Supplementary Information

High strength, self-activating and fast adhesion of polyurethane adhesives based on rosin structure in different environments

Rui Yang [1], Li Tan [2], Zheng Pan [2], Linfeng Tian [2], Tianchen Zhang [2], Baozheng Zhao [2], Fei Song [2], Yonghong Zhou [1, 2], Meng Zhang [1,2*]*

[1]College of Chemical Engineering, Nanjing Forestry University, Jiangsu Province, Nanjing 210037, PR China.

[2]Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry (CAF), Key Lab. of Biomass Energy and Material, Jiangsu Province, Nanjing 210042, PR China.

*Correspondence author: Fei Song (18770044853@163.com) and Meng Zhang (zhangmeng@icifp.cn)

1. Characterization and Measurements

1.1 Characterization Methods

FT-IR spectra of the DAP were measured on a Nicolet iS50 FT-IR spectrometer (Madison, WI, USA), with a wavenumber range of 4000-500 cm^{-1} and a resolution of 4 cm^{-1}. ^{1}H NMR spectra were carried out on a Bruker ARX 300 Wave Spectrometer (Bruker Instrument Crop, Germany) with deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal standard. The Differential Scanning Calorimetry (DSC) was conducted using a DSC8000 (PerkinElmer) at a heating of 20 °C/min from -70°C to 120°C. Small Angle X-ray Scattering (SASX) test was carried out on polymer films with a thickness of 1 mm and a sample-to-detector distance of 400 mm on a model Xeuss 3.0 instrument. Rheological properties of the adhesive were characterized by a rheometer (MARS60) with a parallel plate at 25°C. An oscillatory frequency sweep of the samples was carried out over the frequency range of 0.1 to 100 rad/s with a strain amplitude fixed at 1%. The contact angle of water was taken by an optical instrument goniometer (DSA-100, Kruss) at room temperature, with a drop of 5 μL and readings were taken and photographed after the test drop was stabilized.

1.2 Dry/Underwater adhesion 180° peel test

The peel strength of the adhesive was measured by a universal testing machine (The UTM6503, Shenzhen Sansi Zongheng Company) at a peel speed of 100 mm/min at room temperature. The tests were performed according to the national standard GB/T 2790-1995. The adhesive was first placed on a Kapton film and hot pressed for 30 min at 50°C under a pressure of 10 MPa in a flatbed vulcanizing machine. The Kapton film with the adhesive was adhered onto the substrates in the test environment (dry/underwater) over an area of 25 mm × 100 mm. The adhered samples were allowed to stand in the test environment (dry/underwater) for 1 h before testing. The adhesion strengths of the samples were measured under similar conditions in a variety of harsh environments (1 M NaCl, pH 5, and Seawater). Finally, the end of the Kapton film was pulled back at 180°, mounted in the universal testing machine, and pulled at 100 mm/min. The 180° peel test procedure is shown in Figure S1 (a). The peel tests were

repeated five times, and the results were averaged. To compare the adhesive strength, a range of different substrates (stainless steel, aluminum sheet, PMMA, and glass) with dimensions of 80 mm × 25 mm × 2 mm were used. Before the test, the substrates were sonicated in ethanol and deionized water for 10 min, respectively, and then dried in an oven at 50°C.

1.3 Dry/Underwater lap-shear adhesion test

Lap-shear strength of the adhesive was measured by a universal testing machine (The UTM6503, Shenzhen Sansi Zongheng Company) at 100 mm/min at room temperature. The tests were performed according to the national standard GB/T7124-2008. Before preparing lap-shear test samples, all of the substrates (stainless steel, aluminum sheet, PMMA, and glass) were sonicated in ethanol and deionized water for 10 min, respectively, and then dried in an oven at 50°C. The lap-shear test procedure is shown in Figure S1(b). The adhesive was placed between two substrates with an overlap area of 15 mm × 25 mm and left in the test environment (dry/underwater) for 1 h. The shear adhesion strengths of the samples in various harsh environments (1 M NaCl, pH 5, and Seawater) were measured under similar conditions. Finally, the overlap shear test was performed using a universal testing machine at 25°C at a tensile speed of 100 mm/min. The experiments were repeated five times and the results were averaged.

