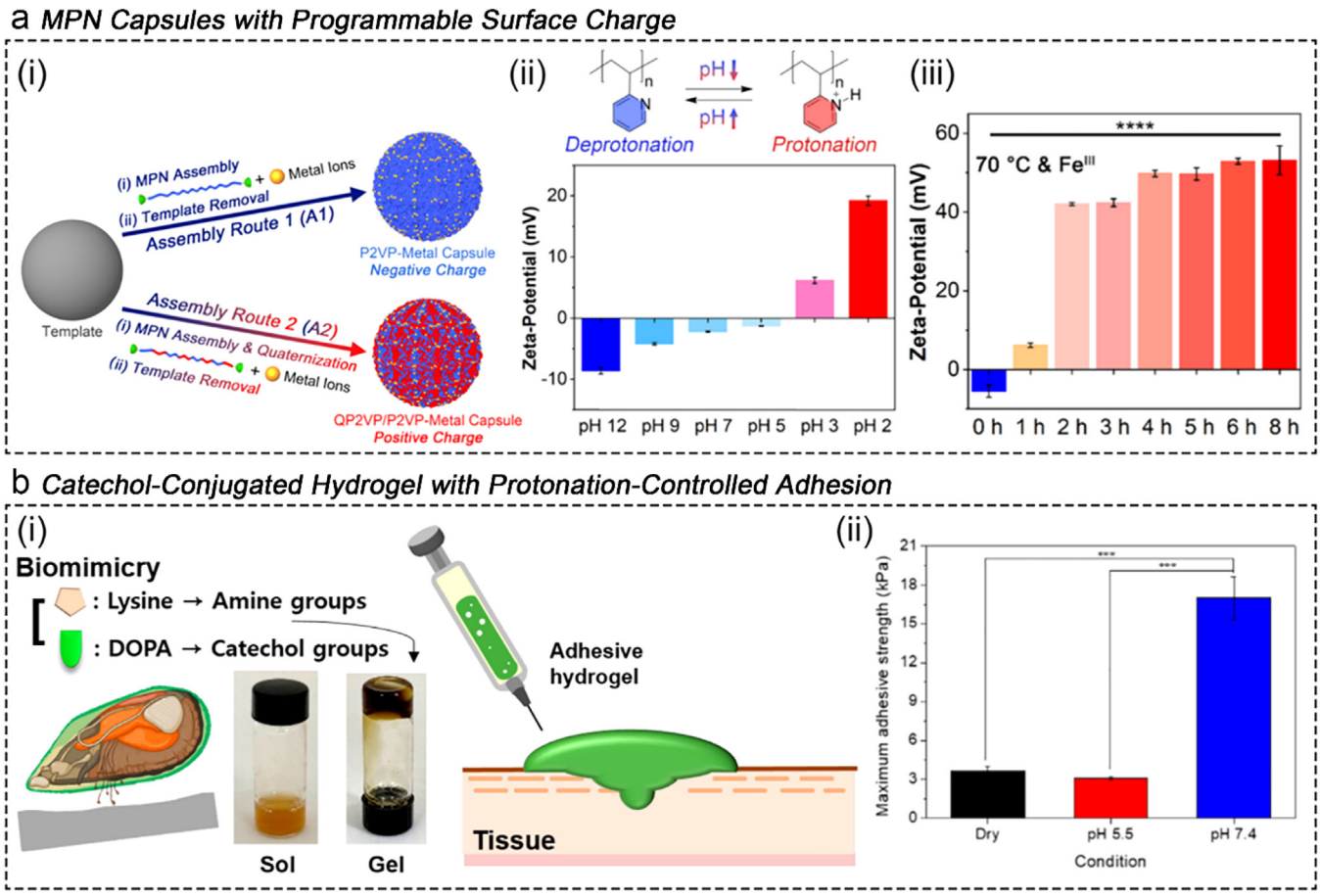


**Fig. 12.** Engineering polyphenol-functionalized polymers with tunable charge properties. (a) Supramolecular assembly of biscatechol-functionalized P2VP into MPN capsules with programmable surface charge. (i) Schematic of two assembly pathways generating negatively charged P2VP–metal and positively charged quaternized QP2VP/P2VP–metal capsules. (ii) Zeta-potential measurements of $P2VP_{76}$–$Fe^{III}$ MPN capsules showing reversible charge switching (−10 to +20 mV) via protonation–deprotonation. (iii) Time-dependent zeta-potential evolution of $QP2VP_m/P2VP_{76-m}$–$Fe^{III}$ MPN capsules at 70 °C, confirming stable charge modulation [61], Copyright 2025. Adapted with permission from the American Chemical Society. (b) Catechol-conjugated poly(allylamine) hydrogel with protonation-controlled adhesion. (i) Schematic illustration of biomimetic hydrogel design inspired by mussel adhesive proteins, showing catechol–amine synergy leading to sol–gel transition and strong tissue adhesion. (ii) Quantitative comparison of adhesive strength under dry, mildly acidic, and physiological conditions [80], Copyright 2021. Adapted with permission from the American Chemical Society.

PDOPA-12) with or without PEG side chains (PDOPA-Si-PEG-400, PDOPA-PEG-400) [96]. As shown in Fig. 13a, PDOPA-Si-12 films are compact and highly hydrophobic (water contact angle = 140°), whereas deprotected PDOPA-12 films are more open and moderately wettable (water contact angle = 81°). Incorporating PEG side chains reduces the contact angles of the PDOPA-Si-12 and PDOPA-12 films to 81° and 17°, respectively, yielding uniform, hydrated surfaces.

At the nanoscale, strong hydrophilic–hydrophobic contrast has been exploited to drive block copolymer microphase separation. Copolymer microphase separation is governed by the segregation strength ($\chi N$), where $\chi$ is the Flory–Huggins interaction parameter describing the incompatibility between the two polymer blocks and N is the degree of polymerization. Catechol-containing styrenic block copolymers, poly(3,4-dihydroxystyrene)-*block*-poly(4-trimethylsilylstyrene) (PDHS-*b*-PTMSS), exhibit a high $\chi$ value, enabling sufficiently high segregation strength even at low molecular weight, and thus undergo microphase separation into 8–10 nm lamellar or cylindrical morphologies [125]. The strong hydrophilicity of the catechol-rich PDHS block contrasts sharply with the hydrophobic, silicon-containing PTMSS segment, producing $\chi \approx 0.7$—over 20-fold higher than that of the benchmark poly(styrene)-*block*-poly(methyl methacrylate) (PS-*b*-PMMA, $\chi \approx 0.03$)—and enabling sub-10 nm pattern formation at a low molecular weight. This large hydrophilic–hydrophobic disparity not only drives nanoscale ordering but also allows post-assembly chemical transformation, as the PDHS domains coordinate metals while the PTMSS domains convert into silicon oxide ($SiO_x$) masks for nanolithography.

Extending hydrophobicity control to supramolecular assemblies, biscatechol-functionalized hydrophobic polymers (i.e., PMA and PBA) have been employed as building blocks for MPN assembly [60]. Biscatechol-PBA shows higher hydrophobicity than biscatechol-PMA, and increasing the hydrophobicity of the biscatechol-functionalized polymer results in a denser coordination network, yielding thicker (≈ 10–21 nm), stiffer (≈ 10–126 mN $m^{-1}$), and less permeable capsules. Hydrophobic interactions have also been employed in conjunction with metal–catechol coordination to tune film compactness, permeability, and particle–cell association, establishing hydrophobicity as a programmable structural parameter in MPNs (Fig. 13b). Lancelot et al. have shown that increasing the metal–phenol coordination density within catechol-containing polymer networks reduces the number of free hydroxyls, lowers surface polarity, and enhances both hydrophobicity and wet adhesion [126].

A key unresolved challenge in the field is to distinguish whether changes in material performance arise from polarity itself or from accompanying changes in phenolic reactivity and polymer organization. For example, PEGylation increases hydration but can also sterically shield phenolic ligands, deprotection

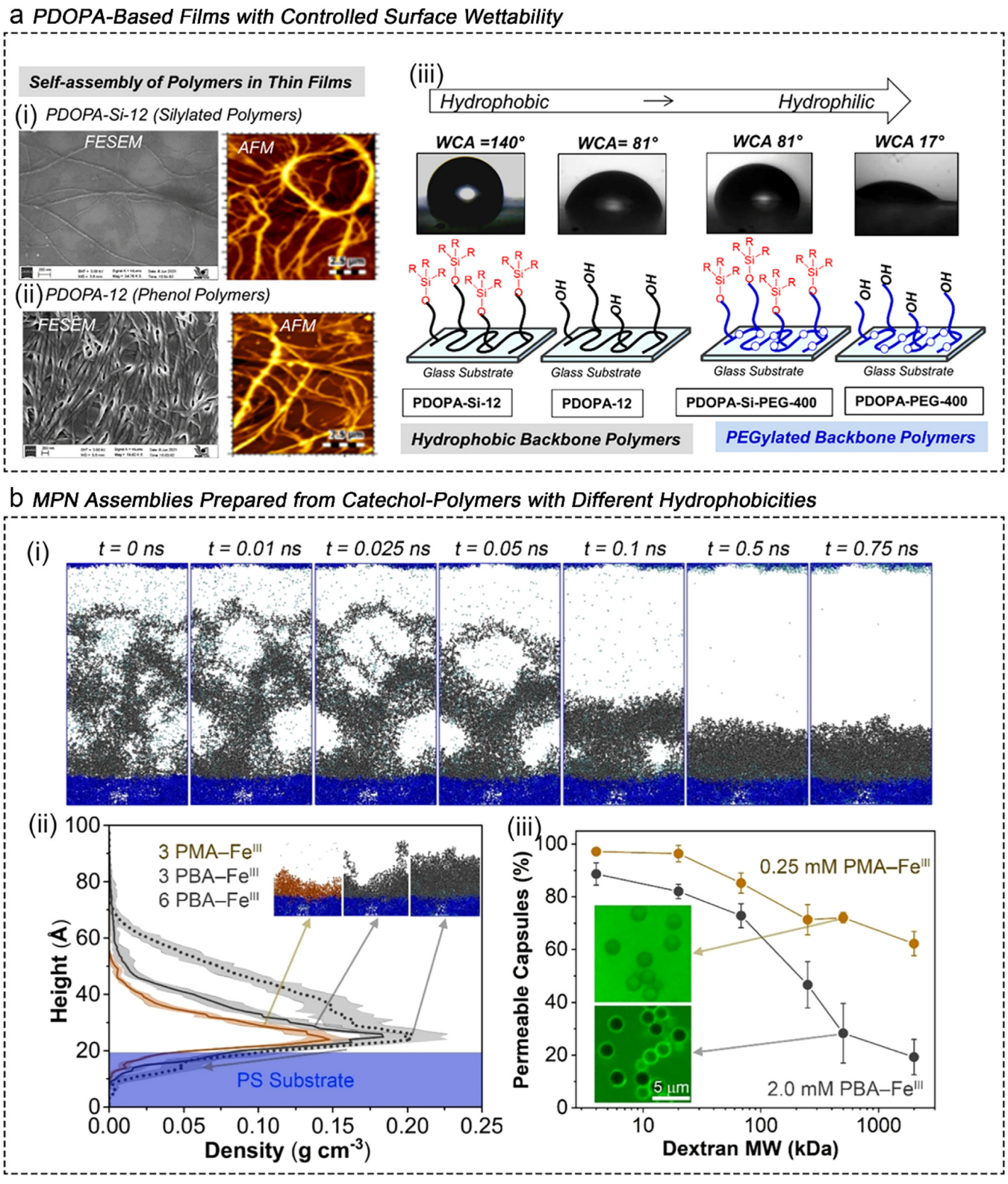


**Fig. 13.** Engineering polyphenol-functionalized polymers with tunable hydrophobicity properties. (a) Self-assembly and surface wettability control of catechol-functionalized polymers. Field-emission scanning electron microscopy (FESEM) and atomic force microscopy images of polymer films drop-cast from tetrahydrofuran solutions of (i) PDOPA-Si-12 and (ii) PDOPA-12 (0.1 mg $mL^{-1}$). (iii) Water contact angle (WCA) measurements illustrating the surface wettability of the respective polymer coatings [96], Copyright 2022. Adapted with permission from the American Chemical Society. (b) Molecular dynamics (MD) simulations and permeability analysis of biscatechol–polymer/$Fe^{III}$ assemblies assembled from PMA and PBA polymers with different hydrophobicities. (i) Time-lapse MD snapshots illustrating the formation and compaction of biscatechol–PBA–$Fe^{III}$ coordination networks on a PS substrate over nanosecond timescales. (ii) Density profiles of PMA–$Fe^{III}$ and PBA–$Fe^{III}$ coordination films as a function of distance from the PS substrate, showing that higher hydrophobicity (PBA) leads to denser film packing and reduced porosity. (iii) Permeability of $PMA_{100}$–$Fe^{III}$ and $PBA_{118}$–$Fe^{III}$ MPN capsules toward fluorescein isothiocyanate–dextran with molecular weights ranging from 4 to 2000 kDa, demonstrating tunable transport behavior governed by polymer hydrophobicity and assembly concentration (insets: representative confocal fluorescence images, scale bars = 5 $\mu$m) [60], Copyright 2023 Kim *et al.* Adapted with permission from Wiley-VCH.

of DOPA units increases polarity while exposing redox-active catechols, and increasing hydrophobic polymer content can densify MPN shells while simultaneously changing coordination density and chain packing. Therefore, future studies should move towards designing polymer libraries in which polarity, phenolic content, molecular architecture, and coordination chemistry are varied independently. Such studies would clarify how local hydration and phenolic interactions propagate into macroscopic properties such as permeability, adhesion, assembly morphology, and biological interactions.

### 4.3. Biocompatibility

The engineering of polyphenol-functionalized polymers has opened new avenues for designing biointerfaces that combine robust interfacial stability of polyphenol units with intrinsic biocompatibility of hydrophilic polymers such as PEG, chitosan, and cellulose. Early progress was inspired by the adhesive proteins of mussels, whose catechol and amine residues enable strong yet reversible interactions with diverse substrates. Building on this principle, Ling et al. developed a polymeric multi-interaction ligand composed of a polyDOPA–PEG–PEI block structure that could anchor to metal and metal oxide nanoparticles through multivalent catechol coordination and electrostatic interactions [106]. This mussel-mimetic architecture endowed the resulting nanoparticles with colloidal stability—retaining dispersibility across extreme pH and salt conditions—while the PEG corona conferred low cytotoxicity and prolonged blood circulation, which represented an early demonstration of the first paradigms of a biocompatible catechol-based polymer system. In other catechol-modified polymers, such as heparin-mimetic polymers, their intrinsic anticoagulant activity has been combined with catechol-mediated Ag-nanoparticle immobilization to yield antibacterial, endothelial-compatible coatings (Fig. 14a) [127].

Polyphenol-functionalized polymers can also form hydrogels through oxidative coupling or metal–phenolic coordination. The catechol or gallol groups act as dynamic cross-linking motifs, enabling the formation of covalent or coordination bonds under physiological conditions [63,70]. When grafted onto biocompatible backbones such as PEG [128], HA [70,129], chitosan [65,66,130], polyethylenimine ethoxylated [59], or cellulose [131,132], these polyphenol motifs confer wet adhesion and dynamic cohesion while preserving the inherent hydrophilicity and cytocompatibility of the host polymer. For example, an enzymatically cross-linked catechol–chitosan hydrogel has been constructed through horseradish peroxidase (HRP)/$H_2O_2$-mediated oxidative coupling, enabling rapid gelation under physiological conditions (Fig. 14b-i) [65]. The resulting hydrogel provides a highly biocompatible 3D environment that supports the adhesion and proliferation of bone marrow-derived mesenchymal stem cells, as confirmed by live/dead fluorescence imaging (Fig. 14b-ii). Quantitative CCK-8 analysis has shown enhanced cell viability and growth within the enzymatically cross-linked catechol–chitosan hydrogel network, indicating negligible cytotoxicity and favorable potential for tissue-engineering applications (Fig. 14b-iii). Such hydrogels can be formed under physiological conditions without toxic initiators, and can be applied for tissue sealing, wound healing, and cell encapsulation in regenerative medicine, highlighting their potential as multifunctional bioadhesive and injectable materials.

These studies show that polyphenol functionalization can integrate interfacial stability with the cytocompatibility of established hydrophilic polymer backbones. However, the biocompatibility of these materials should not be inferred solely from the identity of the parent polymer. Phenolic groups introduce additional chemical reactivity, including oxidation to quinones, metal coordination, hydrogen bonding with biomolecules, and dynamic cross-linking, all of which can alter cellular responses, protein adsorption, degradation behavior, and local oxidative environments. In many studies, biocompatibility is mainly supported by short-term cell viability or live/dead assays, whereas longer-term inflammatory responses, hemocompatibility, immune activation, degradation products, and in vivo persistence remain less systematically examined. A more critical understanding of additional chemical reactivity induced by phenolic groups influencing biological outcomes will be important for generating biocompatible systems for biomedical applications.

### 4.4. Stealth and targeting

Beyond engineering biocompatible materials, polyphenol-functionalized polymers have been exploited to engineer nano- and microscale assemblies with stealth and targeting properties. Incorporation of polyphenol moieties into PEG and HA building blocks has enabled the modular assembly of MPN capsules with tunable biointeractions [71,133]. In this system, PEG–catechol provides low-fouling surfaces that minimize nonspecific cell–capsule interactions, whereas HA–catechol confers CD44-mediated recognition properties toward CD44-overexpressed cancer cells. This modular design allows continuous tuning between “stealth” behavior and receptor-specific “targeting”, thereby enabling precise control of bio–nano interactions (Fig. 15a). Subsequently, macromolecular design strategies have been introduced to program the physicochemical properties and biological interactions of MPN capsules. By varying the architecture and molecular weight of PEG–catechol conjugates, systematic modulation of capsule shell thickness, permeability, and cell association is achieved, thereby establishing a structure–function relationship that governs the stealth performance of PEGylated materials in biological environments (Fig. 15b) [16]. In addition to leveraging the metal coordination of polyphenol moieties to engineer nano- and microscale assemblies, the reversible boronate–catechol covalent interaction has been harnessed to design a dynamically PEGylated nanoparticle system for tumor therapy [134]. In this design, nanoparticles remain PEG-shielded and stable under physiological conditions, but undergo acid-triggered de-PEGylation in the mildly acidic tumor microenvironment, exposing phenylboronic acid groups that specifically recognize sialic acid residues on cancer cells. This environmentally responsive de-shielding mechanism enables synergistic passive and active tumor targeting, while effectively minimizing off-target cytotoxicity.

