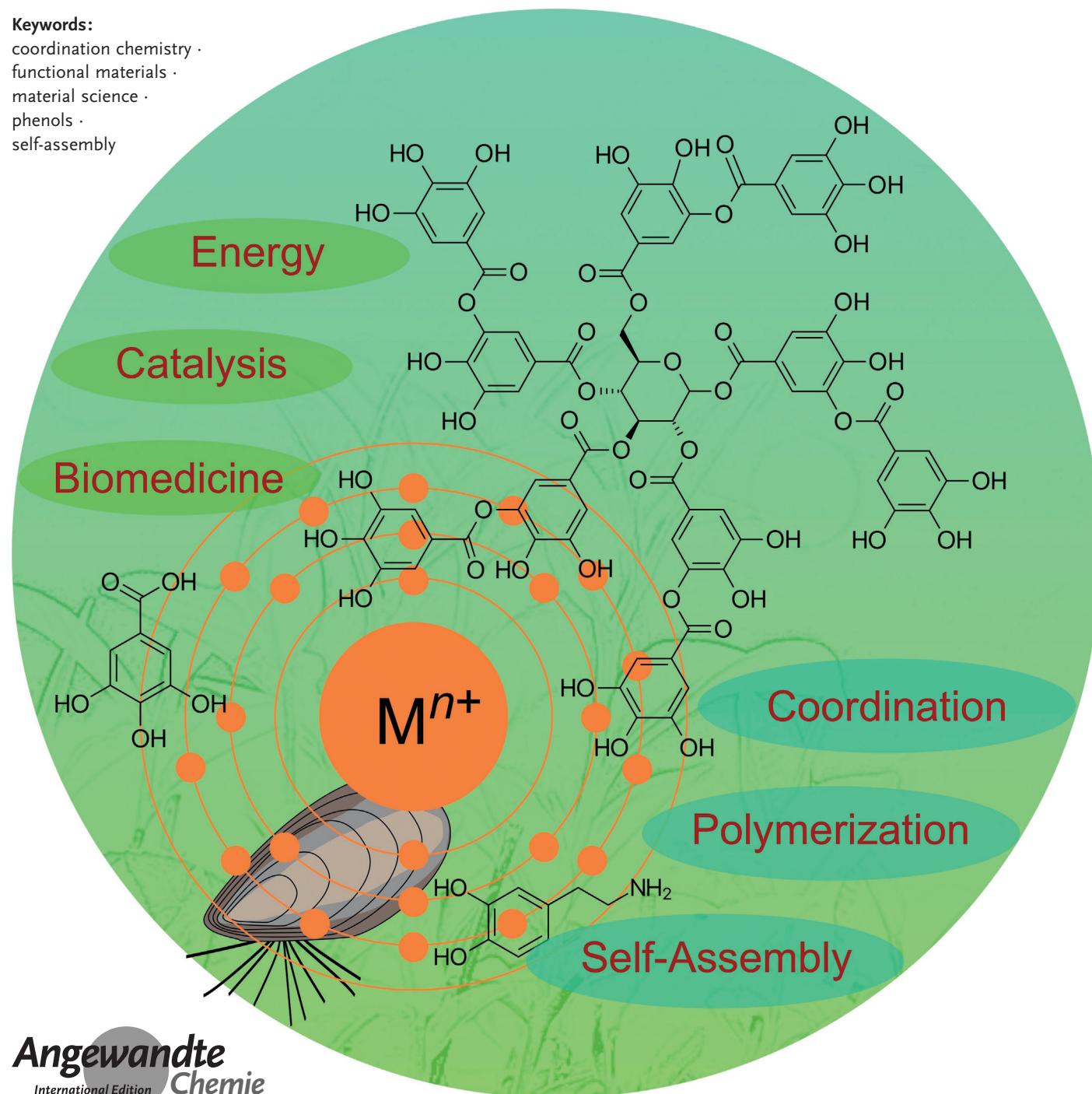


Phenolic Building Blocks for the Assembly of Functional Materials

Md. Arifur Rahim, Samantha L. Kristufek, Shuaijun Pan, Joseph J. Richardson, and Frank Caruso*

Keywords:

coordination chemistry ·
functional materials ·
material science ·
phenols ·
self-assembly



Phenolic materials have long been known for their use in inks, wood coatings, and leather tanning. However, there has recently been a renewed interest in engineering advanced materials from phenolic building blocks. The intrinsic properties of phenolic compounds, such as metal chelation, hydrogen bonding, pH responsiveness, redox potentials, radical scavenging, polymerization, and light absorbance, have made them a distinct class of structural motifs for the synthesis of functional materials. Materials prepared from phenolic compounds often retain many of these useful properties with synergistic effects in applications ranging from catalysis to biomedicine. This Review provides an overview of the diverse functional materials that can be prepared from natural and synthetic phenolic building blocks, as well as their applications.

1. Introduction

Phenolic compounds display diverse functions in a variety of natural systems, ranging from bacteria and fungi to plants and animals.^[1,2] Largely found as secondary plant metabolites, these compounds not only play a pivotal role in the defense mechanisms of plants, but also exhibit a wide range of properties including pigmentation and flavoring of plants and food products, protein complexation, metal coordination, and radical scavenging.^[1,3–6] For example, flavonoids, a major subclass of polyphenols, are primarily responsible for the colors (from non-chlorophyll origin) of fruits, flowers, and vegetables, and protect plants against the sun's ultraviolet (UV) radiation by preventing UV-induced tissue damage.^[7–10] Furthermore, the antioxidant activity of dietary phenolics is generally attributed to their ability to scavenge reactive oxygen species (ROS) and regulate certain metal coordination interactions that inhibit metal ions from generating ROS.^[5]

In addition, other living organisms use phenolic moieties to perform various complex tasks. Investigations into the mechanism of microbial iron transport have revealed that bacteria employ siderophores, such as enterobactin (a tris-catechol derivative), to accumulate iron and subsequently facilitate cellular iron transport. Another prominent example is the protein-based adhesives produced by several marine organisms.^[11–13] Mussels can attach their soft invertebrate bodies to various surfaces underwater by secreting mussel foot proteins that form byssal threads. Sandcastle worms construct protective shells by assembling sand grains with a proteinaceous glue.^[13,14] Both the mussel byssus and sandcastle glue are known to be heavily decorated with catecholamine functional groups (i.e. 3,4-dihydroxyphenyl-L-alanine (DOPA)).^[12,13]

Over the last two decades, progress in understanding these natural systems and the underlying diverse chemistry of phenolic compounds has spurred tremendous interest in the use of phenolic building blocks within the scientific community and has led to numerous major breakthroughs in the fields of chemistry and materials science. For example, the discovery in 1981 that catechol-containing proteins are responsible

From the Contents

1. Introduction	1905
2. Phenolic Building Blocks	1906
3. Thin Films	1908
4. Particles	1914
5. Bulk Materials	1916
6. Applications	1920
7. Summary and Outlook	1922

for the adhesion of mussels^[15] led to a surge in synthetic mussel-inspired materials; to date over 8000 articles have been published in that field. Simultaneously, a wide variety of functional materials have also been developed by taking inspiration from other natural products, such as plant-derived phenols.^[16] Although the various synergistic interactions of catechol- and gallol-containing phenolic compounds are still being studied,^[17] they have been used in the design of various synthetic materials, including conformal coatings,^[18] particles,^[16] gels,^[19] elastomers,^[20] and adhesives.^[21] The field has moved so rapidly that it is difficult to even claim inspiration from nature anymore, as the chemicals and materials have integrated with the everyday lexicon of science.

As a consequence of the natural abundance of phenolic compounds and their varied applications as writing inks, tanned leather, and protective coatings for teeth, phenolic-based materials lie at the intersection of chemistry, material sciences, biology, and engineering.^[1,22] Therefore, a near limitless number of functional phenolic materials can be engineered. However, a comprehensive review is implausible because of the large amount of activity surrounding these compounds. This Review, instead, provides an overview of functional materials that can be engineered from phenolic building blocks, in an attempt to bridge the gaps among the currently disparate fields that use phenols to fabricate materials. Following an overview of naturally abundant phenolic building blocks commonly used for the preparation of functional materials and a summary of their diverse interactions, a brief introduction on the chemistry surrounding synthetic phenolic derivatives is provided, as these compounds have allowed for numerous advances in the

[*] Dr. M. A. Rahim, Dr. S. L. Kristufek, Dr. S. Pan, Dr. J. J. Richardson, Prof. F. Caruso
ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, and the Department of Chemical Engineering
The University of Melbourne
Parkville, Victoria 3010 (Australia)
E-mail: fcaruso@unimelb.edu.au

 The ORCID identification numbers for the authors of this article can be found under: <https://doi.org/10.1002/anie.201807804>.

field of functional materials. The use of the natural phenolic lignin or its synthetic derivatives has been a prominent approach for designing functional materials. However, given the extensive number of reviews on this building block,^[23–26] this will not be discussed herein. The polymerization of molecules with catechol and gallo groups is not always straightforward. Thus, Section 2.1, which is devoted to synthetic phenolic derivatives, can help guide researchers to the most relevant studies and methods. The phenolic-based functional materials discussed are grouped into three broad categories: thin films (Section 3), particles (Section 4), and bulk materials (Section 5). These cover a broad range of synthetic materials from soft to hard and one-dimensional to three-dimensional structures, with applications ranging from nanotechnology to macromolecular science. Section 3 covers films prepared from the assembly of metal–phenolic networks (MPNs), layer-by-layer (LbL) assembly, and by oxidative self-polymerization (e.g. polydopamine (PDA)), thus representing surface-confined or surface-initiated materials from phenolic building blocks with tunable thicknesses ranging from several nanometers to hundreds of nanometers. Section 4 covers capsules, crystalline particles, nanoparticles, micelles, and

superstructures, all of which are commonly formed in solution as discrete materials, ranging in size from tens of nanometers to tens of micrometers. Section 5 covers gels, plastics, and elastomers, which can be formed by diverse techniques that typically result in macroscopic materials of arbitrary size and dimensionality. Following the overview of these three major categories of phenol-based functional materials, their applications in various established and emerging fields including adhesives, stretchable and self-healing materials, drug delivery, sensing, sporulation, separation, catalysis, antioxidant and antimicrobial coatings, micronutrient delivery, and drug crystallization are discussed. We conclude the Review by highlighting where continued integration of separate phenol-focused fields could yield fruitful breakthroughs, and we provide some possible future directions of interest for researchers studying phenols and phenol-based materials.

2. Phenolic Building Blocks

Phenolic compounds are widely distributed in nature and constitute a major class of phytochemicals.^[27] More than 8000 phenolic compounds of the polyphenol family have been identified and are divided into two major groups based on their chemical structures: flavonoids and non-flavonoids.^[28] In addition to plant-based phenolic compounds, catecholamines, such as dopamine and melanin, are found in many living organisms.^[13,15] Some of the common phenolic compounds extracted from natural sources and used as building blocks for functional materials synthesis are shown in Figure 1a–d. Although significant research has focused on using natural building blocks, such as dopamine and tannic acid (TA), to



Md. Arifur Rahim received his Bachelor's degree in Applied Chemistry and Chemical Engineering from the University of Dhaka and his Master's degree in Nanoscience and Technology from Chonbuk National University. He completed his PhD in 2016, working on metal–phenol thin films and gels under the supervision of Frank Caruso at The University of Melbourne. Since then, he has been working as a postdoctoral fellow in Frank Caruso's group, exploring various applications of metal–phenol materials.



Samantha L. Kristufek obtained her BS in Chemistry in 2011 from Penn State Behrend College in Erie, Pennsylvania. She moved to Texas A&M University and obtained a PhD in 2017 under the supervision of Karen L. Wooley, where she worked on the synthesis of poly(phenolic carbonate)s and cross-linked epoxy networks from the natural starting material quercetin for advanced engineering applications. She is currently a postdoctoral researcher in Frank Caruso's group at The University of Melbourne.



Shuaijun Pan received his Bachelor's degree in Chemical Engineering and Technology from Henan Normal University in 2008. He completed his PhD in 2015, studying wetting fundamentals under the supervision of Weijian Xu at Hunan University. He is now conducting surface wetting research under the supervision of Frank Caruso at The University of Melbourne.



Joseph J. Richardson received his Bachelor's degree in Philosophy and his Master's degree in Industrial and Systems Engineering from the University of Florida. He completed his PhD in 2015, researching thin-film deposition strategies under the supervision of Frank Caruso at The University of Melbourne. After a 2-year postdoctoral fellowship at CSIRO studying metal-organic hybrid systems, he returned to Frank Caruso's group to investigate metal-organic thin films.



Frank Caruso received his PhD in 1994 from The University of Melbourne and thereafter conducted postdoctoral research at the CSIRO Division of Chemicals and Polymers. He was an Alexander von Humboldt Research Fellow and a group leader at the Max Planck Institute of Colloids and Interfaces from 1997 to 2002. Since 2003, he has been a professor and is currently an NHMRC Senior Principal Research Fellow at The University of Melbourne. He is Deputy Director of the ARC Centre of Excellence in Convergent Bio-Nano Science and Technology. His research focuses on developing advanced nano- and biomaterials for biotechnology and medicine.

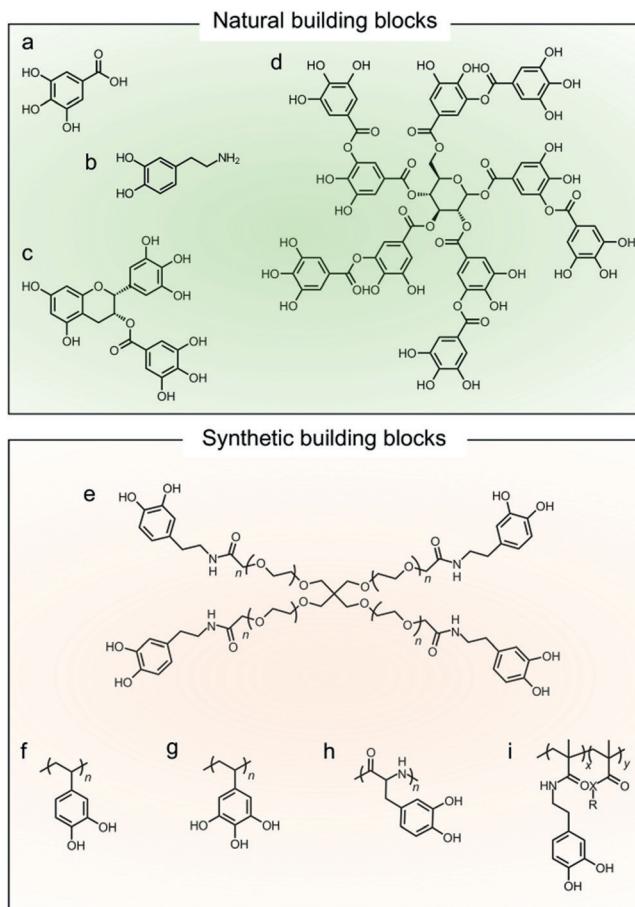


Figure 1. Examples of some common phenolic building blocks used for the preparation of functional materials. Examples of natural building blocks: a) gallic acid, b) dopamine, c) epigallocatechin gallate, and d) tannic acid. Examples of synthetic building blocks: e) PEG-catechol, f,h,i) polycatechols, and g) polygallo.

form functional materials,^[16,29] the synthesis of synthetic phenols and phenolic polymers allows for a near limitless variety of functionalities to be incorporated into phenol-based materials. Some of the common synthetic polymers are shown in Figure 1e–i.

Synthetic phenolic polymers offer a wide range of functionalities, as a large number of non-phenolic side groups, such as block copolymers, spacers, and reactive groups, can be incorporated. Catechol and gallo groups are regularly included in linear and dendritic polymers through a variety of synthetic routes. However, careful choice of synthesis parameters, such as monomer type, polymerization route, and reaction conditions, is necessary because of the reactivity of phenolic moieties. Early synthetic phenolic polymers involved the reaction between commercially available polymers and DOPA,^[30] and since then the field has evolved into synthesizing polymers containing catechols and gallos. Synthetic phenolic polymers have been prepared through different routes, including functional initiators,^[31–33] post-polymerization,^[34,35] and incorporation within the backbone, with the latter approach being the main focus of this section. Other useful synthetic techniques are also briefly mentioned.

One of the simplest routes for functionalizing polymers with phenolic moieties is through the use of dopamine. Dopamine itself can be used to prepare functional materials^[29] (as discussed at length below). However, owing to the presence of its terminal amine, dopamine can also be coupled to diverse chemical moieties by using simple conjugation strategies. Phenolic moieties can be incorporated into commercially available synthetic and natural polymers by a variety of reactions. One of the most common strategies has been the functionalization of different polyethylene glycol (PEG) structures through common amide coupling reactions with various catechol-containing compounds including DOPA,^[30] 3,4-dihydroxyhydrocinnamic acid,^[36] and dopamine.^[37] Other synthetic polymers such as poly(acrylic acid)^[38] and polyethyleneimine^[39] have been conjugated with catechol- and gallo-based compounds. In addition to the functionalization of synthetic polymers, naturally occurring polymers such as chitosan^[40] and hyaluronic acid^[41,42] have been functionalized with catechol groups. Together, these simple chemical reactions allow for the rapid development of advanced materials. However, when specific functionalities need to be incorporated, the polymers often have to be synthesized from simple building blocks, likely necessitating the use of phenolic monomers.

As DOPA is an amino acid containing a catechol structure, it can be combined with the widely available library of amino acid co-monomers to allow for additional functionality to be incorporated during polymerization. Amino acid monomers can be synthesized to form *N*-carboxyanhydride (NCA) compounds followed by ring-opening polymerizations of various monomer combinations. Anderson et al.^[43] synthesized a random copolymer of DOPA and *N*⁵-(2-hydroxyethyl)-L-glutamine, where the amount of DOPA was varied to study the effect on the adhesive and cohesive properties of the polymer.^[43] Inspired by the sandcastle glue, DOPA-NCA was incorporated into two polypeptides with opposite charges. Mixing these together led to the formation of tunable coacervates, depending on the mixing ratios and conditions.^[44]

One common monomer containing a catechol unit is dopamine methacrylamide (DMA), which can be synthesized from dopamine and a methacrylate-containing compound. DMA has been copolymerized with various co-monomers such as aminoethyl methacrylamide^[45] and 2-methoxyethyl acrylate^[46] to allow for DNA immobilization and adhesion under wet conditions, respectively. The polymerization conditions for DMA have allowed for the incorporation of monomers with additional functionality either through copolymerization or the formation of block copolymers. Recent examples include a fluorine-containing polymer, such as poly(2,2,3,3,3-pentafluoropropyl acrylate), grafted brushes for antifouling applications,^[47] and the incorporation of glycopolymer-based monomers to mimic the immunogenic properties of natural pathogens.^[48] Additionally, host-guest chemistry can be incorporated into DMA systems with an adamantyl co-monomer, thereby allowing for reversible adhesion.^[21]

The use of protecting groups is a commonly used synthetic strategy when preparing synthetic phenolic polymers, as catechols can scavenge radicals and thereby limit polymerization and induce side reactions. Studies on the synthesis of

protected monomers have focused on both the accessibility and ease of removing protecting groups post-polymerization. For example, an acetonide protecting group shows promise and limited degradation upon deprotection.^[49] Although the use of protecting groups is generally the most commonly explored strategy, controlled polymerization with DMA has been achieved in specific instances.^[47,50]

To extend the scope of catechol- and gallop-containing synthetic polymers beyond dopamine-based compounds, a range of other polymers and monomers have been explored. One well-studied monomer is the commercially available styric compound 3,4-dimethoxystyrene. The use of this monomer led to poly[(3,4-dihydroxystyrene)-*co*-styrene] being synthesized, and its adhesive properties were studied under various conditions.^[51,52] A homopolymer of 3,4-dimethoxystyrene^[53] was accessed through reversible addition-fragmentation chain-transfer (RAFT) polymerization, and upon demethylation, the free catechol moieties were investigated for their metal-binding capacity, which was independent of molecular weight. Commercially available phenolic monomers have, therefore, allowed for rapid access to functional polymers. However, it has recently been demonstrated that RAFT-prepared gallop-containing polymers have superior free-radical scavenging ability over catechol polymers.^[54] This finding demonstrates the trade-offs between synthesizing the required monomer from simple building blocks and the use of a commercially available monomer that can be readily polymerized.

