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Modular Assembly of Host–Guest Metal–Phenolic Networks Using Macrocyclic Building Blocks

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Abstract: The effective manipulation of interfacial properties has broad implications for the development of high-performance coatings. Metal–phenolic networks (MPNs) are an emerging class of responsive, universally adherent materials. Herein, we integrate host–guest chemistry with MPNs to modulate their surface chemistry and interfacial properties. Macrocyclic cyclodextrins (host) are conjugated to catechol or galloyl groups and subsequently used as components for the assembly of functional MPNs. The assembled cyclodextrin-based MPNs are highly permeable (even to high molecular weight polymers, e.g., 250–500 kDa), yet they specifically and noncovalently interact with various functional guests (including small molecules, polymers, and carbon nanomaterials), allowing for modular and reversible control over interfacial properties. Specifically, by using either hydrophobic or hydrophilic guest molecules, the wettability of the MPNs can be readily tuned between superrepellency ($>150^\circ$) and superwetting ($\sim 0^\circ$). This work, combining MPN assembly and host–guest chemistry, provides a versatile approach for advanced engineering of materials.

The development of robust coating strategies for engineering interfaces is important in diverse fields including materials science and surface engineering.^[1–3] Coordination chemistry, involving metal ions and organic ligands, enables the versatile assembly of composite materials. Metal–phenolic networks (MPNs), an emerging class of coatings formed through coordination chemistry,^[4] can rapidly assemble on diverse materials, regardless of the physicochemical properties of the substrate.^[2,5] However, the universal adherence of MPNs can also lead to nonspecific interactions due to the multidentate

properties of polyphenols and their ability to form multiple interactions with different surfaces.^[6,7] The incorporation of components that allow noncovalent, reversible, and specific interactions into MPN materials would extend their functionality and hence range of potential applications.^[8]

Host–guest chemistry is a branch of supramolecular chemistry that involves molecular complexes that specifically interact through molecular recognition.^[9] Supramolecular structures assembled through host–guest interactions have various applications^[10,11] and can be used to engineer surfaces through noncovalent interactions.^[12] Cyclodextrins (CDs), cyclic oligosaccharides,^[13] are extensively employed as host building blocks for nanomaterials^[11] owing to their hydrophobic cavities (typical diameter <1 nm). These hydrophobic cavities facilitate the formation of inclusion complexes with hydrophobic guest molecules (e.g., adamantane derivatives, ADs). Conversely, the exteriors of CDs are highly polar owing to the abundant hydroxyl groups, making them suitable for processing in aqueous solutions. Therefore, CDs represent suitable building blocks for the assembly of MPNs, as they would allow for the noncovalent functionalization of MPNs using host–guest interactions, thus opening new avenues for the application of MPNs.^[14]

In the present work, host–guest chemistry is introduced into MPN building blocks through the one-pot conjugation of catechols and galloyls to CDs. The resulting phenolic building blocks can subsequently interact with metal ions to coat and functionalize substrates to form a metal–phenolic network (Figure 1). Our modular assembly strategy takes advantage of the universal adherence of MPNs and the specific recognition of guest molecules by the CD host motifs within the network. In the presence of metal ions (e.g., Fe^{III}), host MPNs (MPNs with host motifs) can form thin films on various substrates with different physicochemical properties (i.e., size, shape, and structure). In addition, other physicochemical properties (e.g., fluorescence, wettability) of the MPN films can be precisely tuned via the incorporation of functional guest molecules. Specifically, adamantane-tagged functional molecules have been synthesized to demonstrate both the host–guest binding affinity and the versatile engineering of micro- and macroscopic interfacial properties (i.e., surface wettability).

CD-based host phenolic building blocks were prepared through one-pot synthetic strategies in either organic or aqueous conditions (Figure S1, Supporting Information). In organic solvents, the carbonyldiimidazole-promoted carbamylation strategy enabled conjugation of catechol or galloyl groups to the exterior of the CD ring via the conversion of the pristine CD into imidazole intermediates, yielding phenolic building blocks (cyclodextrin catechol, CC; cyclodextrin galloyl, CG). In aqueous conditions, amidation strategies between carboxylated CD and dopamine, though less effective than the carbamylation strategy,

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Supporting information for this article is given via a link at the end of the document.