These studies highlight a central design challenge in biointeractive polyphenol-functionalized assemblies: the same surface features that suppress nonspecific interactions can also limit receptor engagement and cellular uptake. This challenge is particularly important for dynamic systems such as pH-triggered de-PEGylated nanoparticles, where therapeutic performance depends not only on the presence of stealth and targeting motifs, but also on the kinetics and location of the transition between these two states. Future studies should therefore place greater emphasis on how protein corona formation, ligand accessibility, and microenvironment-triggered de-shielding determine targeting selectivity under biologically relevant conditions.

### 4.5. Stimuli-responsiveness and bioactivity

Dynamic materials that undergo reversible structural and physicochemical transformations in response to environmental or external stimuli have emerged as a versatile platform for constructing advanced functional systems. These adaptive materials have a wide range of applications, including self-healing materials [135], drug and gene delivery systems [136], biosensing [137], catalysis [138], membranes [139], and electronic devices [140]. Stimuli-responsive polymers, in particular, serve as key building

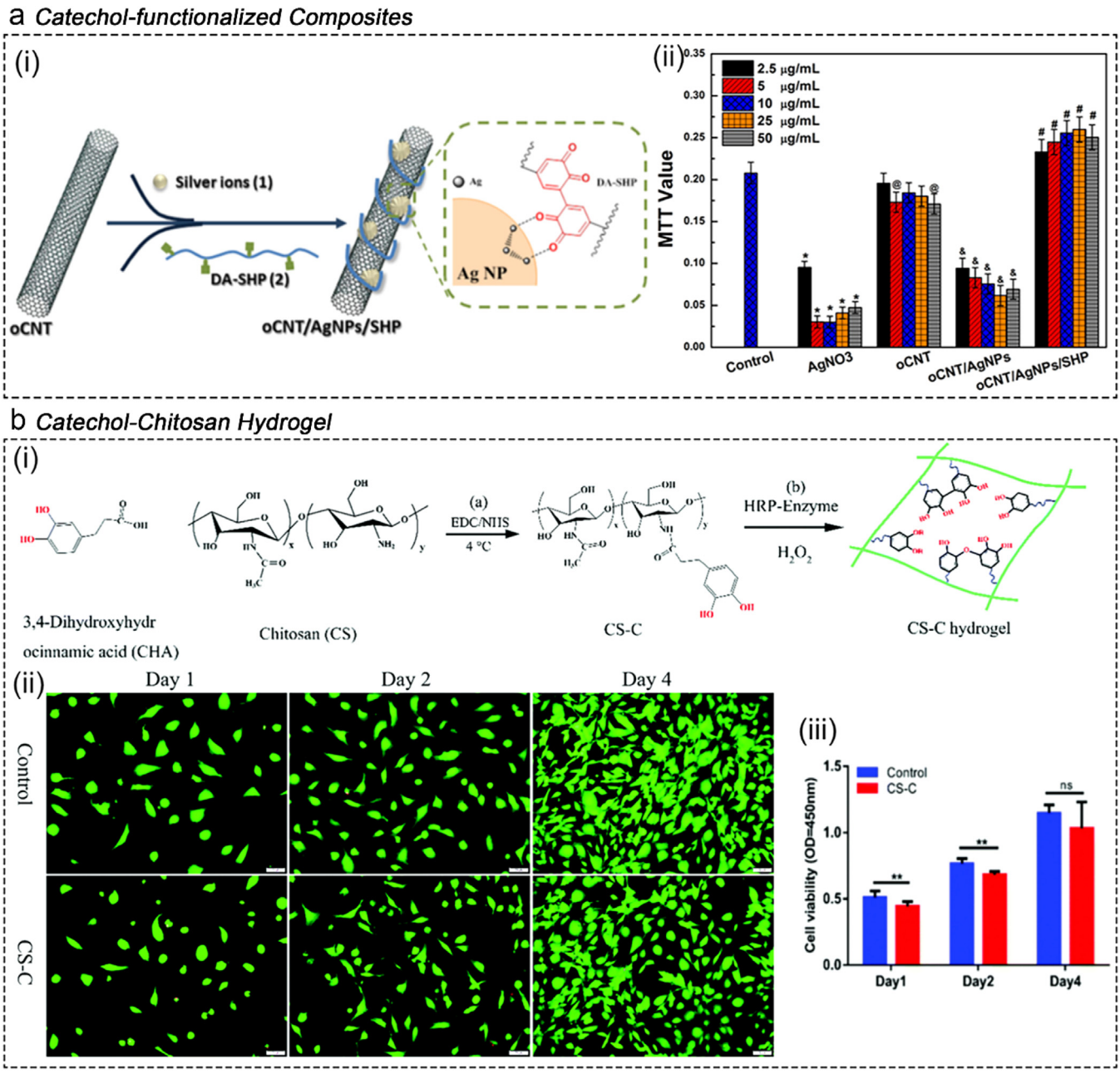


**Fig. 14.** Engineering polyphenol-functionalized polymers with biocompatible properties. (a) Mussel-inspired synthesis and cytocompatibility of catechol–polymer-functionalized antibacterial nanocomposites ($\alpha$CNT/AgNPs/SHP). SHP, self-healing hydrophobic polymer [127], Copyright 2016. Adapted with permission from the American Chemical Society. (b) Mussel-inspired enzymatically cross-linked catechol–chitosan (CS–C) hydrogel with enhanced biocompatibility and cell adhesion. (i) Synthesis and enzymatic cross-linking mechanism of CS–C hydrogel prepared via EDC/NHS coupling of chitosan and 3,4-dihydroxyhydrocinnamic acid, followed by HRP/$H_2O_2$ catalysis. (ii) Live/dead fluorescence staining images showing high viability and proliferation of bone marrow-derived stem cells within CS–C hydrogels over 4 days. (iii) Quantitative CCK-8 assay confirming enhanced cell proliferation and negligible cytotoxicity compared with the control group [65], Copyright 2022. Adapted with permission from The Royal Society of Chemistry.

blocks for dynamic systems due to their tunable responsiveness to diverse stimuli such as pH [141], redox potential [142], temperature [143], light [144], DNA [145], or enzymes [146]. Polyphenols are known to form coordination complex with diverse metal ions (i.e., MPNs) and to engage in hydrogen bonding with biomolecules (e.g., polysaccharides, nucleic acids, and proteins), synthetic polymers, and other polyphenols. These interactions can be modulated by external stimuli (e.g., pH, solvent composition, and temperature), enabling dynamic regulation of material properties [14,78,147]. Accordingly, polyphenol-functionalized polymers that integrate responsive polymer backbones with phenolic moieties have been increasingly used to design multifunctional materials with tailored physicochemical properties.

Coordination of catechol-like amino acid DOPA to $Fe^{III}$ ions has been identified as a key molecular interaction responsible for the hardness and extensibility of mussel byssal thread cuticles [84]. Holten-Andersen et al. engineered synthetic hydrogels by integrating catechol-functionalized 4-arm PEG with $Fe^{III}$ ions to generate bis- and tris-catechol–$Fe^{III}$ coordination networks under alkaline conditions (pH 8 and 12) [85]. The resulting hydrogels exhibited elastic moduli comparable to covalently cross-linked systems, while maintaining self-healing capabilities. In subsequent stud-

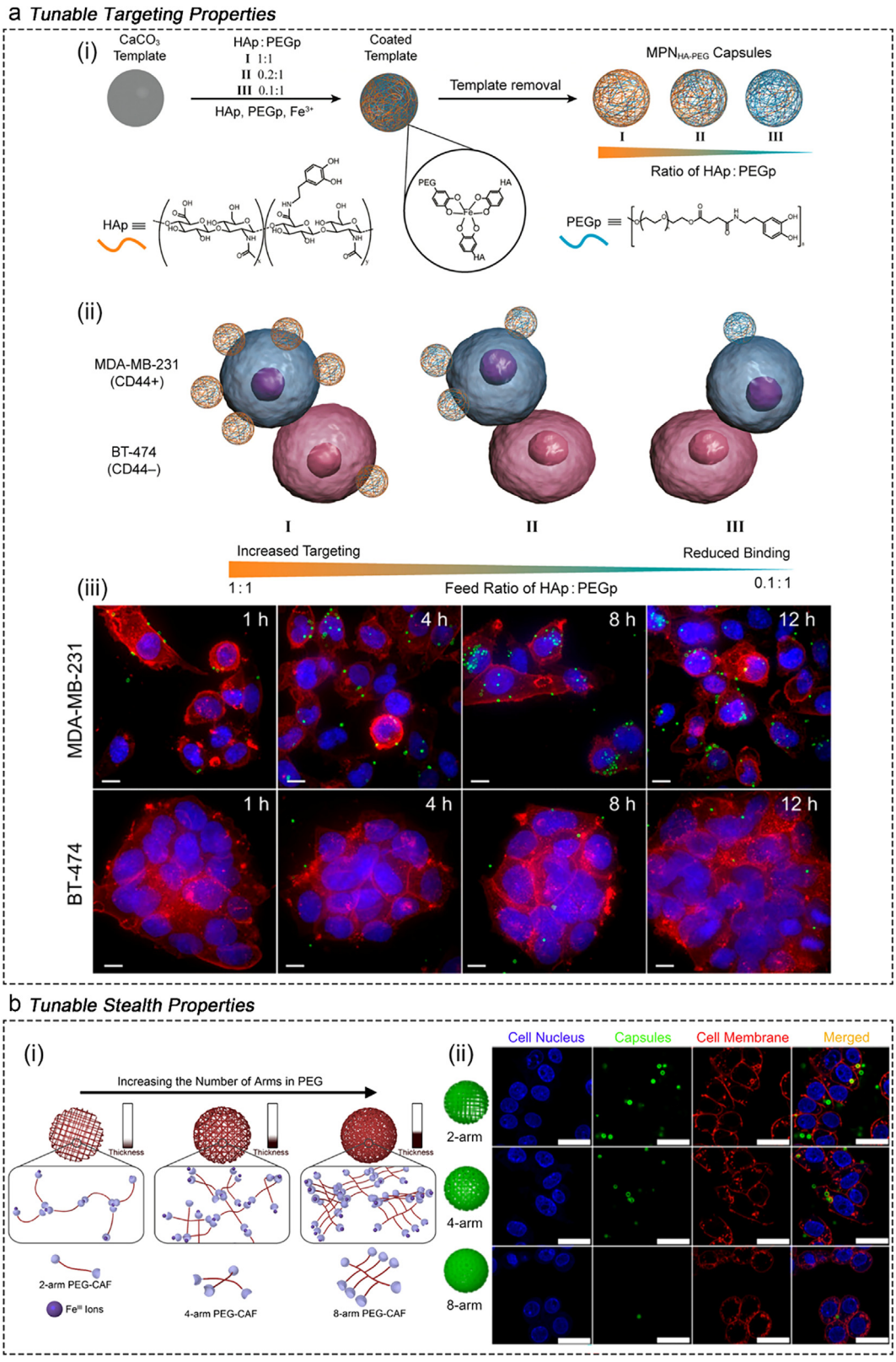


**Fig. 15.** Polyphenol-engineered polymer capsules with tunable targeting and stealth. (a) MPN capsules with tunable targeting properties to cancer cells. (i) Co-deposition of hyaluronic acid–phenol (HAp) and PEG–phenol (PEGp) with $Fe^{III}$ on $CaCO_3$ templates yields $MPN_{HA-PEG}$ capsules with varied HAp:PEGp feed ratios (I = 1:1, II = 0.2:1, III = 0.1:1). (ii) Increasing HAp content in $MPN_{HA-PEG}$ capsules enhances CD44-mediated recognition of MDA-MB-231 ($CD44^+$) over BT-474 ($CD44^-$). (iii) Time-lapse confocal laser scanning microscopy confirms ratio-dependent capsule uptake—HAp-rich capsules associate strongly with $CD44^+$ cells, whereas PEGp-rich shells suppress nonspecific cell binding [71], Copyright 2016. Adapted with permission from the American Chemical Society. (b) MPN capsules with tunable stealth properties. (i) PEG–caffeamide (CAF)–$Fe^{III}$ MPN capsules assembled with 2-, 4-, or 8-arm PEG ligands; increasing arm number thickens the PEG corona and reduces cell association ("stealth"). (ii) Confocal laser scanning microscopy images (capsules, green; membranes, red; nuclei, blue) show markedly diminished cellular binding for 8-arm versus 2-arm PEG capsules [16], Copyright 2021. Adapted with permission from the American Chemical Society.

ies, catechol-functionalized acrylic polymers (i.e., polyacrylates and polymethacrylates) were synthesized to prepare materials that exhibited self-healing behaviors in metal-free aqueous environments [148]. These materials showed self-mending at damaged interfaces, initiated by catechol-mediated hydrogen bonding and subsequently reinforced by additional attractive interactions such as van der Waals forces, hydrophobic interactions, and polymer interpenetration. Collectively, these studies underscore the versatility of catechol chemistry in constructing dynamic polymeric materials. Dual-responsive polymers have been engineered by conjugating self-immolative polymers, capable of depolymerizing into monomeric species upon exposure to specific stimuli, with catechol moieties [149]. Specifically, poly(dithiothreitol), which undergoes rapid depolymerization through thiol–disulfide exchange upon the addition of dithiothreitol, has been functionalized with catechol groups via esterification between the hydroxyl groups of the repeating units and the carboxylic acid of DHCA. The resulting catechol-functionalized polymers are cross-linked through catechol–metal coordination, forming a dual-responsive gel (Fig. 16a). This material integrates the pH-dependent metal ion coordination chemistry of catechol with the on-demand degradability of the self-immolative polymer backbone. Gel degradation is triggered under two conditions: (i) thiol-induced degradation under alkaline conditions and (ii) cleavage of catechol–metal coordination under acidic conditions. In another example, thermoresponsive capsules have been prepared by coordination chemistry between biscatechol-PNIPAM and $Fe^{III}$ ions to display temperature-dependent size contraction and expansion (Fig. 16b-i) [45]. The incorporation of PNIPAM chains into the capsule shell endows the system with thermal responsiveness. Upon heating above the lower critical solution temperature, the PNIPAM segments transition from a hydrated coil to a dehydrated globule conformation, resulting in capsule shrinkage, increased shell thickness, and reduced permeability. The temperature-dependent modulation of permeability is harnessed for the encapsulation and release of cargo molecules (i.e., fluorescein isothiocyanate-labeled dextran, 500 kDa), with approximately 70% release over 90 min at 25 °C, demonstrating the potential of such systems for smart delivery applications (Fig. 16b-ii). Near-infrared (NIR) light-responsive shape memory polymers with permanent shape reconfiguration capability have been prepared via coordination-based cross-linking between DOPA-functionalized PEG and $Fe^{III}$ ions (Fig. 16c) [54]. The formation of catechol–$Fe^{III}$ complexes endows the polymer complexes with broad NIR absorption, enabling photothermal actuation. Rectangular polymer sheets are folded into temporary shapes through origami design, which remain stable at room temperature. Exposure to NIR irradiation restores the original shape of the polymer sheets. In addition, coiled stent-like structures have been shown to expand within 60 s of exposure under NIR light, demonstrating effective photothermal-triggered actuation of the cross-linked polymer networks. The sequence-specific recognition of DNA has been extensively exploited to program the assembly of dynamic nanostructures [150]. In this context, a polyphenol-functionalized DBC (DNA-*b*-poly(MMA-*co*-DHCAF)) enabled the fabrication of nanostructured materials with tunable properties [47]. Sequence-specific hybridization of DNA1 on the surface of DBC–$Fe^{III}$ MPN capsules was performed using its complementary strand DNA1′. The capsules, labeled with fluorescein on DNA1, exhibited a loss of green fluorescence upon addition of Cy3-labeled $DNA1'_{12}$ ($DNA1'_{12}$(Cy3)) due to Förster resonance energy transfer, while red fluorescence from Cy3 was observed on the capsule surface (Fig. 16d). Subsequent strand displacement with a longer complementary DNA sequence ($DNA1'_{18}$), having six more complementary bases, restored green fluorescence and diminished red fluorescence, indicating the exchange of DNA strands. This hybridization exchange enables programmable assembly through sequence-specific molecular recognition, offering new opportunities for the design of micromachine platforms [150] and colloidal architectures [151]. The incorporation of enzyme-cleavable motifs into polymer frameworks offers a rational approach for designing bio-responsive assembled materials. For example, polyphenol-functionalized polymers bearing aliphatic ester linkages, such as DOPA-based poly(esterurethane)s, were designed to undergo esterase-catalyzed degradation [152]. To evaluate the enzyme-responsiveness of the resulting assemblies, hydrophobic drugs including DOX and TPT were encapsulated within the polymeric nanostructures. Drug release kinetics were examined in phosphate-buffered saline at 37 °C in the absence and presence of esterase (Fig. 16e) [96]. In the presence of the enzyme, the assemblies exhibited pronounced drug release, confirming enzymatically triggered degradation and demonstrating the potential of such systems for controlled drug delivery applications.

The incorporation of functional polymers into polyphenol-based assemblies has considerably expanded opportunities to engineer physicochemical and biological properties beyond those attainable using polyphenol chemistry alone. Nevertheless, only a limited range of polymer functionalities has been explored to date, with most studies focusing on hydrophilic polymers, charged polymers, and a few stimuli-responsive systems. Expanding the molecular toolbox of functional polymers to include diverse stimuli-responsive, ionic, bioactive, and programmable polymer architectures will further diversify the accessible property space of assembled nanostructures. Such efforts will also facilitate the establishment of general structure–property–function relationships, enabling the rational design of multifunctional polyphenol-functionalized materials with desired performance.