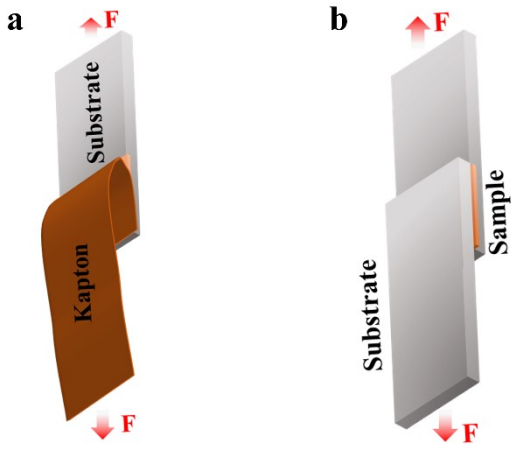


Figure S1. (a) Schematic diagram of 180° peeling test for adhesion. (b) Schematic diagram of lap-shear test for adhesion.

1.4 Theoretical Simulations

1.4.1 Density Functional Theory Simulation

The Density Functional Theory (DFT) was used to simulate the adsorption of DAP-PU fragments on iron and glass surfaces, respectively. SiO_2 molecules were used instead on the glass surface. In this work, all calculations were carried out through the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) functional with the generalized gradient approximation (GGA) method was used to do with the exchange-correlation functional, in combination with the DFT-D3 correction. The cut-off energy of the plane-wave basis is set at 500 eV. A thickness of 30 Å of vacuum was added for all surface models. In the calculations, we have used the Brillouin zone integration with 1*1*1 Gamma-center point sampling. The self-consistent calculations apply a convergence energy threshold of 10-5 eV, and the equilibrium geometries are optimized with maximum stress on each atom within 0.05 eV/Å. Coulombic interaction (DFT+U) for Fe with a U-J value is set as 4.3 eV. For the adsorption reaction of molecules, the energy is calculated through the following equations:

Formula 1: $E_{ad} = E_{sur+adsorbate} - E_{sur} - E_{adsorbate}$

Where $E_{sur+adsorbate}$ is the total energy of adsorption model, E_{sur} is the total energy of surface and $E_{adsorbate}$ is the total energy of adsorbate.