The synthesis of novel phenolic monomers has also been crucial for expanding the scope of functional phenolic materials. One widely studied monomer, triethylsilane-protected eugenol acrylate (TES-EA), can be prepared in three steps from eugenol. TES-EA has been copolymerized with four other monomers to form a polymeric mussel foot protein analogue^[55] or assembled as a block copolymer for further complexation and quaternization with chitosan.^[56] In another recent example of synthesized phenolic monomers, linear polymeric antioxidants were prepared with complex catechol- and gallop-like functional groups, which allowed for control over a variety of material properties such as hydrophobicity.^[57]

Although an array of synthetic monomers and polymers have been synthesized, with near endless possibilities for future structures, other factors beyond simply the addition of phenolic moieties need to be considered. Specifically, numerous fundamental studies have begun to explore the structure-function relationships between the components of synthetic phenolic polymers. For example, a fundamental study on the polarity of the backbone of a synthesized polymer containing catechol moieties has shown additional complexity in the synthesis because the polarity changes specific functional properties of the polymer, such as underwater adhesion.^[58] Other investigations into redox-active catechol-containing polymers have shown that changing the catechol-containing monomer as well as the co-monomer can have performance effects for electrochemical energy storage.^[59] Switching from catechol to gallop moieties has also been observed to change the properties of materials, for example, the underwater adhesion of a polymer can be increased sevenfold.^[60]

These studies demonstrate a few examples of the structure–function relationships of the various components within phenolic polymers, highlighting the importance of these relationships for designing future materials. Collectively, a variety of routes of different complexity and versatility exist for synthesizing phenolic polymers, and many high-performance functional materials can be engineered by combining the attributes of phenols with carefully designed polymers.

3. Thin Films

Phenolic compounds tend to be universally adherent and, therefore, are suitable for use as building blocks in constructing thin films on diverse substrates.^[16] Three general approaches for the formation of thin films with phenolic compounds have been developed to date: MPN assembly,^[16] LbL assembly,^[61] and one-pot synthesis of PDA coatings.^[29] MPNs are formed rapidly through a combination of metal–phenol coordination bonds and adherence between the phenolic materials and the substrate. Alternatively, LbL-assembled films are constructed by first adhering a phenol to the substrate, followed by sequential buildup of metal ions or polymers and phenols. PDA-based materials are prepared from the self-polymerization of dopamine under mild conditions on a substrate. The choice of the deposition methods and materials allows for control over the physicochemical properties of the resultant thin films.^[62] For example, when TA and iron ions are assembled into MPNs, they have different disassembly kinetics than when they are assembled into LbL films.^[63] The following sections focus on these three approaches for assembling phenolic thin films and highlight some of the different building blocks and substrates applicable for preparing phenolic thin films, as well as the physicochemical differences arising from the different assembly mechanisms.

3.1. Assembly of Metal–Phenolic Networks

The recent introduction of MPNs has expanded the scope of phenolic thin films to a variety of different materials, applications, and deposition techniques, as highlighted in recent reviews.^[22,64] This section provides a general overview of the methods, building blocks, substrates, and technologies that have to date been used for forming MPNs (Figure 2a–h). MPNs were originally constructed from metal ions, such as Fe^{III} or Al^{III}, coordinated with multidentate phenolic ligands, such as TA and epigallocatechin gallate (EGCG).^[16] The deposition process is independent of the substrate—silica, gold, iron oxide, emulsions, and even bacteria could be coated in a matter of seconds after mixing the metal ions and phenolic building blocks. Generally, the pH value is raised to stabilize the complexes in the tris complex form after mixing the building blocks, with acidic environments leading to slow disassembly of the MPNs.^[16] Other substrates such as lignin,^[65] collagen,^[66] yeast (Figure 2e–h),^[67] adherent mammalian cells, and red blood cells have been used as substrates, with unique

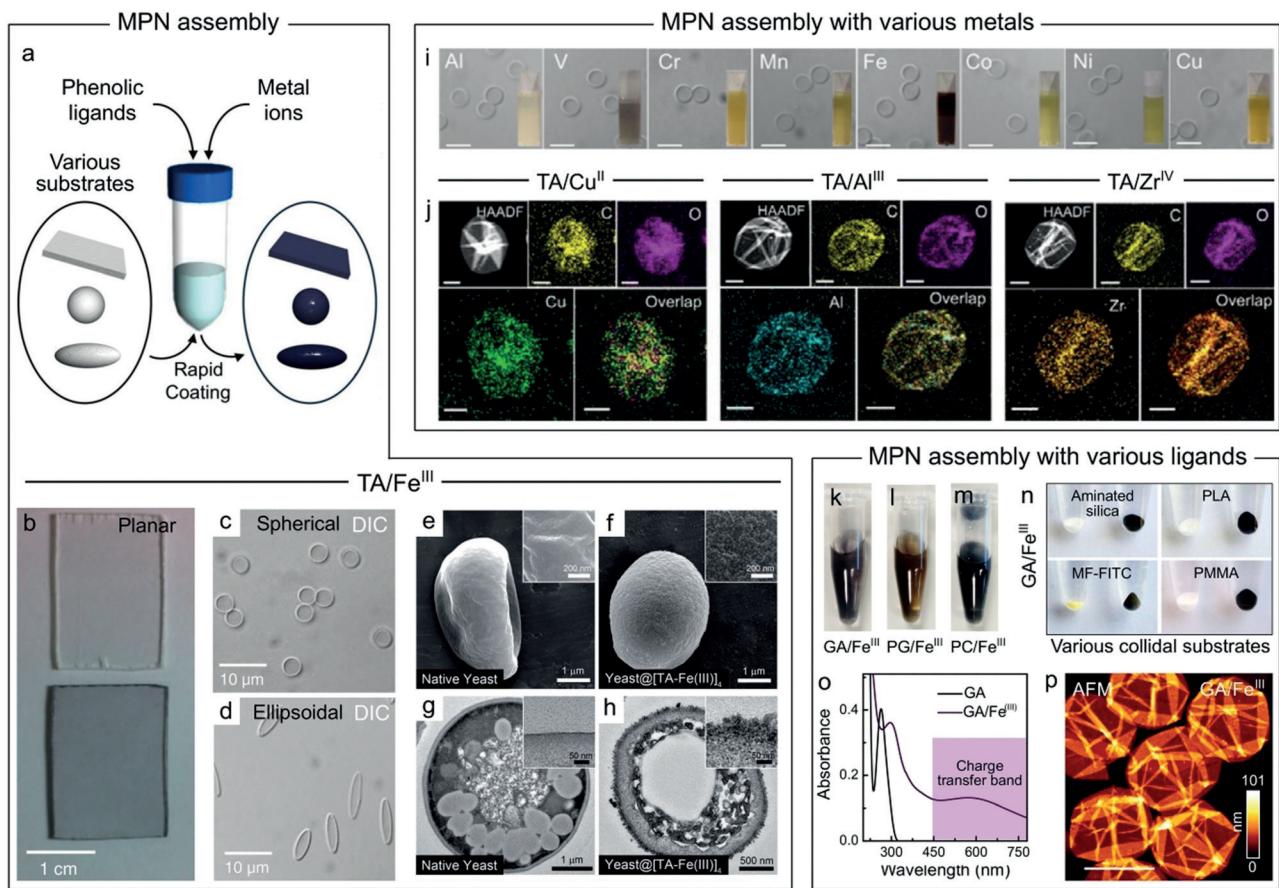


Figure 2. a) Schematic representation of MPN assembly. Adapted with permission.^[16] Copyright 2013 American Association for the Advancement of Science. TA/Fe^{III} films and capsules synthesized on diverse substrates: b) planar (photographs), c) spherical, and d) ellipsoidal (differential interference contrast (DIC) images), and e–h) yeast cells (scanning electron microscopy images). (b–d) Reproduced with permission.^[16] Copyright 2013 American Association for the Advancement of Science. (e–h) Reproduced with permission.^[67] Copyright 2016 Wiley-VCH. MPN assembly with various metals: i) capsules obtained from different TA/M systems ($M = \text{Al}^{\text{III}}$, V^{III} , Cr^{III} , Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , and Cu^{II} ; DIC images) and the corresponding j) high-angle annular dark-field spectra of the capsules. Scale bars: 5 μm in (i) and 1 μm in (j). Reproduced with permission.^[70] Copyright 2014 Wiley-VCH. k–p) MPN assembly with various phenolic ligands: photographs showing the colors of capsule dispersions of GA/Fe^{III} (k), PG/Fe^{III} (l), and PC/Fe^{III} (m) systems, and different colloidal substrates coated with GA/Fe^{III} (n); and o) absorption spectra of GA and a GA/Fe^{III} capsule dispersion and p) atomic force microscopy (AFM) image showing the morphology of dried GA/Fe^{III} capsules. Reproduced with permission.^[75] Copyright 2015 American Chemical Society.

applications, such as sporulation or reduced immune responses, thus demonstrating the wide utility of these materials.^[62,68,69]

The choice of applicable building blocks rapidly expanded after the introduction of MPNs. Different metals have been explored to yield both novel applications for MPN films and to control the physicochemical properties of the films (Figure 2i). Applications such as fluorescence imaging, magnetic resonance imaging (MRI), positron emission tomography (PET) imaging, and catalysis were realized by appropriate choice of the incorporated metal—Eu^{III}, Gd^{III}, Cu^{II}, and Rh^{III}—for each application.^[70] The choice of metal additionally determined the disassembly of the MPN film at different pH values, with the Al^{III}-based film showing disassembly within a physiological pH range (pH 5–7.4), thus being suitable for drug-delivery applications.^[71] Additionally, the metalloid-containing molecule diphenylboronic acid has been used instead of a metal ion to allow for the formation of films that disassemble in the presence of *cis*-diols.^[72]

A wide variety of synthetic and biological phenolic ligands have also been used, including flavonoids, tea infusions, and single-ring phenolic moieties.^[73–75] Small phenolic ligands, namely gallic acid (GA), pyrogallol (PG), and pyrocatechol (PC), were used to demonstrate that at least one vicinal diol group is necessary for the formation of MPN films (Figure 2k–p).^[75] The choice of phenolic ligand (small or multidentate ligands) used for deposition strongly influences the final disassembly kinetics of the MPN films.^[75]

Additionally, hybrid synthetic analogues including PEG-DOPA polymers,^[76] HA-DOPA polymers,^[77] or TA modified with peptides^[78] can be used to form MPNs, thereby allowing for new functionalities and applications to be realized.

Early MPN studies used solution-based batch processing for the formation of MPNs.^[16,70,71] Since then, other approaches commonly used for the formation of LbL films and capsules have been used. Specifically, spray assembly has been used for the formation of MPNs; the technique readily allows the coating of large substrates such as fruits or shoe

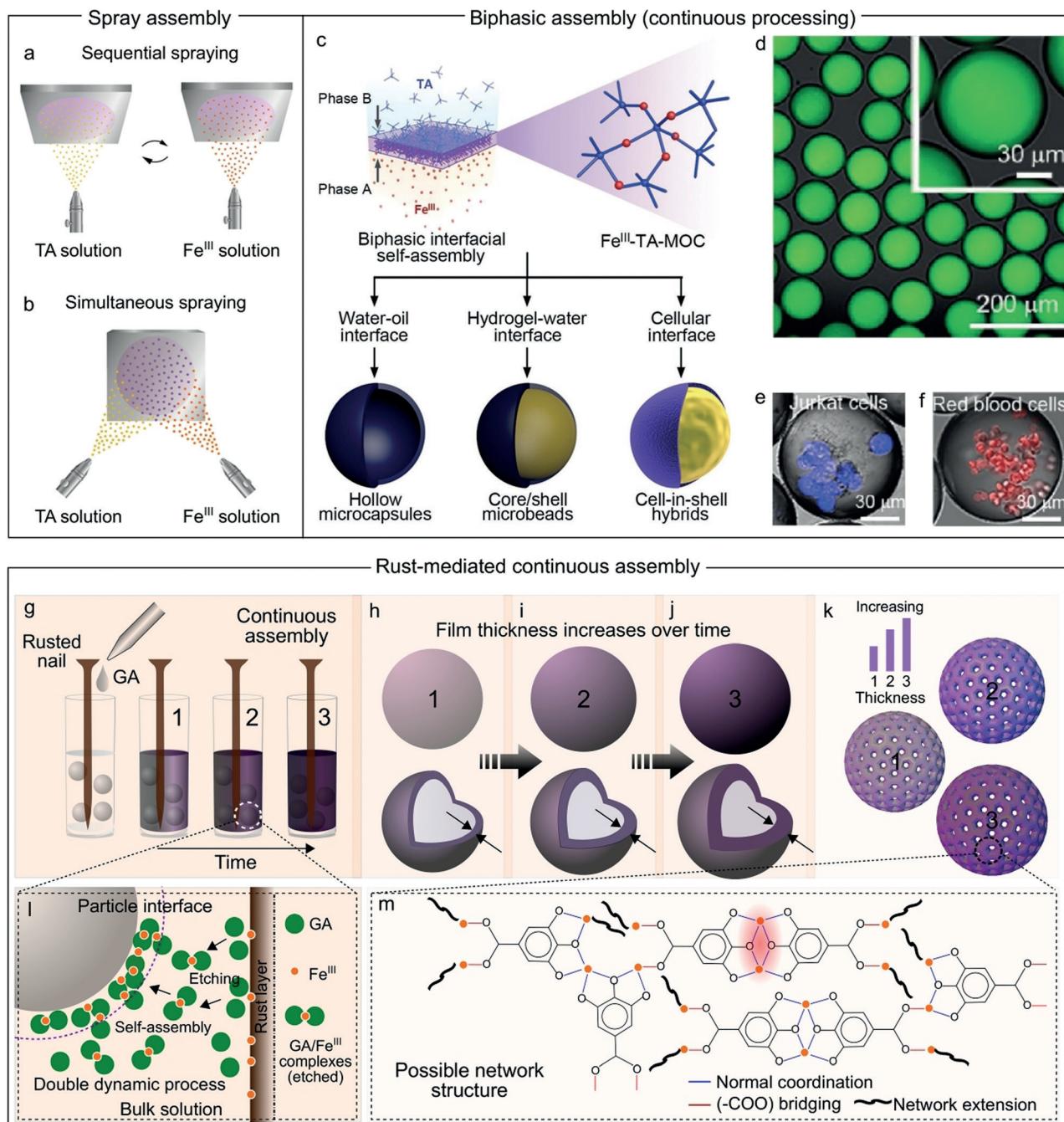


Figure 3. Schematic representations of different methods for MPN assembly. a,b) Spray coating (sequential and simultaneous) assembly method. Reproduced with permission.^[79] Copyright 2017 Springer Nature. c–f) Biphasic assembly for continuous processing: schematic representation of the method (c); dextran-fluorescein isothiocyanate (d); and cell-encapsulated microcapsules in solution (e,f). Reproduced with permission.^[80] Copyright 2016 Wiley-VCH. g–k) Rust-mediated continuous assembly method, l) interfacial interactions, and m) possible network structure of assembled films obtained using this method. Reproduced with permission.^[81] Copyright 2017 Wiley-VCH.

inserts (Figure 3 a,b).^[79] This is an important development for the application of MPNs, as spraying can be incorporated into industrial supply chains to allow for continuous processing. Similarly, the continuous processing of MPN capsules has recently been demonstrated using microfluidics (Figure 3 c–f). However, careful choice of solvents for both the phenolic ligand and metal ions was crucial because of the fast kinetics of the complexation.^[80]

In previous studies,^[16, 70, 75] MPN film formation was observed to proceed in discrete steps of about 10 nm, with interfacial assembly ceasing beyond a finite time (< 60 s). This limitation has been addressed in recent studies, where it has been shown that the assembly process for MPNs can be modulated from discrete to continuous by using solid-state metal precursors such as rusted nails (Figure 3 g–m).^[81] This continuous assembly method has not only yielded the thinnest

MPN films (ca. 5 nm) to date, but also produced high-quality multiligand MPN capsules from crude phenolic extracts such as green-tea infusions.^[82] Another recently demonstrated continuous MPN assembly method used an electro-triggered assembly approach, where a mixture of TA and Fe^{II} was incubated in the presence of an electrode.^[83] Fe^{II} was electrically converted *in situ* into Fe^{III}, thereby allowing for the continuous growth of MPNs on the electrode, modulated by the metal/ligand ratio as well as the intensity and duration of the applied current.