## 5. Applications

### 5.1. Multifunctional interfaces

Surface interfaces represent the primary locus where polyphenol chemistry manifests its multifunctionality, enabling adhesion, redox activity, coordination, and charge modulation across synthetic and biological systems. This section covers interfaces in which catechol/gallol units are chemically integrated into polymer matrices and directly mediate interfacial functionalities, e.g., adhesion, charge mediation at the biointerface, and antifouling and catalytic activity. In this section, we focus on translating the chemical foundations of polyphenol-based polymers into functional interfacial designs and practical applications, highlighting how molecular design principles translate into tunable and multifunctional surface performance.

#### 5.1.1. Adhesive interfaces

The design of adhesive interfaces using polyphenol-functionalized polymers originated from the chemical insights of marine mussel adhesion. Waite and Tanzer first isolated the L-DOPA-rich adhesive proteins of *Mytilus edulis*, identifying catechol oxidation and quinone tanning as the molecular basis of interfacial binding and cohesive curing [153]. Building on this discovery, Sever et al. revealed that $Fe^{III}$–DOPA coordination triggered oxidative cross-linking and radical generation in mussel foot proteins, establishing a durable MPN responsible for wet adhesion under seawater conditions [154]. These biological findings have provided the molecular blueprint for designing synthetic catechol- and gallol-based adhesives. Bridging natural architecture and synthetic materials, Lee et al. pioneered a biohybrid “Geckel” adhesive that combined the nanoscale contact-splitting geometry of gecko foot hairs with the chemical adhesion of mussel catechols (Fig. 17a) [155]. Arrays of polymeric nanopillars coated with a thin catechol-functionalized layer achieved reversible adhesion up to 15 N $cm^{-2}$ in both wet and dry environments, sustaining

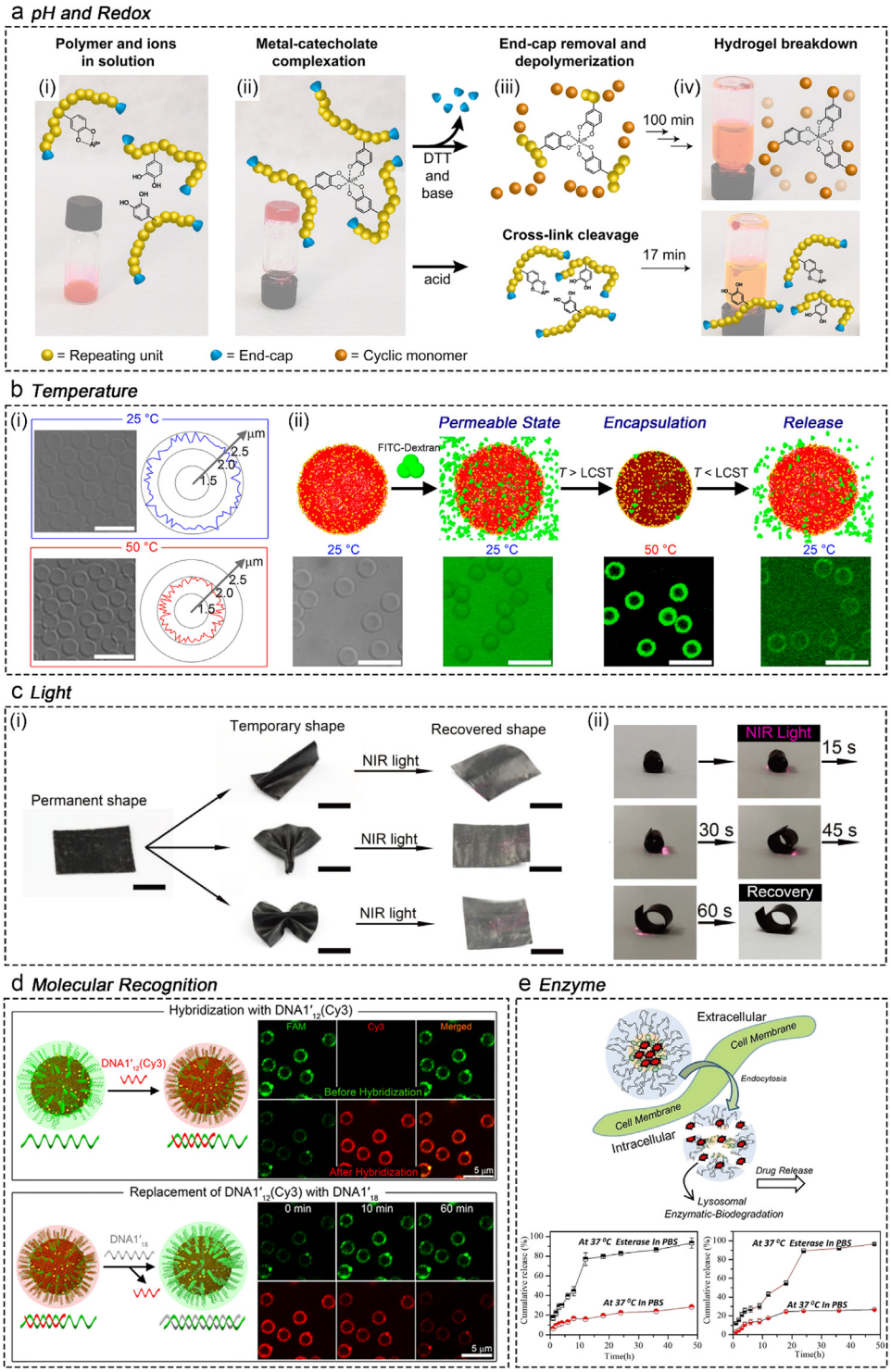


**Fig. 16.** Polyphenol-engineered polymeric materials with stimuli-responsive properties. (a) Hydrogel formation and disassembly. (i) Solution of catechol-functionalized poly(dithiothreitol), $Al^{III}$, and rhodamine 6 G, and (ii) corresponding hydrogel formation induced by base addition (NaOH, pH > 10). (iii) Gel breakdown via depolymerization through decapping upon addition of 10 equiv. dithiothreitol (DTT) and 5 equiv. $Et_3N$ (top) or cleavage of $Al^{III}$–catecholato cross-links under acidic conditions (1 M HCl in methanol) (bottom). (iv) Liquefaction of the hydrogel and concomitant release of rhodamine 6 G into solution following 100 min depolymerization or 17 min metal coordination cleavage [149], Copyright 2021 Agergaard *et al.* Adapted with permission from Wiley-VCH GmbH. (b) Thermoresponsive MPN capsules. (i) Differential interference contrast images and size distribution radar maps of PNIPAM–$Fe^{III}$ MPN capsules at 25 °C (2.3 ± 0.1 $\mu$m) and 50 °C (1.9 ± 0.1 $\mu$m). Scale bars = 5 $\mu$m. (ii) Temperature-controlled encapsulation and release of fluorescein isothiocyanate (FITC)-dextran (500 kDa) from thermoresponsive capsules [45], Copyright 2022. Adapted with permission from the American Chemical Society. (c) Light-triggered shape memory. (i) Temporary shape fixation and NIR-induced recovery under 0.52 W $cm^{-2}$ irradiation. Scale bars = 1 cm. (ii) NIR-triggered expansion of polymer stent [54], Copyright 2021. Adapted with permission from Wiley-VCH GmbH. (d) Molecular recognition. Attachment and detachment of dye-tagged oligonucleotides on DBC–$Fe^{III}$ MPN capsules through hybridization with 12 base- ($DNA1'_{12}(Cy3)$) and 18 base- ($DNA1'_{18}$) complementary sequences. The fluorescence of DNA1(FAM) strands on the capsule surface decreases upon addition of $DNA1'_{12}(Cy3)$ and is restored upon addition of $DNA1'_{18}$ [47], Copyright 2022. Adapted with permission from the American Chemical Society. (e) Enzyme-responsiveness. Controlled release of DOX (left graph) and TPT (right graph) from PDOPA-PEG-400 nanoparticles [96], Copyright 2022. Adapted with permission from the American Chemical Society. LCST, lower critical solution temperature; PBS, phosphate-buffered saline.

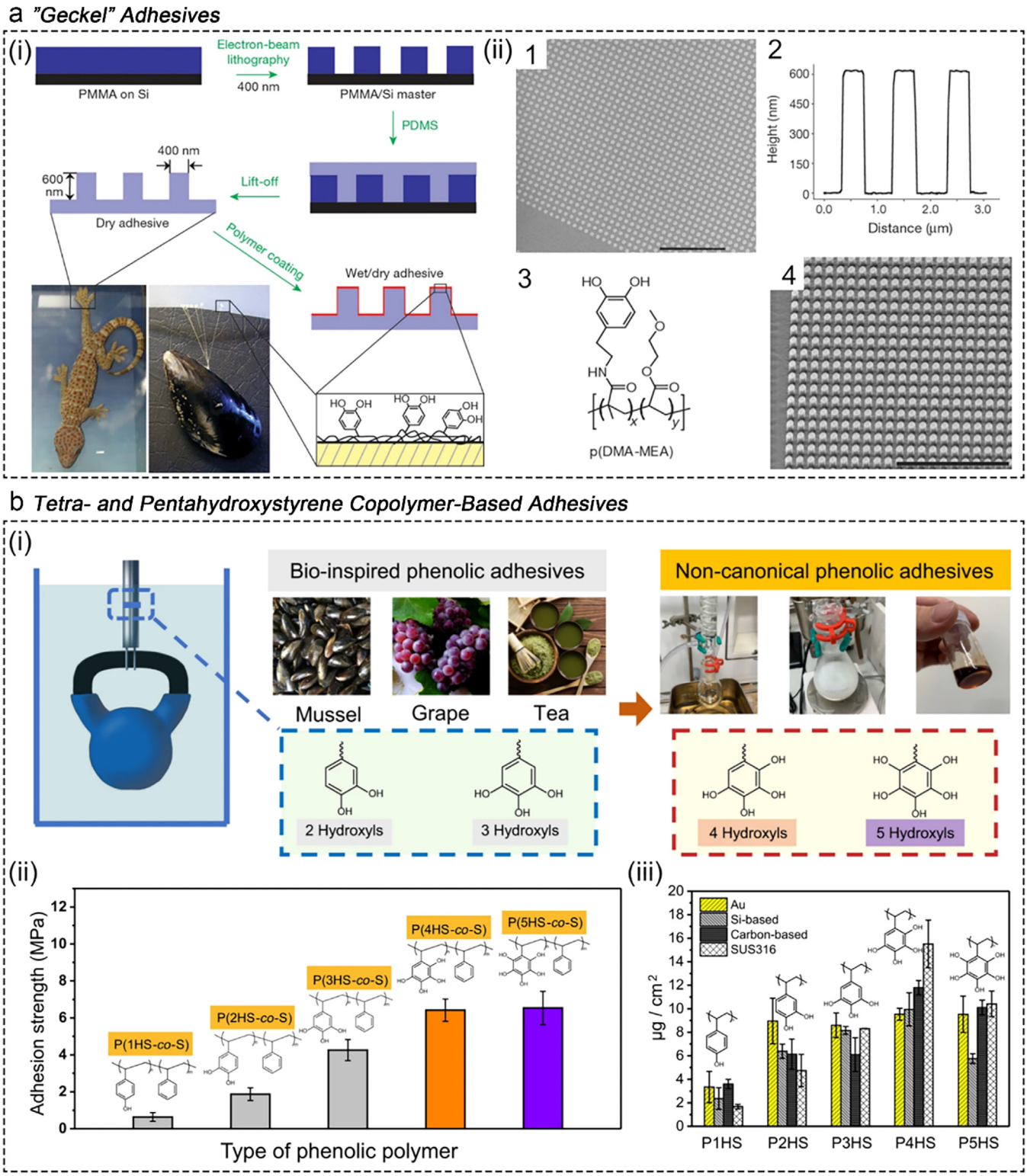


**Fig. 17.** Polyphenol-functionalized polymer adhesives. (a) Hybrid adhesive systems combining nanoscale contact-splitting architectures with catechol-mediated interfacial chemistry. (i) Schematic illustration of microstructured polymeric arrays inspired by gecko setae and mussel adhesion principles. (ii) Cross-sectional and surface micrographs showing periodic nanopillar patterns enabling reversible wet/dry adhesion through synergistic van der Waals and metal–catechol coordination [155], Copyright 2007. Adapted with permission from Springer Nature Limited. (b) Non-canonical phenolic polymers exhibiting ultrahigh underwater adhesion. (i) Molecular design of polyphenolic copolymers with increased hydroxyl multiplicity (from catechol to tetra- and pentahydroxystyrene) that enhance hydrogen-bond density and hydrophobic confinement. (ii) Adhesion strength of different types of phenolic polymers. (iii) Adhesion performance of the different phenolic polymers on multiple substrates, demonstrating bonding strengths exceeding 10 MPa and reversible detachment enabled by dynamic hydrogen-bond networks [166], Copyright 2022 Cheng *et al.* Adapted with permission from Springer Nature.

>1000 attachment–detachment cycles. This seminal work established a design paradigm that merges physical microarchitecture with polyphenolic surface chemistry, demonstrating that catechol groups can bridge disparate adhesion mechanisms—van der Waals interactions and metal coordination—to enable reusable, universal bonding. The molecular principles of polyphenolic adhesion have been refined in subsequent mechanistic studies. An optimal catechol content (~30 mol%) has been shown to maximize wet adhesion (~10 MPa) by balancing cohesive and adhesive interactions [156], while intramolecular proximity between catechol and lysine residues has been found to generate strong multivalent binding on mineral surfaces [157]. Further studies have correlated polymer backbone polarity with underwater adhesion, showing up to a 5-fold enhancement from nonpolar to polar systems [158]. Extension from catechol to trihydroxylated phenolic motifs has enabled further increased adhesion strength, achieving values exceeding 4 MPa at 10 mol% gallol [159]. The incorporation of phenolic chemistry into polymer backbones has also enabled substantially enhanced adsorption on inorganic substrates through multidentate hydrogen bonding, expanding phenolic-mediated adhesion to optoelectronic and sensing interfaces [160].

Building on mussel-inspired chemistry, PDA has emerged as a universal adhesive coating. Kim et al. used PDA priming to pattern low-surface-energy substrates such as Teflon, graphene, and gold with block-copolymer nanodomains, establishing PDA as a versatile interfacial anchor [161]. This concept has been extended to a one-step co-deposition process, enabling simultaneous immobilization of polymers, small molecules, and biomacromolecules to yield multifunctional surfaces for antibacterial and angiogenic applications [162]. Recent studies have redefined the adhesion mechanism of PDA, showing that bonding arises from aggregation-induced assembly stabilized by $\pi$–$\pi$ and cation–$\pi$ interactions rather than static covalent cross-links [163]. Catechol units mediate substrate binding through hydrogen bonding and metal coordination, while amine and indole groups enhance cohesion and assembly. This insight reframes PDA as a dynamic supramolecular adhesive governed by solubility and molecular aggregation.

Molecule-level optimization has enabled advanced engineering of polyphenol-based adhesives with high strength and durable adhesion. By inserting nanometer-scale catechol primers into polymer–mineral interfaces, stronger binding can be achieved—Seo et al. developed 1 nm catechol-acrylate primers that increased polymer–mineral adhesion by 10-fold through forming bidentate interfacial bonds [164]. Building on the idea that interfacial bond multiplicity must be matched with cohesive energy, Tiu et al. incorporated DMA into acrylic pressure-sensitive adhesives, achieving 6-fold higher peel strength and long-term wet adhesion [165]. Cheng et al. furthered phenolic design beyond biomimicry by synthesizing tetra- and pentahydroxystyrene copolymers that reached substantially high (>10 MPa) reversible underwater adhesion through dense hydrogen-bonding clusters within hydrophobic matrices (Fig. 17b) [166]. Additional research has shown that excessive catechol contents in photocrosslinkable systems quench radical polymerization, defining new guidelines for balancing adhesion and cross-linking [77]. As design moved from catechol to multidentate plant-inspired motifs, substantially higher underwater adhesion (≈1.3 MPa in seawater) could be achieved, for instance, using gallol-functionalized copolymers that demonstrate tridentate coordination and oxidation-driven network reinforcement [100]. This principle of coordination-density-driven cohesion also underpins long-term durable assemblies. For example, tannic acid/PVA multilayers have been reported to sustain >100 kPa adhesion for 60 days in seawater [167]. Additionally, solvent exchange-triggered assembly has been leveraged to achieve rapid and high-strength underwater sealing. Sandcastle worm-inspired coacervate-like systems formed by coupling PAAcat with quaternized chitosan display strong adhesion properties ($W_{ad}$ > 2 J m$^{-2}$) without curing owing to their microporous, highly dissipative networks [98]. In contrast, solvent-exchange-activated catechol adhesives rapidly develop dense hydrogen-bonded networks upon hydration, achieving 600 kPa underwater adhesion and rapid hemostasis in vivo [59]. In parallel, considerable effort has been directed toward simplifying fabrication pathways and adopting more sustainable phenolic material platforms. Simple zwitterionic catechol surfactants have been shown to form ultrathin (<4 nm) nanocoatings [168], whereas biodegradable poly(lactic acid)–catechol copolymers combine strong adhesion to diverse substrates with hydrolytic debonding under mild aqueous conditions [169]. Cellulose-based catechol adhesives reinforced through $Fe^{III}$ coordination display further improved mechanical performance [131], with enhanced strength (5.5 MPa on steel) achieved via incorporation of cellulose nanofibrils [132]. This green chemistry approach has been furthered through the use of lignin-derived catechol copolymers, which achieve 8.1 MPa adhesion on steel and durability across pH 3–11 [39]. In summary, these studies chart the evolution of polyphenol-functionalized polymers from biological prototypes to multifunctional synthetic architectures. Through controlled hydroxyl multiplicity, polymer polarity, metal coordination, and supramolecular assembly, phenolic polymers provide adaptive, strong, and even recyclable adhesive interfaces for marine coatings, nanolithography, and biomedical sealing applications.

