

# Green Wood Adhesives from One-Pot Coacervation of Folic Acid and Branched Poly(ethylene imine)

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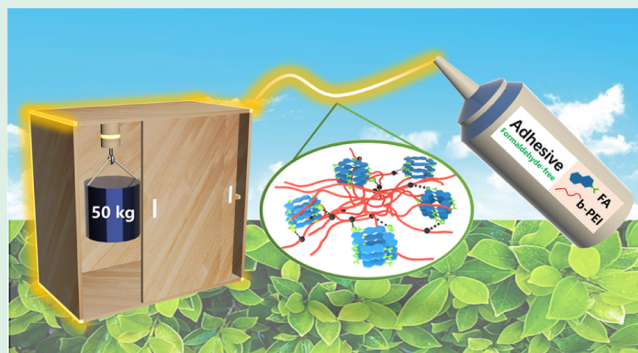
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Supporting Information

**ABSTRACT:** Adhesives are extensively used in furniture manufacture, and most currently utilized furniture glues are formaldehyde-based chemicals, which emit formaldehyde throughout the entire life of the furniture. With increasing concerns about formaldehyde emission effects on human health, formaldehyde-free and environmentally friendly wood adhesives from bio-based resources are highly desired. In this study, we developed an eco-friendly, high-strength, and water-based wood adhesive from one-pot coacervation of the hierarchical self-assembly of folic acid (FA, a biomolecule, vitamin B9) with a commercially available biocompatible polymer—branched poly(ethylene imine) (b-PEI). The coacervation is caused by multiple hydrogen bonds between b-PEI and the stacks of FA quartets, which demonstrates a continuous robust 3D network, thus realizing adhesion and cohesion behaviors. This coacervate has the strongest adhesion toward wood compared with other substrates. The long-lasting shear bonding strength is up to 3.68 MPa, which is much higher than that of commercial super glue, but without releasing any toxic components. Since all the fabrication and application processes are under ambient conditions without any heating and high-pressure procedures, this work provides a facile yet powerful strategy to develop formaldehyde-free, eco-friendly, and high-performance bio-based waterborne adhesives for wood bonding.

**KEYWORDS:** folic acid, branched PEI, co-assembly, coacervate, wood adhesive



## INTRODUCTION

Wood-based products, such as plywood, particleboard, fiberboard, and oriented strand board, are closely related to the everyday life of human beings. For example, furniture is used in every house and offices, and most furniture is an ensemble of different pieces of wood joined together with adhesives.<sup>1,2</sup> However, most of the adhesives used in wood products like furniture are formaldehyde-based chemicals, such as phenolic resin, urea formaldehyde resin, and melamine urea formaldehyde resin, which would release formaldehyde and other volatile organic compounds during the process of use.<sup>3–5</sup> Because formaldehyde is a human carcinogen, people have to make a lot of efforts to get rid of formaldehyde emitted by furniture.<sup>6</sup> Since formaldehyde release could be a life-long process for some furniture, the formaldehyde-based adhesives have loaded unneglectable harms to human beings. Therefore, it is highly desired to develop a new generation of high-performance wood adhesives that do not release any toxic gases to replace the synthetic petroleum-based adhesives in the industry of woody composites.

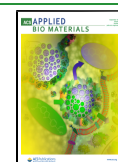
So far, numerous adhesive materials have been developed, but most of them are catechol-based, which rely on covalently incorporating catechol into polymers or by expressing