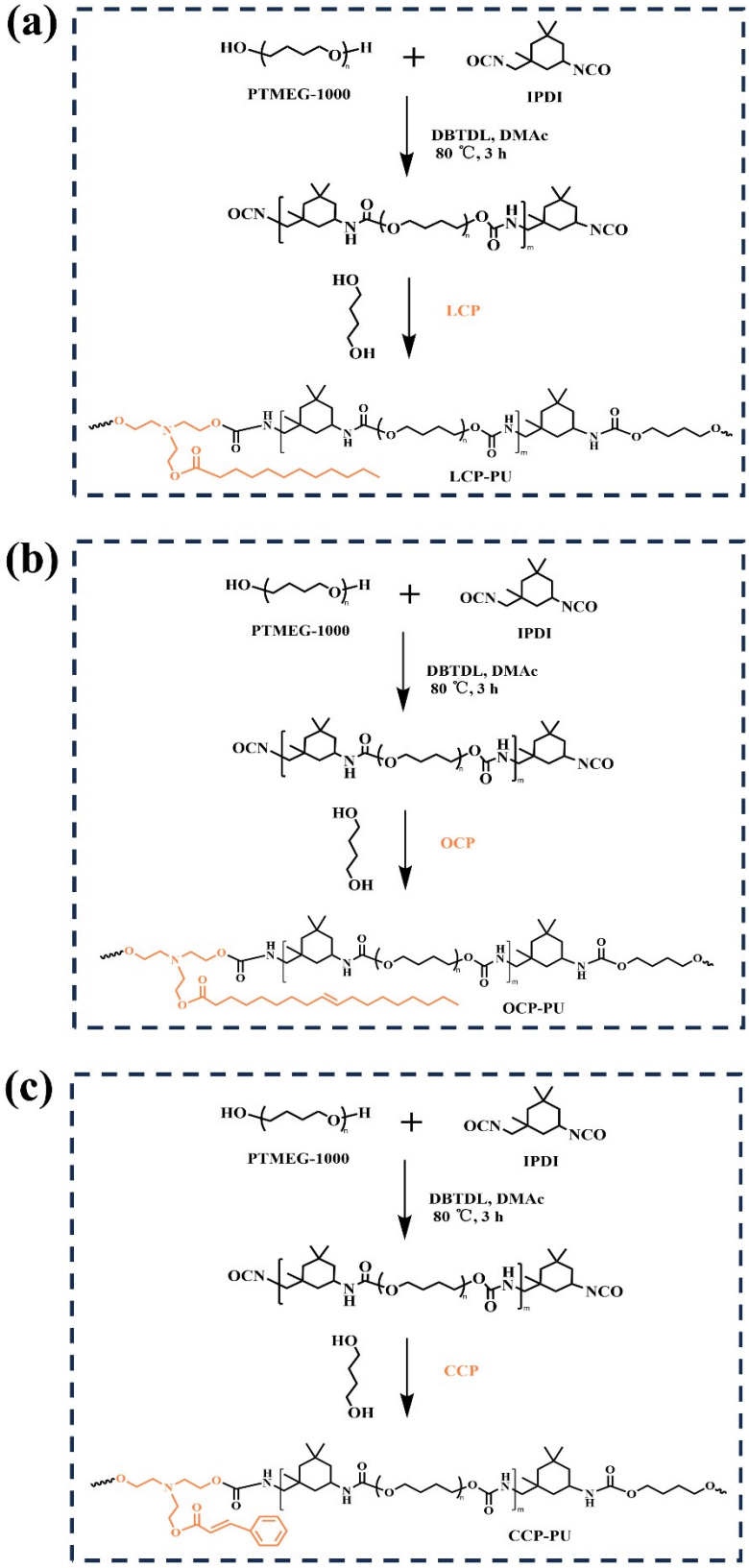
1.4.2 Molecular Dynamics Simulation

To study the underwater adhesion mechanism of polymer, the interaction between DAP-PU and stainless steel or glass substrates can be calculated by the following Formula 2 for molecular dynamics simulation. Materials Studio software was utilized to construct the molecular models. DAP-PU was chosen as the simulation object to construct a molecular chain of DAP: PTMEG-1000: BDO as 8:9:3, and the polymer consisted of two chains. Stainless steel was replaced by using iron atoms and glass by using SiO_2 molecules. Each system contains 200 water molecules. The lowest energy model of DAP-PU was constructed on two different substrates, respectively. The

optimized potential of the condensed phase is used in the Atomic Simulation Study (COMPASS II) force field. The COMPASS II force field is usually used to provide atomic interactions. Then, the Ewald method and the atom-based method were used to analyze the Coulomb interaction and Van der Waals (VDW) interaction between the polymer and the substrate. A geometry optimization using smart method with an energy convergence criterion of 1.0×10^{-3} kcal·mol $^{-1}$ and force convergence criteria of 0.5 kcal·mol $^{-1}$ ·Å $^{-1}$ was used to get a global minimum energy configuration. To equilibrate the model, a equilibrate process was followed under constant temperature and constant volume (NVT ensemble) at 298 K for 500 ps. During the simulation, the temperature control was performed using Nose. The interaction between the adhesive and the iron or glass substrate was calculated by the following equation:

Formula 2: $E_{interfacial} = E_{total} - E_{adhesive} - E_{substrate}$

Here, where $E_{interfacial}$ denotes the interaction energy between the adhesive and the surface; $E_{adhesive}$ and $E_{substrate}$ are the potential energies of the adhesive and the iron or glass surface, respectively, and E_{total} represents the total potential energy of the model system. The larger the negative E_{total}, the stronger the interaction.



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111 Figure S2. Synthesis routes of LCP-PU, OCP-PU, and CCP-PU.

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Table S1. Feeding rations of xDAP-PU adhesion.

Samples	PTMEG-1000 (mol)	BDO (mol)	DAP (mol)	IPDI (mol)
0.3DAP-PU	0.55	0.15	0.3	1.1
0.4DAP-PU	0.45	0.15	0.4	1.1
0.5DAP-PU	0.35	0.15	0.5	1.1

Table S2. Feeding rations of LCP-PU, OCP-PU, and CCP-PU adhesion.