Figure 1. Schematic of MPNs with structural motifs for host–guest interactions. Host phenolic ligands are referred to as cyclodextrin catechol (CC) and cyclodextrin galloyl (CG). The average degree of substitution per cyclodextrin ring is three. In the presence of coordinating metal ions (e.g., Fe^{III} , Al^{III} , Ce^{III} , Co^{II} , Cu^{II} , Ti^{IV} , Zn^{II}), MPNs coatings can rapidly form on diverse substrates. Up to three catechol/galloyl groups can be bound per Fe^{III} center (i.e., mono-complex, bis-complex, and tris-complex coexist, with the bis-complex as the dominant form, see Figures S7–S10 for detailed interactions and stoichiometry). Note that the structure shown here is for illustration purposes only and is not meant to display the exact structural order of the amorphous MPN network. Tunable interfacial properties of the resulting MPNs can be achieved via specific and modulated interactions with the desired guest molecules that can bind into the cavities of the macrocyclic rings cross-linked by Fe^{III} .

were used, yielding a mono-substitution component (Figure S2). The degree of substitution (DS) per CD ring was consistent, as determined from different analysis techniques, including matrix-assisted laser desorption/ionization time-of-flight (MALDI-ToF) mass spectrometry and ^1H NMR spectroscopy (Figures S3–S6). This observation highlights that the phenolic groups were chemically conjugated to CD rather than existing as free inclusion complexes.^[15] In general, the average DS of the host ligands studied herein was three (i.e., three catechol or galloyl groups are chemically attached to the macrocyclic ring of a single β -CD molecule; see MALDI-ToF mass spectra in Figure S5), suggesting that these phenolic ligands readily cross-linked into networks in the presence of metal ions. (Hereafter, β -CD is referred to simply as CD unless specified otherwise.) Simulations on molecular dynamics suggest that up to three catechol/galloyl motifs of these macrocyclic ligands can be

potentially coordinated per one Fe^{III} ion center (Figures S7 and S8; Movies S1 and S2).

Solutions of Fe^{III} mixed with CC or CG rapidly turned purple, suggesting complexation ($\text{CC}/\text{Fe}^{\text{III}}$ or $\text{CG}/\text{Fe}^{\text{III}}$, respectively) between the metal ions and the CC or CG ligands (Figures S9–S11). Host MPNs, $\text{CC}/\text{Fe}^{\text{III}}$ or $\text{CG}/\text{Fe}^{\text{III}}$, were deposited on sacrificial CaCO_3 templates (see Section S1.5, Supporting Information) and formed replica particles or capsules following template removal (via selective binding of calcium with ethylenediaminetetraacetic acid (EDTA)) (Figure 2, Figure S12). Capsules were synthesized from polystyrene sulfonate-stabilized CaCO_3 templates (Figure S13), as well as different organic templates (polystyrene, PS and polymethyl methacrylate, PMMA), resulting in capsules with a wall thickness of less than 10 nm (Figure 2c, Figures S14 and S15). The capsules are

Figure 2. a) Scheme of the preparation of the host MPNs. b) TEM images of CaCO₃-templated host structures: (i) coated CaCO₃ particles before template removal; (ii) replica particles after template removal; and (iii) nanoporous structure. Scale bars in i–iii are 1 μm, 1 μm, and 500 nm, respectively. c) PS-templated host MPN capsules: (i) atomic force microscopy image; (ii) corresponding line profile; and (iii) TEM image. Scale bars are 2 μm. d) UV-Vis spectra and differential interference contrast microscopy image (inset) of the host MPN capsules. Scale bar is 5 μm. e) Permeability of the host MPN capsules (CaCO₃-templated). Inset shows a confocal image of the capsules incubated with FITC-dextran_{250k} (the capsule permeability can be inferred by the contrast in fluorescence between the inner and outer environment). Scale bar is 5 μm.