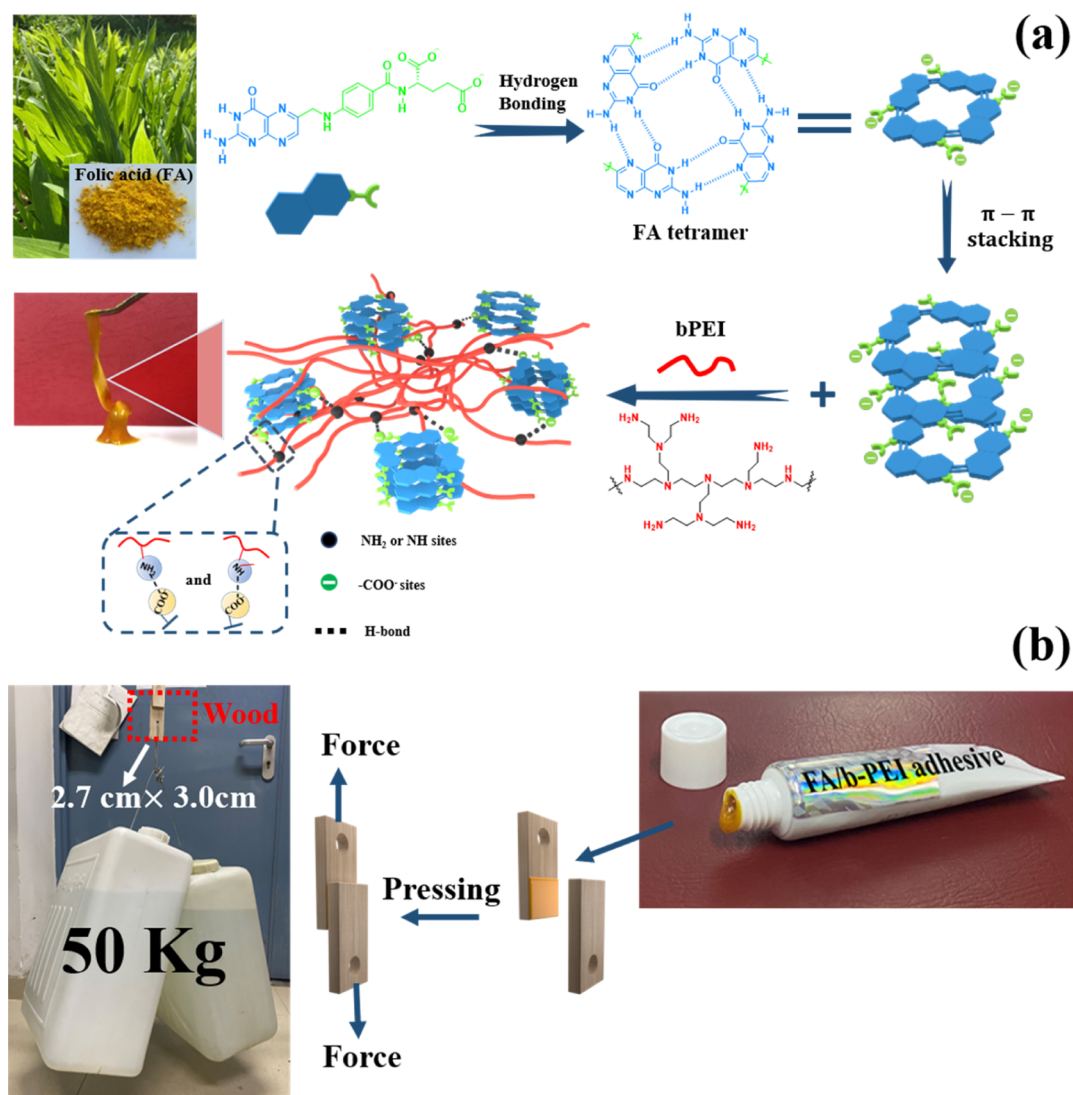
recombinant mussel adhesive proteins.<sup>7,8</sup> In this case, the material preparation often requires tedious synthesis, purification, and expensive reagents.<sup>9</sup> The whole preparation process is time-consuming and costly, which makes it difficult for large scale-up production. There are also some excellent non-catechol-based adhesives, such as low-molecular weight supramolecular adhesive comprising crown ether monomers with structural water,<sup>10</sup> crystal-based adhesive based on polymerization of 1-methyl-3-methylimidazolium hexafluorophosphate, *N,N*-dimethylacrylamide and poly(ethylene glycol) diacrylate,<sup>11</sup> and supramolecular hot melt adhesive fabricated from the naturally existing small molecules of thioctic acid, divinyl compounds, 1,3-diisopropenylbenzene, and Fe<sup>3+</sup> ions in a specific proportion.<sup>12</sup> Despite these achievements in wood adhesion, their fabrication processes require either necessary synthesis or heat input, which is not advantageous in the global