Recent experiments on the growth behavior of MPNs using precursor solutions of various ionic strengths have shown that salts can shield the chelation complex and thereby enable the formation of thicker and rougher films.^[84] Additionally, the redox properties of MPNs have been elucidated in a recent electrochemical study.^[82] Although many previous studies have provided useful insights into various aspects of MPN assembly,^[16,75,81] more fundamental studies are required to elucidate the kinetic and thermodynamic aspects. The structure–function relationship of MPNs, when assembled from different phenolic building blocks, is another aspect that

needs to be investigated to establish design principles for future MPNs. Finally, it is foreseeable that other thin-film assembly techniques adopted from LbL assembly, including vacuum filtration or dewetting, could be used to assemble MPNs with unique properties.^[85]

3.2. Layer-by-Layer Assembly

TA has been used extensively as a building block for LbL film formation because of its ability to form hydrogen bonds and electrostatically interact with a wide range of biological and synthetic polymers such as chitosan, poly(dimethyldiallylamine) (PDDA), poly(vinylpyrrolidone) (PVPON), and poly(allylamine hydrochloride). Some of these structures are shown in Figure 4.^[61] Generally, the pH value of the growth solutions has a significant influence on the growth behavior and mechanical properties (e.g. permeability) of the resulting films, as the degree of protonation or deprotonation of the phenolic moieties varies with the pH value.^[86] Thermoresponsive polymers, such as poly(*N*-isopropylacrylamide)

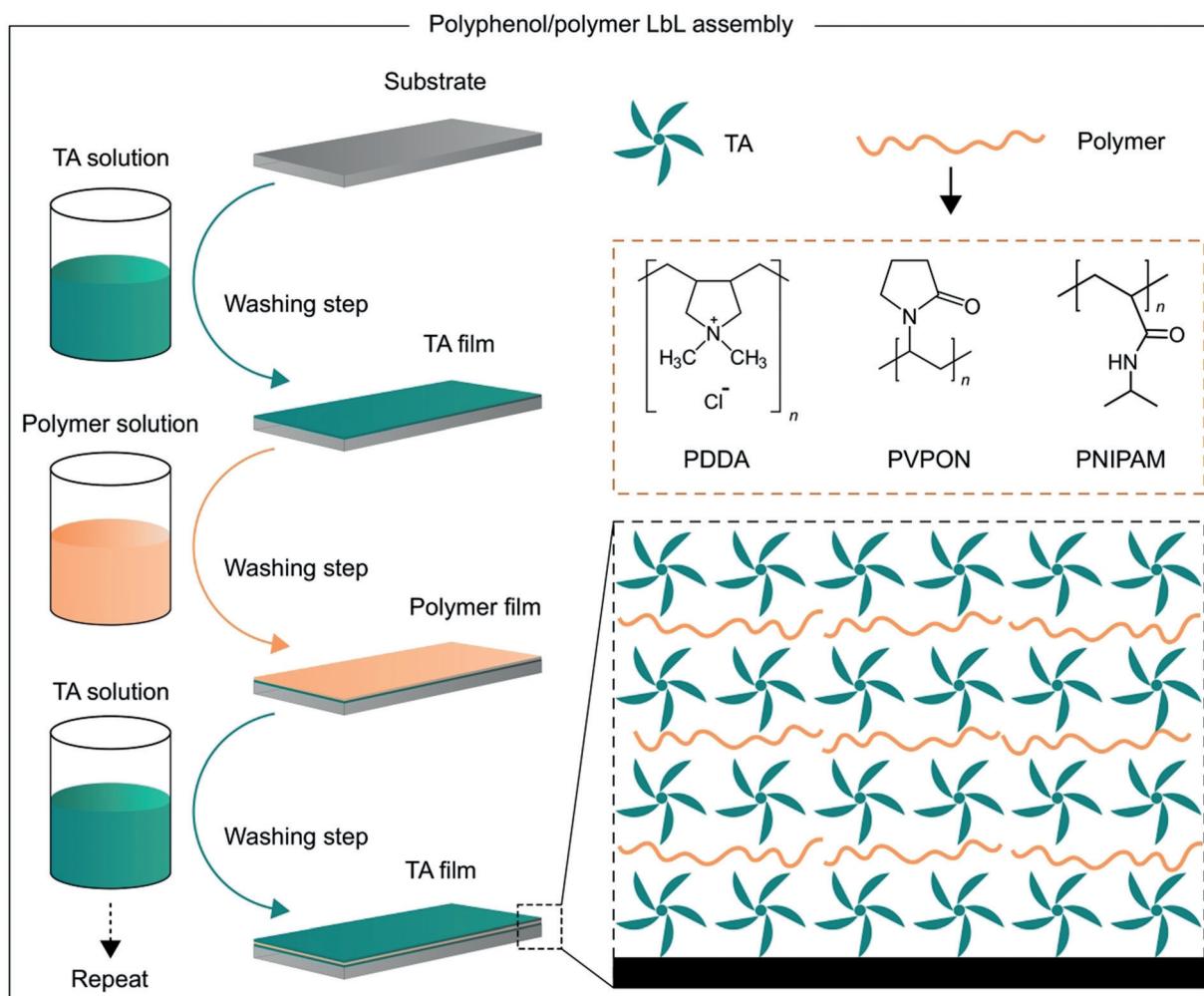


Figure 4. Illustration of the general method for the LbL assembly of TA with different polymers such as poly(dimethyldiallylamine) (PDDA), poly(vinylpyrrolidone) (PVPON), and poly(*N*-isopropylacrylamide) (PNIPAM).

(PNIPAM), can be used with TA to engineer both temperature- and pH-responsive thin films.^[87] A more recent development has been the modification of synthetic polymers, such as poly(acrylic acid), with catechol groups to allow for multilayer growth with PVPON.^[88]

Detailed investigations into the assembly process of TA-containing LbL films have demonstrated a pH dependence of the film growth, depending on whether the layer buildup is accomplished through hydrogen bonding or electrostatic interactions.^[89] For example, TA and poly(*N*-vinylamide) displayed higher affinities for each other at lower pH values, where the gallo groups of TA are protonated, and thus formed hydrogen bonds efficiently with the carbonyl groups of the poly(*N*-vinylamide)s. Consequently, a larger mass was deposited for each layer at a low pH value.^[89] PVPON was deposited by LbL assembly with TA through hydrogen bonding. The molecular weight of PVPON played an important role in controlling the permeability of the resultant thin films, with lower molecular weight PVPON yielding films of higher permeability. Furthermore, for a given PVPON molecular weight, the permeability of the TA-PVPON films decreased when the incubation pH value was changed from 6 to 9.^[87] Poly(2-ethyl-2-oxazoline) can also be used to form LbL thin films through hydrogen bonding with TA.^[90]

Alternatively, thermodynamically stabilized materials, such as micelles,^[91] can be assembled into thin films with phenolic compounds without disruption. Similarly, proteins can be used as an intermediary layer for TA-based LbL films,^[92] and it has been demonstrated that TA does not inhibit the enzymatic activity of the incorporated enzymes after film growth.^[93] These thin films have allowed for a variety of applications to be targeted, including wound healing and metal sequestration,^[94] as a consequence of the antioxidant properties^[95] and metal affinity of phenolic compounds, respectively.^[91]

More recently, the multilayer assembly of phenols has also been accomplished using metal ions instead of polymers.^[63,96] These films are assembled in a LbL (multistep) process and have different physicochemical properties from MPN films prepared from the same components (i.e. TA and Fe^{III}), such as different disassembly kinetics and permeability.^[63] As metal ions and phenolic substrates are soluble in a wide range of solvents, multilayer assembly can be conducted in both organic and aqueous solvents.^[63,96] The layer order, that is, whether TA or Fe^{III} is deposited first, has a significant effect on the final film properties, as does post-treatment at different pH values.^[97] Investigations are ongoing to elucidate the differences between MPNs and LbL films, and it is likely that the wide range of LbL assembly techniques used for other polymer combinations^[85] will be applied to phenolic materials in the near future.

3.3. Oxidative Self-Polymerization Assembly

Adhesive biomaterials produced by marine organisms are known to possess superior mechanical properties (e.g. strength, toughness, and durability) compared to many synthetic materials.^[12,98,99] The exceptional ability of mussels

to strongly attach to diverse substrates (Figure 5a), including wet surfaces, with high binding strength has been the focus of extensive research over the past two decades.^[98,99] Early investigations into the wet adhesion properties of mussels have shown that DOPA and lysine-enriched proteins at the plaque–substrate interface play critical roles for the robust adhesion of mussels.^[12,13,98] Based on these initial observations, in 2007, Lee et al.^[29] demonstrated a surface coating technique based on the polymerization of dopamine (Figure 5b–f). The resulting material is known as PDA. Recent reviews have extensively detailed and summarized the numerous studies conducted on PDA to date,^[100,101] and in the present section we provide a brief overview of the versatility and functionality of PDA-based materials. In addition, we briefly discuss the plant-derived phenolic building blocks capable of forming films through oxidative self-polymerization, such as dopamine.

The distinct advantage of PDA film formation is that it can be achieved on a wide range of substrates, including inorganic, organic, and hydrophobic surfaces, by the oxidative self-polymerization of dopamine under mild basic pH conditions (Figure 5b–g).^[29,99] Besides planar substrates, PDA coatings can also be applied to various particulate substrates to prepare functional core–shell particles and capsules through removal of the core (Figure 5g).^[102,103] Despite the wide applicability and methodological simplicity of the PDA films, the actual mechanism of PDA formation has remained controversial, possibly because of the generation of a series of reaction intermediates during the polymerization reaction and the complex redox process associated in each step.^[104] In earlier studies, the formation of PDA was believed to involve a process akin to the pathway of melanin (eumelanin, a natural pigment commonly found in bacteria, fungi, plants, and animals) production in living organisms.^[104,105] This is known as the “eumelanin” model of PDA formation, where covalent interactions are regarded as the dominant driving force (Figure 5g).^[102,104,106] Alternatively, a physical self-assembly pathway has been proposed, wherein a combination of different noncovalent interactions, such as hydrogen bonding, charge transfer, and π–π stacking, contribute to the formation of PDA films.^[107]

As the field progressed, various chemical routes, including selective chemical reactions, such as the secondary treatments shown in Figure 5h, have been explored to modify PDA films and yield materials with alternative functionalities. For example, the anticancer drug doxorubicin (DOX) was conjugated to PDA capsules through the formation of an acid-labile covalent bond on thiolated poly(methacrylic acid) for drug delivery applications.^[108] In another example, a potentiometric sensor designed from a polymeric membrane ion-selective electrode was imprinted in the PDA layer for the detection of biological analytes.^[109]

PDA surfaces have also been used to conduct various polymerization reactions. For example, atom transfer radical polymerization (ATRP) initiators were immobilized in PDA-coated carbon nanotubes,^[110] magnetic nanoparticles,^[111] and ordered mesoporous carbon (Figure 5h)^[112] to allow for the surface-initiated growth of polymer brushes. PNIPAM polymers were also grown on PDA particles and capsules using

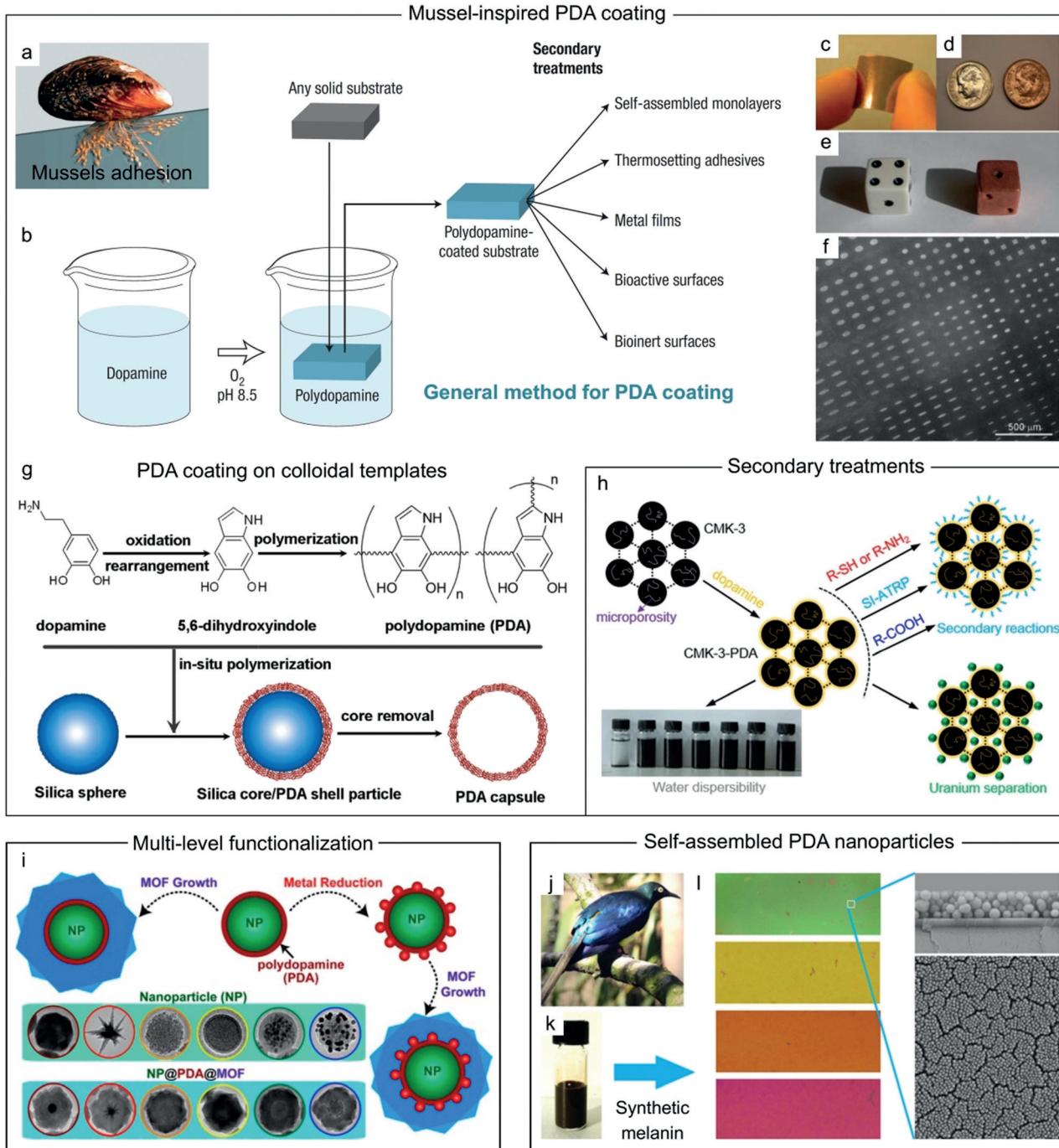


Figure 5. a) Adhesion of the marine mussel *Mytilus californianus* to a surface. Reproduced with permission.^[98] Copyright 2011 Annual Reviews. b) Schematic representation of the mussel-inspired polydopamine (PDA) coating method and subsequent treatment (secondary) to fabricate functional materials. Reproduced with permission.^[99] Copyright 2008 Springer Nature. c–e) PDA coating on different solid substrates and f) electroless silver metallization of a photoresist-patterned surface coated with PDA. Reproduced with permission.^[29] Copyright 2007 American Association for the Advancement of Science. g) Schematic representation of PDA coating on colloidal templates and the resulting PDA capsules after template removal. Reproduced with permission.^[102] Copyright 2009 American Chemical Society. h) Illustration of the surface modification of the ordered mesoporous carbon CMK-3 with PDA, which led to improved water dispersibility, uranium binding ability, and the potential for post-functionalization through secondary reactions. Reproduced with permission.^[112] Copyright 2016 American Chemical Society. i) Schematic illustration of the stepwise synthesis of nanoparticle@PDA, nanoparticle@PDA@metal-organic framework (MOF) and metal nanocatalyst-loaded nanoparticle@PDA@MOF core–shell hybrid nanostructures and examples of the as-synthesized structures. Reproduced with permission.^[116] Copyright 2015 American Chemical Society. j–l) Avian-feather-inspired periodic assembly of PDA-based synthetic melanin nanoparticles to fabricate colored films. Reproduced with permission.^[119] Copyright 2015 American Chemical Society.

activators regenerated by electron-transfer ATRP. The inward and outward growth of the polymer chains could be controlled by solvation effects and hydrothermally induced regulation of the pore network of the PDA.^[113] Polymerization techniques other than ATRP have been exploited, for example, a carbonyl-azide RAFT agent was coupled to the surface of PDA-coated silica particles to perform “grafting from” polymerization reactions.^[114]

As a consequence of the presence of abundant catechol groups, PDA films can display diverse properties, including metal chelation and reduction.^[2,115] A multilevel functionalization strategy to construct PDA-based single nanoparticle@metal-organic framework (MOF) core–shell nanohybrid systems has recently been demonstrated by combining these properties (Figure 5*i*).^[116] Besides conformal coatings, the polymerization of dopamine can lead to the formation of self-assembled PDA nanoparticles under appropriate conditions.^[117,118] Inspired by the structural colors produced from the self-assembled melanosomes in avian feathers, Xiao et al.^[119] demonstrated the assembly of PDA-based synthetic melanin nanoparticles to fabricate colored films (Figure 5*j–l*). These nanoparticles showed a high refractive index and broad optical absorption in the UV/Vis range.

In addition to dopamine, plant-derived phenolic compounds have been observed to undergo oxidative self-polymerization at slightly basic pH values and form colorless coatings on various substrates (Figure 6 *a–d*).^[120] In a pioneering study, Sileika et al.^[120] illustrated this phenomenon using plant polyphenols such as EGCG, PG, and TA. The resulting coatings not only showed antibacterial and antioxidant properties, but could also be used to modulate the optical properties of inorganic nanoparticles such as gold nanorods (Figure 6 *d*). Many examples have followed, thus affording a large family of plant-derived phenolic compounds to be used for surface modification through oxidative self-polymerization.^[121,122] Instead of using basic pH conditions, UV radiation can induce the oxidative self-polymerization of phenolic compounds^[123] and has been used to construct patterned thin films (Figure 6 *e–g*).^[124] As the field grows through expanding the library of building blocks and different methods, a wide variety of new materials and applications are expected to emerge.

4. Particles

The diverse chemistry of phenolic moieties has led to the development of a variety of phenol-based particulate materials including hollow capsules, crystalline particles (such as MOFs), nanoparticles, micelles, and superstructures. Similar to thin films, phenolic particles are most commonly formed by self-assembly of a variety of phenolic building blocks. GA has been traditionally used as a ditopic ligand for MOF synthesis, although other natural and synthetic phenolic ligands have been used more recently with a variety of metal ions. Other self-assembled structures include nanoparticles, micelles,^[125] vesicles,^[126] and brushes,^[127] which can be produced by controlling the assembly conditions. Moreover, metal ions can be used to assemble phenol-coated particles into super-

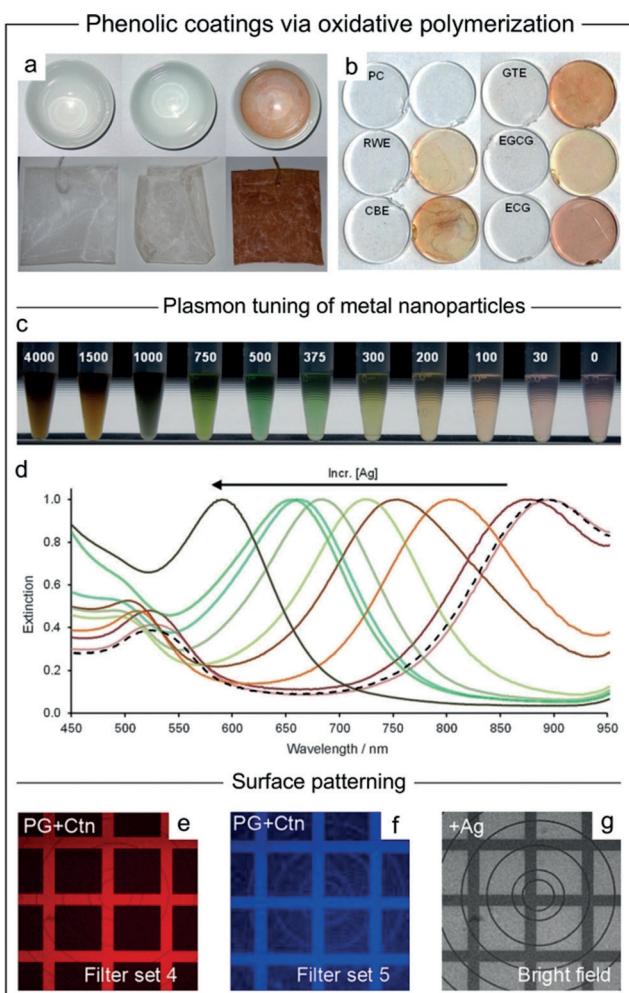


Figure 6. a) Adherent polyphenol coatings deposit on surfaces exposed to tea infusions. b) Coatings of various natural polyphenols deposited onto clear polycarbonate (PC) disks. For each pair of disks, the disk on the right has also been treated with aqueous silver nitrate to visualize the coatings. Plasmonic tuning of metal nanoparticles through templated synthesis of core–shell nanorods using coatings inspired by plant polyphenols: c) blue shift of the longitudinal surface plasmon resonance wavelength as indicated by a color change of the nanorod suspension and d) normalized optical extinction spectra of Au-pyrogallol (PG)-Ag nanorods, illustrating plasmon tuning through control of the Ag shell thickness. Reproduced with permission.^[120] Copyright 2013 Wiley-VCH. Patterning of the polyphenol coating by UV irradiation: e) overlaid pattern formed on the surface by first UV irradiation of the PG solution through a photomask with circular patterns, followed by washing and rhodamine modification; f) pattern formed on the surface by UV irradiation of the catechin (Ctn) solution through a photomask with square patterns (fluorescence microscopy images were taken using filter sets 4 and 5); and g) bright-field microscopy image of the silver-modified pattern. Reproduced with permission.^[124] Copyright 2018 American Chemical Society.

structures.^[128] The wide structural diversity in these self-assembled particles has made phenolic building blocks powerful motifs in the design of nanomaterials. This section gives a broad summary of the current state of the field.

