Tuning the Mechanical Behavior of Metal–Phenolic Networks through Building Block Composition

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ABSTRACT

Metal–phenolic networks (MPNs) are an emerging class of functional metal–organic materials with a high degree of modularity in terms of the choice of metal ion, phenolic ligand, and assembly method. Although various applications, including drug delivery, imaging, and catalysis, have been studied with MPNs, in the form of films and capsules, the influence of metals and organic building blocks on their mechanical properties is poorly understood. Herein, we demonstrate that the

mechanical properties of MPNs can be tuned through choice of the metal ion and/or phenolic ligand. Specifically, the pH of the metal ion solution and/or size of phenolic ligand influence the Young's modulus (E_Y) of MPNs (higher pHs and smaller ligands lead to higher E_Y). This study systematically investigates the roles of both metal ions and ligands on the mechanical properties of metal–organic materials and lends new insight into engineering the mechanical properties of coordinated films.

INTRODUCTION

Metal–ligand complexation is emerging as a versatile cross-linking strategy for simultaneously assembling and strengthening nano- and micromaterials.^{1–3} Coordination-based cross-linking is a rapid process^{4,5} and can impart unique functionalities to materials such as adhesion, load-bearing, and abrasion resistance.^{6–11} For example, Fe^{III} –catechol complexes in mussel byssus threads and Zn^{II} –histidine complexes in wandering spider fangs have remarkable mechanical properties (e.g., low density, and high extensibility and hardness).^{2,6} Fundamental studies on metal complexation provide vital insights not only for understanding the hierarchical structuring and mechanical behavior of biological organisms, but also for designing bio-inspired materials for industrial and biomedical applications.^{4–14} The roles of metal ions and their coordination states have been extensively studied in biological and bio-inspired materials, including borate cross-linking in the cell walls of plants¹² and metal ion complexation in proteins,⁷ peptides,¹¹ and synthetic materials.^{8,10,11,13} However, systematic studies on the influence of metal ions and organic ligands on the physical properties of biological and bio-inspired materials are scant, likely because researchers either focus on a specific ligand (e.g., dopamine, histidine) or a specific metal ion (e.g., Fe^{III} , Zn^{II}).⁷

Phenolic compounds are a class of several thousand molecules with unique physical, chemical, and biological properties that are widely found in living organisms.^{15–18} For instance, the catechol and galloyl moieties of some phenolic compounds act as multivalent chelation sites that can coordinate to various metal ions; the coordination state of the complexes is dictated by pH, and this phenomenon can be exploited to prepare functional metal–phenolic materials.^{3,13,14,19,20} In a previous study, we reported the self-assembly of metal–phenolic network (MPN) films on substrates through the complexation of Fe^{III} ions with a natural polyphenol, tannic acid (TA).²¹ This self-assembly process was extended to a wide variety of metal ions (i.e., Mn^{II}, Zn^{II}, Cu^{II}, Eu^{III}, Al^{III}, Zr^{IV})²² and phenolic molecules (i.e., gallic acid (GA), pyrogallol (PG), pyrocatechol (PC), flavonoids),^{23,24} yielding a broad and modular library of metal–phenolic complexes with promise for drug delivery, bioimaging, separation, antimicrobials, and catalysis.^{22–27} Owing to this modularity, MPNs are a suitable model system for systematically investigating the effects of metals and ligands on the physical properties of metal chelation systems.

Figure 1. (a) Digital photographs of MPN films (top view) formed using various metal ions and phenolic molecules on a planar glass substrate. Scale bars are 1 cm. (b) Chemical structure of tannic acid. (c) UV-Vis absorbance spectra of MPN films on glass. All MPN films were grown for 20–30 days following our previously reported method.³¹

Herein, we investigate the effects of different metal ions and phenolic ligands on the mechanical behavior of MPN films (Figure 1). The mechanical properties (i.e., Young's modulus (E_Y)) of the MPN films were measured using atomic force microscopy (AFM), which revealed that the choice of metal ion and phenolic ligand used for self-assembly strongly influences the mechanical properties of the MPN films. We studied the effects of the modular component on the internal structure of the MPN films to understand the metal- and ligand-dependent mechanical behavior. Specifically, the pH of the metal solution and the molecular structure of the organic ligand are important factors that influence the properties of the films; a higher pH of the starting solution and smaller phenolic ligands both produce MPN films with higher E_Y values. Mixed multi-metal films ($\text{Fe}^{\text{III}}/\text{Ga}^{\text{III}}\text{-TA}$) further elucidated the important role of the pH of the starting solution; the mechanical properties of the mixed multi-metal films were higher than that of the corresponding single metal ion films. In contrast, mixed multi-ligand films ($\text{Fe}^{\text{III}}\text{-PC/TA}$) showed mechanical properties in between those of the corresponding single ligand films, likely because of the difference in ligand size. These insights lead to improved control over the mechanical behaviors of MPN-based materials and could provide useful design principles for the fabrication of bio-inspired materials with desired properties. In addition, this study is of fundamental importance as it helps in elucidating the formation mechanism, stability, and disassembly kinetics of MPNs.