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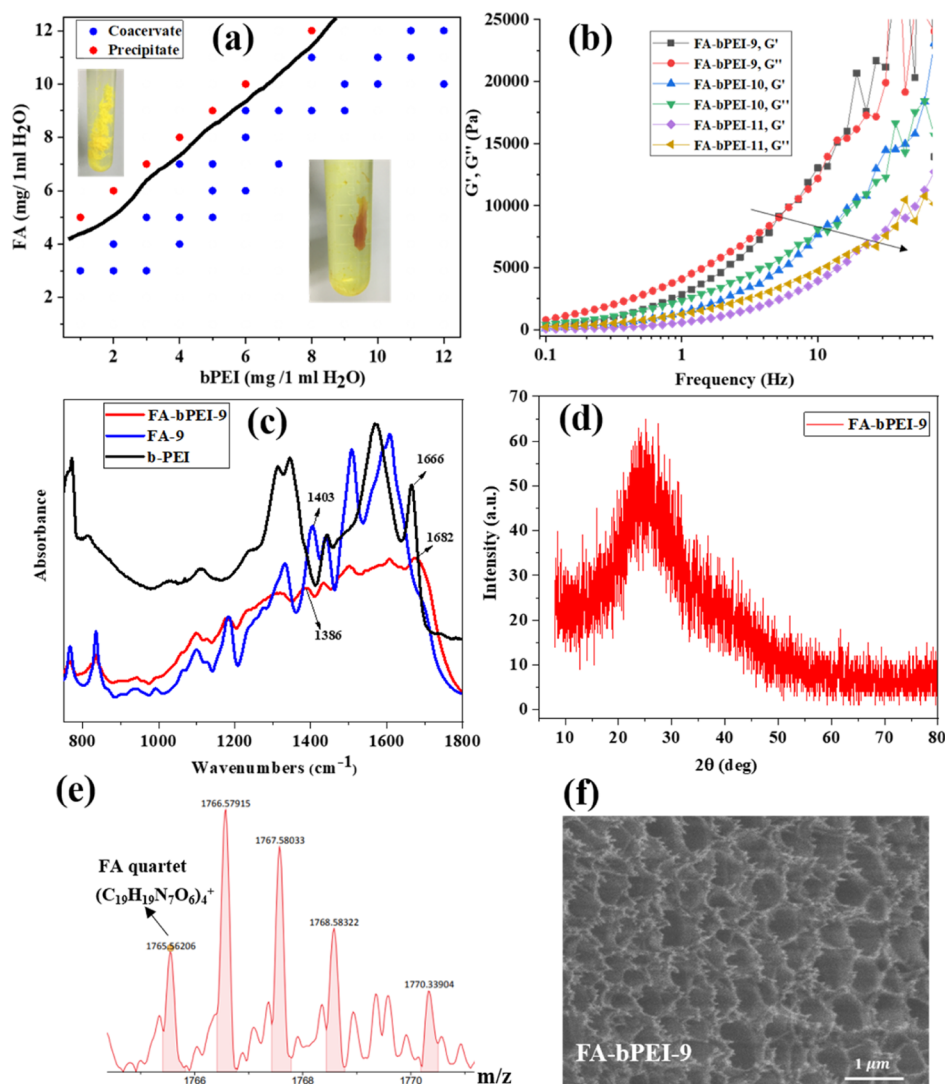
**Figure 1.** (a) Chemical structure of folate and b-PEI and the mechanism of the interactions between FA and b-PEI. (b) Schematic illustrating the FA-b-PEI coacervate adhesion procedure; photo of sustaining a 50 kg load with the adhered wood (2.7 cm × 3.0 cm).

background of peak carbon dioxide emissions and carbon neutrality.

Alternatively, bio-adhesives are the substitute of petroleum-based adhesives that have received great attention from environmental concern point of view, academic researchers, and industries.<sup>13,14</sup> Till now, various bio-based polymers, such as lignin,<sup>15–18</sup> starch,<sup>19,20</sup> zein,<sup>21</sup> tannin,<sup>22</sup> dialdehyde cellulose,<sup>23</sup> proteins,<sup>24–26</sup> and chitin/chitosan,<sup>27</sup> have been introduced in the creation of wood adhesives in recent years. However, for lignin adhesives, the main problem is their extremely low reactivity, which leads to long pressing times and thus increases production costs in panel manufacturing.<sup>16,28,29</sup> In most studies, lignin-based adhesives still require the incorporation of phenol formaldehyde (PF) or polymeric methylene diphenyl diisocyanate to satisfy the requirements with acceptable mechanical properties.<sup>23</sup> For instance, Moubarik et al. reported lignin-based wood adhesives prepared with PF, in which bagasse lignin could be used to replace 30% of the PF resins used to bond plywood panels, without adversely affecting bond properties.<sup>30</sup> Moreover, protein-based adhesives exhibit a few disadvantages including fragility and low structural bond strengths because there is a lack of satisfied

cohesion due to the hydrophilic molecular interactions within protein structures, which limits their practicability in the plywood manufacturing industry.<sup>13,14,25,31</sup> Currently, few other natural materials are found that can be used to construct green adhesives with similar or much better adhesive performance with a much better economic pathway. Therefore, the development of new bio-based environmentally friendly wood adhesives with high cost efficiency and high adhesion performance still needs further exploration.