4.1. Capsules

Capsules are an important class of particle systems that find applications ranging from biomedicine to catalysis.^[85] The synthetic strategy for capsule formation generally involves two stages: 1) film formation on colloidal templates and 2) subsequent removal of the templates.^[62,85] Phenolic capsules can be prepared by all of the different coating techniques (i.e. MPN, LbL, and PDA assembly) described in Section 3. The methodological details for phenolic capsule formation have been recently reviewed^[129] and will not be discussed separately in this section.

4.2. Crystalline Particles

The use of phenolic compounds as organic ligands for the formation of crystalline coordination polymers or MOFs can be traced back to at least 1991, when Fe^{III}-gallate MOFs were prepared using GA and Fe^{III} salts as precursors.^[130] However, unlike carboxylate and imidazole-based ligands, the explora-

tion of phenolic ligands has not flourished in MOF research, although a recent upsurge in interest is noticeable.

The synthesis of Fe^{III}-gallate MOFs was reinvestigated using a solvothermal route and extended to other transition metals such as Mg^{II}, Mn^{II}, Co^{II}, and Ni^{II}, and Zr^{IV}.^[131–133] The GA-based MOFs are isostructural and composed of infinite chains of corner-sharing MO₆ octahedra (where, M=Zr^{IV}, Fe^{III}, Mn^{II}, Co^{II}, Ni^{II}, Mg^{II}) connected by the gallates (an example is provided in Figure 7 a).^[131,132] Expanding on GA-based MOF structures, a synthetic digallate ligand can be used to form phenolic Zr^{IV}-MOFs (Figure 7 b,c).^[134] Both GA- and digallate-based MOFs show enhanced chemical and hydrolytic stability, owing to the high pK_a values of the phenolate groups which strengthens the Zr–O bonds, compared with the typical Zr^{IV}-carboxylate MOFs.^[133,134]

Crystalline metal catecholates are another emerging class of MOFs that use synthetic catechol derivatives and metals such as Co^{II}, Ni^{II}, Fe^{II}, Ti^{IV}, and V^{IV} (Figure 7 d–f).^[135,136] Fe-catecholate MOFs show mixed oxidation states of Fe and an ultrahigh proton conductivity comparable to that of Nafion.^[136] Ellagic acid has also been used to form crystalline

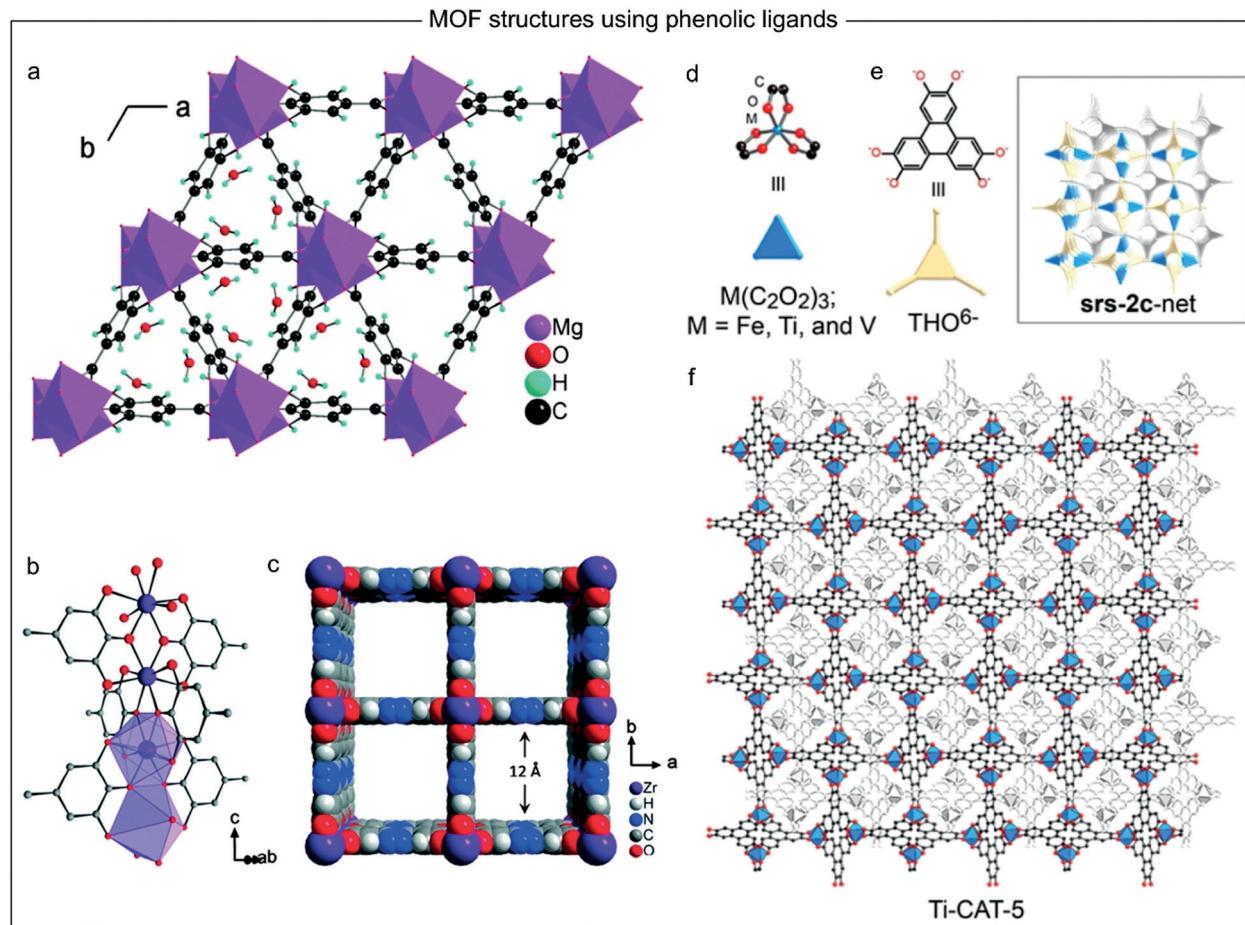


Figure 7. a) Structural representation of the Mg^{II}-gallate MOFs. Reproduced with permission.^[131] Copyright 2014 Wiley-VCH. Structure of the Zr^{IV}-gallate MOFs: b) view of a single chain showing the Zr atoms coordinated by gallol groups and c) view of the structure along the [001] direction. Reproduced with permission.^[134] Copyright 2015 Wiley-VCH. d,e) Crystalline metal-catecholate frameworks constructed from H₆THO ligands (THO⁶⁻=triphenylene-2,3,6,7,10,11-hexakis(olate)) with Fe^{II}, Ti^{IV}, and V^{IV}; and f) simplified representation of the resulting topology. Reproduced with permission.^[136] Copyright 2012 American Chemical Society.

materials with metal ions (in this instance Zn^{II}).^[137] Finally, catechol-containing molecules can also be used for the surface functionalization of MOFs, as demonstrated by the use of a gallol-containing lipid molecule to modify the dispersibility of MOF particles.^[138]

4.3. Nanoparticles, Micelles, and Superstructures

Self-assembled nanostructures from phenolic compounds can be prepared through various interactions including hydrogen bonding, metal coordination, oxidative self-polymerization, and any combination thereof. Examples of a few of these nanoparticle systems have been provided in Section 3.3, and herein we highlight some of the recent advances in the field. For example, Wang et al.^[139] reported a self-assembled nanoparticle system with an average size of about 140 nm by using TA and the poloxamer Pluronic F-127. After incorporating ^{89}Zr into the system, the composite particles were used for PET imaging of tumors. PEG-modified Pt prodrug nanocomplexes were prepared through metal–phenol coordination by using an emulsion-based process.^[140] The resulting particles with an average size of about 100 nm showed a high drug loading capacity and low fouling properties. Another recent study described a series of metal-loaded PDA nanoparticles prepared by the oxidative self-polymerization of metal–dopamine complexes in the presence of free dopamine.^[141] Among the various metal-loaded systems investigated, Mn^{III} -loaded PDA nanoparticles showed high spin, low anisotropy, and weak magnetic coupling and, therefore, superior relaxivity behavior compared with Fe^{III} -loaded PDA nanoparticles.^[141]

Phenolic micellar structures can be formed through metal or boron complexation with various catechol derivatives. For example, micelles from telodendrimers with either catechol or boron functionalities can be assembled using dual-responsive boronate cross-linking.^[125] These micelles are pH- and diol-responsive, and when functionalized with a catechol-based dye exhibit dramatic changes in color.^[125] Catechols have been incorporated into linear diblock copolymers, instead of branched dendrimers, and used to incorporate drugs with boronic acid groups, such as bortezomib, into micelles.^[142] In an alternative strategy towards pH- and diol-responsive micelles, block copolymers of either PEG-*b*-catechol or PEG-*b*-phenylboronic acid were synthesized and mixed to form well-defined, stable, core-cross-linked polyion complex micelles (Figure 8a).^[143] A small-molecule polyion complex micelle system has also been developed for drug delivery using EGCG as a cross-linker in the assembly to prevent DOX-induced cardiotoxicity during drug release.^[144] Alternatively, metal–catechol coordination can be used to cross-link micelles, allowing for drug loading and pH-responsive release.^[140,145] For example, a PEG-*b*-PDOPA copolymer can be cross-linked using Fe^{III} –catechol coordination to generate drug-loaded theranostic micelles, which can assemble and disassemble through a change in acidity enabled by the coordination cross-links.^[146]

Block copolymers with a catechol-containing segment can also be used for phenol-specific drug loading. In an example

by Chan et al.,^[147] DOX was loaded into the core of catechol/imidazole mixed micelles through the organocatalytic Raper-Mason reaction between the amine groups of the drug and the catechol groups of the phenolic polymer. The resulting imine bond was hydrolyzable, and pH-dependent drug release from the micelles *in vitro* was demonstrated. These micelles can also be embedded into a hydrogel using strain-promoted alkyne–azide reactions to form a composite material, further advancing the use of phenolic micelles.^[148]

In an elegant synthesis of a norbornene-containing macromonomer with a pendant silyl-protected catechol, bottle brushes were synthesized and cross-linked using ketone functional groups. This design allowed for the presence of free catechols after gel formation, and the catechols could slow the rate of drug release from the network compared to individual micelles.^[127] Other macrostructures can be achieved by using copolymers of poly(*N*-(4-aminophenyl)methacrylamide-*co*-polyethylene glycol monomethyl ether methacrylate), where post-polymerization functionalization through formation of a Schiff base with 3,4-dihydroxybenzaldehyde allowed for assembly with cosolvent mixtures of Fe^{III} or Cu^{II} into either solid particles or vesicles (Figure 8b,c).^[126] Very recently, fiber-like self-assembled materials were obtained from TA and poly(2-ethyl-2-oxazoline) by using a thin-film templating approach followed by rearrangement with acidic buffer.^[190]

Coordinative metal–phenol interactions can also be used to bridge nano- and microstructures to form complex superstructures.^[128] For example, nanoparticles and microparticles were separately coated with phenolic films (MPNs or PDA), mixed, and then cross-linked with metal ions. By using this approach, a range of particle systems (including living cells) with different functionalities could be assembled into superstructures (Figure 8d–l). A recent study described a different approach to assemble particles into superstructures, by using the Mo-PDA complex as the binder and curing agent.^[149] This strategy has been applied to assemble superstructures from particles with various shapes (e.g. nanospheres, nanocubes, and hollow spheres) in the size range of 10 to 500 nm. Although the field of phenol-based superstructures is still in its infancy, it can be envisioned that the use of metal–phenol coordination bonds to form complex hierarchies could pave the way for unique applications of structured assemblies, such as synthetic cells or artificial organs.^[128]

5. Bulk Materials

In addition to the nano- and microsystems discussed in earlier sections, bulk, macroscopic materials, including gels,^[30] epoxy networks,^[150] polycarbonates,^[151] and elastomers,^[20] can be engineered from phenolic compounds. Some of these materials have been thoroughly reviewed elsewhere.^[198] Thus, the present section briefly covers these phenolic bulk materials, while highlighting the building blocks used in their design and assembly.

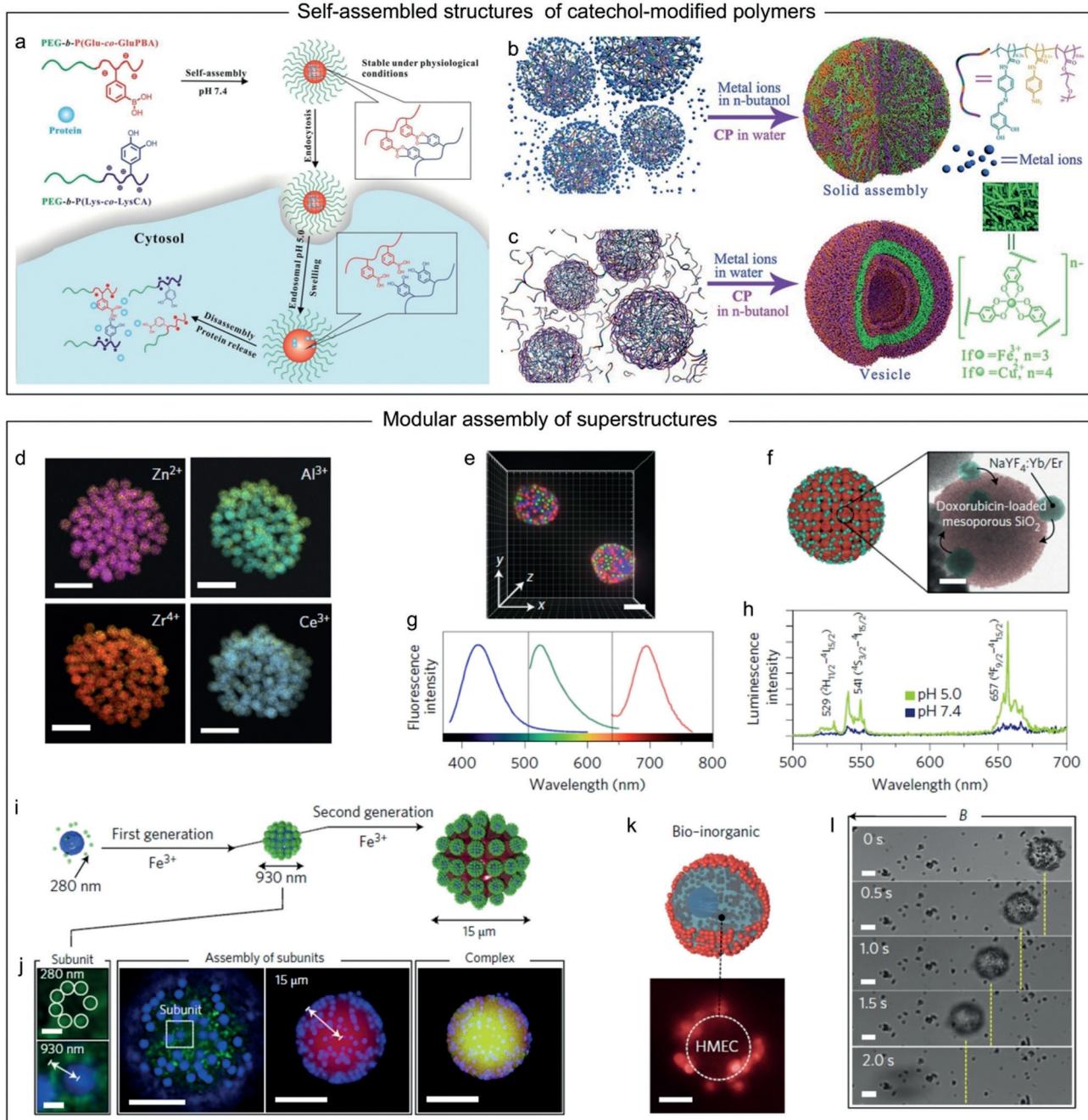


Figure 8. Self-assembled structures of catechol-modified polymers using different cross-linking strategies such as a) core-cross-linked polyion complex micelles (using catechol–boron complexation), and either b) solid assemblies or c) vesicles (using catechol–metal complexation). (a) Reproduced with permission.^[143] Copyright 2013 American Chemical Society. (b,c) Reproduced with permission.^[126] Copyright 2015 Royal Society of Chemistry. d–l) Structural tailorability of modular-assembled superstructures using phenolic coatings, as characterized by various spectroscopic methods. Reproduced with permission.^[128] Copyright 2016 Springer Nature.