EXPERIMENTAL METHODS

Materials. Tannic acid (ACS reagent), gallic acid (97.5–102.5%), pyrogallol (99.0%), pyrocatechol ($\geq 99.0\%$), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), gallium(III) nitrate hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), indium(III) nitrate hydrate ($\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$), terbium(III) nitrate hexahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), 3-(N-morpholino)propanesulfonic acid (MOPS), and polyethyleneimine (PEI, $M_w \sim 25,000$) were purchased from Sigma-Aldrich. Planar glass substrates ($76 \text{ mm} \times 26 \text{ mm}$) were obtained from Waldemar Knittel. Water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was obtained from an inline Millipore RiOs/Origin water purification system. All solutions were freshly prepared for immediate use in each experiment.

Characterization. AFM experiments were carried out on a JPK NanoWizard II BioAFM. Typical scans were recorded in intermittent contact mode with MikroMasch silicon cantilevers (NSC/CSC). The thickness and roughness of the metal–phenolic network (MPN) films were analyzed using JPK SPM image processing software (version V.3.3.32). AFM force measurements were carried out with an MFP-3D from Asylum Research using biosphere cantilevers that have a 50 nm radius spherical tip and a nominal spring constant of 40 N m^{-1} (NanoTools, Munich). UV-Visible absorption measurements were carried out on an Analytik Jena SPECORD 250 PL. Small-angle X-ray scattering (SAXS) data were collected at the SAXS beamline of the Australian Synchrotron facility, part of ANSTO. The samples were investigated using the small/wide angle X-ray scattering beamline (16 keV , 900 mm camera length using Pilatus 1M and 200 k detectors, transmission mode). Scatterbrain software was used for analysis.

Preparation of MPN Films. All solutions were freshly prepared for immediate use. Aliquots (10 mL) of fresh metal ions in water (37 mM of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, or $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solutions) and phenolic molecule in water (23.5 mM of TA, or 37 mM of GA, PC, or PG) were vigorously mixed by a vortex mixer for 10 s . For the preparation of the

Ga^{III}–TA, In^{III}–TA, and Tb^{III}–TA films, 5 mL of MOPS buffer (10 mM, pH 8) was added to the pre-complexed metal–phenolic solutions. The addition of the MOPS buffer negligibly raised the pH (~0.05–0.3 pH units). To increase the interaction between MPN films and the substrate and prevent the possibility of delamination of the MPN films from the substrate during AFM experiments, planar glass substrates were primed with a PEI layer by dipping the substrates into a PEI solution (1 mg mL⁻¹, 0.5 M NaCl) for 15 min, rinsing in water three times, and drying under a stream of nitrogen. The substrates were then immersed in each pre-complexed metal–phenolic solution in a 50 mL tube for 20–30 days. The substrates were washed with water three times to remove excess metal ions and TA. The coated substrates were subsequently immersed in MOPS buffer (40 mL, 10 mM, pH 8) in a 50 mL tube to strongly cross-link the metal ions with phenolic molecules.

Preparation of Multi-Metal and Multi-Ligand Systems. The preparation of the Fe^{III}/Ga^{III}–TA network films (multi-metal system) followed a similar protocol to that described for the preparation of MPN films. Aliquots (5 mL) of FeCl₃·6H₂O (37 mM) in water, Ga(NO₃)₃ in water (37 mM), and MOPS buffer (10 mM, pH 8) were added to 10 mL of TA in water (23.5 mM), and the solution was vigorously mixed by a vortex mixer for 10 s. Planar glass substrates were primed with a PEI layer by dipping the substrates into a PEI solution (1 mg mL⁻¹, 0.5 M NaCl) for 15 min, rinsing in water three times, and drying under a stream of nitrogen. The substrates were immersed in the pre-complexed metal–phenolic solution in a 50 mL tube for 20–30 days. The substrates were washed with water three times to remove excess metal ions and TA. The coated substrates were subsequently immersed in MOPS buffer (40 mL, 10 mM, pH 8) in a 50 mL tube to strongly cross-link the metal ions with phenolic molecules.