Folic acid (FA) is a naturally abundant B vitamin and can be obtained from various natural supplies, such as green leafy vegetables, legumes, and fruits.<sup>32</sup> It has been well documented that FA is able to form quartets in water, which further undergo  $\pi-\pi$  stacking.<sup>33</sup> In our previous work, we have developed a supramolecular folate-based printable bio-hydrogel and thermo-gene hydrogel with the aid of FA quartets and metal ions.<sup>34,35</sup> As shown in Figure 1a, the structure of FA consists of a pterin ring and a glutamate moiety, which are connected by 4-aminobenzoic acid. Notably, the presence of many functional groups in its chemical structure enables its easy coupling with other materials by noncovalent interactions, such as ion coordination, hydrophobic interaction, hydrogen



**Figure 2.** (a) Phase diagrams of the FA–b-PEI mixture at pH = 9. (b) Rheological behavior of the FA–bPEI-*X* wet adhesive: the storage modulus  $G'$  and the loss modulus  $G''$  as a function of angular frequency. (c) FT-IR spectroscopy of FA, b-PEI, and the FA–bPEI-9 adhesive sample. (d) XRD spectra of the FA–bPEI-9 adhesive. (e) High-resolution mass spectrometry of the FA–bPEI-9. (f) SEM image of the freeze-dried FA–bPEI-9 sample.

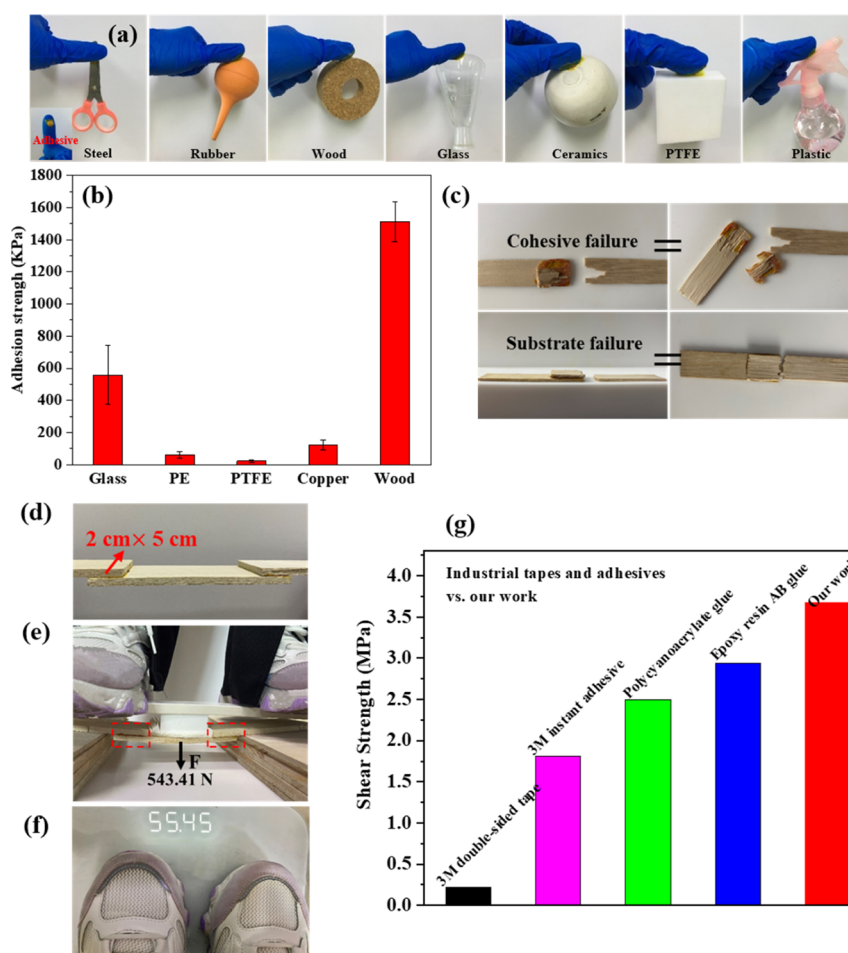
bonding,  $\pi$ – $\pi$  stacking, and electrostatic interaction with other components. These multimode interactions are comparable to what mussel adhesive proteins do,<sup>36</sup> inspiring that FA is probably a potential candidate in the design of novel adhesives.