stable at neutral pH conditions over a period of 7 days but also display pH-responsive degradability in acidic conditions (e.g., pH < 3) (Figure S16), indicating the coordination-based nature of the MPNs. It is noted that the macrocyclic ligands can coordinate with various metal ions and can form MPN coatings

on diverse templates (Figure S17) and with various metal ions (Figures S18 and S19). The coordination bonding of both CC/Fe^{III} and CG/Fe^{III} in the capsules was further confirmed by UV-vis spectroscopy (Figure 2d, Figure S10), with the presence of the broad absorption band at ~580 nm corresponding to the

ligand-to-metal charge transfer band.^[16] In addition, the permeability of the host MPNs was ~10 times higher than that of conventional tannic acid/Fe^{III} MPNs,^[2,3] as determined using a series of fluorescein isothiocyanate-tagged dextran (FITC-dextran) molecules with various molecular weights (4–2000 kDa) (Figure 2e). The effective pore size (i.e., equivalent hydrodynamic size of the permeate) of the host MPNs was thereby determined to be 30–50 nm in diameter (for capsules templated from either CaCO₃ or PS; Figure S20).^[17] This high permeability is unlikely due to the macrocyclic channel of CD (internal diameter is <1 nm), but rather it is more likely due to the large CD coordination units, which are more rigid and sterically restricted in packing than tannic acid-based units (see Figure

S21 and simulations on molecular dynamics in the Supporting Information; Figures S22 and S23; Movies S3 and S4). Other factors may include kinetic trapping during MPN formation, low interactions of the host MPNs with the probe polymer, and the dynamic nature of the coordinated networks.^[18]

Besides the universal adherence and high permeability of the host MPNs, the specific host–guest binding capability of the macrocyclic CD rings in the MPNs was studied. To visualize the guest binding affinity of the macrocyclic phenolic systems (i.e., CC, CC/Fe^{III} 3:1 complex), phenolphthalein was used as the guest molecule (Figure 3a). The aromatic frame of phenolphthalein is similar in size to the interior of the macrocyclic ring. Therefore, a single CD cavity can fit one

Figure 3. Guest binding affinity of the host MPN complexes and structures. a) Host–guest interactions between a model guest (phenolphthalein) and host system (CC or CC/Fe^{III}). The color intensity decreases as the concentration of the host material increases (from left to right: 0.0 to 1.0 mm with an interval of 0.1 mm), indicating the formation of host–guest inclusion complexes. b) UV–Vis spectra of fullerene inclusion: (i) free fullerene C₆₀; (ii) inclusion product with unmodified cyclodextrin (CD/C₆₀); and (iii) inclusion product with cyclodextrin catechol (CC/C₆₀). c) Binding affinity of the host MPNs: (i) fluorescent guest molecule (AD-FITC); (ii) confocal image of the labeled host MPN-coated PS particles through host–guest binding; and (iii) confocal image of the host MPN capsules. Scale bars are 20 μm.

phenolphthalein molecule via hydrophobic forces (i.e., host–guest inclusion complex, 1:1 stoichiometry). When increasing the concentration of the host motifs (CD, CC, CC/Fe^{III} 3:1 complex), the solution changed from pink to colorless (for CD, see Figure S24), light brown (for CC, Figure 3a), and light red (for CC/Fe^{III} 3:1 complex, Figure 3a) owing to a decrease in the absorbance of phenolphthalein at 530 nm (characteristic

absorption) upon formation of the host–guest complexes (Figure S25). The host–guest binding constants K_a can be determined by UV–vis spectroscopy (see Section S1.4, Supporting Information) as follows:

$$A = A_{\infty} - \frac{1}{K_a} \frac{A - A_0}{C_0} \quad (1)$$

where C_0 and A_0 are the initial concentration and absorbance of phenolphthalein, respectively, A and A_∞ are the absorbance values of the solution containing excess phenolphthalein and excess CD, respectively. Therefore, by plotting A versus $(A - A_0)/C_0$, the binding constant K_a is determined from the slope of $-1/K_a$. The K_a of the unmodified CD with phenolphthalein was determined to be $6.7 \times 10^3 \text{ L mol}^{-1}$ (Figure S24), in good agreement with the literature ($\sim 10^3 \text{ L mol}^{-1}$).^[19] The formation of inclusion complexes between the phenolic (modified) CDs (CC and CC/Fe^{III}) and phenolphthalein was also examined. Although slightly lower binding constants were obtained for CC ($K_a = 3.8 \times 10^3 \text{ L mol}^{-1}$) and CC/Fe^{III} ($K_a = 3.5 \times 10^3 \text{ L mol}^{-1}$), the results suggest that both systems maintain a high binding capacity. The lower binding constants might result from the potentially

deformed macrocyclic CD rings upon chemical modification. However, the formation of MPN complexes did not reduce the binding capacity further.

Additionally, the macrocyclic phenolic building blocks displayed a high binding affinity for water-insoluble guest molecules (ADs; fullerene, C_{60}). Compared with the unmodified CD, CC displayed higher binding capacities to C_{60} , as indicated by the significant decrease in the absorbance at 330 nm (characteristic absorption of C_{60}) after inclusion complex formation (Figure 3b). The enhanced binding capacity can be attributed to the improved intermolecular forces (i.e., π - π stacking between C_{60} and CC) and the host-guest attractions between C_{60} and the hydrophobic cavity of the macrocyclic

Figure 4. Surface wettability engineering of host MPNs. a) Glass substrates before (left) and after (right) host MPN (CG/Fe^{III}) deposition. Scale bars are 1 cm. b) Hydrophobic guest molecule (AD-C16) and hydrophilic guest molecule (AD-PEG). c) Tunable surface wettability (from superhydrophilicity to superhydrophobicity) through specific guest binding of the host MPN coating.

catechols. To further confirm the host-guest binding capability of the host MPNs, a fluorescein-tagged adamantane derivative (AD-FITC; Figures S26 and S27) was synthesized for the direct observation of the binding of the guest AD-FITC to the coated particles and capsules (Figure 3c). After incubation of the host MPN-coated particles and host MPN capsules in the AD-FITC solution (1 mg mL^{-1} in methanol), the particles and capsules were thoroughly washed and examined using fluorescence microscopy, which confirmed the inclusion complex formation between the host MPNs and AD-FITC guest molecules. Guest recognition is achieved by the host-guest chemistry between CD cavities and the hydrophobic AD motifs rather than nonspecific adsorption of FITC on MPNs. Control experiments involving incubation with free FITC did not show any fluorescence after washing (data not shown). **Note that thorough washing is needed to exclude nonspecific binding.** These results,

collectively, suggest the superior interfacial properties of the host MPNs.

Besides particle engineering, the macroscopic surface properties (e.g., wettability) of the surfaces could be tuned using the modular assembly of host-guest MPNs (Figure 4). Planar substrates (i.e., glass) were first incubated with CG/Fe^{III} complexes, and a conformal dark film was deposited, suggesting adherence of the macrocyclic phenolic CD when mixed with Fe^{III} (Figure 4a). Two energetically different guest molecules, adamantane-tagged hydrophilic poly(ethylene glycol) (AD-PEG) and adamantane-tagged hydrophobic hexadecane (AD-C16) (Figures S26 and S28), were then used to tune the macroscopic surface properties of the CG/Fe^{III} coatings (Figure 4b). The intrinsically hydrophilic host MPN coating (water contact angle is $\sim 35^\circ$) could be made either superhydrophilic ($<10^\circ$) by hosting the hydrophilic guest AD-PEG or superhydrophobic ($>150^\circ$) by hosting the hydrophobic guest AD-C16 (Figure 4c). Moreover,

the wetting was readily switched simply by guest exchange. The surface repellency could be further enhanced (i.e., roll-off angle $<5^\circ$) by coating hierarchically textured substrates (e.g., fabrics). These results indicate that the modular assembly of host–guest MPNs can serve as a promising technique for advanced surface engineering, with potential for tuning the surface wettability.