5.1. Gels

Gel-based materials represent an important class of soft materials that find applications in diverse fields, including tissue engineering, drug delivery, catalysis, pollutant sequestration, filtration, and chemical sensing.^[152–158] The driving forces for the assembly of these viscoelastic soft materials can be covalent and noncovalent in nature. Among the diverse noncovalent driving forces, metal-ligand coordination has

become an attractive route to gel both organic and aqueous solvents, and the resulting materials are commonly known as metallogeels.^[159–161] The growing interest in metallogeel research stems from the prospects of integrating properties pertaining to the metal (e.g. redox, optoelectronic, and magnetic)^[152–154, 162, 163] into a gel matrix and exploiting the dynamic nature of coordination bonding to design systems with stimuli-responsiveness or specific mechanical properties for targeted applications.^[152–154, 159, 164]

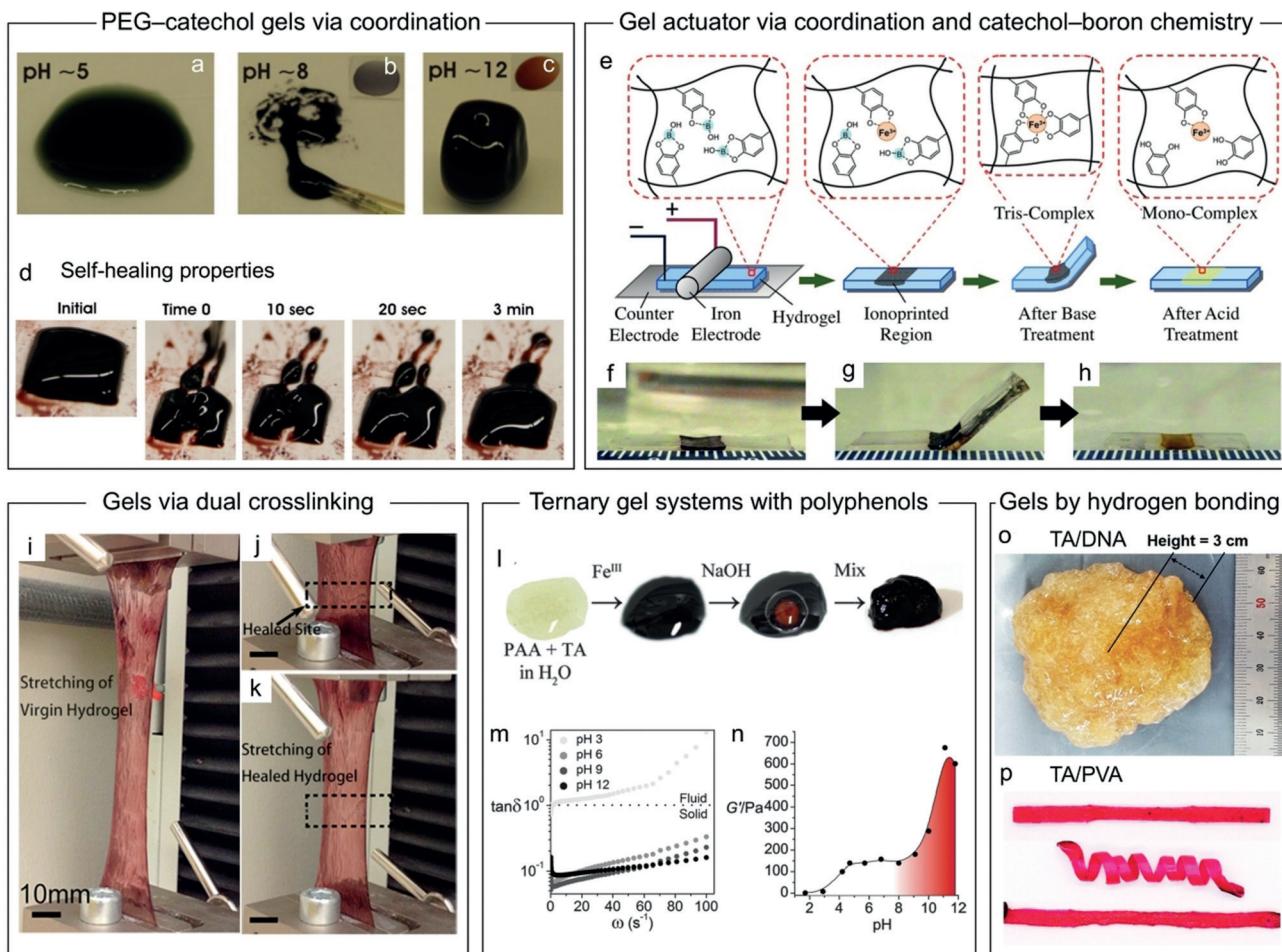


Figure 9. a–c) Gelation behavior of PEG-catechol with Fe^{III} at different pH values and d) self-healing properties of the resulting gels. Reproduced with permission.^[19] e–h) Gel actuator fabricated using catechol–boron and catechol–Fe^{III} coordination through ionoprinting. Reproduced with permission.^[171] Copyright 2014 Wiley-VCH. i–k) High extensibility and the fast self-healing property of a photopolymerized (covalent cross-linking) hydrogel using pre-coordinated catechol–Fe^{III} complexes as dynamic cross-linkers. Reproduced with permission.^[173] Copyright 2015 American Chemical Society. Ternary gel system: l) using a mixture of poly(allylamine hydrochloride) (PAA), TA, and Fe^{III}, and m,n) its rheological properties as a function of the pH value. Reproduced with permission.^[174] Copyright 2014 Royal Society of Chemistry. Examples of gels obtained through hydrogen bonding between TA and o) biopolymer (DNA) or p) synthetic polymer poly(vinyl alcohol) (PVA). Shape-memory property of the TA/PVA gel. (o) Reproduced with permission.^[177] Copyright 2015 Wiley-VCH. (p) Reproduced with permission.^[176] Copyright 2016 American Chemical Society.

Early examples of metallogels based on phenolic derivatives have their roots in the field of mussel-inspired chemistry, where iron–catechol coordination, in particular, has been the subject of extensive research.^[19,161,165,166] To date, the most established approach for the formation of such metallogels consists of two steps: 1) covalent modification of natural or synthetic polymers with phenolic moieties and 2) gelation of these modified polymers through coordinative cross-linking induced by the addition of transition metals.^[19,165,167–170] The most widely used combination is PEG modified with catechol functional groups (PEG-catechol) and Fe^{III} ions (Figure 9a–c).^[19,165,166] Some of the properties exhibited by these gels include self-healing (Figure 9d) and stimuli-responsiveness, thereby illustrating the dynamic and reversible nature of coordination interactions.^[19,166,169] By using the differences in the pH-responsiveness and reversibility of catechol–boron and catechol–Fe^{III} complexes, Lee and Konst^[171] designed a gel-based actuator

system by an ionoprinting approach (Figure 9e–h). Additionally, Li et al.^[172] reported a variant of this approach through the use of Fe₃O₄ nanoparticles as cross-linking motifs (instead of using of Fe^{III} ions as cross-linkers) for PEG-catechol. The resulting gels showed remarkably different mechanical properties from their ionic counterparts (e.g. solid-like, but, reversible hydrogel mechanics), which can be attributed to the dynamics of multiple catechol–Fe^{III} cross-links formed on the surface of Fe₃O₄ nanoparticles. Furthermore, Hou and Ma^[173] demonstrated a supramolecular hydrogel system using photopolymerizable, precoordinated catechol–Fe^{III} complexes as multifunctional cross-linkers and acrylamide as a monomer. The resulting dual-cross-linked (i.e. coordination and covalent) gels showed high extensibility and self-healing capacity (Figure 9i–k).

An alternative approach has also been developed, where a native polyphenol, a polyelectrolyte, and a transition metal are mixed to form a ternary gel system.^[174,175] Krogsgaard

et al.^[174] used TA, poly(allylamine hydrochloride), and Fe^{III} ions to form one such system ((Figure 9l–n), where both the TA-poly(allylamine hydrochloride) covalent cross-linking through a Michael-type or Schiff base reaction and TA-Fe^{III} cross-linking through coordination were essential for gelation to occur.^[174] This approach was later extended to other transition metals and hydrogen-bonding (with TA) polymer motifs.^[174,175]

Besides metal coordination, polyphenols can form gels with biopolymers or synthetic polymers solely through hydrogen bonding.^[176,177] For example, Shin et al. have reported the spontaneous gelation of a DNA/TA (named as TNA hydrogel) mixture, where the gallo groups of TA cross-link the phosphate groups in the DNA backbone through hydrogen bonding (Figure 9o).^[177] The TNA hydrogel exhibits adhesiveness, extensibility, and superior *in vivo* hemostatic ability. Very recently, Hu et al.^[178] demonstrated the formation of a hydrogel by adding polyphenols such as EGCG to amyloid fibrils present in the nematic phase. The resulting gels have been observed to be shear thinning and thermo-stable in the range of 25 to 90°C without the occurrence of a phase transition. Chen et al.^[176] reported a temperature-responsive shape-memory gel (Figure 9p) based on hydrogen-bonding interactions between TA and poly(vinyl alcohol) (PVA). Deformed or elongated TA/PVA hydrogel samples in wet or dried conditions, can recover their original shape when immersed in water at 60°C in a few seconds or at 125°C in approximately 2.5 min, respectively.

Despite the progress mentioned above, the direct gelation of native phenolic compounds with transition metals remained elusive until recently, when the combination of TA and Group IV transition metals (e.g. Ti^{IV}; Figure 10) was used.^[179] Interestingly, this gelation was observed to be specific to this group. TA in combination with transition metals from other groups, for example, Fe^{III} from Group III, resulted in only coacervates or soluble complexes (also observed by Krogsgaard et al.^[174]). Considering such specificity, it was hypothesized that the high oxidation state and formal charge of Group IV metals could, in addition to coordinative cross-linking, play a critical role in the solvent trapping process, thereby enabling the overall gelation process.^[179] The TA-Ti^{IV} metallogels could be formed by a simple mixing process under ambient conditions in various organic and aqueous solvents (Figure 10a–d) and display a range of properties, including optical transparency, self-healing, shape persistence, injectability, adhesiveness, and tunable mechanics (examples of these are provided in Figure 10f,g).^[179] One of the remarkable features of this system is its robust and adaptive nature that allows the *in situ* cogelation of diverse additives (Figure 10h) and regulation of other concomitant assembly processes such as the crystallization (Figure 10i) of MOFs.

5.2. Plastics and Elastomers

The study of plastics and elastomers based on phenolic compounds has been ongoing for decades, and herein we highlight some of the more recent examples. Commercially

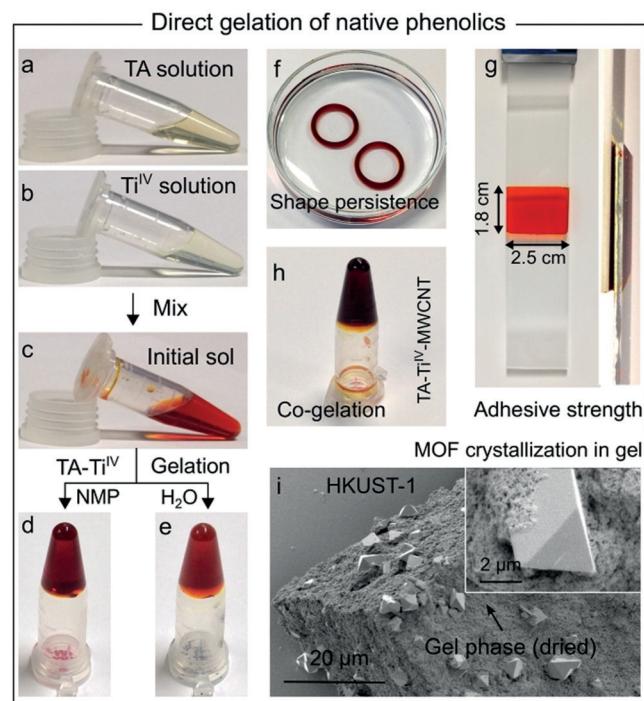


Figure 10. a–e) Gelation process of the TA-Ti^{IV} gel system. f) Shape persistence and g) adhesiveness of the TA-Ti^{IV} gel system. h) Example of *in situ* co-gelation of multiwalled carbon nanotubes (MWCNTs) in the TA-Ti^{IV} gel system. i) Crystallization of HKUST-1 (Cu-benzene-1,3,5-tricarboxylate MOFs) in the TA-Ti^{IV} gel system. Reproduced with permission.^[179] Copyright 2016 Wiley-VCH.

available phenolic compounds, such as bisphenol A (BPA), have been extensively and successfully used as monomers for the industrial synthesis of epoxy resins and polycarbonates. However, there has been recent interest in replacing BPA and similar estrogenic phenolic analogues because of concerns over health risks and the petroleum-based origin of the starting materials.^[180] In this context, phenolic compounds of natural origin are of interest.^[181,182] Examples include the use of phenolic lipids (e.g. cardanol), phenolic acids (e.g. GA and hydroxybenzoic acid), and polyphenols (e.g. quercetin).^[183–187] For polycarbonates, phenolic compounds such as ferulic acid, honokiol, and lignin can be used directly in the polymerization reactions.^[151,161,188,189] The range of natural phenolic compounds has, therefore, allowed for a multitude of structural materials with different properties to act as replacements for the conventionally used BPA.

Phenolic elastomers containing catechol and gallo functional groups and their composites are also of interest to fabricate materials with superior mechanical properties.^[60,190] For example, Li et al.^[190] designed a catechol-functionalized elastomer that showed self-healing properties in seawater through hydrogen bonding and coordination interactions with metal ions (such as Ca^{II} and Mg^{II}) found in seawater. In another approach, catechol-based self-healing elastomers were synthesized in seawater by using reversible boron-catechol chemistry.^[191] Recently, Filippidi et al.^[20] prepared a high-performance composite elastomer by using catechol-Fe^{III} coordination chemistry. The introduction of the reversible coordination cross-links in the initial epoxy network

simultaneously increased the cross-link density and energy dissipation characteristics of the network in the dry state, thereby resulting in a stiff, yet tough elastomer.

6. Applications

Traditionally, phenol-based materials have been used as pigments, antioxidants, photographic developers, and inks.^[70] However, in recent times, their broad range of chemical properties and functions have made them useful precursors for constructing a range of smart, advanced materials including stimuli-responsive materials,^[192,193] antibacterial and chemical-resistant materials,^[194,195] superstructures,^[128] unique polymeric materials,^[196] DNA origami-based materials,^[197] and other nanosystems.^[198,199] Moreover, natural polyphenols have recently been shown to provide enhanced blood circulation after complexation with proteins.^[200] This section focuses on recent scientific advances regarding applications of materials composed of phenolic building blocks.

6.1. Mechanical Applications

6.1.1. Adhesives

Nature often serves as an inspiration to scientists to engineer novel adhesives, and one commonly referenced example deals with the phenolic-based adhesive of mussels. Pioneering investigations have revealed that the byssal adhesion property of mussels arises from the abundance of phenolic amino acids in the adhesive protein (DOPA)^[15] and their synergistic interplay with lysine residues.^[17] Mussels have the ability to permanently stick to nearly any available surface, even in the most turbulent intertidal zones (Figure 11a).^[18] Unlike mussels, which maintain permanent adhesion in wet and dry states, many natural reversible adhesives, such as gecko feet, lose adhesion when exposed to water.^[18] A reversible wet/dry adhesive was designed by combining the robust wet/dry adhesion of marine mussels and the reversibility of the foot hair structures of geckos (Figure 11a).^[18] This system displayed excellent performance over 1000 adhesion tests both in dry and wet states. Another hybrid adhesive was fabricated from mussel foot proteins and amyloidogenic proteins (a major subunit of amyloid curli fibers produced by *Escherichia coli*). These two compounds can be assembled together into higher-order hierarchical structures with a high underwater adhesion energy (20.9 mJ m^{-2}).^[201] Alternatively, conjugating phenolic moieties to stimuli-responsive polymers allows for the fabrication of wet adhesives with reversible triggered adhesion, which can be useful as a sealant for repair of the fetal membrane.^[202] In another strategy, the thermoresponsive polymer PNIPAM was introduced into catechol-containing polymers through host–guest chemistry.^[21] Owing to the conformational transition of PNIPAM around its lower critical solution temperature (LCST), the adhesive exhibits tunable interfacial forces. At temperatures lower than the LCST (e.g. 25°C), the hydrophilic PNIPAM chains form a swelling layer with water molecules, thus preventing adhesion. In contrast, at

temperatures greater than the LCST (e.g. 40°C), the PNIPAM chains transition into the hydrophobic state, thus exposing the adhesive groups. In addition to these selected examples, adhesives for tissue engineering applications have been discussed in a recent review.^[203]

6.1.2. Materials with Superior Mechanical Properties

Phenolic materials have been engineered with a wide range of mechanical properties. For example, drawing inspiration from the excellent mechanical properties displayed by squid beaks,^[204] scientists have designed stiff and compliant phenolic materials. A catechol cross-linking method that has been used is metal complexation, where inorganic ions (e.g. Fe^{III}) are used to generate the desired mechanical properties (e.g. hardness, extensibility,^[205] and gelation).^[81] For example, iron–catechol cross-linking can be used to enhance the toughness of elastomers (Figure 11b)^[20] owing to the sacrificial, reversible coordination bonds. In another approach, interface-assisted formation of self-healing and self-sealing films was achieved by using a range of phenolic ligands,^[206] as polyphenols preferentially form at the air–water interface where phenolic ligands oxidize and polymerize given sufficient oxygen (Figure 11c). Upon damage, the films can easily self-heal upon regeneration at the air–water interface. Alternatively, metalloid-based systems (e.g. boron–catechol complexation) can be used to form self-healing materials.^[191]

6.2. Biological Applications

6.2.1. Drug Delivery

In recent years, particles and hollow capsules fabricated from MPNs have been engineered for drug delivery using a variety of assembly methods.^[63,70,71,76,77,80,140,207] A notable advantage of MPN-based systems is that the incorporated therapeutic cargo can be released through changes in the pH value, with the incorporated metal determining the pH value of the disassembly.^[16,70,71] As tumor sites have a lower local pH value than healthy tissues, as well as different intracellular and extracellular pH values, these MPN-based systems may have potential for use in anticancer therapy. In addition to pH changes, controlled release has been achieved with UV light.^[208] An example of a photoresponsive release system consisted of TA–Cu^{II} coordination networks coated on a mesoporous silica core loaded with photoacid generators and therapeutic cargo. Irradiation with UV light resulted in generation of the photoacid, which degraded the coordination coatings and released the cargo. Additionally, the surface chemistry of drug delivery vehicles has been engineered to show tunable targeting and stealth behavior by using phenolic building blocks (Figure 11d).^[77]

6.2.2. Sensing and Imaging

Dopamine-modified quantum dots were first used as cell-based biosensors to investigate the interplay between cell labeling and redox states.^[209] A nonconductive nanocoating of polyphenols was used as a molecular-imprinting nanosensor