Since sufficient internal adhesiveness is crucial for a qualified adhesive, it is necessary to co-assemble FA into a three-dimensional network.<sup>37</sup> To achieve this goal, we proposed in this work a novel supramolecular adhesive derived from one-pot coacervation of FA and branched poly(ethylene imine) (b-PEI, Figure 1a). B-PEI is a commercially available biocompatible polycation, which is extensively used as an agent for the transfection of genes and for the construction of functional materials and drug delivery systems.<sup>38,39</sup> Importantly, water-soluble b-PEI has a history in wood composite research, applied as a priming layer for adhesives, and it was recently investigated in mixtures with reactive biopolymers to form durable crosslinked adhesives.<sup>40–43</sup> Depending on solution pH, b-PEI also contains a large amount of primary, secondary, and tertiary amino groups. Thus, both electrostatic interactions and hydrogen bonding may occur between b-PEI and the FA quartet, which would build a continuous robust 3D network

favored by an adhesive. In this work, we show that b-PEI and FA are capable of forming coacervate adhesives via a one-pot aqueous co-assembling process. Notably, this new complex coacervate exhibits a stronger adhesion property on the wood substrate than all the tested commercial adhesives (Figure 1b) with long-lasting adhesiveness. In contrast to the heat-initiated curing of plywood manufacture using resin-based adhesives, this novel waterborne adhesive can be cured at room temperature and without releasing toxic formaldehyde. This one-step procedure is green, facile, and time-saving and has low cost and thus is advantageous for the global goal of reducing peaking carbon dioxide emissions and achieving carbon neutrality.

## RESULTS AND DISCUSSION

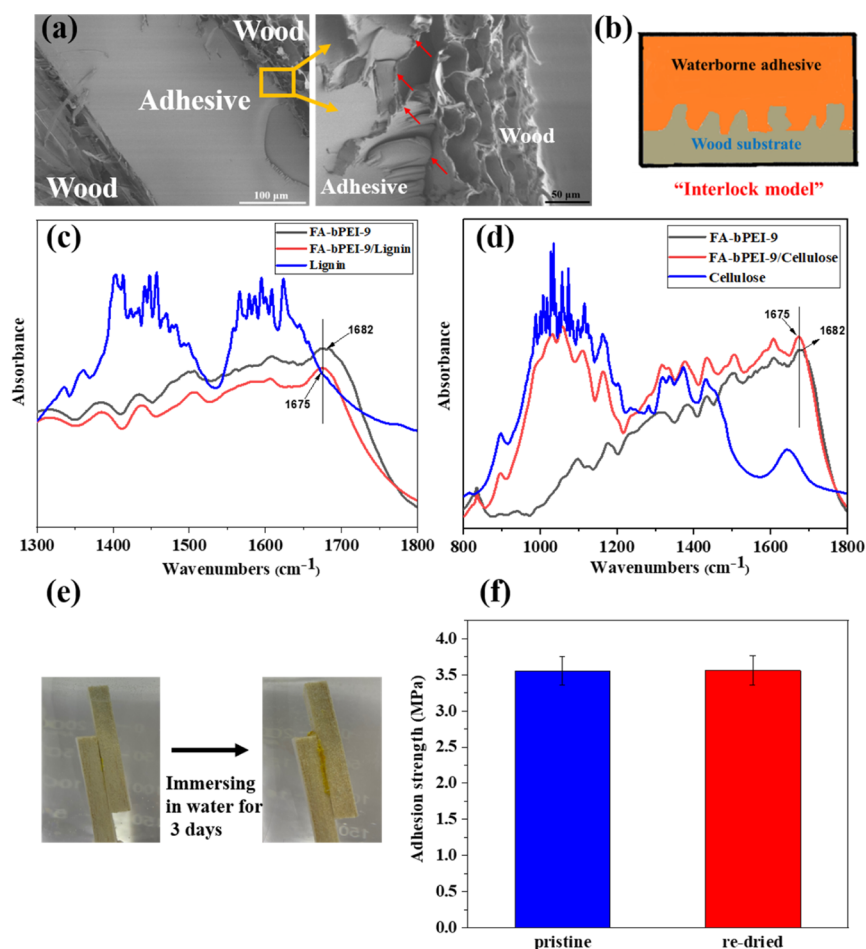
Figure 2a shows the phase diagram of the complexed system of FA and b-PEI. Upon mixing the aqueous solution of FA and b-PEI of weight ratio 1:1 at different concentrations, either coacervates or precipitates were obtained. The coacervates obtained at different pHs (Figure S1), termed as FA–bPEI-*X*



**Figure 3.** (a) Bulk wet adhesive adhering to various hydrophobic and hydrophilic surfaces. (b) Adhesion strength of the FA–bPEI-9 adhesive measured for different substrates. (c) Photos of wood test pieces after shear test; representative failure mode (in wood) of test sample curing for 4 h (above); and curing for 7 h (below). (d) Wooden bridge constructed by gluing three pieces of boards. The gluing area is 2 cm × 5 cm. (e,f) The bridge can hold a volunteer with a weight of 55.45 kg. (g) Comparison of adhesion strengths of industrial tapes and commercial glues vs FA–bPEI-9 wood adhesive.