#### 5.1.2. Antifouling interfaces

Polyphenol-functionalized polymers have been broadly employed to engineer antifouling surfaces that prevent unwanted adhesion of proteins, microorganisms, or hydrophobic contaminants. The antifouling function arises from catechol moieties that can mediate both surface anchoring and chemical modification, enabling robust adhesion to diverse substrates while providing reactive sites for constructing hydration layers or hierarchical structures. At the molecular level, Fischer et al. introduced a precision-engineered strategy to inhibit bioadhesion using sequence-defined glycomacromolecules bearing terminal catechol groups [170]. After lectin recognition, the oxidation of catechol to quinone enables covalent Michael coupling with nucleophilic residues on bacterial lectins, converting reversible carbohydrate–protein binding into irreversible conjugation. This covalent locking mechanism efficiently suppresses *E. coli* attachment and has defined a molecular paradigm for antifouling interfaces that exploit catechol oxidation for programmable adhesion inhibition. At the mesoscopic scale, hierarchical and biomimetic architectures have been used to impart underwater repellence. Ma et al. integrated mussel-inspired catechol adhesion with fish-skin-like microstructural design [171]. In this study, a catechol-rich copolymer base layer enables layer-by-layer assembly of polyelectrolytes to generate fish-scale-like nanostructures (root mean square ≈ 170 nm). The resulting films exhibit durable underwater superoleophobicity (oil contact angle ≈ 163°) and non-sticky behavior after 2 weeks of immersion, demonstrating that catechol anchoring combined with hierarchical structuring can produce cross-linkable antifouling surfaces across inorganic and polymeric materials. Beyond structural design, advanced antifouling coatings have been developed based on metal–phenolic coordination and hydration-layer engineering. PEG–polyphenol derivatives coordinated with $Fe^{III}$ have been engineered into PEG–MPN capsules that exhibit low protein adsorption (1.8 ng mm$^{-2}$) and minimal cell association (<2%), while remaining pH-responsive for controlled release [55]. In another example, engineered dopamine-containing terpolymer coatings that can undergo self-cross-linking via Michael addition/Schiff-base reactions yield ~30 nm PEG-based layers that resist bacterial, diatom, and barnacle adhesion by >90% under seawater flow [172]. These studies illustrate how $Fe^{III}$–catechol coordination, PEG stealth, and

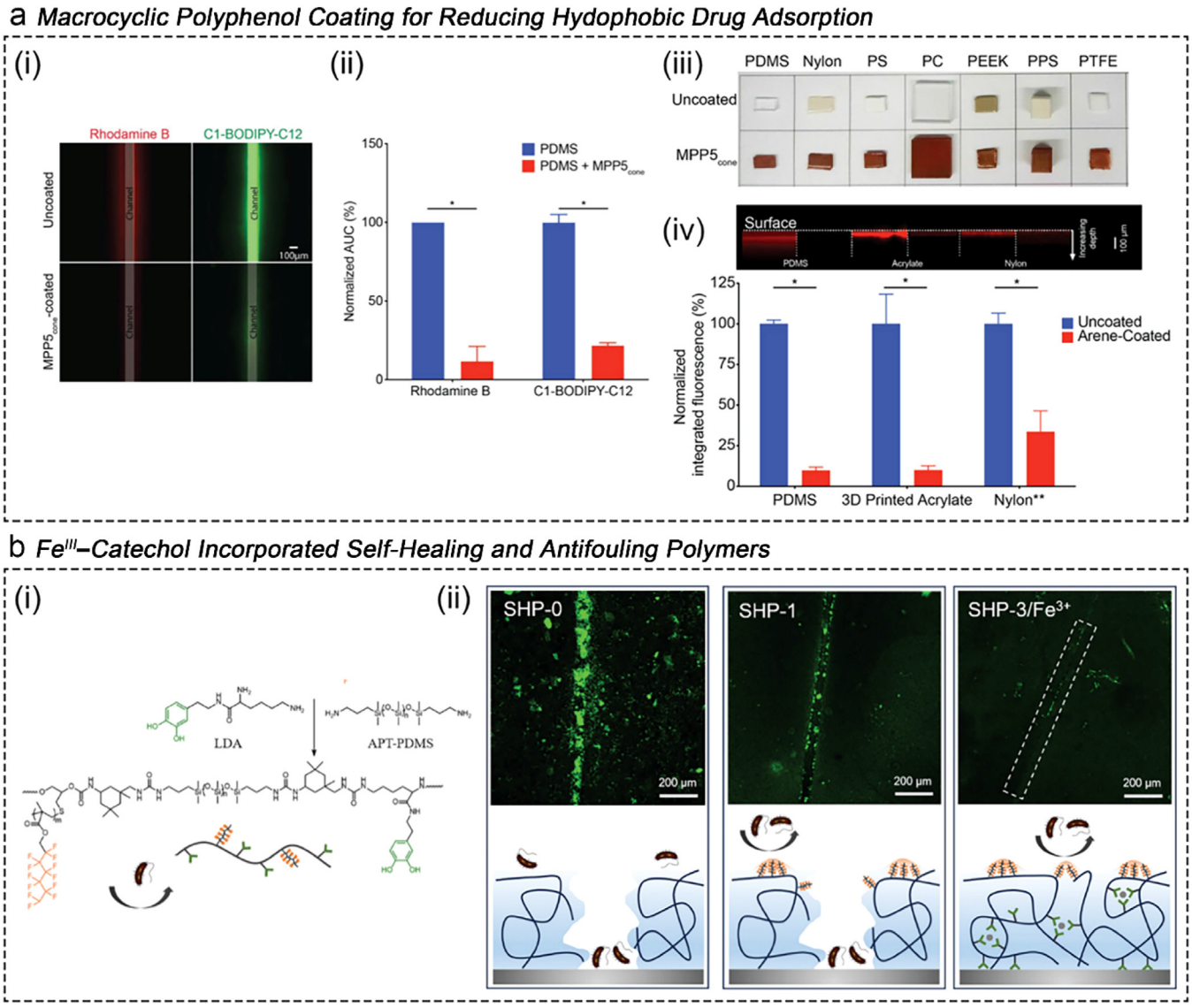


**Fig. 18.** Polyphenol-functionalized polymer-based antifouling coatings. (a) Macrocyclic polyphenol coatings based on catechol-functionalized calix[4]resorcinarenes ($MPP5_{cone}$) providing dense surface coverage and hydrophobic molecule blocking on various polymer substrates. (i) Fluorescence microscopy images showing strong suppression of Rhodamine B and C1-BODIPY-C12 absorption on coated PDMS microchannels. (ii) Amount of dye infused into uncoated and $MPP5_{cone}$-coated channels. (iii) Photographs of uncoated and coated polymer substrates (PDMS, polydimethylsiloxane; nylon, PS, polystyrene; PC, polycarbonate; PEEK, polyether ether ketone; PPS, poly(*p*-phenylene sulfide); PTFE, poly(tetrafluoroethylene)) demonstrating uniform coloration and substrate-independent adhesion. (iv) Quantitative fluorescence analysis confirming >90% reduction in small-molecule uptake by $MPP5_{cone}$ coating, establishing an oxygen-permeable, cytocompatible antifouling barrier layer [173], Copyright 2020. Adapted with permission from Wiley-VCH. (b) Fluorinated PDMS-based antifouling polymers incorporating $Fe^{III}$–catechol coordination for underwater self-healing and fouling resistance. (i) Synthetic scheme and schematic of phase-separated low-surface-energy nanodomains with dynamic $Fe^{III}$–catechol linkages. (ii) Confocal images and corresponding schematic representations showing minimized bacterial attachment and autonomous healing of surface defects in $Fe^{III}$-coordinated formulations. SHP-*x*, self-healing hydrophobic polymer (where *x* denotes the feed component ratio used during synthesis) [175], Copyright 2024. Adapted with permission from Wiley-VCH. LDA, lysine-dopamine; APT-PDMS, $\alpha,\omega$-aminopropyl-terminated polydimethylsiloxane.

hydration-induced repulsion produce long-lasting, environmentally benign antifouling coatings.

Studies have also extended polyphenol chemistry to polymer-primer and grafting strategies for functional antifouling coating. Macrocyclic polyphenols have been developed based on catechol-functionalized calix[4]resorcin arene that forms dense molecular coatings on PDMS, suppressing hydrophobic molecule absorption by ~90% while maintaining oxygen permeability and cytocompatibility (Fig. 18a) [173]. Dopamine-based copolymer bottlebrush primers integrating ATRP-initiating moieties have been designed to enable the growth of poly(oligoethylene glycol methacrylate) brushes on inert polyolefins [174]. The resulting smooth (~50 nm) hydrophilic layers reduce bovine serum albumin adsorption by ~95%. Recent studies have advanced antifouling coatings toward dynamic and self-healing systems. This is exemplified through the engineering of fluorinated PDMS-based polymers that contain lysine–dopamine linkers and $Fe^{III}$–catechol coordination that form phase-separated nanodomains (~50 nm) with low surface energy and high toughness (Fig. 18b) [175]. Upon immersion, the dynamic $Fe^{III}$–catechol bonds reorganize to autonomously close scratches, restoring antifouling capability against *Pseudomonas* sp. after mechanical damage. This system represents a new generation of mussel-inspired dynamic antifouling polymers, merging low-surface-energy chemistry, metal–phenolic coordination, and marine-grade durability. Together, these studies delineate the evolution of polyphenol-based antifouling interfaces from molecular-

scale adhesion inhibition to dynamic, self-healing surface systems. Through hierarchical structuring, hydration-layer and metal–phenolic engineering, and polymer-brush grafting, polyphenol chemistry provides a unifying framework for constructing robust, multifunctional coatings that maintain long-term cleanliness and biocompatibility across biomedical and marine environments.

#### 5.1.3. Antibacterial interfaces

Polyphenol-functionalized polymers have been extensively exploited to engineer antibacterial interfaces that integrate metal coordination, redox chemistry, and bioadhesion. Early studies focused on exploiting the redox and chelating duality of catechols to anchor antimicrobial metals. For instance, a DOPA-functionalized cationic copolymer was introduced to form micellar coatings on stainless steel, where catechol–metal coordination ensured firm adhesion and in situ reduction of $Ag^{I}$ yielded confined $Ag^{0}$/AgCl nanoparticles [176]. Two silver-loaded bilayers were sufficient to achieve >99.999% *E. coli* eradication within 2 h, establishing a refillable, mussel-inspired antibacterial coating. Extending this concept, Nie et al. employed a dopamine-functionalized heparin-mimetic polymer to simultaneously reduce $Ag^{I}$ and immobilize Ag nanoparticles on carbon nanotubes (CNTs), generating surfactant-free, biocompatible nanohybrids with strong and durable antibacterial activity [127]. Similarly, dopamine-containing glycopolymer coatings were developed to reduce $Ag^{I}$ to Ag nanoparticles in situ, creating transparent and antifogging antimicrobial films applicable to optical and medical devices (Fig. 19a) [177]. Collectively, these studies demonstrate how catechol–metal redox coordination can produce self-anchoring and Ag-generating antimicrobial interfaces with sustained performance and minimal cytotoxicity.

Beyond Ag-based systems, Kim et al. constructed multilayered alginate–catechol films cross-linked by $Fe^{III}$–catechol coordination that achieved tunable thickness and chemical robustness under harsh pH conditions [86]. The $Fe^{III}$-coordinated alginate–catechol films exhibit strong antifouling and antibacterial behavior (>99.9% *E. coli* inhibition) while maintaining hydrophilicity and removability through ethylenediaminetetraacetic acid treatment, representing a durable and reversible catechol–metal framework. Building on the principle of charge balance and hydration, Gao et al. designed mussel-inspired mixed-charge polypeptide coatings that combined zwitterionic and cationic residues with DOPA to yield hemocompatible, antibiofilm catheters that reduced bacterial load by six orders of magnitude in vivo [27]. Similarly, catechol–zwitterion copolymers were synthesized for hydroxyapatite surfaces, achieving up to 85% reduction in *Streptococcus oralis* adhesion via synergistic catechol anchoring and hydration-driven antifouling [120]. These studies highlight how metal–phenolic coordination and surface charge modulation can cooperatively endow biointerfaces with long-term antibacterial and antifouling properties. The intrinsic redox activity of catechols has also been harnessed to generate reactive oxygen species (ROS) or thermal energy for on-demand antimicrobial action. Kord Forooshani et al. designed hematin–catechol microgels that produce •OH radicals through a self-activated Fenton-like process at physiological pH, achieving complete bacterial and viral inactivation without external reagents (Fig. 19b) [121]. In a complementary approach, magnetic poly(catechol–hexanediamine) particles were engineered to combine electrostatic capture with NIR-triggered photothermal killing, effectively eradicating biofilms and bacterial contaminants [178]. These systems illustrate how catechol redox chemistry can be transformed into dynamic antibacterial platforms powered by self-oxidation or light activation. At the macroscopic and biological scale, catechol-functionalized hydrogels have emerged as multifunctional antibacterial adhesives. Ag–lignin nanoparticles have been used as redox mediators and cross-linkers to construct dynamic hydrogels with sustained underwater adhesion, high stretchability, and broad-spectrum antibacterial efficacy, enabling complete wound closure in vivo [179]. A polyampholyte hydrogel combining methacrylamide dopamine, acrylic acid, and quaternized chitosan has been synthesized to achieve contact-active bactericidal behavior, high toughness, and tissue affinity [180]. In addition, dopamine-initiated, photo-cross-linkable hydrogels have been developed in which dopamine acts as both the radical initiator and adhesion promoter, forming strong wet-adhesive, bacteriostatic gels within seconds [181]. These studies collectively underscore the chemical versatility of catechols in coupling adhesion, mechanical resilience, and antibacterial functionality into tissue-compatible hydrogels. Further, these studies define a consolidated framework for polyphenol-mediated antibacterial interfaces, spanning nanoscale coatings to macroscopic adhesives. Catechol chemistry underpins this evolution by offering a single chemical handle for anchoring, redox activation, metal coordination, and covalent reactivity. Through integration with metals ($Ag^{I}$, $Fe^{III}$), charged polymers, and soft matrices, these systems achieve multifunctional outcomes, ranging from self-regenerating antibacterial coatings and ROS-generating microgels to tissue-adhesive hydrogels that simultaneously prevent infection and promote regeneration.

#### 5.1.4. Other functional interfaces

Polyphenol chemistry provides a versatile molecular toolkit for engineering functional interfaces that integrate universal adhesion, programmable polymerization, and metal-coordination-driven reactivity. Catechol moieties act as both adhesive anchors and reactive ligands, enabling robust coupling between organic polymers and inorganic substrates while introducing dynamic coordination and redox properties that endow materials with mechanical, chemical, and catalytic functionality. At the interface-engineering level, Wang et al. have demonstrated a dual-function catechol-based photoiniferter (dopamine–diethylcarbamodithioate) that combines mussel-inspired adhesion with light-controlled radical polymerization [182]. The dopamine– diethylcarbamodithioate molecule anchors to diverse materials (Ti, Au, polyvinyl chloride) through catechol–metal coordination, while its *N,N*-diethyldithiocarbamate group enables surface-confined polymerization under UV irradiation. Using this single-step photochemical route, hydrophilic polymer brushes, such as PNIPAM, poly(2-(dimethylamino)ethyl methacrylate), and P(DMAEMA-*b*-BA), are grafted directly onto various substrates with tunable thickness (5–45 nm) and hydrophilicity (contact angle 36–54°). This catalyst-free, substrate-independent process establishes a universal and programmable foundation for covalently tethered polymer interfaces. Beyond surface grafting, metal–polyphenol coordination diversifies polyphenol chemistry into structural, redox-active, and catalytic interface design. Coordination between catechol groups and Ce ions has been shown to govern electron transfer and colloidal stability in redox-active systems [183,184]. Specifically, catechol–PEG coatings can induce the reduction of $Ce^{IV}$ to $Ce^{III}$ and oxygen-vacancy formation, enhancing ROS-scavenging capacity [183], while catechol-containing block copolymers can tune $Ce^{III}$/$Ce^{IV}$ ratios and dispersion stability through controlled catechol density [184]. These studies highlight redox-coupled coordination as a route to developing self-regenerating antioxidant interfaces with balanced activity and stability.