In summary, host–guest chemistry was introduced into MPNs by the coupling of phenolics and cyclodextrins. The resultant macrocyclic phenolic ligands rapidly assembled into complexes and conformal coatings on diverse substrates via metal–phenolic coordination chemistry (an important feature for versatile assemblies). The high permeability (regardless of the nature of the solute, i.e., hydrophilic dextran, hydrophobic PS, hydrophobic/hydrophilic PMMA, and EDTA/ Ca^{2+} complex), the specific host–guest interactions (guest molecules including phenolphthalein, C_{60} , ADs), and the tunable wettability exhibited by the host MPNs have significant implications for the engineering of advanced materials for various applications, e.g., building nanopores,^[20] macroscopic switches,^[21] superstructures,^[22] host-directed therapy,^[23] and bioresponsive materials,^[24] and should expedite advances in other coordination-based assemblies.^[25]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: hollow structures • host–guest systems • membranes • superhydrophobic surfaces • tunable wettability

- [1] L. Li, G. Zhang, Z. Su, *Angew. Chem.* **2016**, *128*, 9239; *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 9093.
- [2] 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.
- [3] a) S. Karan, Z. Jiang, A. G. Livingston, *Science* **2015**, *348*, 1347; b) J. J. Richardson, M. Bjornmalm, F. Caruso, *Science* **2015**, *348*, aaa2491.
- [4] a) H. Ejima, J. J. Richardson, F. Caruso, *Nano Today* **2017**, *12*, 136; b) J. Guo, T. Suma, J. J. Richardson, H. Ejima, *ACS Biomater. Sci. Eng.* **2019**, DOI: 10.1021/acsbomaterials.8b01507.
- [5] M. A. Rahim, S. L. Kristufek, S. Pan, J. J. Richardson, F. Caruso, *Angew. Chem.* **2019**, *131*, 1920; *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 1904.
- [6] a) Y. Ju, J. Cui, M. Mullner, T. Suma, M. Hu, F. Caruso, *Biomacromolecules* **2015**, *16*, 807; b) Y. Ju, J. Cui, H. Sun, M. Mullner, Y. Dai, J. Guo, N. Bertleff-Zieschang, T. Suma, J. J. Richardson, F. Caruso, *Biomacromolecules* **2016**, *17*, 2268; c) M. Krogsgaard, V. Nue, H. Birkedal, *Chem. Eur. J.* **2016**, *22*, 844; d) H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007**, *318*, 426.
- [7] D. Hong, K. Bae, S. P. Hong, J. H. Park, I. S. Choi, W. K. Cho, *Chem. Commun.* **2014**, *50*, 11649.
- [8] N. Huang, K. Wang, H. Drake, P. Cai, J. Pang, J. Li, S. Che, L. Huang, Q. Wang, H. C. Zhou, *J. Am. Chem. Soc.* **2018**, *140*, 6383.
- [9] G. Yu, K. Jie, F. Huang, *Chem. Rev.* **2015**, *115*, 7240.
- [10] a) J. Tian, Z. Y. Xu, D. W. Zhang, H. Wang, S. H. Xie, D. W. Xu, Y. H. Ren, H. Wang, Y. Liu, Z. T. Li, *Nat. Commun.* **2016**, *7*, 11580; b) Z. Zhou, Z. Han, Z. R. Lu, *Biomaterials* **2016**, *85*, 168; c) M. I. Bodnarchuk, S. Yakunin, L. Piveteau, M. V. Kovalenko, *Nat. Commun.* **2015**, *6*, 10142; d) X. Hou, C. Ke, C. J. Bruns, P. R. McGonigal, R. B. Pettman, J. F. Stoddart, *Nat. Commun.* **2015**, *6*, 6884; e) 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; f) A. K.-W. Chan, W. H. Lam, Y. Tanaka, K. M.-C. Wong, V. W.-W. Yam, *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 690; g) G. Yu, W. Yu, L. Shao, Z. Zhang, X. Chi, Z. Mao, C. Gao, F. Huang, *Adv. Funct. Mater.* **2016**, *26*, 8999; h) D. Tanaka, A. Henke, K. Albrecht, M. Moeller, K. Nakagawa, S. Kitagawa, J. Groll, *Nat. Chem.* **2010**, *2*, 410.