Sample	PTMEG-1000 (mol)	BDO (mol)	Polyol (mol)	IPDI (mol)
LCP-PU	0.45	0. 15	0.4 LCP	1.1
OCP-PU	0.45	0.15	0.4 OCP	1.1
CCP-PU	0.45	0.15	0.4 CCP	1.1

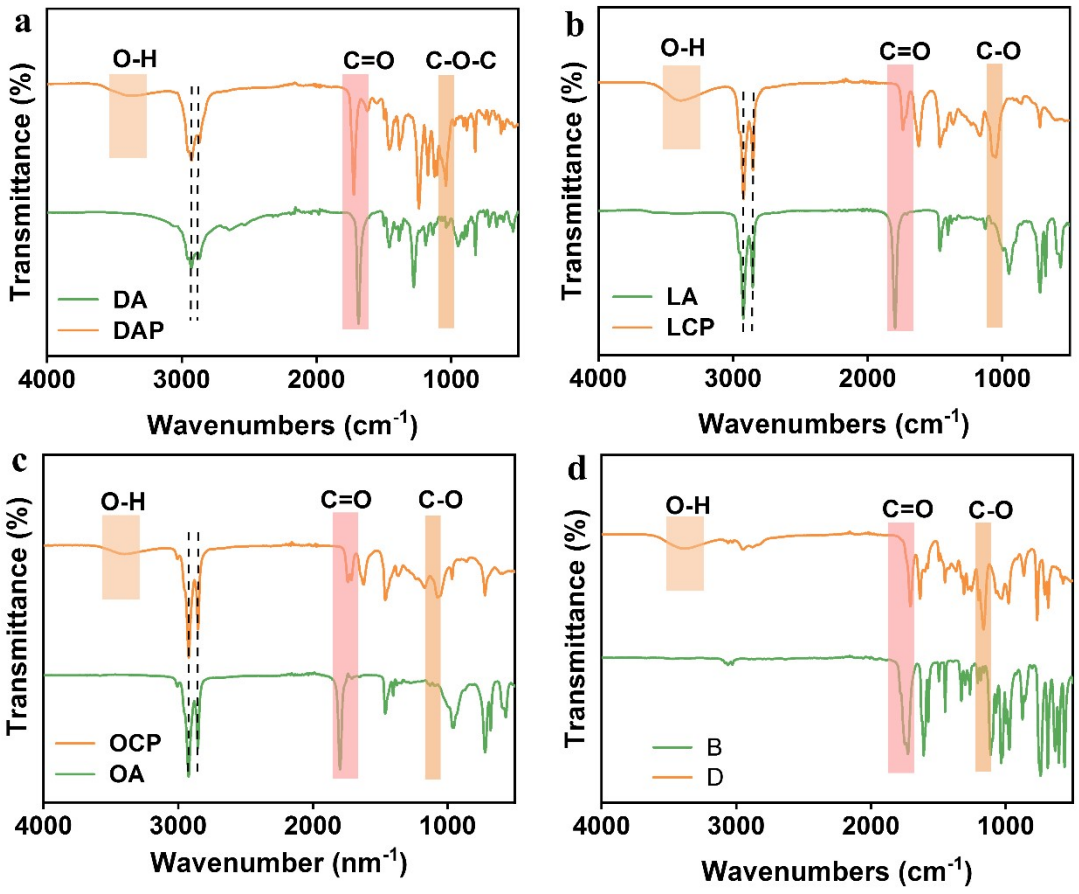
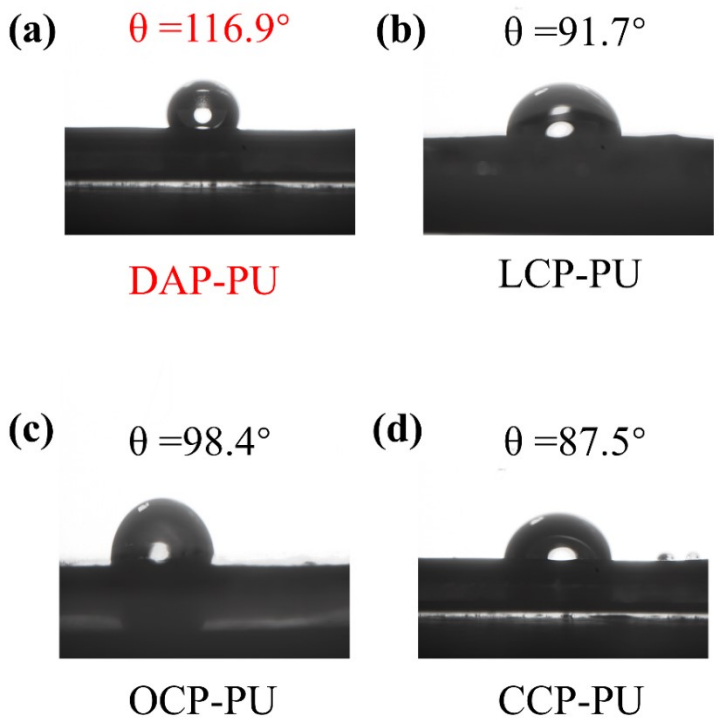


Figure S3. (a) FT-IR spectra of the DA and the DAP. (b) FT-IR spectra of the LA and the LAP. (c) FT-IR spectra of the OA and the OAP. (d) FT-IR spectra of the CA and the CA.