The same coordination mechanism underlies anticorrosion coatings that merge redox buffering with physical barrier effects. Faure et al. have reported the fabrication of hybrid multilayer coatings on galvanized steel via layer-by-layer assembly of DOPA-functionalized cationic polymers and clay platelets [185]. The catechol groups promote adhesion and $Fe^{II}$/$Fe^{III}$ chelation, while the clay nanolayers create tortuous diffusion paths to block ions and oxygen, increasing impedance by 10 fold and achieving chromium-free corrosion protection. In addition, Payra et al. have demonstrated that incor-

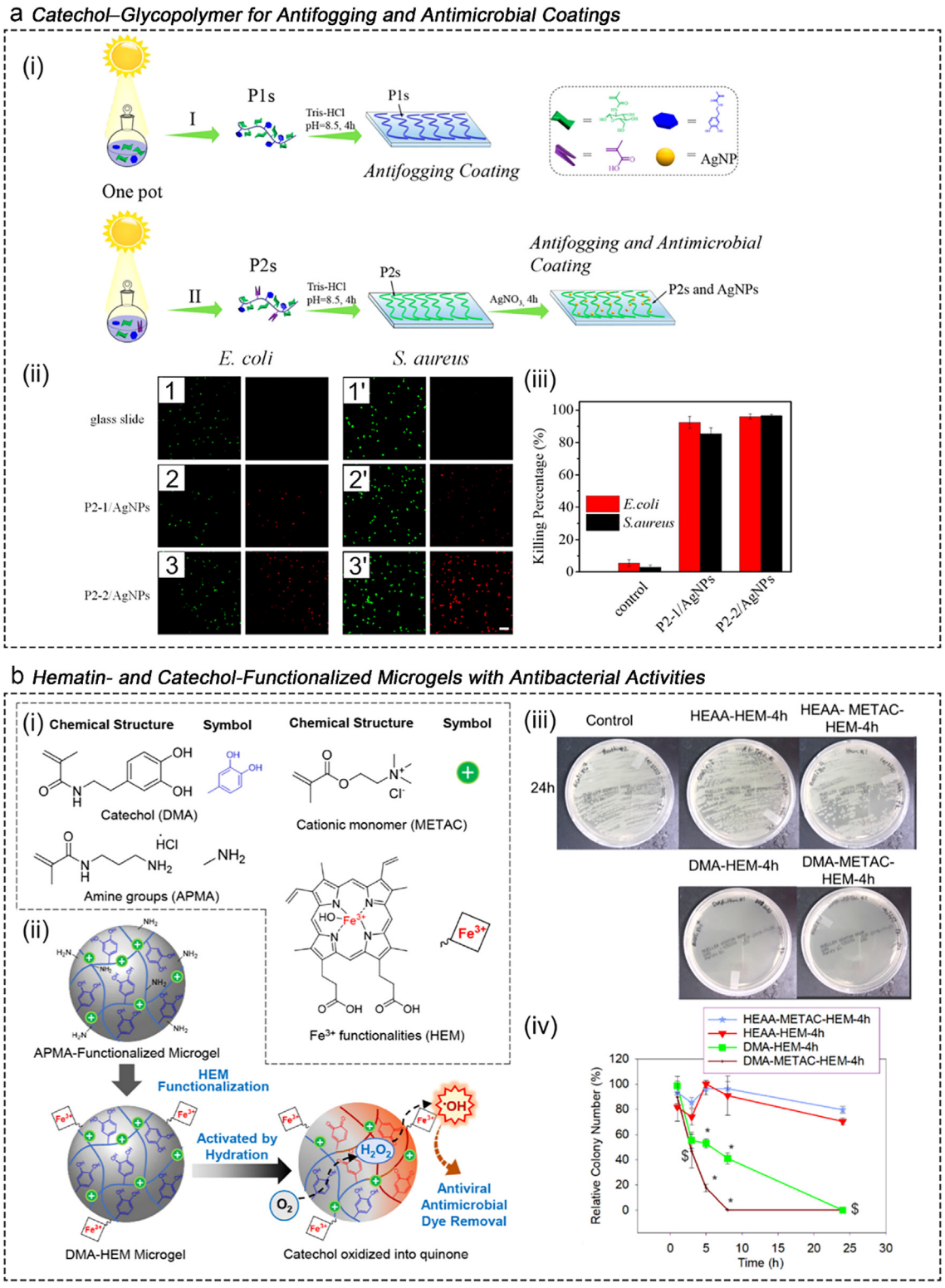


**Fig. 19.** Polyphenol-based antibacterial interfaces. (a) Catechol–glycopolymer as antifogging and antimicrobial coatings. (i) Schematic of sunlight-induced one-pot formation of catechol–glycopolymer films and subsequent in situ silver nanoparticle (AgNP) generation. P1 and P2 are poly(*N*-3,4-dihydroxybenzenethyl methacrylamide-*co*-2-deoxy-2-(methacrylamido)glucopyranose) and poly(*N*-3,4-dihydroxybenzenethyl methacrylamide-*co*-methacrylic acid-*co*-2-deoxy-2-(methacrylamido)-glucopyranose), respectively. (ii) Live/dead fluorescence microscopy images of *E. coli* (1–3) and *Staphylococcus aureus* (*S. aureus*) (1′–3′) on glass and AgNP-containing coatings showing efficient bacterial killing. (iii) Quantitative antibacterial performance indicating >95% elimination of both strains [177], Copyright 2020. Adapted with permission from the American Chemical Society. (b) Hematin- and catechol-functionalized microgels exhibiting self-activated Fenton-like antibacterial behavior. (i) Chemical structures of the catechol, cationic, and $Fe^{III}$–porphyrin components used to fabricate HEM–CAT microgels. (ii) Schematic mechanism illustrating catechol oxidation to $H_2O_2$ and its catalytic conversion by $Fe^{III}$–porphyrin centers into •OH radicals for broad-spectrum antimicrobial and antiviral activity. (iii) Photographs of bacterial colonies on control and hematin- and catechol-functionalized microgel-treated plates after 24 h incubation. (iv) Time-dependent bacterial survival curves confirming near-complete eradication [121], Copyright 2020. Adapted with permission from the American Chemical Society. HEM, hematin; HEAA, *N*-hydroxyethyl acrylamide.

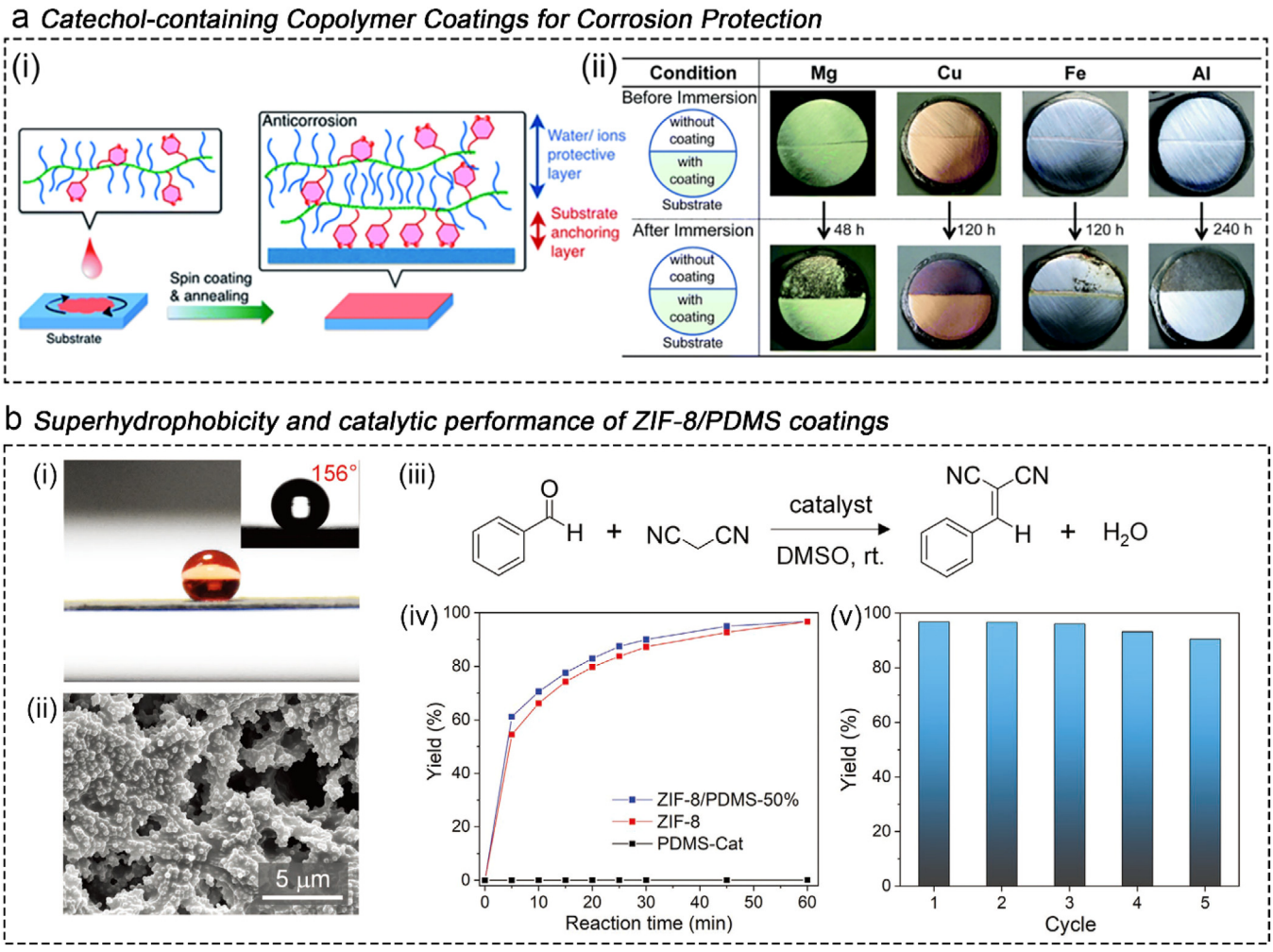


**Fig. 20.** (a) Bioinspired catechol-containing copolymer coatings for corrosion protection on diverse metals. (i) Schematic illustration of spin coating and annealing to form dense, hydrophobic, and water-ion-blocking layers through substrate anchoring and molecular packing. (ii) Photographs showing corrosion resistance of coated versus uncoated Mg, Cu, Fe, and Al substrates after immersion for up to 240 h [186], Copyright 2015. Adapted with permission from The Royal Society of Chemistry. (b) Superhydrophobic ZIF-8/PDMS coatings with catalytic functionality. (i) Water droplet on ZIF-8/PDMS-coated carbon cloth exhibiting a contact angle of 156 ° (ii) SEM image of the ZIF-8/PDMS-coated surface. (iii) Knoevenagel condensation reaction of benzaldehyde and malononitrile at room temperature. (iv) Reaction yields obtained with ZIF-8/PDMS, pristine ZIF-8, and catechol-functionalized PDMS (PDMA-Cat). (v) Catalytic recyclability of the ZIF-8/PDMS coating in the Knoevenagel reaction [117], Copyright 2020. Adapted with permission from Wiley-VCH GmbH.

porating DMA into hydrophobic alkyl methacrylate matrices produces transparent, defect-free films (0.3–1 $\mu$m) that reduce corrosion current densities by four orders of magnitude and maintain stability across pH 1–11 (Fig. 20a) [186]. Together, these systems establish metal–phenol anticorrosion interfaces as durable, eco-friendly alternatives to $Cr^{VI}$-based protective coatings. At the catalytic frontier, catechol–metal coordination has been harnessed to stabilize and modulate active centers across multiple length scales. Au@Ag@PDA nanoparticles have been assembled into robust interfacial monolayers, where PDA simultaneously reduces, anchors, and stabilizes nanocrystals for efficient and recyclable 4-nitrophenol reduction [187]. Wong et al. have extended this catechol-coordination strategy by directing the coordination-driven growth of ZIF-8 coatings on catechol-functionalized PDMS, generating superhydrophobic catalytic surfaces with sustained activity toward Knoevenagel condensation (Fig. 20b) [117]. The resulting ZIF-8/PDMS coating retained catalytic activity comparable to pristine ZIF-8, while catechol-mediated strong adhesion enabled facile recovery and excellent recyclability after repeated catalytic cycles. Collectively, these studies illustrate how polyphenol-based interface chemistry evolves from a universal modification tool to a multifunctional coordination framework. Through the integration of covalent grafting, dynamic metal coordination, and redox-active interactions, catechol-functionalized polymers enable interfaces that are mechanically reinforced, redox-active, chemically protective, and catalytically active. This convergence of adhesion chemistry and coordination dynamics defines a unifying molecular principle for designing adaptive coatings, protective barriers, and catalytic platforms across engineering and biomedical applications.

Polyphenol-functionalized polymers provide a broadly adaptable strategy for engineering multifunctional interfaces across diverse applications, including antifouling coatings, antibacterial surfaces, adhesive hydrogels, and catalytically or redox-active interfaces. However, the reactivity of phenolic groups can be both advantageous and disadvantageous: while it underpins strong adhesion and versatile interfacial chemistry, it may also promote nonspecific interactions, oxidative changes, or instability under complex application-relevant conditions. For example, exposed phenolic groups can strengthen surface binding and enable further coordination or redox reactions, but they may also promote nonspecific biomolecular adsorption or oxidative changes over time. Similarly, antibacterial or catalytic functions often require active metal ions, redox cycling, or charged groups, which may influence coating stability and biological compatibility. Therefore, fu-

ture work should not simply expand the range of functions introduced into polyphenol-based interfaces, but should more carefully define how phenolic anchoring layers, functional polymer segments, and outer-surface chemistries contribute to interfacial performance. Long-term evaluation under application-relevant conditions, including aqueous aging, mechanical stress, biofouling, oxidative environments, and complex biological media, will be essential for determining whether these interfaces can maintain their intended function beyond initial proof-of-concept demonstrations.

### 5.2. Responsive and adaptive materials

Polyphenol–functionalized polymer systems provide dynamic platforms that exploit reversible coordination, redox reactions, and hydrogen bonding to create materials capable of healing or responding to environmental stimuli. This section covers supramolecular architectures, such as hydrogels, in which catechol or gallol groups promote self-healing and actively regulate material responses to pH, ions, temperature, light, or mechanical stress, highlighting how rational molecular and network design enables programmable, reversible, and functionally adaptive material behavior.

#### 5.2.1. Self-healing hydrogels

The earliest generation of mussel-inspired hydrogels established $Fe^{III}$–catechol coordination as a reversible, pH-tunable cross-linking motif for dynamic network design. Holten-Andersen et al. recreated the self-healing behavior of mussel byssal threads by controlling bis- and tris-$Fe^{III}$–catechol complexes in PEG–dopamine hydrogels, achieving reversible gelation and mechanical recovery through pH adjustment [85]. Building on this concept, catechol, nitrocatechol, and 3–hydroxy-4-pyridinone ligands have been examined to tune coordination stability and gel mechanics [188]. The 3–hydroxy-4-pyridinone–$Fe^{III}$ hydrogels display robust gelation at physiological pH, enhanced oxidative resistance, and controllable viscoelastic relaxation, providing injectability and degradability for potential drug delivery. These studies defined metal–phenolic coordination as a chemically programmable and biologically compatible framework for creating self-healing, adaptive hydrogels, laying the foundation for subsequent generations of polyphenol-based materials. Subsequent research has expanded beyond $Fe^{III}$ coordination to incorporate hydrogen bonding, boronate ester, and oxidative coupling as alternative dynamic linkages for wet adhesion and self-healing. For instance, Ahn *et al.* have demonstrated metal-free self-healing of catechol-functionalized polyacrylates in water via bidentate hydrogen bonding and hydrophobic interactions, revealing that catechols alone can drive underwater cohesion [148]. To enhance the service life of polyolefin composites, Chen et al. developed a lignin cluster polymerization strategy to prepare lignin-functionalized polyolefin composites through nickel-catalyzed copolymerization of ethylene and lignin cluster monomers. The resulting composites exhibited rapid autonomous self-healing ($\leq$30 s) under diverse harsh environments, including underwater conditions, seawater, cryogenic temperatures (−60 °C), and organic solvents, while maintaining excellent mechanical properties and reprocessability through dynamic cross-linking networks [189]. Through exploiting synergistic $Fe^{III}$ coordination and $NaIO_4$-mediated oxidation, a polyurethane–dopamine system has been developed to achieve rapid gelation and reprocessability [190]. In another example, metal cross-links have been replaced by boronate–catechol dynamic esters to produce non-swellable marine elastomers, achieving 91% toughness recovery and excellent durability in seawater [191]. Collectively, these studies diversify mussel-inspired chemistry into multitype dynamic bonding, enabling versatile self-healing and biomedical sealing interfaces beyond classical $Fe^{III}$ coordination.

The integration of hierarchical structural design, dynamic coordination chemistry, and reversible cross-linking mechanisms has enabled the development of catechol-based gels into robust, adaptive self-healing systems displaying wet adhesion, mechanical recovery, and tissue adhesion properties. Combining imine formation and ionic cross-linking within poly(allylamine)–hydrocaffeic acid/nanoclay networks yields fully self-healing and pH-reversible hydrogels with enhanced underwater adhesion [80]. In a related strategy, catechol–phenolic intermolecular interactions have been shown to drive self-growing hydrogel particles, enabling spontaneous interparticle coalescence and long-term cohesion under high temperature and salinity [192]. Park et al. introduced cryo-triggered chitosan–catechol hydrogels with freeze–thaw-induced condensation of catechol-containing polymers, yielding porous, self-recoverable scaffolds suitable for fibroblast growth [66]. Mechanistic investigations into $Fe^{III}$–nitrocatechol coordination have revealed how supramolecular clustering and metal–ligand exchange kinetics govern the viscoelastic lifetime of catechol hydrogels. Rheology and small-angle X-ray scattering studies have revealed multiple relaxation regimes—from rapid bond dissociation ($\approx$0.1–1 s) to ultra-slow segment disengagement ($>10^5$ s)—establishing a relationship between coordination kinetics and cluster formation and long-lived elasticity [193]. These mechanistic insights provide a quantitative framework for understanding how metal–ligand association and polymer aggregation collectively dictate the self-healing behavior of catechol-based hydrogels. Beyond bulk gels, $Fe^{III}$ cross-linking of catechol-functionalized block copolymers at liquid–liquid interfaces has enabled the formation of self-healing viscoelastic microcapsules, bridging nanoscale MPNs with macroscopic mechanical constructs (Fig. 21a) [194]. The incorporation of photo-cross-linking alongside catechol H-bonding in PEG–poly(lactic acid) elastomers has led to biodegradable polymers that heal within 1 h at 37 °C [195]. In parallel, bioinspired redox regulation via ferritin-mediated $Fe^{III}/Fe^{II}$ cycling has been applied to sustain long-term self-healing of HA–catechol hydrogels, achieving 5× longer lifetimes than $FeCl_3$ gels (Fig. 21b) [129]. Collectively, these studies illustrate how hierarchical design, dynamic coordination, and bioinspired redox regulation converge to produce durable, reconfigurable self-healing materials with extended mechanical and biological lifetimes.