(where  $X = 9, 10,$  and  $11,$  denoting the solution pH), are all viscous, which are subjected to further study as adhesives. Figure 2b shows the viscoelastic properties of the FA–b-PEI coacervate. The elastic modulus  $G'$  is smaller than the viscous modulus  $G''$  in the low-frequency region for all the coacervates, verifying their viscous nature. The cross-over frequency  $\omega$  increases with increasing pH from 9 to 11, indicating that the relaxation time  $\tau$ , which equals  $1/\omega$ , becomes shorter. This means that the coacervation becomes looser with increasing pH. The solution  $pK_a$  of b-PEI was estimated to be 8.5 from the titration curve of b-PEI (Figure S2); thus, b-PEI turns out to be a neutral polymer at higher pH values. To prove the presence of strong H-bonding between b-PEI and FA, Fourier transform infrared spectroscopy (FT-IR) characterization of b-PEI, FA, and FA–b-PEI coacervates was performed. As shown in Figure 2c, the N–H bending vibrations of primary amines of b-PEI shift from 1666 to 1682  $\text{cm}^{-1}$ , and the symmetric vibration of  $\text{COO}^-$  of FA shifts from 1403 to 1386  $\text{cm}^{-1}$ , clearly revealing the formation of hydrogen bonding between b-PEI and FA (Figures 2c, S3). Only one broad peak was observed at  $2\theta = 23.3^\circ$  in the broad angle range of  $0\text{--}40^\circ$  in X-ray diffraction (XRD) and wide-angle X-ray scattering (WAXS) measurements (Figures 2d, S4a, and S5). According to the Bragg equation  $d = \lambda/2 \sin \theta$ , this distance is calculated

to be 3.8 Å, featuring the occurrence of  $\pi\text{--}\pi$  stacking. Fourier transform mass spectrometry (FT-MS) measurements were carried out to confirm that FA molecules have formed quartets in the coacervate by the occurrence of a series of species with  $m/z$  ranging from 1765 to 1770. Because the  $M_w$  of the folate ion is about 441, the species with  $m/z = 1765.56206$  is assigned as  $(\text{C}_{76}\text{H}_{77}\text{N}_{28}\text{O}_{24})^+$ , which is exactly the composition of 4 FA charged by  $1\text{H}^+$ . The other peaks, such as  $m/z = 1766.57915, 1767.58033, 1768.58322,$  and  $1770.33904,$  are the species of the FA quartet containing different isotopes (Figures 2d and S6), further suggesting that the  $\pi\text{--}\pi$  stacking originates from the stacking of the FA quartets in the coacervates. The absence of diffractions in the low-angle region (Figure S4b) indicates that the FA tetramers are not aligned in the coacervates. They crosslink the amide groups on the b-PEI via hydrogen bonding, thus leading to strong cohesive internal interactions, as illustrated in Figure 1a. The lyophilized coacervates of FA–bPBI- $X$  under scanning electron microscopy (SEM) were an interconnected 3D porous network (Figures 2e and S7), which was caused by the loss of water during the freeze drying procedure. Notably, quantitative measurements indicate that the FA–bPEI-9 coacervate has the strongest adhesion ability among the three adhesives (Figure S8). At pH 9, the FA is partially dissociated, and the ratio of FA to folate is



**Figure 4.** (a) SEM images of the glued area. (b) “Interlock Model”. (c,d) FT-IR spectra of the mixtures of FA–bPEI-9/lignin and FA–bPEI-9/cellulose. (e) Separation of wooden boards glued with the FA–bPEI-9 adhesive after being immersed in water for 3 days. (f) Adhesion strength of the pristine adhered wood substrates and the re-dried wood substrates from water-soaked detached wood.

close to 1:6 calculated based on the integral area ratios of the X-ray photoelectron spectroscopy (XPS) subpeaks (Figure S9). This means that hydrogen bonding between carboxylic acid and carboxylates might occur, providing desired internal cohesive force for the coacervate adhesive. With increasing pH to 10 and 11, the FA is almost completely converted into its sodium salt (Figure S9). Since b-PEI is neutral at all these pHs, the increased charges in the system may introduce repulsive forces, which is not advantageous for effective cohesive forces. Gravimetric analysis reveals that the water content in the fresh coacervate FA–bPEI-9, FA–bPEI-10, and FA–bPEI-11 is 52.5, 54.8, and 59.6%, respectively. Thus, the increased ionic degree in the coacervate has increased the content of water, which causes a dilution of the entanglement. This will inevitably lower the modulus and result in a poor adhesion. For this reason, the freshly prepared FA–bPEI-9 adhesive was chosen for further study. In addition, the thermogravimetric analysis (TGA) curve in Figure S10 indicates that all the supramolecular composite materials display good thermal stability with a degradation temperature of around 285 °C.