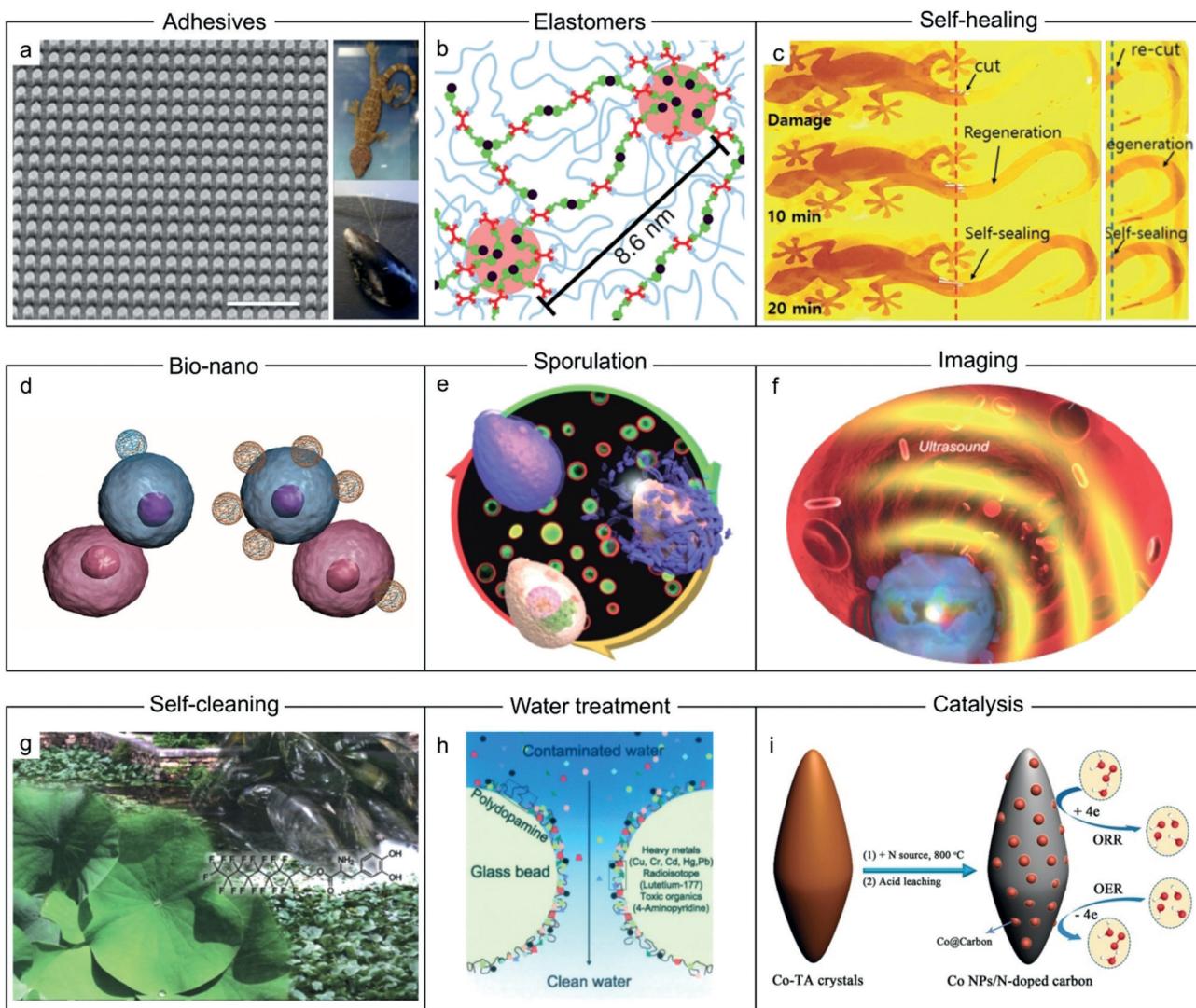


Figure 11. Diverse applications of phenolic materials. a) Biomimetic adhesive inspired by mussels and geckos. Reproduced with permission.^[18] Copyright 2007 Springer Nature. b) Elastomer toughening through metal–catechol cross-links. Reproduced with permission.^[20] Copyright 2017 American Association for the Advancement of Science. c) Biologically inspired regenerative self-healing and self-sealing films. Reproduced with permission.^[206] Copyright 2016 Wiley-VCH. d) Drug carriers with tunable cellular adhesion and targeting performance. Reproduced with permission.^[77] Copyright 2016 American Chemical Society. e) Single-cell encapsulation and artificial sporulation. Reproduced with permission.^[67] Copyright 2014 Wiley-VCH. f) Application of metal–phenol particles in ultrasound imaging. Reproduced with permission.^[212] Copyright 2015 Wiley-VCH. g) Mussel-inspired coating for self-cleaning applications. Reproduced with permission.^[214] Copyright 2014 Royal Society of Chemistry. h) Detoxification of water by polydopamine. Reproduced with permission.^[219] Copyright 2012 Wiley-VCH. i) Metal–polyphenol crystals and the derived composites for catalytic applications. Reproduced with permission.^[222] Copyright 2016 Wiley-VCH.

for the recognition of proteins with ultrahigh sensitivity.^[210] This system not only showed specific recognition for human ferritin and papillomavirus, but also responded to the conformational changes of proteins such as calmodulin. GA-based self-assembled nanodots obtained by iron coordination were used in the enhancement of tumor-imaging sensitivity and the promotion of renal clearance.^[211] The incorporation of metal ions in MPNs has enabled their use as imaging agents in biological applications through PET, MRI, ultrasound (Figure 11 f), and fluorescence imaging.^[70,212]

6.2.3. Artificial Sporulation

The TA–Fe^{III} MPN system has been used for the encapsulation of single cells (Figure 11 e).^[16,67,147] After coating yeast cells with MPNs, cell division was suppressed, but could be fully restored upon disassembly of the coatings.^[67] The MPN coatings could protect the yeast cells from multiple external aggressors such as irradiation with UV-C and lytic enzymes, which mimics the sporulation process in nature.^[67]

6.3. Energy and Environmental Applications

6.3.1. Controlled Wetting and Self-Cleaning

Conformal coatings prepared from PDA and MPNs are also of interest to modify the wetting properties of various surfaces. Superhydrophobic particles were engineered by attaching silver nanoparticles to silica particles with PDA as bridging coatings, followed by reaction with thiol to lower the surface energy.^[213] The resultant particles were super-repellent to water owing to the modified composite structure and low surface energy. Superhydrophobic self-cleaning coatings have also been obtained in a single dip-coating step using a perfluorinated dopamine derivative (Figure 11g).^[214] Moreover, antifouling phenolic coatings were prepared using catechol-containing polymers or thiol-containing peptide-dopamine conjugates.^[76,215,216]

6.3.2. Separations

Oil–water separation is important for environmental remediation and a wide range of industrial applications.^[217] TA–Fe^{III} MPN coatings have been used to fabricate multi-functional filtration membranes.^[218] MPN-coated poly(ether sulfone) membranes exhibited high water flux and antifouling properties against proteins and cells, thus demonstrating potential applications in water purification.^[218] Owing to the high binding affinity of catechol to metals, catechol-coated substrates could also be used in environmental remediation for the removal of heavy metals (Figure 11h)^[219] and organic contaminants.^[220] Additionally, films with embedded PDA-modified nanoparticles could be used for CO₂ separation.^[221]

6.3.3. Catalysis

The ability to chelate a variety of metals makes phenolic materials ideal candidates in catalytic reactions. Crystalline cobalt-polyphenol MOFs can be used as high-performance catalysts for oxygen reduction and oxygen evolution reactions (Figure 11i).^[222] Catalytic applications of MPNs include the Suzuki–Miyaura coupling reaction in water,^[223] the Fenton reaction,^[65] the photocatalytic degradation of organic dyes (thermally treated MPNs),^[66] and the hydrogenation of quinoline,^[70] as well as radical and ROS scavengers.^[54,73,224]

6.4. Emerging Applications

In addition to the applications mentioned above, phenolic materials have recently been explored for some interesting emerging applications based on their adhesive, antibacterial, antioxidant, astringent, and metal-chelating properties. For example, Ma et al.^[225] studied the astringent effect of polyphenols originating from protein-mediated lubrication failure, and engineered a tongue-like polyacrylamide hydrogel that exhibited high polyphenol sensitivity. By using this property, a scientific strategy has been demonstrated to efficiently catch fish (the epidermal layer of fish is rich in various biologically active proteins) with a TA-modified glove (Figure 12a–c). A physical mixture of TA and PEG has been

shown to have superior mucoadhesive properties originating from the pH-dependent intermolecular interactions between TA and mucin.^[226] Park et al. demonstrated that TA-based MPNs could be used as edible coatings to preserve the post-harvest shelf-life of perishable fruits (Figure 12d,e).^[79] Meurer et al. designed a biohybrid microgel particle system containing catechol moieties to deliver micronutrients (e.g. Fe^{III}) as a foliar fertilizer system.^[227] The TA-Ti^{IV} metallogel system has recently been used as a medium for the controlled crystallization of active pharmaceutical ingredients (APIs), which is critical in optimizing the processing and performance of drug formulations.^[228] The method for API crystallization in the TA-Ti^{IV} metallogel is shown in Figure 12g,h. The gel-grown API crystals were observed to be significantly different in size, morphology, and polymorphism compared with those grown in controls without the gelators (Figure 12i,j). Additionally, the size and morphology of the API crystals could be tailored by altering the reaction parameters and gel composition.

7. Summary and Outlook

The ubiquity of phenolic compounds and their facile combination with synthetic and biopolymers have allowed for the engineering of a wide variety of functional materials. Phenolic materials can be assembled across a wide range of length scales (in the nanometer to centimeter range) for a variety of applications. The three broad classes of phenolic materials described herein, namely films, particles, and bulk materials, overlap in some cases, but act as categories for classifying past studies reported in the literature. Films are classified by being surface-confined, and encompass MPN films, LbL films, PDA films, and other self-polymerized films. If film formation is performed on nano- or microparticles, film-coated particles are obtained. Phenol-based particles encompass diverse materials ranging from MOFs to micelles and superstructures. Finally, bulk materials, such as gels and elastomers, represent some of the most established phenolic materials in the literature.

We have highlighted that the building blocks play a key role in the final material properties, and that a wide variety of attractive and stabilizing forces, such as electrostatic, hydrogen bonding, and metal chelation, can be used to form functional phenolic materials. Moreover, building blocks of similar types can be blended together to allow for emergent properties. The extensive research studies on phenolic materials, arising separately from mussel-inspired chemistry and phytochemistry, are starting to merge into a single cohesive and productive field. Therefore, the present Review has aimed to collate knowledge from seemingly unrelated fields and research topics that share the use of phenols as the point of similarity, so that researchers can find inspiration from outside traditional avenues.

There are also challenges to overcome to advance this important field of research. For example, the assembly of MPN- and PDA-based materials is poorly understood at the molecular level, in part because of the amorphous nature of these materials. As a result, many of the biomimetic materials

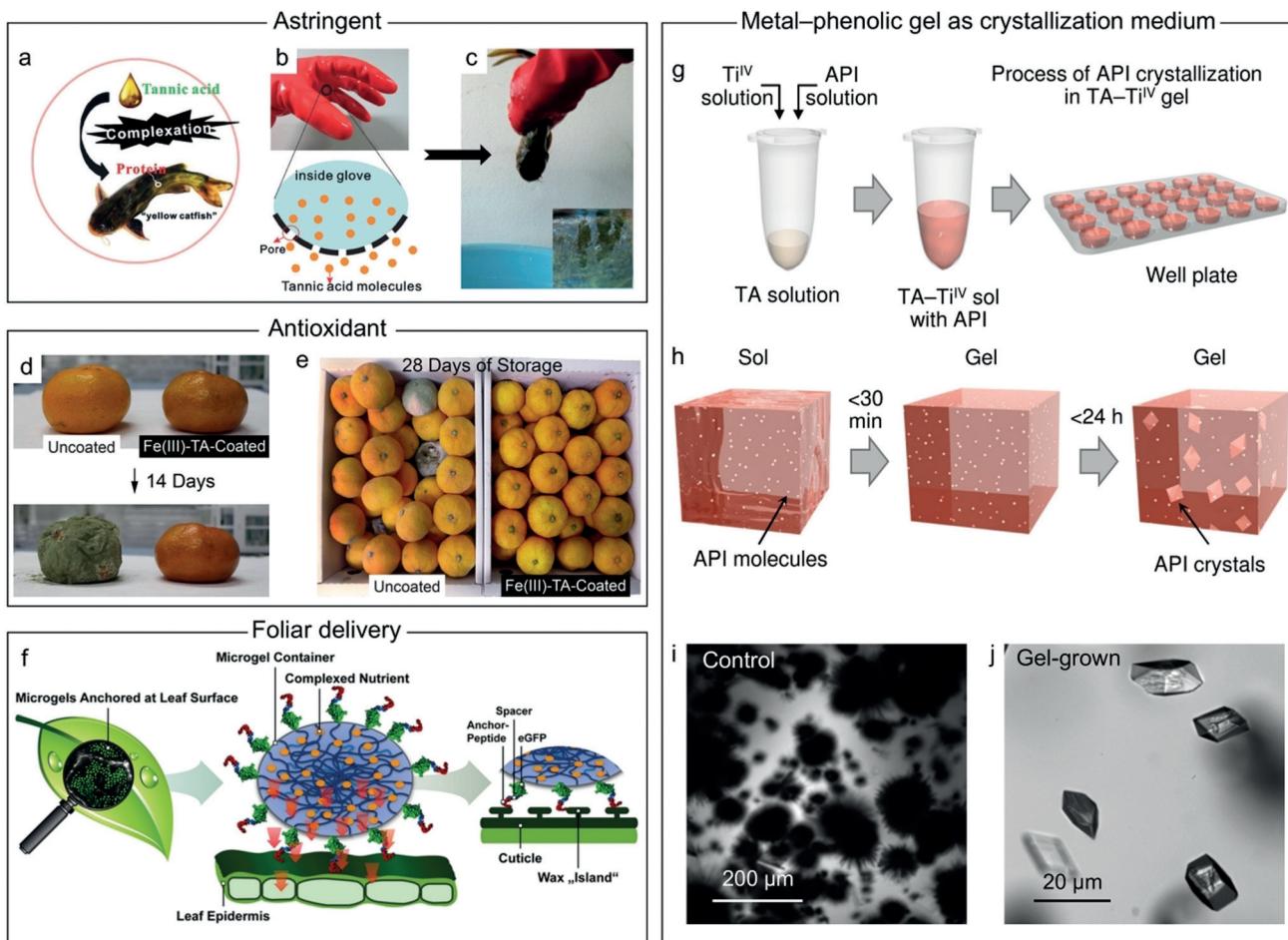


Figure 12. Emerging applications of phenol-based materials. a) Responsiveness of a fish to TA owing to astringency. b) Schematic representation and c) photograph of fish capture using a TA-modified glove. Reproduced with permission.^[225] Copyright 2016 Wiley-VCH. d,e) Spray-coated MPNs on fruits showing antioxidant activity. Reproduced with permission.^[79] Copyright 2017 Springer Nature. f) Schematic representation of microgel-based fertilizers for specific attachment to leaf surfaces and controlled foliar delivery of nutrients to plants. Reproduced with permission.^[227] Copyright 2017 Wiley-VCH. g) Illustration of the crystallization of an active pharmaceutical ingredient (API) in the TA-Ti^{IV} gel system. h) Sol–gel transition and subsequent crystallization of the API in the gels. Optical microscopy images showing piroxicam crystallization in i) solution (without the gelators) and j) the TA-Ti^{IV} gel. Reproduced with permission.^[228] Copyright 2018 Wiley-VCH.

are yet to replicate the performance of living systems such as the underwater adhesion of mussels. Fundamentals of the structure–function relationship and synergistic impact of the organic–inorganic components of MPNs assembled from different combinations of metals and phenolic building blocks are also critical aspects that need to be addressed.

Moving forward, the use of strategically designed, multi-component phenolic composites will be important for next-generation applications. The synergistic combination of various phenolic materials and methods used in disparate fields is expected to yield unique materials with emergent properties. For example, the coating of phenolic gels with phenolic thin films could allow for capsule-like structures with phenol or metal gradients and a defined distribution of high and low modulus regions. Additionally, the combination of amorphous and crystalline materials (such as gel-MOF composites)^[179] could allow for the fabrication of unique composites with synergistic functions.

Beyond the use of catechol- and gallo-containing building blocks, expansion into other phenolic compounds, such as phenolic lipids, would allow for the generation of a broad range of materials as well as the possible generation of emergent properties. Moving tangential to phenols, the amino acid histidine is responsible for significant functional metal chelation in biological systems,^[229] where histidine–metal complexes have recently begun to emerge for constructing functional materials and sensors.^[230] Finally, a deeper understanding into the physical and chemical interactions of phenolic materials is necessary for designing materials with even better performance, which requires interdisciplinary collaborations between chemists, materials scientists, engineers, and biologists. Along these lines, advanced analytical techniques and computational chemistry will play pivotal roles in rationalizing design principles for the preparation of advanced phenolic materials.

Acknowledgements

This research was conducted and funded by the Australian Research Council (ARC) Centre of Excellence in Convergent Bio-Nano Science and Technology (project number CE140100036) and by the ARC through the Discovery Project Scheme (DP170103331). F.C. acknowledges the award of a National Health and Medical Research Council Senior Principal Research Fellowship (APP1135806).

Conflict of interest

The authors declare no conflict of interest.

How to cite: *Angew. Chem. Int. Ed.* **2019**, *58*, 1904–1927
Angew. Chem. **2019**, *131*, 1920–1945