The preparation of the Fe^{III}–PC/TA films (multi-ligand system) followed a similar protocol to that described for the preparation of MPN films. Aliquots (5 mL) of PC in water (37 mM) and TA in water (23.5 mM) were added to 10 mL of FeCl₃·6H₂O in water (37 mM), and the solution was vigorously mixed by a vortex mixer for 10 s. Planar glass substrates were primed with a PEI layer by dipping the substrates into a PEI solution (1 mg mL⁻¹, 0.5 M NaCl) for 15 min, rinsing in water three times, and drying under a stream of nitrogen. The substrates were then immersed in the pre-complexed metal–phenolic solution in a 50 mL tube for 20–30 days. The substrates were washed with water three times to remove excess metal ions and TA. The coated substrates were subsequently immersed in MOPS buffer (40 mL, 10 mM, pH 8) in a 50 mL tube to strongly cross-link the metal ions with phenolic molecules.

Mechanical Test. To investigate the compressional behavior and topographical variability of the metal–phenolic network films, AFM force measurements were performed in air with an MFP-3D from Asylum Research using BioSphere™ cantilevers that have a 50 nm radius diamond-like carbon spherical tip and a nominal spring constant of 40 N m⁻¹ (NanoTools, Munich) to reduce and exclude adhesion issues between the AFM tip and the films. Prior to use, the cantilevers were washed consecutively in ethanol and water, and the tip area was checked via reverse imaging with a TipCheck grid (BudgetSensors, Sofia).²⁸ The spring constant was determined via the thermal noise method,²⁹ and the InvOLS was calibrated prior to every measurement on a glass slide.

Maps of the force vs indentation were taken at a minimum of 500 nm from each indentation center within flat areas on the surface of the MPN films, where an indentation velocity of 1 μm s⁻¹ was used. The resultant curves are a function of force vs Z piezo sensor displacement, where

the indentation depth can be determined by subtracting the cantilever deflection from the Z piezo sensor displacement. Owing to low adhesion, the Hertz model³⁰ was chosen to estimate the Young's modulus of the material from the force vs indentation data as follows:

$$F = \frac{4}{3} \frac{E}{(1-\nu^2)} R^{\frac{1}{2}} d^{\frac{3}{2}} \quad (1)$$

where E is the elastic modulus (Pa), ν is Poisson's ratio, R is the radius of the indenter (m), and d is the indentation depth (m). As Poisson's ratio is unknown, a value of 0.4 was used.³⁰ To ensure the validity of the Hertz model, the areas used for analysis were imaged prior to compression and were found to have a root mean square roughness of less than 1.5 nm within a 100 nm × 100 nm area, where the indentation depth into the film was a minimum of 10 nm including plastic deformation. The material showed significant plastic deformation. Therefore, the retract curve was used to determine the material properties.

RESULTS AND DISCUSSION

The MPN films were prepared by soaking a substrate in a pre-complexed metal–ligand solution, according to our previously reported method.³¹ Briefly, simply mixing metal ions (Fe^{III}, Ga^{III}, In^{III}, Tb^{III}) with phenolic ligands (TA, GA, PG, PC) in solution led to complexes, followed by immersion of a planar glass substrate pre-coated with PEI into the pre-complexed solutions led to the spontaneous formation of MPN films on the substrate surface (Figure S1). Each system (Ga^{III}–TA, In^{III}–TA, Tb^{III}–TA, Fe^{III}–GA, Fe^{III}–PG, or Fe^{III}–PC) produced films (Figure 1a,b). The UV-vis spectra of the MPN films showed absorbance peaks between 400 and 700 nm, indicating deposition of the metal–phenolic complexes on the substrate (Figure 1c).^{22,23}

Figure 2. Influence of metal ions (M^{3+}) on the mechanical properties of M^{III} -TA films assessed by AFM force measurements: representative force curves for (a) Ga^{III} -TA, (b) In^{III} -TA, and (c) Tb^{III} -TA films. (d) Mechanical properties of the MPN films, as measured by AFM force measurements in (a–c). (e) Normalized radius of gyration of the complexes, as determined by SAXS. (f) pH of the pre-complexed metal-phenolic solutions. Fe indicates Fe^{III} -TA films, Ga indicates Ga^{III} -TA films, In indicates In^{III} -TA films, and Tb indicates Tb^{III} -TA films in (d–f). The E_Y of the Fe^{III} -TA film was obtained from our previous report.³¹