Next, the adhesive ability of the FA–bPEI-9 coacervate was systematically examined. As illustrated in Figure 3a, the bulk adhesive could readily adhere to different substrates, such as plastics, wood, steel, Teflon [polytetrafluoroethylene (PTFE)], ceramics, and glass, indicating that the coacervate-based adhesive has a substantially broad application in various

substrates. Figure 3b shows the shear adhesion strength for different plates adhered by the FA–bPEI-9 coacervates. After curing for 4 h under air conditions, the adhesion strengths for copper, glass, PE, PTFE, and wood were 121.7, 559.1, 62.1, 22.2, and 1510 kPa, respectively. Overall, tough adhesion could be seen on hydrophilic surfaces, while the adhesion effect of coacervates on hydrophobic substrates with low surface energy is relatively weak. Compared with the copper substrate, we assume that the higher adhesion strength of glass comes from the high-density H-bonds. Moreover, the PTFE surface is more hydrophobic than that of PE, thus leading to the weakest adhesion strength. Clearly, the coacervate displays the strongest adhesion toward wood. Typically, to establish the maximum adhesion strength, the adhesive needs to penetrate the surface boundary layers, spread, and develop intimate interfacial contacts with the substrates’ surfaces and thereafter cure and set within a reasonable period of contact time.<sup>7,44</sup> As a result, it was found that the adhesion strength on wood amounts to 3.68 MPa after curing for 7 h and levels off for further prolongation of the curing time. This long term of curing is due to the slow evaporation of water from the small gaps between the two wood plates.<sup>45</sup> Control experiments revealed that a firm adhesion strength of around 3.6 MPa can be achieved within 1 h under heating or N<sub>2</sub> blowing to accelerate the curing process (Figure S11). This adhesion is so strong that the two pieces of the adhered wood would not be

separated under a large shear force that would break the wood itself (Figure 3c), suggesting that the dry adhesive strength was higher than the intrinsic strength of the wood. Figure 1b shows that for a glue area of 2.7 cm × 3.0 cm, the adhered slices of wood are able to easily support a load of 50 kg after curing for 12 h, showing the excellent macroscopic adhesive behavior of FA–bPEI-9 coacervates (Movie S1). This adhesion is long-lasting. The adhered wood substrates are still able to hold weights up to 50 kg after storage for 180 days. As shown in Figure 3d, the adhesion strength can also be demonstrated with a bridge constructed by adhering three pieces of wooden boards through two joints (each joint has an area of 2 cm × 5 cm). Figure 3e,f shows that the wooden bridge can withstand a total weight of 55.45 kg. Figure 3g shows the comparison of the adhesion strengths of several robust commercial adhesives versus our FA–bPEI-9 wood adhesive, which were measured with exactly the same procedures. The results revealed that the FA–bPEI-based waterborne adhesive displays the best adhesion property, indicating that it is very attractive in practical applications to replace the formaldehyde-based wood adhesives.

In order to unravel the reason for the excellent adhesive ability of the FA–bPEI-9 coacervate toward wood substrates, SEM and FT-IR measurements were conducted. It is well known that wood is a hygroscopic material, and the hydrophilic surface of wood is very coarse, with its internal structure full of pores of 20–30 μm (Figures 4a and S12). As the flowable coacervate FA–bPEI-9 adhesive is applied, it would fill in the concave and coat on the convex wood surface to form an “interlock”,<sup>46</sup> as illustrated in Figure 4b. Furthermore, the waterborne adhesive can easily penetrate into the microstructure of the wood.<sup>47</sup> As such, more mechanical interlock joints (red arrows in Figure 4a) would be produced, which is beneficial for a strong adhesion.<sup>11</sup> Considering that the major components for wood are cellulose and lignin,<sup>43</sup> in vivo FT-IR measurements were further carried out to study the interaction between the adhesive and woods. Figure 4c,d shows the FT-IR spectra for the complexes of FA–bPEI-9/cellulose and FA–bPEI-9/lignin, respectively. The wavenumber of the N–H bending vibration is red-shifted in both systems, indicating that H-bonding has occurred between FA–bPEI-9 and cellulose and FA–bPEI-9 and lignin. Additionally, the hydroxyl group of lignin has shifted from 3403 to 3190 cm<sup>-1</sup> (Figure S13), indicating the weakened vibrational energy of the O–H bonding. Renneckar and Zhou reported that hydrogen bonds may form between wood and b-PEI, leading to physical adsorption of b-PEI to the surface of wood. The adsorption was maximized under basic pH when the b-PEI molecule is neutral.<sup>43</sup> Therefore, we anticipate that the superstrong wood adhesive ability of FA–bPEI-9 should be attributed to a sequence of steps: polymer adsorption, penetration of the waterborne adhesive, mechanical interlocking, and formation of hydrogen bonds between the FA–bPEI-9 coacervate and active sites on the wood surface such as hydroxyl groups.