#### 5.2.2. Stimuli-responsive hydrogels

Catechol–metal ion coordination and redox-active bonds impart polyphenol-functionalized polymer hydrogels with tunable gelation and degradation under environmental stimuli. Spatial control over $Fe^{III}$–catechol coordination has enabled pH-driven actuation through ionoprinted metal-ion gradients within catechol-containing networks [92]. In parallel, the integration of boronate–catechol complexation and disulfide chemistry has produced hydrogels exhibiting reversible sol–gel transitions, in which pH or redox stimuli dynamically cleave and reform boronate–diol and disulfide linkages to enable self-healing and adaptive mechanical behaviors [196]. Orthogonal degradation pathways have also been realized by combining $Fe^{III}$ coordination with disulfide depolymerization, allowing independent pH- and thiol-triggered network disassembly [149]. Additionally, charge-switchable catechol–chitosan hydrogels have been engineered to reversibly adapt their structure and properties in response to pH variations [130]. Similarly, lignin-based hydrogels have been engineered to exploit the intrinsic protonation and ionization behavior of lignin for rapid pH-responsive mechanical switching and actuation. Cross-linking industrial kraft lignin with poly(ethylene glycol) diglycidyl ether produces an all-lignin-based hydrogel that reversibly transitions between soft and stiff states and undergoes repeated bending and recovery within approximately 1 min in response to alternating acidic and alkaline conditions [197]. These systems highlight how protonation and re-

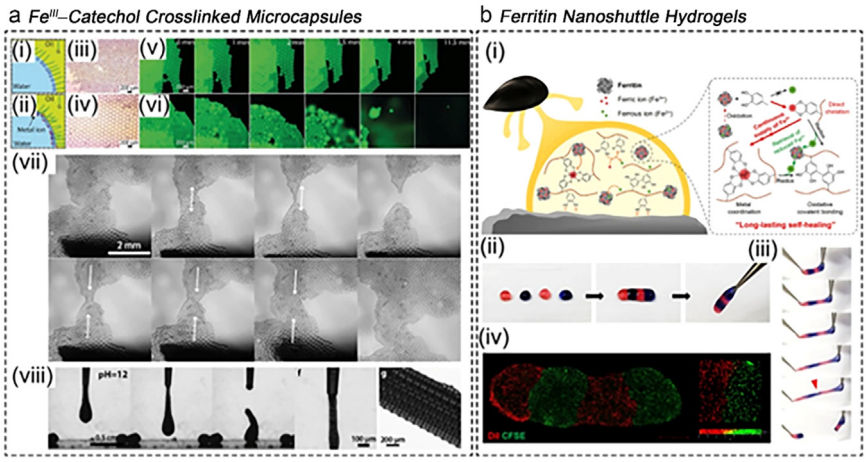


**Fig. 21.** Catechol-based self-healing polymeric materials. (a) Formation and dynamic behavior of $Fe^{III}$–catechol cross-linked microcapsules at liquid–liquid interfaces. (i,ii) Schematic illustration of interfacial assembly at oil–water and metal-ion-mediated oil–water interfaces. (iii,iv) Optical microscopy images of monolayered microcapsules formed without (iii) and with (iv) $Fe^{III}$ cross-linking, showing increased interfacial stability upon metal coordination. (v,vi) Fluorescence microscopy images of water-in-oil droplets stabilized by catechol-functionalized (v) or non-functionalized (vi) surfactants floating on an $Fe^{III}$-containing aqueous phase (pH = 8.5). Catechol-bearing droplets cross-link at the interface to form stable viscoelastic capsules, whereas control droplets collapse upon oil evaporation. (vii) Time-lapse optical microscopy sequence demonstrating self-healing of viscoelastic capsule films when fractured regions are brought into contact (arrows indicate the direction of the force applied on the film). (viii) Time-lapse photographs of capsule inks extruded into a basic solution (pH = 12), showing continuous filament formation and structural retention during deposition [194], Copyright 2019. Adapted with permission from Wiley-VCH & Co. KGaA, Weinheim. (b) Ferritin nanoshuttle enables long-lasting self-healing and assembly of catechol-functionalized hydrogels. (i) Schematic illustration of ferritin-mediated $Fe^{III}/Fe^{II}$ exchange sustaining dual cross-linking—metal coordination and oxidative covalent bonding—within HA–catechol hydrogels. Continuous $Fe^{III}$ supply and $Fe^{II}$ retrieval by ferritin establish a redox cycle that prolongs self-healing. (ii) Photographs of color-dyed HA–catechol hydrogels demonstrating autonomous fusion and cohesive recovery through ferritin-mediated cross-linking. (iii) Sequential images showing reversible bending and recovery of a ferritin-cross-linked hydrogel strip under repeated mechanical deformation. (iv) Confocal fluorescence image of coassembled red (DiI) and green (CFSE) cell-laden hydrogel modules, illustrating self-healing-driven formation of continuous 3D tissue-like constructs [129], Copyright 2023. Adapted with permission from the American Chemical Society.

dox control can program adhesion, disassembly, and biocompatibility in catechol-based hydrogels.

Besides chemical stimuli, light has emerged as a powerful external trigger to remotely and reversibly modulate cross-linking dynamics in catechol-containing networks. Photocleavable nitrodopamine motifs have enabled light-induced bond scission that drives programmable disassembly and underwater debonding, while maintaining $Fe^{III}$-mediated self-healing through reversible coordination [198]. Additionally, Liang et al. have exploited $Fe^{III}$–catechol photothermal complexes in PEG-based shape-memory polymers, enabling rapid NIR-triggered recovery (<60 s) and reversible actuation driven by localized heating [54]. These studies represent functional extensions of $Fe^{III}$–catechol coordination, demonstrating how optical and photothermal energy can control mechanical reconfiguration in reconfigurable adhesives, soft actuators, and biomedical devices.

Thermal modulation of catechol interactions enables temperature-dependent adhesion and soft actuation. The incorporation of catechol units into thermoresponsive PNIPAM networks yields hydrogels that display lower critical solution temperature behaviors and undergo heat-induced stiffening while maintaining cell-adhesive properties even below the phase-transition threshold [199]. In a related system, thermally reversible underwater adhesion has been achieved by exploiting temperature-controlled catechol hydration, where heating exposes catechol moieties to promote strong interfacial bonding and subsequent cooling induces detachment through rehydration (Fig. 22a) [200]. These studies demonstrate how temperature-triggered phase transitions and catechol hydration dynamics can generate reversible, biocompatible adhesive interfaces.

Beyond single-stimulus control, the integration of multiple responsive mechanisms has expanded catechol chemistry toward practical bioadhesive and printable scaffolds. Water- and pH-triggered hyperbranched catechol polymers have been shown to spontaneously coacervate, enabling rapid underwater adhesion and hemostatic wound sealing [201]. In parallel, coupling pH-dependent gallol oxidation with UV polymerization in HA methacrylate–gallic acid-functionalized HA bioinks has produced injectable and printable hydrogels that combine strong tissue adhesion with antioxidant functionality (Fig. 22b) [72]. Collectively, these studies exemplify next-generation multistimuli catechol networks capable of coupling environmental responsiveness with biological functionality for tissue engineering and wound repair.

The studies summarized in Section 5.2 demonstrate that polyphenol-functionalized polymers are particularly powerful for constructing responsive and adaptive soft materials because phenolic motifs can form reversible coordination bonds, hydrogen-bonding networks, boronate esters, and redox-active cross-links. These dynamic interactions allow hydrogels and supramolecular networks to self-heal, deform, debond, degrade, or recover in response to pH, redox conditions, light, temperature, and mechanical stress. However, the dynamic chemistry that enables adaptivity also introduces a possible limitation: responsiveness is often achieved by weakening or rearranging the network, which can compromise long-term mechanical integrity, dimensional stability, or fatigue resistance. A key challenge is therefore not simply to increase responsiveness, but to control the lifetime, spatial distribution, and reversibility of phenolic cross-links within the polymer network. Future studies should more rigorously evaluate these materials under repeated stimulus cycles, prolonged mechanical deformation, aqueous aging, and physiologically or application-relevant environments.

### 5.3. Energy and electronic devices

The redox-active and adhesive nature of polyphenol-functionalized polymers underpin their dual utility in electronic sensing and energy storage applications. This section covers systems that integrate catechol and gallol chemistries into conductive polymers, electrode binders, and interfacial coatings to enhance

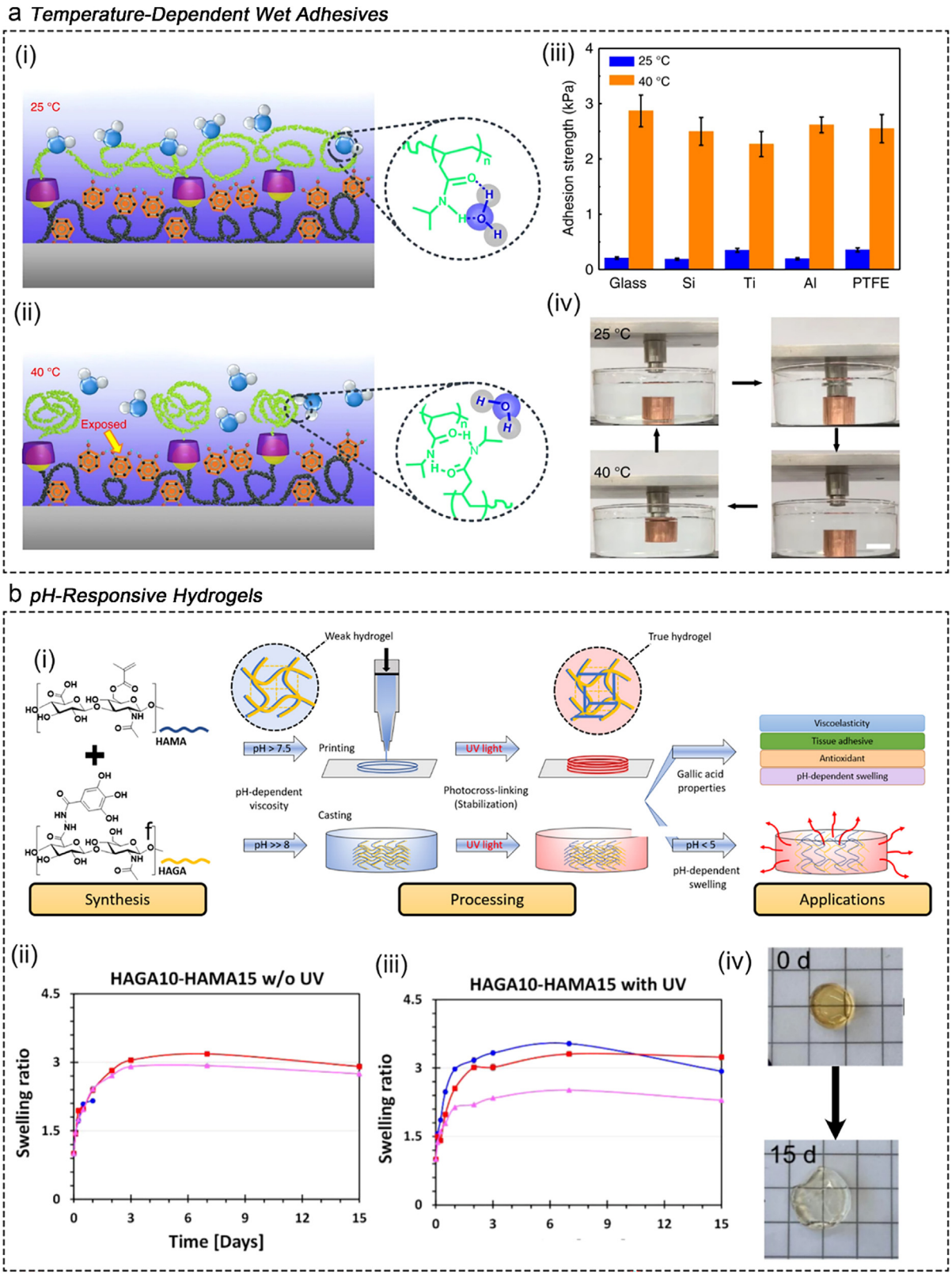


**Fig. 22.** Thermo- and pH-responsive catechol/gallol hydrogels with tunable adhesion and swelling behavior. (a) Temperature-dependent interfacial adhesion of PNIPAM–catechol hydrogel. (i, ii) Schematic illustrations showing enhanced hydrophobic collapse and catechol-mediated bonding at 40 °C. (iii) Quantitative adhesion strength of the hydrogel across different substrates confirming increased interfacial adhesion under an elevated temperature. (iv) Demonstration of the reversible underwater attachment and detachment behavior of the hydrogel [200], Copyright 2017 Zhao *et al.* Adapted with permission from Springer Nature. (b) (i) pH-responsive hyaluronic acid methacrylate (HAMA) and gallic acid-functionalized hyaluronic acid (HAGA) hybrid hydrogels exhibiting complementary pH- and light-induced cross-linking. The HAGA component modulates viscosity for injectability and 3D printability under weakly basic conditions, while UV-cross-linked HAMA stabilizes the network. (ii–iv) The resulting hydrogel displays tunable viscoelasticity, reversible swelling, and multifunctional antioxidant and adhesive properties [72], Copyright 2023 Jongprasitkul *et al.* Adapted with permission from the American Chemical Society.

charge transport, interfacial stability, and mechanical durability, as well as materials that harness reversible redox and coordination processes for chemical, biological, or mechanical signal transduction. By emphasizing the molecular-level control of these hybrid systems, we highlight how the precise modulation of redox and coordination interactions enables tunable electron transfer and robust/responsive performance in energy and electronic devices.

*5.3.1. Sensors*

Catechol-based polymers have been applied as building blocks for constructing multifunctional sensors, owing to their combined characteristics of adhesion, redox activity, and coordination chemistry. An early milestone was established by Ham et al., who introduced a catecholamine copolymer, p(*N*-(3,4-dihydroxyphenethyl) methacrylamide (DOMA)-*co*-aminoethylmethacrylamide (AEMA)), as a universal surface primer enabling direct immobilization of oligonucleotides on diverse substrates [202]. The simple aqueous deposition strategy provides strong adhesion and high-density hybridization, establishing catechol-mediated molecular recognition as a viable strategy for biosensor fabrication. Extending catechol chemistry to optical platforms, Zhan et al. have reported the design of fluorescent conjugated polymers bearing pendant catechol groups to enhance surface retention and photostability [160]. The multidentate catechol–oxide interactions produce robust fluorescent coatings with 14-fold higher signal durability under dynamic or aqueous conditions, exemplifying how catechol anchoring can stabilize optical sensors.

In mechanically coupled systems, PDA infiltration has been leveraged to repair intersheet defects in graphene fibers, achieving a 4-fold conductivity and 8-fold tensile strength improvement through $\pi-\pi$ and hydrogen-bond-mediated interlayer adhesion [203]. The resulting defect-healed fibers highlight catechol chemistry as a route to reconcile strength and conductivity in flexible electronic sensors. Similarly, catechol-terminated PMMA has been employed as a macromolecular coupling agent at ceramic/polymer interfaces in lead-free piezoelectric composites, where strong catechol–oxide binding preserves ferroelectric domains and improves local piezoresponse [204]. Metal ion-catechol coordination-driven polymer networks have been engineered for programmable stiffness control [205], suggesting structural patterning as a complementary strategy to enhance mechanical adaptability in soft sensor systems.

Recent research has shifted toward hydrogel-based biointeractive sensors, where dynamic catechol coordination governs adhesion, conductivity, and responsiveness. Metal-ion-responsive catechol hydrogels have been shown to exhibit colorimetric and electrochemical switching through reversible $Fe^{III}/Ag^{I}$ coordination [206]. Building on this concept, catechol-lignin/reduced-graphene-oxide hybrids embedded within double-network hydrogels have enabled the development of skin-conformal, adhesive, and UV-stable bioelectronic sensors [207]. The integration of catechol-modified PVA with $Ti_3C_2T_x$ MXene nanosheets yields self-healable, oxidation-resistant strain sensors, compatible with deep learning model-assisted signal analysis and long-term durability (Fig. 23) [114]. Such systems underscore the multifunctionality of catechol coordination in imparting robustness, signal stability, and biological compatibility to next-generation soft sensor technologies.

*5.3.2. Electrodes*

Electrochemical energy storage requires electrode materials that collectively display high-energy density, rapid kinetics, and long-term stability. Achieving greener and more sustainable energy storage requires hybrid electrode architectures that integrate battery-like redox reactions with capacitor-like charge transport [208–211]. In this context, catechol-based polymers offer a bioinspired molecular platform that combines reversible redox activity, metal coordination, and strong interfacial adhesion for next-generation organic electrodes. Early studies established catechol and quinone derivatives as reversible redox motifs for organic energy storage. For example, Kim et al. embedded $Q/QH_2$ couples within ordered polypyrrole networks to realize rapid proton-coupled electron transfer with pseudocapacitive behavior [212]. Liu et al. demonstrated a PDA–CNT hybrid cathode, in which the indolequinone units of PDA underwent multi-electron faradaic reactions while the nanotube framework provided electrical continuity and mechanical stability, yielding a sustainable organic cathode for $Li^+/Na^+$ batteries [213]. Patil et al. engineered a $Li^+$-conducting catechol copolymer that integrated redox activity with single-ion transport, and its combination with CNTs produced flexible buckypaper electrodes, which exhibited rate capability and a long cycle life (Fig. 24a) [214]. Building on these developments, the redox–coordination concept has been extended to multivalent ions ($H^+$, $Zn^{2+}$, $Al^{3+}$), establishing quantitative correlations between metal–catechol binding strength and electrode potential [215]. Further molecular and structural optimization have been achieved through the use of mesoporous PDA–graphene hybrids, which enhance ion diffusion and charge-transfer kinetics [216], as well as through molecularly defined catechol polymer platforms featuring near-complete functional substitution and fully reversible redox cycling [217]. Lignin-derived nitrogen-doped carbon aerogels assembled from co-electrospun nanofibers preserve wood-inspired cellular architectures, while generating interconnected multichannel porous networks during carbonization. The combination of hierarchical porosity, nitrogen doping, and continuous ion/electron transport pathways facilitates efficient charge storage, resulting in excellent cycling stability and a high energy density in symmetric supercapacitors [218]. These studies delineate a quinone-based faradaic framework, in which controlled molecular design enables tunable electron transfer and electrochemical stability in sustainable organic cathodes.

Catechol-based coordination chemistry has also been widely applied to engineer interfacial architectures that stabilize electrochemical interfaces and maintain electrode integrity under repeated cycling. For example, catechol–Ce coordination has been employed to construct antioxidative protective layers on proton-exchange membrane electrodes, where the dynamic $Ce^{III}/Ce^{IV}$ cycle scavenges radicals and enhances oxidative endurance in fuel-cell cathodes [219]. Jeong and Choi have introduced $Fe^{III}$–tris(catechol) dynamic networks as self-healing polymer binders for Si anodes, enabling autonomous crack repair and capacity retention during prolonged cycling [220]. Ko et al. have reported PEG–catechol cross-linked binders that combine ionic conductivity with strong adhesion to Si and Cu substrates, mitigating pulverization and delamination under electrochemical strain [109]. In addition, Battaglia et al. have demonstrated that polymer backbone flexibility and $\pi-\pi$/coordination interactions dictate cohesion and electrochemical durability of the electrode composites (Fig. 24b) [221]. Looking forward, integrating catechol coordination with emerging conductive or self-adaptive polymers may offer new pathways to design greener electrodes that autonomously regulate redox stability and mechanical resilience under practical operating conditions.