The interaction between catechol moieties and trivalent metal ions typically involves the displacement of the six protons on the catechol group (Figure 1a). We thus first explored the

effect of different trivalent metals on the mechanical properties of the Fe^{III}-TA, Ga^{III}-TA, In^{III}-TA, and Tb^{III}-TA films. Owing to its ionic radius, Fe^{III} has an optimum fit for a cation in an octahedral complex with three catechol molecules;^{7,32} thus, Fe^{III}-TA complexes have exceptionally high stability. Trivalent metal ions with larger (Ga^{III}, In^{III}, Tb^{III}) radii than that of Fe^{III} bind to catechol less tightly, resulting in weaker complexation of the metal ions with catechol groups.³² We hypothesized that the high stability of Fe^{III}-TA complexes would translate to a high E_Y for the Fe^{III}-TA films but this was not the case. Interestingly, the E_Y trend of the MPN films was independent of the stability of the metal-phenolic complex. All of the MPN films studied showed small deformation regimes and hysteresis between the approach and retract curves, indicating the occurrence of plastic deformation during AFM indentation (Figure 2a-c and Figure S2),³³ likely due to disruption of the microstructure. The moduli were calculated from the elastic response of the samples indented by the AFM tip using the Hertz model for data fitting. The modulus of the Tb^{III}-TA film showed up to a 7-fold increase in E_Y compared to that of Fe^{III}-TA films prepared previously (2.9 ± 1.0 GPa),³¹ however there is a large margin of error as the thin layer thickness and high roughness of the Tb^{III}-TA films could result in variable influences by the substrate and uncertainties in contact geometry. In contrast, the moduli of the Ga^{III}-TA and In^{III}-TA films were only two times higher than that of the Fe^{III}-TA films (Figure 2d). The estimated E_Y values of Tb^{III}-TA, In^{III}-TA, and Ga^{III}-TA films were 21.9 ± 7.3 , 5.9 ± 1.5 , and 5.9 ± 1.9 GPa, respectively. We note that the distribution for the Tb^{III}-TA film was broad, likely because the large radius of the Tb^{III} ions allows for more variable complexation states and because the films measured were relatively rough (root mean square roughness of ~ 12 nm, in $\sim 25 \mu\text{m}^2$ area) and relatively thin compared with the other films (base thickness ~ 50 nm, Figure S1). This wide distribution also means that the average E_Y might be less representative of

the overall material properties of the film. The metal–TA films were analyzed using SAXS to rule out the possibility of metal nanoparticle formation and to better understand the metal-dependent internal structure of the films. The normalized complex size³⁴ decreased in the order of $\text{Fe}^{\text{III}}\text{--TA} > \text{Tb}^{\text{III}}\text{--TA} > \text{In}^{\text{III}}\text{--TA} > \text{Ga}^{\text{III}}\text{--TA}$ (Figure 2e), which does not correspond to the E_{Y} trend observed for the films (Figure 2d). These results indicate that the effect of metal ion on the mechanical properties of MPN films might be influenced by factors other than the chelation strength or internal packing of the building blocks. For example, it has been shown previously that metal–phenolic complexes in solution have limited diffusion owing to the relatively large complex size, and this can interfere with layer deposition, which could play a role on the subsequent stiffness of the formed films.³¹

We then investigated the effect of external factors on the mechanical properties of the MPN films, as it is well known that the properties of self-assembled materials depend on both internal factors (e.g., type of bond, long-range order, and defects) and external factors (e.g., assembly conditions such as solvent, pH, and temperature).^{7,35,36} For example, the charge-transport performance of organic semiconductor films, which can be tuned by varying π – π interactions between the organic molecules, determines the orientation and phase state of the components in the film.³⁷ Because the complexation state of metals and phenolic ligands can be controlled by pH,²¹ we first investigated the effect of pH. For example, the $\text{Fe}^{\text{III}}\text{--TA}$ complex is predominantly in the mono-complex state at $\text{pH} < 2$, the bis-complex state at $3 < \text{pH} < 6$, and the tris-complex state at $\text{pH} > 7$, suggesting that the pH of the pre-complexed metal–phenolic solution could influence the properties of the resultant MPN films. The pH of the pre-complexed metal–phenolic solutions was 1.8 for $\text{Fe}^{\text{III}}\text{--TA}$, 1.9 for $\text{Ga}^{\text{III}}\text{--TA}$, 2.1 for $\text{In}^{\text{III}}\text{--TA}$, and 3.2 for $\text{Tb}^{\text{III}}\text{--TA}$ (Figure 2f), owing to differences in the pH of the metal solutions. The trend observed

in the pH of the pre-complexed solutions strongly correlates to the E_Y trend observed for the MPNs films, as assessed from AFM force measurements; increased pH corresponds to increased E_Y . In addition, we have previously reported that high ionic strength solutions change the film properties, and pH outside of the range of ~ 1.7 – 2.9 inhibits the continuous growth process.^{31,34} This result suggested that the self-assembly conditions of metal–TA complexes strongly influence the metal-dependent mechanical behavior of the resultant films.