The water resistance of wood composites is a crucial parameter to evaluate an adhesive application performance. As shown in Figure 4e, the glued wooden plate (thickness of 6 mm) cannot be separated until after being immersed in water for 3 days, while the on-demand separation of the adherends is an important character of supramolecular adhesives.<sup>48</sup> It should also be noted that water-soaked detached wet wood products could be re-adhered simply under mild mechanical

pressing under ambient conditions, and the adhesion strength of the re-dried woods nearly returns to its initial value, as shown in Figure 4f, different from the heat-initiated curing process for the epoxy resin-based adhesive, which is generally incapable of reversible adhesion upon being detached. Finally, since both FA and b-PEI have been recognized to be biocompatible and can be easily obtained with mature synthetic chemistry, the current adhesive can be easily scaled up, which would open up a new paradigm in developing environmentally friendly wood adhesives.

## CONCLUSIONS

In conclusion, we developed a new type of non-catechol-based waterborne adhesive via complex coacervation of FA with b-PEI polycation. FA is induced to form quartets after complexing with b-PEI in the coacervate, which further undergo  $\pi$ – $\pi$  stacking and crosslink the b-PEI chains into a more robust network. The multiple hydrogen bonds between the COO<sup>-</sup> of FA quartets and the amide groups on the b-PEI are crucial for this crosslinking and provide strong internal cohesive interactions in the adhesive. The maximum adhesion strength can be 3.68 MPa shear strength on wood substrates when curing at room temperature, greater than that of commercial formaldehyde-based wood adhesives, but without releasing any toxic components. Since FA is not easy to be oxidized, the adhesion is long-lasting under ambient conditions, paving the way for obtaining novel formaldehyde-free wood adhesives.

## EXPERIMENTAL SECTION

**Materials.** FA hydrate (>98.0%) was purchased from Tokyo Chemical Industry Co., Ltd. b-PEI (30 wt % in water,  $M_w = 100,000$ ) was obtained commercially from Beijing Hwrk Chemical Co., Ltd and used without further purification. Wood substrates (*Paulownia fortunei* (seem.)Hemsl) are used in this study with a thickness of 1 and 6 mm. Sodium hydroxide (NaOH) was purchased from Xilong Chemicals with a purity of above 99.0%. All the abovementioned chemicals were used as received. Water used in all experiments was purified using a Milli-Q Advantage A10 ultrapure water system.

**Preparation of the Bulk Wet Adhesive.** The solubility of FA in water is very poor (1.6 mg L<sup>-1</sup> at 25 °C) due to intramolecular hydrogen bonding, but it dissolves easily on addition of NaOH. First, a FA solution at 0.025 Mol/L with pH values from 9.0 to 11.0 was prepared and adjusted with a few drops of concentrated NaOH. Then, the b-PEI solution (0.012 g/mL) was prepared. When mixing the two FA-X (X = 9, 10, and 11) and b-PEI solutions (1:1 v/v) with shaking, a bright-yellow coacervate occurred instantly and was applied directly.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsabm.1c00825>.

Sample preparation; experimental titration data of b-PEI; FT-IR spectroscopy of FA, b-PEI, and the FA–bPEI-X adhesive sample; XRD patterns of the FA–bPEI-X samples; WAXS profile of the FA–bPEI-9 sample; FT-MS of the prepared samples; SEM images of the freeze-dried FA–bPEI-10 and FA–bPEI-11 samples; effect of pH on the adhesion strength of FA–bPEI-X coacervates on the copper surface; high-resolution XPS spectra (O 1s) of FA at pH = 9 and pH = 10; TGA curve of the samples; adhesion strength of the FA–bPEI-9 adhesive on the wood surface measured under different curing conditions; SEM images of the wood

surface and the adhesion interface between the adhesive and wood; and FT-IR spectra of the mixtures of b-PEI/lignin (PDF)

Adhered slices of wood easily supporting a load of 50 kg (MP4)

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### Notes

The authors declare no competing financial interest.

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