- [1] S. Quideau, D. Deffieux, C. Douat-Casassus, L. Pouységou, *Angew. Chem. Int. Ed.* **2011**, *50*, 586; *Angew. Chem.* **2011**, *123*, 610.
- [2] J. Yang, S. M. A. Cohen, M. Kamperman, *Chem. Soc. Rev.* **2014**, *43*, 8271.
- [3] A. Soto-Vaca, A. Gutierrez, J. N. Losso, Z. Xu, J. W. Finley, *J. Agric. Food Chem.* **2012**, *60*, 6658.
- [4] G. M. Robinson, R. Robinson, *Biochem. J.* **1932**, *26*, 1647.
- [5] N. R. Perron, J. L. Brumaghim, *Cell Biochem. Biophys.* **2009**, *53*, 75.
- [6] F. J. Francis, P. C. Markakis, *Crit. Rev. Food Sci. Nutr.* **1989**, *28*, 273.
- [7] A. E. Stapleton, *Plant Cell* **1992**, *4*, 1353.
- [8] P. W. Barnes, M. A. Tobler, K. Keefover-Ring, S. D. Flint, A. E. Barkley, R. J. Ryel, R. L. Lindroth, *Plant Cell Environ.* **2016**, *39*, 222.
- [9] V. Cheynier, G. Comte, K. M. Davies, V. Lattanzio, S. Martens, *Plant Physiol. Biochem.* **2013**, *72*, 1.
- [10] P. Bandyopadhyay, A. K. Ghosh, C. Ghosh, *Food Funct.* **2012**, *3*, 592.
- [11] R. J. Stewart, J. C. Weaver, D. E. Morse, J. H. Waite, *J. Exp. Biol.* **2004**, *207*, 4727.
- [12] J. H. Waite, N. H. Andersen, S. Jewhurst, C. Sun, *J. Adhes.* **2005**, *81*, 297.
- [13] A. H. Hofman, I. A. van Hees, J. Yang, M. Kamperman, *Adv. Mater.* **2018**, *30*, 1704640.
- [14] P. K. Forooshani, B. P. Lee, *J. Polym. Sci. Part A* **2016**, *55*, 9.
- [15] J. H. Waite, M. L. Tanzer, *Science* **1981**, *212*, 1038.
- [16] H. Ejima, J. J. Richardson, K. Liang, J. P. Best, M. P. van Koeverden, G. K. Such, J. Cui, F. Caruso, *Science* **2013**, *341*, 154.
- [17] G. P. Maier, M. V. Rapp, J. H. Waite, J. N. Israelachvili, A. Butler, *Science* **2015**, *349*, 628.
- [18] H. Lee, B. P. Lee, P. B. Messersmith, *Nature* **2007**, *448*, 338.
- [19] N. Holten-Andersen, M. J. Harrington, H. Birkedal, B. P. Lee, P. B. Messersmith, K. Y. C. Lee, J. H. Waite, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 2651.
- [20] E. Filippidi, T. R. Cristiani, C. D. Eisenbach, J. H. Waite, J. N. Israelachvili, B. K. Ahn, M. T. Valentine, *Science* **2017**, *358*, 502.
- [21] Y. Zhao, Y. Wu, L. Wang, M. Zhang, X. Chen, M. Liu, J. Fan, J. Liu, F. Zhou, Z. Wang, *Nat. Commun.* **2017**, *8*, 2218.
- [22] H. Ejima, J. J. Richardson, F. Caruso, *Nano Today* **2017**, *12*, 136.
- [23] S. L. Kristufek, K. T. Wacker, Y. Y. Timothy Tsao, L. Su, K. L. Wooley, *Nat. Prod. Rep.* **2017**, *34*, 433.
- [24] A. L. Holmberg, K. H. Reno, R. P. Wool, T. H. Epps III, *Soft Matter* **2014**, *10*, 7405.
- [25] K. J. Yao, C. B. Tang, *Macromolecules* **2013**, *46*, 1689.
- [26] A. Gandini, T. M. Lacerda, *Prog. Polym. Sci.* **2015**, *48*, 1.
- [27] B. K. Tiwari, N. P. Brunton, C. Brennan, *Handbook of Plant Food Phytochemicals: Sources, Stability and Extraction*, Wiley, Hoboken, **2013**.
- [28] G. R. Beecher, *J. Nutr.* **2003**, *133*, 3248S.
- [29] H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007**, *318*, 426.
- [30] B. P. Lee, J. L. Dalsin, P. B. Messersmith, *Biomacromolecules* **2002**, *3*, 1038.
- [31] Q. Zhang, G. Nurumbetov, A. Simula, C. Zhu, M. Li, P. Wilson, K. Kempe, B. Yang, L. Tao, D. M. Haddleton, *Polym. Chem.* **2016**, *7*, 7002.
- [32] X. Xiong, L. Xue, J. Cui, *ACS Macro Lett.* **2018**, *7*, 239.
- [33] X. Fan, L. Lin, J. L. Dalsin, P. B. Messersmith, *J. Am. Chem. Soc.* **2005**, *127*, 15843.
- [34] L. Q. Xu, H. Jiang, K.-G. Neoh, E.-T. Kang, G. D. Fu, *Polym. Chem.* **2012**, *3*, 920.
- [35] F. Zhang, S. Liu, Y. Zhang, Z. Chi, J. Xu, Y. Wei, *J. Mater. Chem.* **2012**, *22*, 17159.
- [36] J. Su, F. Chen, V. L. Cryns, P. B. Messersmith, *J. Am. Chem. Soc.* **2011**, *133*, 11850.
- [37] H. Lee, K. D. Lee, K. B. Pyo, S. Y. Park, H. Lee, *Langmuir* **2010**, *26*, 3790.
- [38] Y. Min, P. T. Hammond, *Chem. Mater.* **2011**, *23*, 5349.
- [39] Y. Lee, S. H. Lee, J. S. Kim, A. Maruyama, X. Chen, T. G. Park, *J. Controlled Release* **2011**, *155*, 3.
- [40] J. H. Ryu, Y. Lee, W. H. Kong, T. G. Kim, T. G. Park, H. Lee, *Biomacromolecules* **2011**, *12*, 2653.
- [41] H. Lee, Y. Lee, A. R. Statz, J. Rho, T. G. Park, P. B. Messersmith, *Adv. Mater.* **2008**, *20*, 1619.
- [42] J. H. Cho, J. S. Lee, J. Shin, E. J. Jeon, S. An, Y. S. Choi, S. W. Cho, *Adv. Funct. Mater.* **2018**, *28*, 1705244.
- [43] T. H. Anderson, J. Yu, A. Estrada, M. U. Hammer, J. H. Waite, J. N. Israelachvili, *Adv. Funct. Mater.* **2010**, *20*, 4196.
- [44] L. Zhang, V. Lipik, A. Miserez, *J. Mater. Chem. B* **2016**, *4*, 1544.
- [45] H. O. Ham, Z. Liu, K. H. Lau, H. Lee, P. B. Messersmith, *Angew. Chem. Int. Ed.* **2011**, *50*, 732; *Angew. Chem.* **2011**, *123*, 758.
- [46] P. Glass, H. Chung, N. R. Washburn, M. Sitti, *Langmuir* **2009**, *25*, 6607.
- [47] B. Xu, X. Sun, C. Wu, J. Hu, X. Huang, *Polym. Chem.* **2017**, *8*, 7499.
- [48] M. Wen, M. Liu, W. Xue, K. Yang, G. Chen, W. Zhang, *ACS Macro Lett.* **2018**, *7*, 70.
- [49] N. Patil, C. Falentin-Daudré, C. Jérôme, C. Detrembleur, *Polym. Chem.* **2015**, *6*, 2919.
- [50] S. Lamping, T. Otremba, B. J. Ravoo, *Angew. Chem. Int. Ed.* **2018**, *57*, 2474; *Angew. Chem.* **2018**, *130*, 2499.
- [51] C. R. Matos-Pérez, J. D. White, J. J. Wilker, *J. Am. Chem. Soc.* **2012**, *134*, 9498.
- [52] M. A. North, C. A. Del Gross, J. J. Wilker, *ACS Appl. Mater. Interfaces* **2017**, *9*, 7866.
- [53] A. Isakova, P. D. Topham, A. J. Sutherland, *Macromolecules* **2014**, *47*, 2561.
- [54] K. Zhan, H. Ejima, N. Yoshie, *ACS Sustainable Chem. Eng.* **2016**, *4*, 3857.
- [55] S. Seo, S. Das, P. J. Zalicki, R. Mirshafian, C. D. Eisenbach, J. N. Israelachvili, J. H. Waite, B. K. Ahn, *J. Am. Chem. Soc.* **2015**, *137*, 9214.
- [56] Q. Zhao, D. W. Lee, B. K. Ahn, S. Seo, Y. Kaufman, J. N. Israelachvili, J. H. Waite, *Nat. Mater.* **2016**, *15*, 407.
- [57] R. Hlushko, H. Hlushko, S. A. Sukhishvili, *Polym. Chem.* **2018**, *9*, 506.
- [58] Y. Mu, X. Wu, D. Pei, Z. Wu, C. Zhang, D. Zhou, X. Wan, *ACS Biomater. Sci. Eng.* **2017**, *3*, 3133.
- [59] N. Patil, A. Aqil, F. Ouhib, S. Admassie, O. Inganas, C. Jerome, C. Detrembleur, *Adv. Mater.* **2017**, *29*, 1703373.

- [60] K. Zhan, C. Kim, K. Sung, H. Ejima, N. Yoshie, *Biomacromolecules* **2017**, *18*, 2959.
- [61] T. Shutava, M. Prouty, D. Kommireddy, Y. Lvov, *Macromolecules* **2005**, *38*, 2850.
- [62] J. J. Richardson, J. Cui, M. Björnalm, J. A. Braunger, H. Ejima, F. Caruso, *Chem. Rev.* **2016**, *116*, 14828.
- [63] M. A. Rahim, H. Ejima, K. L. Cho, K. Kempe, M. Müllner, J. P. Best, F. Caruso, *Chem. Mater.* **2014**, *26*, 1645.
- [64] H. Ejima, J. J. Richardson, F. Caruso, *Polym. J.* **2014**, *46*, 452.
- [65] B. L. Tardy, J. J. Richardson, J. Guo, J. Lehtonen, M. Ago, O. J. Rojas, *Green Chem.* **2018**, *20*, 1335.
- [66] G. Xiao, W. Chen, F. Tian, J. J. Richardson, B. L. Tardy, M. Liu, N. Joshi, J. Guo, *Chem. Asian J.* **2018**, *13*, 972.
- [67] J. H. Park, K. Kim, J. Lee, J. Y. Choi, D. Hong, S. H. Yang, F. Caruso, Y. Lee, I. S. Choi, *Angew. Chem. Int. Ed.* **2014**, *53*, 12420; *Angew. Chem.* **2014**, *126*, 12628.
- [68] S. H. Yang, D. Hong, J. Lee, E. H. Ko, I. S. Choi, *Small* **2013**, *9*, 178.
- [69] T. Park, J. Y. Kim, H. Cho, H. C. Moon, B. J. Kim, J. H. Park, D. Hong, J. Park, I. S. Choi, *Polymers* **2017**, *9*, 140.
- [70] J. Guo, Y. Ping, H. Ejima, K. Alt, M. Meissner, J. J. Richardson, Y. Yan, K. Peter, D. von Elverfeldt, C. E. Hagemeyer, F. Caruso, *Angew. Chem. Int. Ed.* **2014**, *53*, 5546; *Angew. Chem.* **2014**, *126*, 5652.
- [71] Y. Ping, J. Guo, H. Ejima, X. Chen, J. J. Richardson, H. Sun, F. Caruso, *Small* **2015**, *11*, 2032.
- [72] J. Guo, H. Sun, K. Alt, B. L. Tardy, J. J. Richardson, T. Suma, H. Ejima, J. Cui, C. E. Hagemeyer, F. Caruso, *Adv. Healthcare Mater.* **2015**, *4*, 1796.
- [73] N. Bertleff-Zieschang, M. A. Rahim, Y. Ju, J. A. Braunger, T. Suma, Y. Dai, S. Pan, F. Cavalieri, F. Caruso, *Chem. Commun.* **2017**, *53*, 1068.
- [74] M. A. Rahim, M. Björnalm, N. Bertleff-Zieschang, Y. Ju, S. Mettu, M. G. Leeming, F. Caruso, *ACS Appl. Mater. Interfaces* **2018**, *10*, 7632.
- [75] M. A. Rahim, K. Kempe, M. Müllner, H. Ejima, Y. Ju, M. P. van Koeverden, T. Suma, J. A. Braunger, M. G. Leeming, B. F. Abrahams, *Chem. Mater.* **2015**, *27*, 5825.
- [76] Y. Ju, J. Cui, M. Müllner, T. Suma, M. Hu, F. Caruso, *Biomacromolecules* **2015**, *16*, 807.
- [77] Y. Ju, J. Cui, H. Sun, M. Müllner, Y. Dai, J. Guo, N. Bertleff-Zieschang, T. Suma, J. J. Richardson, F. Caruso, *Biomacromolecules* **2016**, *17*, 2268.
- [78] X. Yang, B. Yang, L. He, R. Li, Y. Liao, S. Zhang, Y. Yang, X. Xu, D. Zhang, H. Tan, J. Li, J. Li, *ACS Biomater. Sci. Eng.* **2017**, *3*, 3553.
- [79] J. Park, S. Choi, H. Moon, H. Seo, J. Kim, S.-P. Hong, B. Lee, E. Kang, J. Lee, D. Ryu, I. S. Choi, *Sci. Rep.* **2017**, *7*, 6980.
- [80] B. J. Kim, S. Han, K. B. Lee, I. S. Choi, *Adv. Mater.* **2017**, *29*, 1700784.
- [81] M. A. Rahim, M. Björnalm, N. Bertleff-Zieschang, Q. Besford, S. Mettu, T. Suma, M. Faria, F. Caruso, *Adv. Mater.* **2017**, *29*, 1606717.
- [82] P. V. Cherepanov, M. A. Rahim, N. Bertleff-Zieschang, M. A. Sayeed, A. P. O'Mullane, S. E. Moulton, F. Caruso, *ACS Appl. Mater. Interfaces* **2018**, *10*, 5828.
- [83] C. Maerten, L. Lopez, P. Lupattelli, G. Rydzek, S. Pronkin, P. Schaaf, L. Jierry, F. Boulmedais, *Chem. Mater.* **2017**, *29*, 9668.
- [84] J. Guo, J. J. Richardson, Q. A. Besford, A. J. Christofferson, Y. Dai, C. W. Ong, B. L. Tardy, K. Liang, G. H. Choi, J. Cui, *Langmuir* **2017**, *33*, 10616.
- [85] J. J. Richardson, M. Björnalm, F. Caruso, *Science* **2015**, *348*, aaa2491.
- [86] T. G. Shutava, Y. M. Lvov, *J. Nanosci. Nanotechnol.* **2006**, *6*, 1655.
- [87] V. Kozlovskaya, E. Kharlampieva, I. Drachuk, D. Cheng, V. V. Tsukruk, *Soft Matter* **2010**, *6*, 3596.
- [88] J. Sun, C. Su, X. Zhang, J. Li, W. B. Zhang, N. Zhao, J. Xu, S. Yang, *J. Colloid Interface Sci.* **2018**, *513*, 470.
- [89] Y. Takemoto, H. Ajiro, M. Akashi, *Langmuir* **2015**, *31*, 6863.
- [90] E. Adatoz, S. Hendessi, C. W. Ow-Yang, A. L. Demirel, *Soft Matter* **2018**, *14*, 3849.
- [91] B.-S. Kim, H.-i. Lee, Y. Min, Z. Poon, P. T. Hammond, *Chem. Commun.* **2009**, 4194.
- [92] M. V. Lomova, A. I. Brichkina, M. V. Kiryukhin, E. N. Vasina, A. M. Pavlov, D. A. Gorin, G. B. Sukhorukov, M. N. Antipina, *ACS Appl. Mater. Interfaces* **2015**, *7*, 11732.
- [93] M. Allais, F. Meyer, V. Ball, *J. Colloid Interface Sci.* **2018**, *512*, 722.
- [94] V. Ball, *Colloids Interface Sci. Commun.* **2014**, *3*, 1.
- [95] T. G. Shutava, M. D. Prouty, V. E. Agabekov, Y. M. Lvov, *Chem. Lett.* **2006**, *35*, 1144.
- [96] S. Kim, D. S. Kim, S. M. Kang, *Chem. Asian J.* **2014**, *9*, 63.
- [97] L. Yang, L. Han, J. Ren, H. Wei, L. Jia, *Colloids Surf. A* **2015**, *484*, 197.
- [98] B. P. Lee, P. B. Messersmith, J. N. Israelachvili, J. H. Waite, *Annu. Rev. Mater. Res.* **2011**, *41*, 99.
- [99] J. H. Waite, *Nat. Mater.* **2008**, *7*, 8.
- [100] M. Liu, G. Zeng, K. Wang, Q. Wan, L. Tao, X. Zhang, Y. Wei, *Nanoscale* **2016**, *8*, 16819.
- [101] R. Mrówczyński, *ACS Appl. Mater. Interfaces* **2018**, *10*, 7541.
- [102] A. Postma, Y. Yan, Y. Wang, A. N. Zelikin, E. Tjipto, F. Caruso, *Chem. Mater.* **2009**, *21*, 3042.
- [103] X. Chen, Y. Yan, M. Mullner, M. P. van Koeverden, K. F. Noi, W. Zhu, F. Caruso, *Langmuir* **2014**, *30*, 2921.
- [104] M. d'Ischia, A. Napolitano, V. Ball, C.-T. Chen, M. J. Buehler, *Acc. Chem. Res.* **2014**, *47*, 3541.
- [105] C.-T. Chen, F. J. Martin-Martinez, G. S. Jung, M. J. Buehler, *Chem. Sci.* **2017**, *8*, 1631.
- [106] S. Hong, S. Na Yun, S. Choi, T. Song In, Y. Kim Woo, H. Lee, *Adv. Funct. Mater.* **2012**, *22*, 4711.
- [107] D. R. Dreyer, D. J. Miller, B. D. Freeman, D. R. Paul, C. W. Bielawski, *Langmuir* **2012**, *28*, 6428.
- [108] J. Cui, Y. Yan, G. K. Such, K. Liang, C. J. Ochs, A. Postma, F. Caruso, *Biomacromolecules* **2012**, *13*, 2225.
- [109] R. Liang, J. Ding, S. Gao, W. Qin, *Angew. Chem. Int. Ed.* **2017**, *56*, 6833; *Angew. Chem.* **2017**, *129*, 6937.
- [110] Y. Song, G. Ye, Y. Lu, J. Chen, J. Wang, K. Matyjaszewski, *ACS Macro Lett.* **2016**, *5*, 382.
- [111] Y. Yang, X. Liu, G. Ye, S. Zhu, Z. Wang, X. Huo, K. Matyjaszewski, Y. Lu, J. Chen, *ACS Appl. Mater. Interfaces* **2017**, *9*, 13637.
- [112] Y. Song, G. Ye, F. Wu, Z. Wang, S. Liu, M. Kopeć, Z. Wang, J. Chen, J. Wang, K. Matyjaszewski, *Chem. Mater.* **2016**, *28*, 5013.
- [113] Z. Zeng, M. Wen, G. Ye, X. Huo, F. Wu, Z. Wang, J. Yan, K. Matyjaszewski, Y. Lu, J. Chen, *Chem. Mater.* **2017**, *29*, 10212.
- [114] S. P. Le-Masurier, G. Gody, S. Perrier, A. M. Granville, *Polym. Chem.* **2014**, *5*, 2816.
- [115] M. Lee, U. Kim Jong, S. Lee Joon, I. Lee Byung, J. Shin, B. Park Chan, *Adv. Mater.* **2014**, *26*, 4463.
- [116] J. Zhou, P. Wang, C. Wang, Y. T. Goh, Z. Fang, P. B. Messersmith, H. Duan, *ACS Nano* **2015**, *9*, 6951.
- [117] M. Kohri, Y. Nannichi, T. Taniguchi, K. Kishikawa, *J. Mater. Chem. C* **2015**, *3*, 720.
- [118] T.-F. Wu, J.-D. Hong, *Biomacromolecules* **2015**, *16*, 660.
- [119] M. Xiao, Y. Li, M. C. Allen, D. D. Deheyn, X. Yue, J. Zhao, N. C. Gianneschi, M. D. Shawkey, A. Dhinojwala, *ACS Nano* **2015**, *9*, 5454.
- [120] T. S. Sileika, D. G. Barrett, R. Zhang, K. H. Lau, P. B. Messersmith, *Angew. Chem. Int. Ed.* **2013**, *52*, 10766; *Angew. Chem.* **2013**, *125*, 10966.
- [121] J. S. Lee, J. S. Lee, M. S. Lee, S. An, K. Yang, K. Lee, H. S. Yang, H. Lee, S.-W. Cho, *Chem. Mater.* **2017**, *29*, 4375.