Figure 3. Influence of phenolic ligands on the mechanical properties of Fe^{III}–polyphenol films assessed by AFM force measurements: representative force curves for (a) Fe^{III}–GA, (b) Fe^{III}–PG, and (c) Fe^{III}–PC films. (d) Mechanical properties of the MPN films, as measured by AFM force

measurements in (a–c). (e) Normalized radius of gyration of the complexes, as determined by SAXS. (f) pH of the pre-complexed metal–phenolic solutions. TA indicates Fe^{III}–TA films, GA indicates Fe^{III}–GA films, PG indicates Fe^{III}–PG films, and PC indicates Fe^{III}–PC films in (d–f). The E_Y of the Fe^{III}–TA film was obtained from our previous report.³¹

We then explored the effect of different phenolic ligands on the mechanical behavior of MPN films. The complexation between metal ions and phenolic molecules is a dominant interaction for the formation of tannic acid-based MPN films.³¹ However, small phenolic ligands, such as GA, PG, and PC, are composed of a single aromatic ring with ditopic or tritopic chelating groups; therefore, other non-covalent interactions (e.g., π – π interaction) may contribute to the formation of MPNs in addition to metal complexation.²³ Fe^{III} was selected as the metal ion, while the phenolic ligand was varied (Figure 3a–c) for forming the films. Notably, in general, the E_Y of the Fe^{III}–phenolic films increased as the size of the phenolic ligand decreased (Figure S3). The E_Y values of the Fe^{III}–GA, Fe^{III}–PG, and Fe^{III}–PC films were 2–4 times higher than that of the Fe^{III}–TA film (E_Y of 2.9 ± 1.0 GPa).³¹ The E_Y of Fe^{III}–GA, Fe^{III}–PG, and Fe^{III}–PC films were estimated to be 5.1 ± 1.8 , 11.3 ± 2.7 , and 7.4 ± 2.4 GPa, respectively (Figure 3d).

It is possible that simple and small phenolic molecules (e.g., GA, PG, and PC) could produce more uniform and long-range ordered coordination structures than TA-based materials owing to their molecular geometries (Figure S3). In addition, TA is a dendrimer-like molecule with a flexible macromolecular structure. For example, complexation of Fe^{III} with GA can produce amorphous MPN films, as well as crystalline metal–organic frameworks depending on the synthesis conditions.²³ SAXS analysis suggested that the high E_Y of the Fe^{III}–PG and Fe^{III}–PC films originated from the enhanced molecular orientation and tighter packing of the small

phenolic molecules (Figure 3e). Moreover, the E_Y histograms of Fe^{III} -PG and Fe^{III} -GA films showed a broad distribution, probably due to steric hindrance of the additional hydroxyl of the galloyl group (vs catechol) for PG and GA and the additional carboxyl groups for GA. In contrast, PC only has one catechol group, and the Fe^{III} -PC films showed a Gaussian-shaped distribution likely due to low steric hindrance between PC molecules. Finally, there were negligible pH differences between the pre-complexed Fe^{III} -TA, Fe^{III} -GA, Fe^{III} -PG, and Fe^{III} -PC solutions (approximately pH 1.8) due to the low pH of the Fe^{III} solutions (Figure 3f), suggesting that pH did not dictate the E_Y of the MPN films prepared with different ligands. Although this did not definitively explain the difference in mechanical properties, this contributes toward ongoing studies of elucidating the formation mechanism of MPNs.

Figure 4. Influence of mixed multi-metal and multi-ligand systems on the mechanical properties of MPN films: representative force curves for (a) $\text{Fe}^{\text{III}}/\text{Ga}^{\text{III}}$ -TA and (b) Fe^{III} -PC/TA films. (c)

Mechanical properties of the films, as measured by AFM force measurements in (a, b). (d) pH of the pre-complexed metal–phenolic solutions. The E_Y of the Fe^{III} –TA film was obtained from our previous report.³¹