The application of polyphenol-functionalized polymers in energy and electronic devices has shown considerable promise, but further progress will require a clearer understanding of how phenolic chemistry controls device-level processes. For example, increasing phenolic content may strengthen adhesion or introduce additional redox-active sites, but it may also dilute conductive pathways, restrict ion transport, or alter interfacial resistance. Therefore, an important next step for this field is to move beyond reporting composite-level performance improvements and toward identifying which specific transport, interfacial, or electrochemical processes are regulated by phenolic motifs.

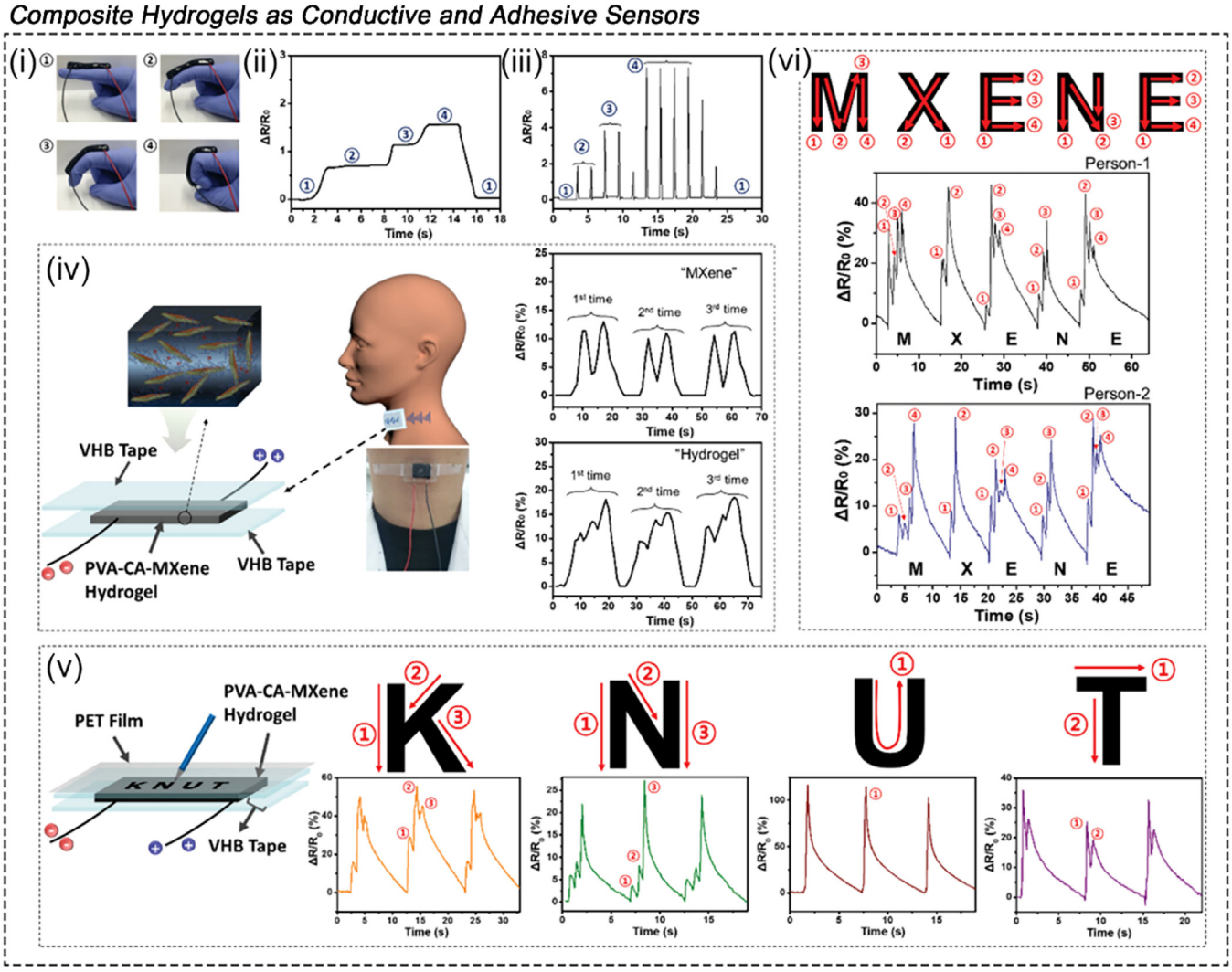


**Fig. 23.** Polyphenol-functionalized polymer-based multifunctional nanomaterials for sensor applications. Poly(vinyl alcohol)–catechol (PVA–CA)–MXene composite hydrogel used as a conductive, stretchable, and adhesive sensor for bioelectronic applications. (i–iii) Motion sensing capability demonstrated by finger bending and tapping tests showing stable, reproducible resistance changes. (iv) Application of the wearable PVA–CA–MXene sensor on the throat for voice monitoring, showing consistent signal response across multiple cycles. (v–vi) Real-time detection and recognition of articulated words ("MXENE" and "KNUT") by decoding resistance waveforms, highlighting high signal fidelity and durability [114], Copyright 2023. Adapted with permission from Wiley-VCH.

### 5.4. Biomedical applications

The intrinsic biocompatibility, adhesion, and redox reactivity of polyphenol-functionalized polymers underpin a wide spectrum of biomedical applications, spanning drug delivery, tissue repair, and regenerative medicine. This section covers polymeric systems where catechol and gallol chemistries are harnessed to achieve bioadhesion, antioxidation, and dynamic crosslinking for therapeutic or diagnostic purposes. We introduce studies that apply polyphenol-functionalized polymers as clinically relevant biointerfaces and therapeutic platforms, highlighting how polyphenol-based molecular design enables tunable interactions with cells and tissues for controlled delivery, healing, and regeneration.

#### 5.4.1. Drug delivery and bioimaging

Polymers have served as versatile and tunable platforms for drug delivery applications [222–224]. The integration of polyphenol coordination into supramolecular assembly of polymer chains has enabled the creation of multifunctional, stimuli-responsive drug delivery and imaging platforms that couple chemical adaptability with structural robustness. Catechol conjugation transforms polymers into bioadhesive materials that prolong residence, guide localization, and enhance tissue interaction. For example, Kim et al. have reported the use of PEI–catechol to immobilize adeno-associated viruses on substrates, producing "sticky viruses" capable of patterned gene transfer and spatial control of neurite outgrowth [225]. Kim et al. have adapted this concept to oral mucoadhesion, where catechol-conjugated chitosan covalently interacts with mucin thiols and amines to increase gastrointestinal retention and insulin bioavailability by 3-fold [226]. Similarly, catechol-modified chitosan/HA nanoparticles have been engineered, combining electrostatic complexation with catechol-mediated tissue adhesion, for sustained local delivery of DOX in oral cancers [227]. Beyond molecular bonding, Zhao et al. have demonstrated the synergy of geometry-assisted adhesion and catechol chemistry in enhancing wet adhesion on leaves and pesticide retention through the engineering of hat-shaped PVA-catechol microparticles that combines hydrogen bonding with mechanical interlocking; thereby suggesting a general strategy for creating robust, adherent coatings and localized therapeutic carriers [228]. Collectively, these studies establish catechol-based adhesion—from

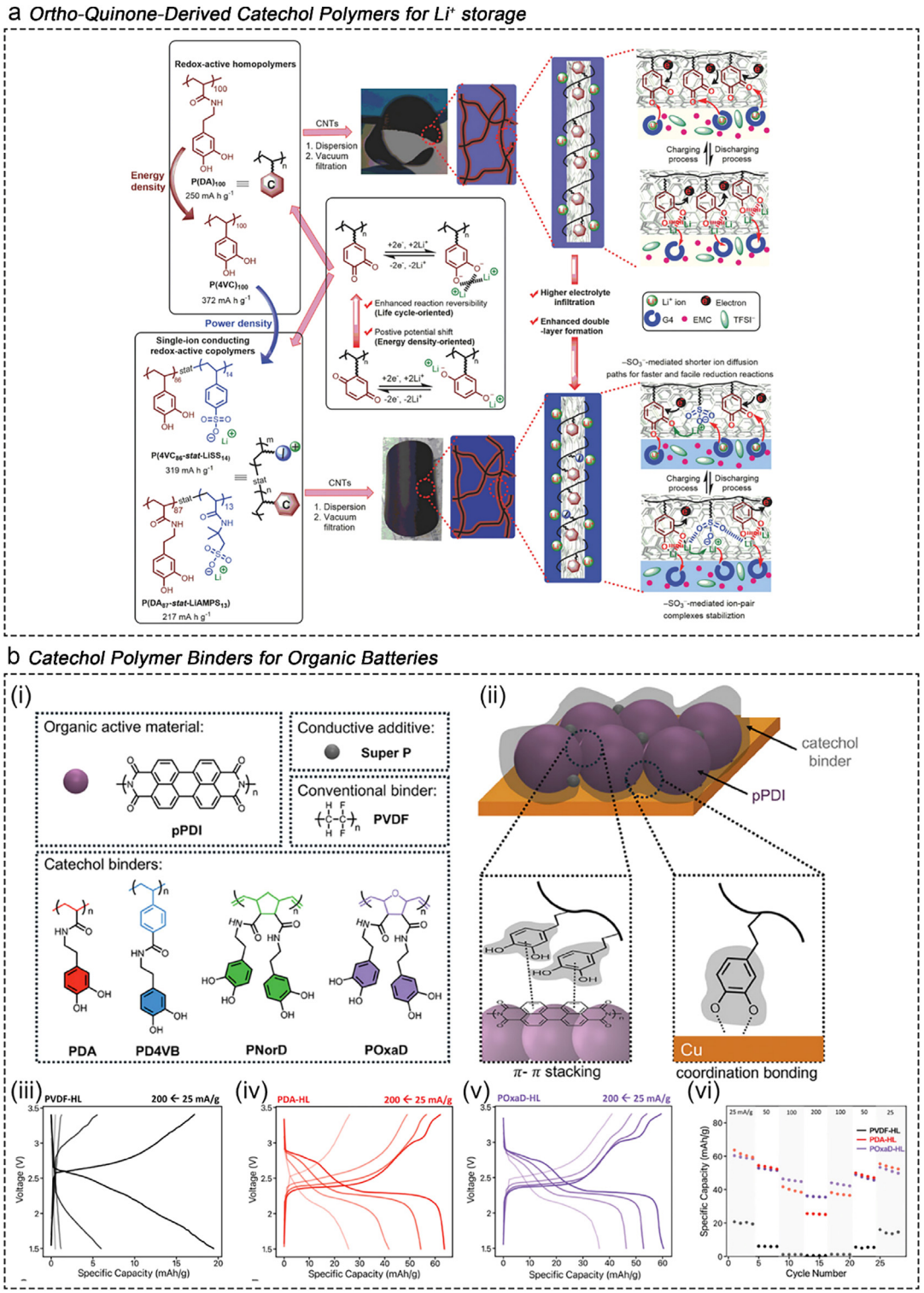


**Fig. 24.** Catechol-bearing redox polymers for robust $Li^+$ energy storage and interfacial stabilization. (a) Bioinspired macromolecular engineering of *ortho*-quinone-derived catechol polymers with tunable redox and ionic functionalities for high-performance $Li^+$ storage. Single-ion-conducting copolymers ($P(DA_{87}$-stat-$LiAMPS_{13})$) achieve enhanced electrolyte infiltration, rapid ion diffusion, and stable ion-pair complexes, enabling high-rate and long-life cycling (98% capacity retention after 3400 cycles). Catechol–CNT interactions provide binder-free, flexible buckypaper cathodes with improved $Li^+$ transport and double-layer capacitance [214], Copyright 2017. Reproduced with permission from Wiley-VCH & Co. KGaA, Weinheim. (b) Mussel-inspired catechol polymer binders for organic batteries. (i) Schematic representation of the cell components, including perylene diimide (pPDI) as the organic active material, Super P as the conductive additive, and various catechol-based polymer binders (PDA, poly(dopamine acrylamide); PD4VB, poly(dopamine 4-vinylbenzamide); PNorD, poly(norbornene dopamine); POxaD, poly(oxanorbornene dopamine)) compared with conventional PVDF. (ii) Illustration of interfacial binding mechanisms showing $\pi$–$\pi$ stacking between pPDI and catechol rings, and $Cu^{II}$ coordination enhancing adhesion and charge transport at the electrode interface. (iii–v) Galvanostatic charge–discharge profiles of electrodes using PVDF, PDA, and POxaD binders at different current densities, highlighting the improved electrochemical reversibility of catechol-containing systems. (vi) Cycling performance comparison demonstrating higher specific capacity and stability of the catechol–binder electrodes relative to PVDF-based controls [221], Copyright 2024 Battaglia *et al*. Adapted with permission from Wiley-VCH.

chemical to structural scales—as a unifying approach for designing delivery systems that integrate fixation, retention, and controlled release.

In addition, dynamic covalent and supramolecular catechol-based interactions enable precise, environment-responsive control of drug loading and release. For example, catechol–boronate dynamic covalency has been introduced as a reversible linkage for pH-triggered drug release, achieving selective liberation of bortezomib under acidic tumor conditions [36]. Building on this concept, Qiu et al. engineered pH-active, glutathione-degradable catechol-bearing nanogels that codelivered DOX and bortezomib via boronate and electrostatic interactions, enabling sequential, redox-coupled release and synergistic tumor inhibition [81]. Liang et al. demonstrated that $\pi$–$\pi$ stacking and hydrogen bonding between DOX and PEG–epigallocatechin gallate generated supramolecular nanocomplexes with high loading efficiency (~88%) and pH-dependent dissociation, highlighting that dynamic noncovalent catechol interactions can direct precise drug release [229]. Degradable nanoparticle systems were designed using L-DOPA-based poly(ester-urethane)s stabilized by aromatic $\pi$ interactions and enzymatically cleavable backbones, achieving enzyme-triggered release of DOX and TPT, and selective cytotoxicity to cancer cells (MCF-7) [96]. Together, these studies illustrate how catechol chemistry—whether through reversible covalent or supramolecular interactions—provides molecular precision for multiresponsive, controllable drug delivery.

Metal–phenolic coordination chemistry generates programmable hybrid carriers whose mechanical, interfacial, and biological properties are governed by reversible $Fe^{III}$–catechol cross-linking. Dopamine-functionalized HA and PEG building blocks have been shown to assemble with $Fe^{III}$ into MPN capsules capable of $CD44^{+}$-targeted delivery, establishing a polyphenol-based hybrid platform that integrates intrinsic bioactivity with antifouling properties [71]. Subsequent studies have revealed that protein corona formation on HA-based MPN capsules enhances, rather than diminishes, receptor-specific interactions, highlighting MPN adaptability within biological fluids [133]. In addition, systematic studies on biomolecular corona formation have shown that precoating nanoparticles with fetal bovine serum effectively alters the biomolecular corona composition, leading to reduced nanoparticle–leukocyte association in human blood [230]. Quantitative correlations between PEG-MPN capsule size and phagocytic uptake further demonstrate that PEG–polyphenol coordination plays a central role in regulating stealth behavior and circulation profiles [231]. More recently, the integration of DNA hybridization with $Fe^{III}$ coordination has enabled the formation of programmable MPN nanocapsules for highly efficient siRNA delivery (Fig. 25a) [47]. Altogether, these studies define MPNs as modular, bioadaptive coordination frameworks capable of translating molecular recognition into tunable mechanical and delivery properties across multiple length scales.

Supramolecular polyphenol assemblies integrate structural modulation and external stimuli into adaptive platforms for therapy and imaging. Mai et al. have extended catechol coordination to magnetically responsive iron oxide nanocubes, where furfuryl–catechol–PEG ligands enable Diels–Alder cleavage under alternating magnetic fields for localized, non-thermal drug release (Fig. 25b) [232]. In addition, the OligoPEG–Dopa-coated $Fe_3O_4$ nanoparticles exhibit high colloidal stability and $T_2$ magnetic resonance imaging contrast ($r_2 \approx 254\ mM^{-1}\ s^{-1}$), introducing a durable, bioinert imaging interface [105]. These studies represent the culmination of polyphenol engineering—from molecular coordination to multimodal actuation—where catechol chemistry underpins magnetically, photothermally, and radiometrically integrated theranostic systems capable of precision treatment and real-time visualization.

*5.4.2. Wound healing*

Catechol- and gallol-derived chemistries have been extensively leveraged to design multifunctional wound-healing biomaterials that combine rapid wet adhesion, antimicrobial defense, and tissue adhesion. For example, poly(acryloyl glycine)–hydroxyapatite hydrogels have been designed to combine $Ca^{II}$–catechol coordination with polymer entanglement, achieving a compressive strength of 5 MPa and strong wet adhesion for rapid wound sealing [233]. Protein-based adhesive systems have been realized using recombinant elastin-like polypeptide hydrogels end-functionalized with catechol groups, which display strong adhesion to porcine skin (≈37–39 kPa), elastic compliance, and complete biodegradation in vivo, establishing a suture-free platform for soft-tissue repair [234]. An all-natural $\varepsilon$-polylysine/gallic acid–collagen network has been shown to display high wet adhesion, intrinsic antibacterial activity, and scar-free healing through gallol–amine cross-linking and lysine–tissue electrostatics (Fig. 26a) [75]. Another study has exemplified a dual-cross-linking catechol–thiol hydrogel that combines rapid gelation, strong mechanical integrity, and ROS-mediated redox signaling, achieving >95% closure of infected burns within 10 days [235]. Catechol chemistry has also enabled instant hemostatic sealing in minimally invasive contexts. For instance, catechol-functionalized chitosan grafted onto medical needles undergoes oxidative catechol–amine cross-linking upon blood contact, triggering a rapid sol-to-gel transition that forms hydrogel plugs to seal puncture wounds and prevent blood leakage [236]. This approach highlights the translational potential of catechol-based adhesives for rapid hemostasis and infection-resistant wound closure, extending mussel-inspired design principles toward clinical applications.