- [122] H. Watanabe, A. Fujimoto, J. Nishida, T. Ohishi, A. Takahara, *Langmuir* **2016**, *32*, 4619.
- [123] F. Behboodi-Sadabab, H. Zhang, V. Trouillet, A. Welle, N. Plumeré, P. A. Levkin, *Adv. Funct. Mater.* **2017**, *27*, 1700127.
- [124] F. Behboodi-Sadabab, H. Zhang, V. Trouillet, A. Welle, N. Plumeré, P. A. Levkin, *Chem. Mater.* **2018**, *30*, 1937.
- [125] Y. Li, W. Xiao, K. Xiao, L. Berti, J. Luo, H. P. Tseng, G. Fung, K. S. Lam, *Angew. Chem. Int. Ed.* **2012**, *51*, 2864; *Angew. Chem.* **2012**, *124*, 2918.
- [126] C. Yuan, J. Chen, S. Yu, Y. Chang, J. Mao, Y. Xu, W. Luo, B. Zeng, L. Dai, *Soft Matter* **2015**, *11*, 2243.
- [127] R. Slegeris, B. A. Ondrusk, H. Chung, *Polym. Chem.* **2017**, *8*, 4707.
- [128] J. Guo, B. L. Tardy, A. J. Christofferson, Y. Dai, J. J. Richardson, W. Zhu, M. Hu, Y. Ju, J. Cui, R. R. Dagastine, I. Yarovsky, F. Caruso, *Nat. Nanotechnol.* **2016**, *11*, 1105.
- [129] M. Björnalm, J. Cui, N. Bertleff-Zieschang, D. Song, M. Faria, M. A. Rahim, F. Caruso, *Chem. Mater.* **2017**, *29*, 289.
- [130] C. H. Wunderlich, R. Weber, G. Bergerhoff, Z. Anorg. Allg. Chem. **1991**, *598*, 371.
- [131] L. Cooper, T. Hidalgo, M. Gorman, T. Lozano-Fernandez, R. Simon-Vazquez, C. Olivier, N. Guillou, C. Serre, C. Martineau, F. Taulelle, D. Damasceno-Borges, G. Maurin, A. Gonzalez-Fernandez, P. Horcajada, T. Devic, *Chem. Commun.* **2015**, *51*, 5848.
- [132] R. K. Feller, A. K. Cheetham, *Solid State Sci.* **2006**, *8*, 1121.
- [133] L. Cooper, N. Guillou, C. Martineau, E. Elkaim, F. Taulelle, C. Serre, T. Devic, *Eur. J. Inorg. Chem.* **2014**, 6281.
- [134] G. Mouchaham, L. Cooper, N. Guillou, C. Martineau, E. Elkaïm, S. Bourrelly, P. L. Llewellyn, C. Allain, G. Clavier, C. Serre, T. Devic, *Angew. Chem. Int. Ed.* **2015**, *54*, 13297; *Angew. Chem.* **2015**, *127*, 13495.
- [135] M. Hmadeh, Z. Lu, Z. Liu, F. Gádara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, E. Perre, V. Ozolins, K. Suenaga, X. Duan, B. Dunn, Y. Yamamoto, O. Terasaki, O. M. Yaghi, *Chem. Mater.* **2012**, *24*, 3511.
- [136] N. T. T. Nguyen, H. Furukawa, F. Gádara, C. A. Trickett, H. M. Jeong, K. E. Cordova, O. M. Yaghi, *J. Am. Chem. Soc.* **2015**, *137*, 15394.
- [137] S. J. Yang, M. Antonietti, N. Fechler, *J. Am. Chem. Soc.* **2015**, *137*, 8269.
- [138] W. Zhu, G. Xiang, J. Shang, J. Guo, B. Motellalli, P. Durfee, J. O. Agola, E. N. Coker, C. J. Brinker, *Adv. Funct. Mater.* **2018**, *28*, 1705274.
- [139] X. Wang, J. Yan, D. Pan, R. Yang, L. Wang, Y. Xu, J. Sheng, Y. Yue, Q. Huang, Y. Wang, R. Wang, M. Yang, *Adv. Healthcare Mater.* **2018**, 1701505. <https://doi.org/10.1002/adhm.201701505>.
- [140] Y. Dai, J. Guo, T. Y. Wang, Y. Ju, A. J. Mitchell, T. Bonnard, J. Cui, J. J. Richardson, C. E. Hagemeyer, K. Alt, F. Caruso, *Adv. Healthcare Mater.* **2017**, *6*, 1700467.
- [141] Z. Wang, Y. Xie, Y. Li, Y. Huang, L. R. Parent, T. Ditri, N. Zang, J. D. Rinehart, N. C. Gianneschi, *Chem. Mater.* **2017**, *29*, 8195.
- [142] S. Wu, R. Qi, H. Kuang, Y. Wei, X. Jing, F. Meng, Y. Huang, *ChemPlusChem* **2013**, *78*, 175.
- [143] J. Ren, Y. Zhang, J. Zhang, H. Gao, G. Liu, R. Ma, Y. An, D. Kong, L. Shi, *Biomacromolecules* **2013**, *14*, 3434.
- [144] T. Cheng, J. Liu, J. Ren, F. Huang, H. Ou, Y. Ding, Y. Zhang, R. Ma, Y. An, J. Liu, L. Shi, *Theranostics* **2016**, *6*, 1277.
- [145] G. H. Hwang, K. H. Min, H. J. Lee, H. Y. Nam, G. H. Choi, B. J. Kim, S. Y. Jeong, S. C. Lee, *Chem. Commun.* **2014**, *50*, 4351.
- [146] K. Xin, M. Li, D. Lu, X. Meng, J. Deng, D. Kong, D. Ding, Z. Wang, Y. Zhao, *ACS Appl. Mater. Interfaces* **2017**, *9*, 80.
- [147] J. M. W. Chan, J. P. K. Tan, A. C. Englert, X. Ke, S. Gao, C. Yang, H. Sardon, Y. Y. Yang, J. L. Hedrick, *Macromolecules* **2016**, *49*, 2013.
- [148] R. J. Ono, A. L. Z. Lee, Z. X. Voo, S. Venkataraman, B. W. Koh, Y. Y. Yang, J. L. Hedrick, *Biomacromolecules* **2017**, *18*, 2277.
- [149] L. Sun, C. Wang, L. Wang, *ACS Nano* **2018**, *12*, 4002.
- [150] R. Auvergne, S. Caillol, G. David, B. Boutevin, J. P. Pascault, *Chem. Rev.* **2014**, *114*, 1082.
- [151] K. T. Wacker, S. L. Kristufek, S.-M. Lim, S. Kahn, K. L. Wooley, *RSC Adv.* **2016**, *6*, 81672.
- [152] P. Dastidar, S. Ganguly, K. Sarkar, *Chem. Asian J.* **2016**, *11*, 2484.
- [153] A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith, *Angew. Chem. Int. Ed.* **2008**, *47*, 8002; *Angew. Chem.* **2008**, *120*, 8122.
- [154] D. Díaz Díaz, D. Kuhbeck, R. J. Koopmans, *Chem. Soc. Rev.* **2011**, *40*, 427.
- [155] B. Adhikari, G. Palui, A. Banerjee, *Soft Matter* **2009**, *5*, 3452.
- [156] C. Keplinger, J.-Y. Sun, C. C. Foo, P. Rothemund, G. M. Whitesides, Z. Suo, *Science* **2013**, *341*, 984.
- [157] D. Das, T. Kar, P. K. Das, *Soft Matter* **2012**, *8*, 2348.
- [158] M. Shibayama, X. Li, T. Sakai, *Ind. Eng. Chem. Res.* **2018**, *57*, 1121.
- [159] A. Y.-Y. Tam, V. W.-W. Yam, *Chem. Soc. Rev.* **2013**, *42*, 1540.
- [160] N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821.
- [161] Q. Chen, W. Huang, P. Chen, C. Peng, H. B. Xie, Z. K. Zhao, M. Sohail, M. Bao, *ChemCatChem* **2015**, *7*, 1083.
- [162] M. Martínez-Calvo, O. Kotova, M. E. Möbius, A. P. Bell, T. McCabe, J. J. Boland, T. Gunnlaugsson, *J. Am. Chem. Soc.* **2015**, *137*, 1983.
- [163] H. B. Aiyappa, S. Saha, P. Wadge, R. Banerjee, S. Kurungot, *Chem. Sci.* **2015**, *6*, 603.
- [164] J. H. Kim, J. Y. Oh, J. M. Lee, Y. C. Jeong, S. H. So, Y. S. Cho, S. Nam, C. R. Park, S. J. Yang, *Carbon* **2018**, *126*, 190.
- [165] M. S. Menyo, C. J. Hawker, J. H. Waite, *Soft Matter* **2013**, *9*, 10314.
- [166] N. Holten-Andersen, A. Jaishankar, M. J. Harrington, D. E. Fullenkamp, G. DiMarco, L. He, G. H. McKinley, P. B. Messersmith, K. Y. C. Lee, *J. Mater. Chem. B* **2014**, *2*, 2467.
- [167] Y. Chan Choi, J. S. Choi, Y. J. Jung, Y. W. Cho, *J. Mater. Chem. B* **2014**, *2*, 201.
- [168] A. Ghadban, A. S. Ahmed, Y. Ping, R. Ramos, N. Arfin, B. Cantaert, R. V. Ramanujan, A. Miserez, *Chem. Commun.* **2016**, *52*, 697.
- [169] P. S. Yavvare, S. Pal, S. Kumar, A. Kar, A. K. Awasthi, A. Naaz, A. Srivastava, A. Bajaj, *ACS Biomater. Sci. Eng.* **2017**, *3*, 3404.
- [170] H. Xu, J. Nishida, W. Ma, H. Wu, M. Kobayashi, H. Otsuka, A. Takahara, *ACS Macro Lett.* **2012**, *1*, 457.
- [171] B. P. Lee, S. Konst, *Adv. Mater.* **2014**, *26*, 3415.
- [172] Q. Li, D. G. Barrett, P. B. Messersmith, N. Holten-Andersen, *ACS Nano* **2016**, *10*, 1317.
- [173] S. Hou, P. X. Ma, *Chem. Mater.* **2015**, *27*, 7627.
- [174] M. Krogsgaard, A. Andersen, H. Birkedal, *Chem. Commun.* **2014**, *50*, 13278.
- [175] H. Fan, L. Wang, X. Feng, Y. Bu, D. Wu, Z. Jin, *Macromolecules* **2017**, *50*, 666.
- [176] Y.-N. Chen, L. Peng, T. Liu, Y. Wang, S. Shi, H. Wang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 27199.
- [177] M. Shin, J. H. Ryu, J. P. Park, K. Kim, J. W. Yang, H. Lee, *Adv. Funct. Mater.* **2015**, *25*, 1270.
- [178] B. Hu, Y. Shen, J. Adamcik, P. Fischer, M. Schneider, M. J. Loessner, R. Mezzenga, *ACS Nano* **2018**, *12*, 3385.
- [179] M. A. Rahim, M. Björnalm, T. Suma, M. Faria, Y. Ju, K. Kempe, M. Müllner, H. Ejima, A. D. Stickland, F. Caruso, *Angew. Chem. Int. Ed.* **2016**, *55*, 13803; *Angew. Chem.* **2016**, *128*, 14007.
- [180] D. Chen, K. Kannan, H. Tan, Z. Zheng, Y. L. Feng, Y. Wu, M. Widelka, *Environ. Sci. Technol.* **2016**, *50*, 5438.
- [181] Q. Q. Ma, X. Q. Liu, R. Y. Zhang, J. Zhu, Y. H. Jiang, *Green Chem.* **2013**, *15*, 1300.

- [182] C. Ding, A. S. Matharu, *ACS Sustainable Chem. Eng.* **2014**, 2, 2217.
- [183] E. Darroman, N. Durand, B. Boutevin, S. Caillol, *Prog. Org. Coat.* **2016**, 91, 9.
- [184] T. K. L. Nguyen, S. Livi, B. G. Soares, G. M. O. Barra, J.-F. Gérard, J. Duchet-Rumeau, *ACS Sustainable Chem. Eng.* **2017**, 5, 8429.
- [185] L. Puchot, P. Verge, S. Peralta, Y. Habibi, C. Vancaeyzeele, F. Vidal, *Polym. Chem.* **2018**, 9, 472.
- [186] G. Yang, B. J. Rohde, H. Tesefay, M. L. Robertson, *ACS Sustainable Chem. Eng.* **2016**, 4, 6524.
- [187] S. L. Kristufek, G. Yang, L. A. Link, B. J. Rohde, M. L. Robertson, K. L. Wooley, *ChemSusChem* **2016**, 9, 2135.
- [188] A. Noel, Y. P. Borguet, J. E. Raymond, K. L. Wooley, *Macromolecules* **2014**, 47, 2974.
- [189] S. F. Koelewijn, S. Van den Bosch, T. Renders, W. Schutyser, B. Lagrain, M. Smet, J. Thomas, W. Dehaen, P. Van Puyvelde, H. Witters, B. F. Sels, *Green Chem.* **2017**, 19, 2561.
- [190] J. Li, H. Ejima, N. Yoshie, *ACS Appl. Mater. Interfaces* **2016**, 8, 19047.
- [191] C. Kim, H. Ejima, N. Yoshie, *RSC Adv.* **2017**, 7, 19288.
- [192] X.-W. Peng, L.-X. Zhong, J.-L. Ren, R.-C. Sun, *J. Agric. Food Chem.* **2012**, 60, 3909.
- [193] J. Huang, J. Liao, T. Wang, W. Sun, Z. Tong, *Soft Matter* **2018**, 14, 2500.
- [194] S. Pan, A. K. Kota, J. M. Mabry, A. Tuteja, *J. Am. Chem. Soc.* **2013**, 135, 578.
- [195] D. Payra, M. Naito, Y. Fujii, Y. Nagao, *Chem. Commun.* **2016**, 52, 312.
- [196] S. C. Grindy, R. Learsch, D. Mozhdehi, J. Cheng, D. G. Barrett, Z. Guan, P. B. Messersmith, N. Holten-Andersen, *Nat. Mater.* **2015**, 14, 1210.
- [197] Y. Tokura, S. Harvey, C. Chen, Y. Wu, D. Y. W. Ng, T. Weil, *Angew. Chem. Int. Ed.* **2018**, 57, 1587; *Angew. Chem.* **2018**, 130, 1603.
- [198] K. Tanaka, G. H. Clever, Y. Takezawa, Y. Yamada, C. Kaul, M. Shionoya, T. Carell, *Nat. Nanotechnol.* **2006**, 1, 190.
- [199] Z. Yi, Z. Sun, G. Chen, H. Zhang, X. Ma, W. Su, X. Cui, X. Li, *J. Mater. Chem. B* **2018**, 6, 1373.
- [200] M. Shin, H.-A. Lee, M. Lee, Y. Shin, J.-J. Song, S.-W. Kang, D.-H. Nam, E. J. Jeon, M. Cho, M. Do, S. Park, M. S. Lee, J.-H. Jang, S.-W. Cho, K.-S. Kim, H. Lee, *Nat. Biomed. Eng.* **2018**, 2, 304.
- [201] C. Zhong, T. Gurry, A. A. Cheng, J. Downey, Z. Deng, C. M. Stultz, T. K. Lu, *Nat. Nanotechnol.* **2014**, 9, 858.
- [202] M. Perrini, D. Barrett, N. Ochsenbein-Koelble, R. Zimmermann, P. Messersmith, M. Ehrbar, *J. Mech. Behav. Biomed. Mater.* **2016**, 58, 57.
- [203] V. Bhagat, M. L. Becker, *Biomacromolecules* **2017**, 18, 3009.
- [204] A. Miserez, T. Schneberk, C. Sun, F. W. Zok, J. H. Waite, *Science* **2008**, 319, 1816.
- [205] M. J. Harrington, A. Masic, N. Holten-Andersen, J. H. Waite, P. Fratzl, *Science* **2010**, 328, 216.
- [206] Y. Wang, J. P. Park, S. H. Hong, H. Lee, *Adv. Mater.* **2016**, 28, 9961.
- [207] W. Xu, P. A. Ledin, Z. Iatridi, C. Tsitsilianis, V. V. Tsukruk, *Angew. Chem. Int. Ed.* **2016**, 55, 4908; *Angew. Chem.* **2016**, 128, 4992.
- [208] C. Park, B. J. Yang, K. B. Jeong, C. B. Kim, S. Lee, B. C. Ku, *Angew. Chem. Int. Ed.* **2017**, 56, 5485; *Angew. Chem.* **2017**, 129, 5577.
- [209] S. J. Clarke, C. A. Hollmann, Z. Zhang, D. Suffern, S. E. Bradforth, N. M. Dimitrijevic, W. G. Minarik, J. L. Nadeau, *Nat. Mater.* **2006**, 5, 409.
- [210] D. Cai, L. Ren, H. Zhao, C. Xu, L. Zhang, Y. Yu, H. Wang, Y. Lan, M. F. Roberts, J. H. Chuang, M. J. Naughton, Z. Ren, T. C. Chiles, *Nat. Nanotechnol.* **2010**, 5, 597.
- [211] F. Liu, X. He, H. Chen, J. Zhang, H. Zhang, Z. Wang, *Nat. Commun.* **2015**, 6, 8003.
- [212] J. Guo, X. Wang, D. C. Henstridge, J. J. Richardson, J. Cui, A. Sharma, M. A. Febbraio, K. Peter, J. B. de Haan, C. E. Hagemeyer, F. Caruso, *Adv. Healthcare Mater.* **2015**, 4, 2170.
- [213] L. Zhang, J. Wu, Y. Wang, Y. Long, N. Zhao, J. Xu, *J. Am. Chem. Soc.* **2012**, 134, 9879.
- [214] D. Hong, K. Bae, S. P. Hong, J. H. Park, I. S. Choi, W. K. Cho, *Chem. Commun.* **2014**, 50, 11649.
- [215] S. Kim, T. Gim, Y. Jeong, J. H. Ryu, S. M. Kang, *ACS Appl. Mater. Interfaces* **2018**, 10, 7626.
- [216] J. Cui, Y. Ju, K. Liang, H. Ejima, S. Lörcher, K. T. Gause, J. J. Richardson, F. Caruso, *Soft Matter* **2014**, 10, 2656.
- [217] Q. Zhu, Q. Pan, *ACS Nano* **2014**, 8, 1402.
- [218] H. J. Kim, D.-G. Kim, H. Yoon, Y.-S. Choi, J. Yoon, J.-C. Lee, *Adv. Mater. Interfaces* **2015**, 2, 1500298.
- [219] M. Lee, J. Rho, D. E. Lee, S. Hong, S. J. Choi, P. B. Messersmith, H. Lee, *ChemPlusChem* **2012**, 77, 987.
- [220] H. Guo, Z. Yao, Z. Yang, X. Ma, J. Wang, C. Y. Tang, *Environ. Sci. Technol.* **2017**, 51, 12638.
- [221] J. Kim, Q. Fu, J. M. Scofield, S. E. Kentish, G. G. Qiao, *Nanoscale* **2016**, 8, 8312.
- [222] J. Wei, Y. Liang, Y. Hu, B. Kong, J. Zhang, Q. Gu, Y. Tong, X. Wang, S. P. Jiang, H. Wang, *Angew. Chem. Int. Ed.* **2016**, 55, 12470; *Angew. Chem.* **2016**, 128, 12658.
- [223] G. Yun, S. Pan, T. Y. Wang, J. Guo, J. J. Richardson, F. Caruso, *Adv. Healthcare Mater.* **2018**, 7, 1700934.
- [224] A. Alford, V. Kozlovskaya, B. Xue, N. Gupta, W. Higgins, D. Pham-Hua, L. L. He, V. S. Urban, H. M. Tse, E. Kharlampieva, *Chem. Mater.* **2018**, 30, 344.
- [225] S. Ma, H. Lee, Y. Liang, F. Zhou, *Angew. Chem. Int. Ed.* **2016**, 55, 5793; *Angew. Chem.* **2016**, 128, 5887.
- [226] M. Shin, K. Kim, W. Shim, J. W. Yang, H. Lee, *ACS Biomater. Sci. Eng.* **2016**, 2, 687.
- [227] R. A. Meurer, S. Kemper, S. Knopp, T. Eichert, F. Jakob, E. Goldbach Heiner, U. Schwaneberg, A. Pich, *Angew. Chem. Int. Ed.* **2017**, 56, 7380; *Angew. Chem.* **2017**, 129, 7486.
- [228] M. A. Rahim, Y. Hata, M. Björnalm, Y. Ju, F. Caruso, *Small* **2018**, 14, 1801202.
- [229] M. Shamsipur, F. Molaabasi, M. Shanehsaz, A. A. Moosavi-Movahedi, *Microchim. Acta* **2015**, 182, 1131.
- [230] F. Jehle, P. Fratzl, M. J. Harrington, *ACS Nano* **2018**, 12, 2160.

Manuscript received: July 8, 2018

Accepted manuscript online: September 16, 2018

Version of record online: December 11, 2018