To further elucidate the role of the metal ion solution pH and ligand size on MPN mechanical properties, MPN films were prepared with multiple metal ions (e.g., $\text{Fe}^{\text{III}}/\text{Ga}^{\text{III}}$ –TA) and multiple ligands (e.g., Fe^{III} –PC/TA), respectively (Figure 4). The $\text{Fe}^{\text{III}}/\text{Ga}^{\text{III}}$ –TA and Fe^{III} –PC/TA films were dark brown owing to the presence of Fe^{III} (Figure 1a), and UV-vis spectroscopy and AFM analysis confirmed the formation of MPN films on the substrates (Figure S4). The E_Y of $\text{Fe}^{\text{III}}/\text{Ga}^{\text{III}}$ –TA film was 6.7 ± 2.2 , and that of the Fe^{III} –PC/TA film was 6.5 ± 2.0 (Figure 4a,b). The $\text{Fe}^{\text{III}}/\text{Ga}^{\text{III}}$ –TA films showed ~2-fold increase in E_Y compared to the Fe^{III} –TA films (2.9 ± 1.0 GPa)³¹ and a marginal increase over the E_Y of the Ga^{III} –TA films (6.7 vs 5.9 GPa) (Figure 4c). This is possibly due to the slightly higher pH of the pre-complexed solution when incorporating Ga^{III} into the $\text{Fe}^{\text{III}}/\text{Ga}^{\text{III}}$ –TA solution (Figure 4d) when compared with the pH of the Fe^{III} –TA solution without Ga^{III} . This result supports our hypothesis that the external factors governing self-assembly strongly influence the final E_Y of MPN films when considering different metal ions. A synergistic effect was not seen for the multi-ligand films and the inclusion of TA in Fe^{III} –PC/TA reduced the E_Y in comparison to the single-ligand Fe^{III} –PC films. This supported our hypothesis that small ligands (exhibiting reduced steric hindrance and improved ability to π – π stack) plays an important role in yielding metal–phenolic films with high E_Y values. Still, it is challenging to decouple the influences of the coordination bonds from the ligand–ligand packing effects as the Young’s modulus of metal–phenolic materials relies on both factors.

CONCLUSIONS

In summary, we have demonstrated that the mechanical behavior of MPN films can be controlled through the choice of the metal ion (Fe^{III} , Ga^{III} , In^{III} , Tb^{III}) and/or phenolic ligand (TA, GA, PC, PG). The modularity of the components enabled control over the mechanical properties of the films. When investigating the effect of different metals, the pH of the pre-complexed metal–TA solution was an important factor that influenced the mechanical behavior of the MPNs films regardless of the stability of the metal–TA complexes or internal packing. For different ligands, the geometry and size of the phenolic molecules were important factors influencing the mechanical behavior of the Fe^{III} –phenolic films. These results were confirmed by examining multi-metal and multi-ligand systems. Overall, our results provide valuable insight in metal–phenolic systems, thus improving our understanding of bio-inspired materials, while also enhancing our control over the design of functional materials. We are currently extending our investigation to other factors (e.g., reaction media) that can also influence the properties of metal–phenolic materials.

ASSOCIATED CONTENT

Supporting Information. AFM data and UV-Vis absorption spectra of MPN films; energy-minimized chemical structures of phenolic molecules.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Lee, S. M.; Pippel, E.; Gösele, U.; Dresbach, C.; Qin, Y.; Chandran, C. V.; Bräuniger, T.; Hause, G.; Knez, M. Greatly Increased Toughness of Infiltrated Spider Silk. *Science* **2009**, *324*, 488–492.
- (2) Harrington, M. J.; Masic, A.; Holten-Andersen, N.; Waite, J. H.; Fratzl, P. Iron-Clad Fibers: A Metal-Based Biological Strategy for Hard Flexible Coatings. *Science* **2010**, *328*, 216–220.
- (3) Filippidi, E.; Cristiani, T. R.; Eisenbach, C. D.; Waite, J. H.; Israelachvili, J. N.; Ahn, B. K.; Valentine, M. T. Toughening Elastomers Using Mussel-Inspired Iron-Catechol Complexes. *Science* **2017**, *358*, 502–505.