Beyond bulk hydrogels, catechol chemistry has enabled the development of composite and fibrous architectures that extend adhesive and regenerative functionality. Poly($\gamma$-glutamic acid)–dopamine hydrogels integrating enzymatic catechol oxidation with nanosilicate cross-linking have achieved rapid wound sealing, strong wet adhesion, and scar-free skin regeneration [237]. Furthermore, injectable composite systems have been realized using catechol-modified chitosan hydrogels incorporating oyster-peptide microspheres, wherein thermosensitive gelation and sustained peptide release act synergistically to enhance wound healing by accelerating re-epithelialization and stimulating angiogenesis [238]. At the fibrous scale, PDA-assisted catechol immobilization has been employed to fabricate polycaprolactone/alginate fibers that covalently bind antimicrobial peptides, resulting in enhanced vascularization and complete wound closure within 2 weeks [239]. Collectively, these advances demonstrate how catechol and gallol chemistries provide a molecular toolkit for engineering adhesive, injectable, and bioactive scaffolds. By integrating physical sealing, biochemical protection, and regenerative signaling within structurally diverse formats, these systems enable efficient and multifunctional wound repair beyond conventional bulk hydrogel platforms.

*5.4.3. Tissue engineering*

Early efforts in integrating catechol chemistry into tissue engineering have established fundamental principles for pH-, redox-, and oxidation-controlled adhesion–cohesion transitions in natural polymer scaffolds. HA–catechol conjugates have been developed for switching between substrate adhesion and hydrogel cohesion via pH modulation, forming biocompatible, porous matrices that supported neural stem cell encapsulation and differentiation [70]. In parallel, Ku and Park have demonstrated that mussel-inspired PDA coatings synergize with nanofibrous alignment to promote skeletal myoblast fusion and maturation, linking catechol surface chemistry to cellular mechanotransduction [240]. Extending this interface control, patterned PDA films with tunable topography

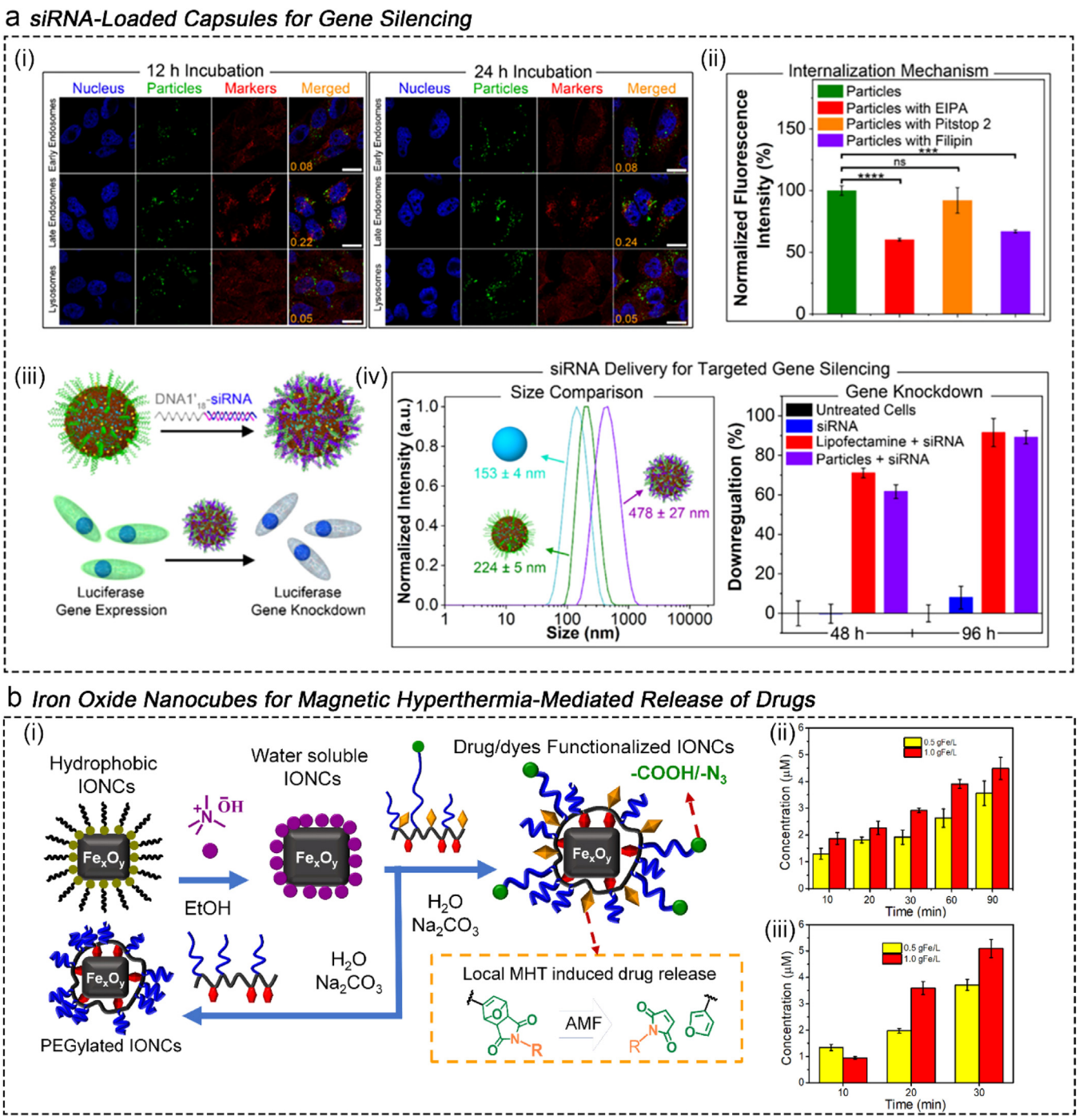


**Fig. 25.** Polyphenol-engineered nanocarriers for nucleic acid and drug delivery. (a) siRNA-loaded capsules for gene silencing. (i) Confocal microscopy images showing intracellular trafficking of MPN capsules loaded with siRNA over 12 and 24 h. (ii) Quantitative analysis of capsule uptake mechanisms using specific endocytic inhibitors. (iii, iv) Schematic illustrations and transfection efficiency of siRNA-loaded MPN capsules, confirming efficient luciferase gene knockdown after 48 and 96 h incubation [47], Copyright 2022. Adapted with permission from the American Chemical Society. (b) Drug/dye-functionalized iron oxide nanocubes (IONCs). (i) Two-step ligand exchange for the preparation of functional IONCs bearing carboxylic acid (–COOH)- or azide ($–N_3$)-terminated groups. Time-dependent release profiles of DOX (ii) and fluorescein (iii) from functional IONCs upon magnetic hyperthermia (MHT, 110 kHz, 16 kA $m^{-1}$) at different Fe concentrations (0.5 and 1.0 g $L^{-1}$) [232], Copyright 2022 Mai *et al.* Adapted with permission from the American Chemical Society. AMF, alternating magnetic field.

have been engineered, revealing that microscale indentation enhances focal adhesion and cell spreading [241]. Collectively, these studies define catechol-mediated surface modification as a versatile strategy to reconcile adhesive stability with cellular compatibility in soft tissue scaffolds.

Building upon this chemical foundation, subsequent research has leveraged multivalent phenolic cross-linking and dynamic hydrogen bonding to achieve rapid gelation, self-healing, and 3D printability. Gallol–epigallocatechin gallate hydrogen bonding has been identified as a metal-free, coordination-independent mechanism for forming dynamic, protein-interactive hydrogels [101]. The application of HA–PG has allowed dual oxidative and alkaline cross-linking, creating elastic, adhesive, and angiogenic hydrogels for stem cell transplantation [74]. In another example, gallol-functionalized HA/gelatin bioinks undergo time-programmed hydrogen bonding and oxidation, yielding printable constructs with

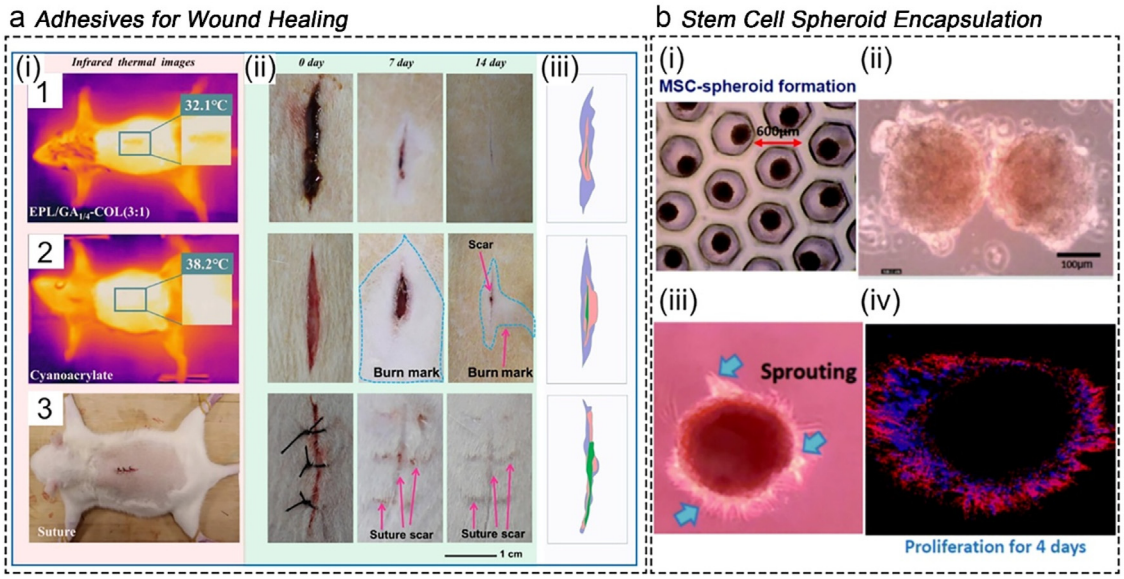


**Fig. 26.** Catechol-reinforced hydrogels for wound healing and tissue engineering. (a) Bioinspired gallol-functionalized collagen adhesive for wet-tissue sealing and wound repair. (i) Infrared thermography comparing the exothermic behavior of EPL/$GA_{1/4}$–COL, $\varepsilon$-polylysine/gallic acid/collagen adhesive, cyanoacrylate glue, and surgical sutures during wound closure, showing lower heat generation with the bioadhesive. (ii) Photographs of skin incisions and burn wounds in mice demonstrating superior healing and minimal scarring with EPL/$GA_1/_4$–COL compared with cyanoacrylate and sutures over 14 days. (iii) Schematic contour representation showing progressive wound contraction [75], Copyright 2020. Adapted with permission from Elsevier B. V. (b) HA–catechol hydrogel supporting mesenchymal stem cell (MSC) spheroid encapsulation and sprouting. (i) MSC-spheroids formed in the hydrogel. (ii) Phase-contrast images of MSC spheroids after 1 day culture. (iii,iv) Hydrogel encapsulation of MSC-promoted cell migration and proliferation, demonstrating a suitable microenvironment for cartilage tissue engineering [246], Copyright 2021. Adapted with permission from The Royal Society of Chemistry.

high cell viability [242]. In parallel, gallic acid-modified methacrylated gelatin bioinks, engineered through combining $Fe^{III}$–phenolic coordination and UV polymerization, enable 3D printing at physiological conditions [243]. These dual-cross-linked hydrogels exhibit high shape fidelity, elasticity ($G' \approx 4.5$ kPa), and tissue-adhesive antioxidant properties, while maintaining excellent cell viability after printing. The printed architectures are also enabled through catechol-mediated double-network hydrogels matching muscle viscoelasticity, demonstrating that phenolic cross-linking imparts both mechanical robustness and cellular permissiveness [244]. These studies have transitioned catechol-based hydrogels from static adhesives to reversible, processable, and biointeractive materials compatible with 3D biomanufacturing.

Recent research has shifted toward functional tissue reconstruction, emphasizing hierarchical mechanics, cell-instructive interfaces, and in vivo regenerative efficacy. Within the context of cartilage regeneration, chondroitin sulfate–catechol hydrogels have been designed with cartilage-matched stiffness (~10 kPa) and controlled degradation profiles, supporting stem cell chondrogenesis and promoting hyaline cartilage regeneration in rabbit defect models [245]. Enzymatically cross-linked systems further extend catechol functionality in cartilage repair. For instance, enzymatically cross-linked catechol–chitosan hydrogels via HRP/$H_2O_2$ chemistry have achieved tunable gelation kinetics, porous microstructure, and seamless integration with native cartilage, while promoting bone-marrow-derived mesenchymal stem cell differentiation [65]. Beyond musculoskeletal tissues, catechol-functionalized hydrogels have demonstrated broad translational potential across diverse tissue contexts. Sprayable oxime-cross-linked star-PEG–catechol hydrogels have been developed for cardiac adhesion prevention [128], while HA–catechol matrices have been used to deliver mesenchymal stem cell spheroids for esophageal fibrosis repair (Fig. 26b) [246]. In parallel, catechol–amine synergistic interactions have been shown to regulate endothelial morphogenesis, underscoring vascular integration as an emerging dimension of catechol-functionalized biointerfaces [73]. Altogether, these studies delineate a trajectory in phenolic-based material design for tissue engineering, from chemical-level adhesion control, through dynamic cross-linking and printing adaptability, to multifunctional, regenerative hydrogels capable of guiding cell fate and tissue morphogenesis in vivo. Catechol and its analogues have thus evolved from mimics of mussel-inspired adhesion into biochemical–mechanical mediators bridging soft materials with living tissue, offering a blueprint for next-generation regenerative scaffolds that unify adhesion, mechanics, and biology.

The biomedical studies summarized in Section 5.4 demonstrate that catechol- and gallol-functionalization on biocompatible polymers can serve as dynamic regulators of biological contact, cargo retention, release, tissue integration, and extracellular matrix remodeling. However, the central challenge lies in the fact that biological media are chemically active: proteins, lipids, metal ions, enzymes, oxidants, and inflammatory microenvironments can alter phenolic oxidation state, coordination stability, cross-linking density, and degradation pathways after administration or implantation. Therefore, future biomedical studies should move beyond initial demonstrations of cytocompatibility, adhesion, or therapeutic efficacy and more rigorously define how phenolic chemistry evolves in vivo over time. Such understanding will be essential for determining whether polyphenol-functionalized polymer systems can maintain the required balance among retention, responsiveness, bioactivity, degradation, and safety in clinically relevant settings.

## 6. Summary and outlook

This review presents a comprehensive overview of the synthetic strategies, hierarchical assembly behaviors, and functionalities of polyphenol-functionalized polymers, highlighting their versatility across chemistry, materials science, and bionanotechnology. These polymers have emerged as a distinctive class of building blocks that integrate polymer chemistry with the versatility of phenolic groups. Advances in polymer synthesis, including ring-

opening polymerization, radical polymerization, controlled/living radical polymerization, and diverse post-functionalization strategies, have enabled the precise incorporation of phenolic motifs into linear, branched, and networked polymer architectures. The resulting polymers can interact with metal ions, small molecules, macromolecules, or nano/microstructures through a broad spectrum of covalent and noncovalent interactions, including oxidation-mediated coupling, cross-linking reactions, dynamic boronate–phenolic complexations, hydrogen bonding, metal coordination, hydrophobic interactions, ionic interactions, and $\pi$–$\pi$ interactions. These chemistries endow polyphenol-functionalized polymers with the capacity to form hierarchical assemblies, spanning molecular complexes, hydrogels, particles, thin films, and organized superstructures. Beyond phenolic reactivity, the intrinsic attributes of polymer scaffolds—such as biocompatibility, stealth and targeting behavior, charge tunability, hydrophilicity/hydrophobicity, stimuli-responsiveness, and bioactivity—can be strategically leveraged to program the physicochemical properties of assembled materials. Collectively, polyphenol-functionalized polymers have emerged as a versatile materials platform that bridges the multifunctionality of phenolic chemistry with the structural adaptability of polymer frameworks, enabling the generation of advanced materials for multifunctional interfaces, responsive and adaptive systems, energy and electronic devices, and biomedical applications.

From a materials science perspective, polyphenol-based systems demonstrate broad utility in interface engineering, energy storage, and sensing. Their ability to mediate charge transfer and redox activity has advanced applications in organic electrodes and electrochemical sensors. The field is now transitioning from phenomenological demonstrations toward predictive design, in which molecular-level insights—such as coordination geometry, oxidation kinetics, and interfacial energy landscapes—can guide the rational engineering of new functional materials. In the biomedical domain, their strong wet adhesion and biocompatibility have inspired tissue adhesives, wound dressings, and 3D-printable bioinks. Polyphenol-functionalized polymers can also actively regulate biological processes by modulating oxidative stress, promoting tissue integration, and enabling controlled delivery of therapeutics and genetic materials. Future directions will likely focus on integrating these systems with lipid, peptide, and nucleic acid technologies to achieve precise biofunctionality and spatiotemporal control in vivo.

Despite considerable progress in the synthesis and application of polyphenol-functionalized polymers, several opportunities remain to advance both fundamental understanding and practical applications. (1) A deeper mechanistic understanding is needed of how phenolic ligands and polymer chains cooperatively dictate the assembly process, and how the resulting assembled structures influence material properties and function. Elucidating these multiscale relationships will be essential for predictive material design. (2) Broadening the library of polymer scaffolds to encompass diverse architectures (e.g., 2-, 4-, 8-arm or dendritic), molecular weights (from 1 to 1000 kDa), and functionalities (e.g., charge, degradability, and responsiveness) may unlock additional assembly modes. (3) Expanding the chemical repertoire of phenolic moieties beyond canonical catechol and gallol derivatives remains an unexplored area. For example, multihydroxylated aromatics [166] and enzymatic-catalyzed synthesized polyphenols [247] may enrich the functional and structural landscape of available building blocks. (4) Data-driven and artificial intelligence-assisted design strategies are expected to accelerate the fabrication of polyphenol-functionalized polymer assemblies with precisely tuned physicochemical properties. Coupled with developed synthetic methods, sustained multidisciplinary collaboration, and improved mechanistic insight, such approaches may enable the development of next-generation materials capable of addressing long-standing challenges across chemistry, materials science, and bionanotechnology.

## CRediT authorship contribution statement

**Chan-Jin Kim:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Conceptualization. **Shiyao Li:** Writing – review & editing, Writing – original draft, Investigation. **Gyeongeun Heo:** Writing – review & editing. **Zhaoran Wang:** Writing – review & editing. **Yi Ju:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization. **Frank Caruso:** Writing – review & editing, Funding acquisition, Conceptualization.

## Declaration of competing interest

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

## Data availability

No data was used for the research described in the article.

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