- [11] a) G. Y. Tonga, Y. Jeong, B. Duncan, T. Mizuhara, R. Mout, R. Das, S. T. Kim, Y. C. Yeh, B. Yan, S. Hou, V. M. Rotello, *Nat. Chem.* **2015**, *7*, 597; b) A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling, W. R. Dichtel, *Nature* **2016**, *529*, 190.
- [12] C. Wang, Z. Wang, X. Zhang, *Acc. Chem. Res.* **2012**, *45*, 608.
- [13] D. Ikuta, Y. Hirata, S. Wakamori, H. Shimada, Y. Tomabechei, Y. Kawasaki, K. Ikeuchi, T. Hagimori, S. Matsumoto, H. Yamada, *Science* **2019**, *364*, 674.
- [14] a) S. Engel, N. Moller, B. J. Ravoo, *Chem. Eur. J.* **2018**, *24*, 4741; b) G. Cutrone, X. Li, J. M. Casas-Solvas, M. Menendez-Miranda, J. Qiu, G. Benkovics, D. Constantin, M. Malanga, B. Moreira-Alvarez, J. M. Costa-Fernandez, L. Garcia-Fuentes, R. Gref, A. Vargas-Berenguel, *Nanomaterials* **2019**, *9*, 1103; c) S. Xu, P. Wang, Z. Sun, C. Liu, D. Lu, J. Qi, J. Ma, *J. Membr. Sci.* **2019**, *569*, 124.
- [15] M. Palomar-Pardavé, G. Alarcón-Ángeles, M. T. Ramírez-Silva, M. Romero-Romo, A. Rojas-Hernández, S. Corona-Avedaño, *J. Inclusion Phenom. Macrocyclic Chem.* **2010**, *69*, 91.
- [16] 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, F. Caruso, *Chem. Mater.* **2015**, *27*, 5825.
- [17] J. K. Armstrong, R. B. Wenby, H. J. Meiselman, T. C. Fisher, *Biophys. J.* **2004**, *87*, 4259.
- [18] E. Filippidi, T. R. Cristiani, C. D. Eisenbach, J. H. Waite, J. N. Israelachvili, B. K. Ahn, M. T. Valentine, *Science* **2017**, *358*, 502.
- [19] I. H. Higuti, P. A. d. Silva, J. Papp, V. M. d. E. Okiyama, E. A. d. Andrade, A. d. A. Marcondes, A. J. d. Nascimento, *Braz. Arch. Biol. Technol.* **2004**, *47*, 837.
- [20] S. Howorka, *Nat. Nanotechnol.* **2017**, *12*, 619.
- [21] Y. Sun, J. Ma, D. Tian, H. Li, *Chem. Commun.* **2016**, *52*, 4602.
- [22] 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.
- [23] R. S. Wallis, R. Hafner, *Nat. Rev. Immunol.* **2015**, *15*, 255.
- [24] Y. Lu, A. A. Aimetti, R. Langer, Z. Gu, *Nat. Rev. Mater.* **2016**, *2*, 16075.
- [25] a) L. Mei, W.-Q. Shi, Z.-F. Chai, *Bull. Chem. Soc. Jpn.* **2018**, *91*, 554; b) K. Ariga, M. Nishikawa, T. Mori, J. Takeya, L. K. Shrestha, J. P. Hill, *Sci. Technol. Adv. Mat.* **2018**, *20*, 51; c) J.-K. Sun, X.-D. Yang, G.-Y. Yang, J. Zhang, *Coord. Chem. Rev.* **2019**, *378*, 533.

COMMUNICATION

The synthesis of host phenolic building blocks, consisting of macrocyclic host rings and phenolic coordinating functions, enables the rapid assembly of universally adherent conformal metal–phenolic network coatings on diverse substrates with modular and tunable interfacial properties using host–guest chemistry.

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