- (4) Xu, Z. Mechanics of Metal-Catecholate Complexes: The Roles of Coordination State and Metal Types. *Sci. Rep.* **2013**, *3*, 2914.
- (5) Lee, H.; Scherer, N. F.; Messersmith, P. B. Single-Molecule Mechanics of Mussel Adhesion. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 12999–13003.
- (6) Politi, Y.; Priewasser, M.; Pippel, E.; Zaslansky, P.; Hartmann, J.; Siegel, S.; Li, C.; Barth, F. G.; Fratzl, P. A Spider's Fang: How to Design an Injection Needle Using Chitin-Based Composite Material. *Adv. Funct. Mater.* **2012**, *22*, 2519–2528.
- (7) Degtyar, E.; Harrington, M. J.; Politi, Y.; Fratzl, P. The Mechanical Role of Metal Ions in Biogenic Protein-Based Materials. *Angew. Chem., Int. Ed.* **2014**, *53*, 12026–12044.
- (8) Grindy, S. C.; Learsch, R.; Mozhdehi, D.; Cheng, J.; Barrett, D. G.; Guan, Z.; Messersmith, P. B.; Holten-Andersen, N. Control of Hierarchical Polymer Mechanics with Bioinspired Metal-Coordination Dynamics. *Nat. Mater.* **2015**, *14*, 1210–1216.
- (9) Li, Y.; Wen, J.; Qin, M.; Cao, Y.; Ma, H.; Wang, W. Single-Molecule Mechanics of Catechol-Iron Coordination Bonds. *ACS Biomater. Sci. Eng.* **2017**, *3*, 979–989.
- (10) Chen, K.; Zhang, S.; Li, A.; Tang, X.; Li, L.; Guo, L. Bioinspired Interfacial Chelating-like Reinforcement Strategy toward Mechanically Enhanced Lamellar Materials. *ACS Nano* **2018**, *12*, 4269–4279.
- (11) Jehle, F.; Fratzl, P.; Harrington, M. J. Metal-Tunable Self-Assembly of Hierarchical Structure in Mussel-Inspired Peptide Films. *ACS Nano* **2018**, *12*, 2160–2168.

- (12) O'Neill, M. A.; Eberhard, S.; Albersheim, P.; Darvill, A. G. Requirement of Borate Cross-Linking of Cell Wall Rhamnogalacturonan II for *Arabidopsis* Growth. *Science* **2001**, *294*, 846–849.
- (13) Holten-Andersen, N.; Harrington, M. J.; Birkedal, H.; Lee, B. P.; Messersmith, P. B.; Lee, K. Y. C.; Waite, J. H. pH-Induced Metal-Ligand Cross-Links Inspired by Mussel Yield Self-Healing Polymer Networks with Near-Covalent Elastic Moduli. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 2651–2655.
- (14) Kim, S.; Peterson, A. M.; Holten-Andersen, N. Enhanced Water Retention Maintains Energy Dissipation in Dehydrated Metal-Coordinate Polymer Networks: Another Role for Fe-Catechol Cross-Links? *Chem. Mater.* **2018**, *30*, 3648–3655.
- (15) Quideau, S.; Deffieux, D.; Douat-Casassus, C.; Pouységu, L. Plant Polyphenols: Chemical Properties, Biological Activities, and Synthesis. *Angew. Chem., Int. Ed.* **2011**, *50*, 586–621.
- (16) Sileika, T. S.; Barrett, D. G.; Zhang, R.; Lau, K. H.; Messersmith, P. B. Colorless Multifunctional Coatings Inspired by Polyphenols Found in Tea, Chocolate, and Wine. *Angew. Chem., Int. Ed.* **2013**, *52*, 10766–10770.
- (17) de Pascual-Teresa, S.; Clifford, M. N. Advances in Polyphenol Research: A *Journal of Agricultural and Food Chemistry* Virtual Issue. *J. Agric. Food Chem.* **2017**, *65*, 8093–8095.
- (18) Hong, S.; Wang, Y.; Park, S. Y.; Lee, H. Progressive Fuzzy Cation- π Assembly of Biological Catecholamines. *Sci. Adv.* **2018**, *4*, eaat7457.

- (19) Xu, H.; Nishida, J.; Ma, W.; Wu, H.; Kobayashi, M.; Otsuka, H.; Takahara, A. Competition between Oxidation and Coordination in Cross-Linking of Polystyrene Copolymer Containing Catechol Groups. *ACS Macro Lett.* **2012**, *1*, 457–460.
- (20) Park, C.; Yang, B. J.; Jeong, K. B.; Kim, C. B.; Lee, S.; Ku, B. C. Signal-Induced Release of Guests from a Photolabile Metal-Phenolic Supramolecular Cage and Its Hybrid Assemblies. *Angew. Chem., Int. Ed.* **2017**, *56*, 5485–5489.
- (21) Ejima, H.; Richardson, J. J.; Liang, K.; Best, J. P.; van Koeveerden, M. P.; Such, G. K.; Cui, J.; Caruso, F. One-Step Assembly of Coordination Complexes for Versatile Film and Particle Engineering. *Science* **2013**, *341*, 154–157.
- (22) Guo, J.; Ping, Y.; Ejima, H.; Alt, K.; Meissner, M.; Richardson, J. J.; Yan, Y.; Peter, K.; von Elverfeldt, D.; Hagemeyer, C. E.; Caruso, F. Engineering Multifunctional Capsules through the Assembly of Metal–Phenolic Networks. *Angew. Chem., Int. Ed.* **2014**, *53*, 5546–5551.
- (23) Rahim, M. A.; Kempe, K.; Müllner, M.; Ejima, H.; Ju, Y.; van Koeveerden, M. P.; Suma, T.; Braunger, J. A.; Leeming, M. G.; Abrahams, B. F.; Caruso, F. Surface-Confined Amorphous Films from Metal-Coordinated Simple Phenolic Ligands. *Chem. Mater.* **2015**, *27*, 5825–5832.
- (24) Bertleff-Zieschang, N.; Rahim, M. A.; Ju, Y.; Braunger, J. A.; Suma, T.; Dai, Y.; Pan, S.; Cavalieri, F.; Caruso, F. Biofunctional Metal–Phenolic Films from Dietary Flavonoids. *Chem. Commun.* **2017**, *53*, 1068–1071.

- (25) Dai, Y.; Guo, J.; Wang, T. Y.; Ju, Y.; Mitchell, A. J.; Bonnard, T.; Cui, J.; Richardson, J. J.; Hagemeyer, C. E.; Alt, K.; Caruso, F. Self-Assembled Nanoparticles from Phenolic Derivatives for Cancer Therapy. *Adv. Healthcare Mater.* **2017**, *6*, 1700467.
- (26) Yun, G.; Pan, S.; Wang, T. Y.; Guo, J.; Richardson, J. J.; Caruso, F. Synthesis of Metal Nanoparticles in Metal-Phenolic Networks: Catalytic and Antimicrobial Applications of Coated Textiles. *Adv. Healthcare Mater.* **2018**, *7*, 1700934.
- (27) Park, J. H.; Choi, S.; Moon, H. C.; Seo, H.; Kim, J. Y.; Hong, S.-P.; Lee, B. S.; Kang, E.; Lee, J.; Ryu, D. H.; Choi, I. S. Antimicrobial Spray Nanocoating of Supramolecular Fe(III)-Tannic Acid Metal-Organic Coordination Complex: Applications to Shoe Insoles and Fruits. *Sci. Rep.* **2017**, *7*, 6980.
- (28) Neto, C.; Craig, V. S. J. Colloid Probe Characterization: Radius and Roughness Determination. *Langmuir* **2001**, *17*, 2097–2099.
- (29) Hutter, J. L.; Bechhoefer, J. Calibration of Atomic-Force Microscope Tips. *Rev. Sci. Instrum.* **1993**, *64*, 1868–1873.
- (30) Dimitriadis, E. K.; Horkay, F.; Maresca, J.; Kachar, B.; Chadwick, R. S. Determination of Elastic Moduli of Thin Layers of Soft Material Using the Atomic Force Microscope. *Biophys. J.* **2002**, *82*, 2798–2810.
- (31) Yun, G.; Besford, Q. A.; Johnston, S. T.; Richardson, J. J.; Pan, S.; Biviano, M.; Caruso, F. Self-Assembly of Nano- to Macroscopic Metal–Phenolic Materials. *Chem. Mater.* **2018**, *30*, 5750–5758.

- (32) Hider, R. C.; Kong, X. Chemistry and Biology of Siderophores. *Nat. Prod. Rep.* **2010**, *27*, 637–657.
- (33) Butt, H.-J.; Cappella, B.; Kappl, M. Force Measurements with the Atomic Force Microscope: Technique, Interpretation and Applications. *Surf. Sci. Rep.* **2005**, *59*, 1–152.
- (34) Guo, J.; Richardson, J. J.; Besford, Q. A.; Christofferson, A. J.; Dai, Y.; Ong, C. W.; Tardy, B. L.; Liang, K.; Choi, G. H.; Cui, J.; Yoo, P. J.; Yarovsky, I.; Caruso, F. Influence of Ionic Strength on the Deposition of Metal–Phenolic Networks. *Langmuir* **2017**, *33*, 10616–10622.
- (35) Mann, S. Self-Assembly and Transformation of Hybrid Nano-Objects and Nanostructures under Equilibrium and Non-Equilibrium Conditions. *Nat. Mater.* **2009**, *8*, 781–792.
- (36) Svatek, S. A.; Perdigão, L. M. A.; Stannard, A.; Wieland, M. B.; Kondratuk, D. V.; Anderson, H. L.; O’Shea, J. N.; Beton, P. H. Mechanical Stiffening of Porphyrin Nanorings through Supramolecular Columnar Stacking. *Nano Lett.* **2013**, *13*, 3391–3395.
- (37) Li, L.; Hu, W.; Fuchs, H.; Chi, L. Controlling Molecular Packing for Charge Transport in Organic Thin Films. *Adv. Energy Mater.* **2011**, *1*, 188–193.

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