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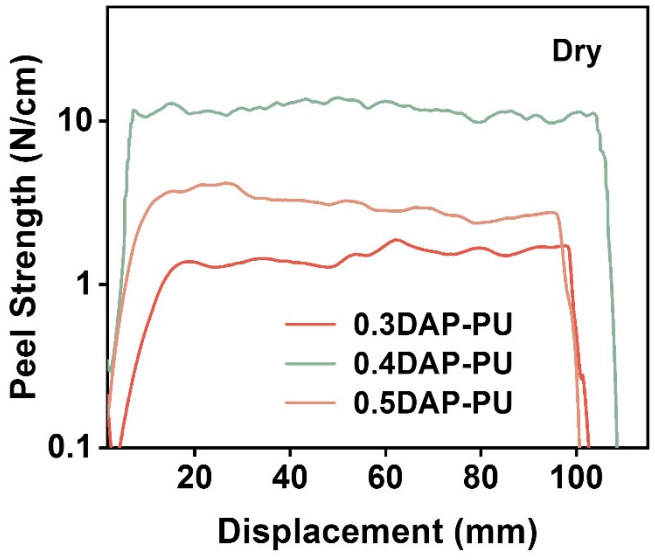
121 Figure S4. Water contact angle images of (a) DAP-PU, (b) LCP-PU, (c) OCP-PU, and (d) CCP-

122 PU.



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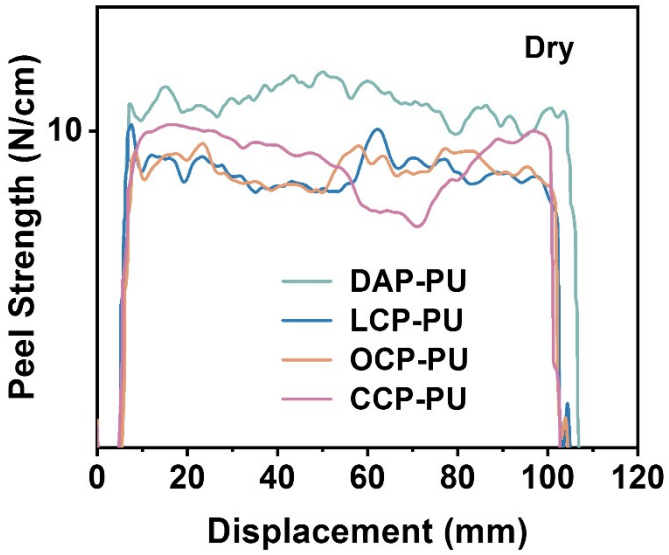
124 Figure S5. Dry 180° Peel test curves of 0.3DAP-PU, 0.4DAP-PU, and 0.5DAP-PU.



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126 Figure S6. Dry 180° Peel test curves of DAP-PU, LCP-PU, OCP-PU and CCP-PU.

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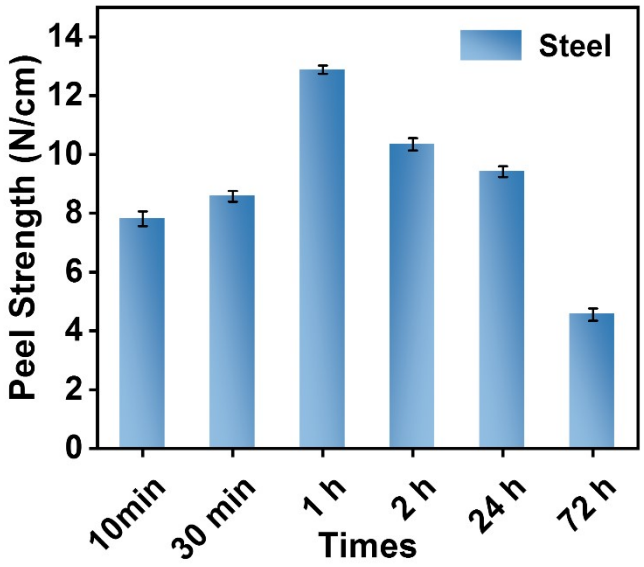

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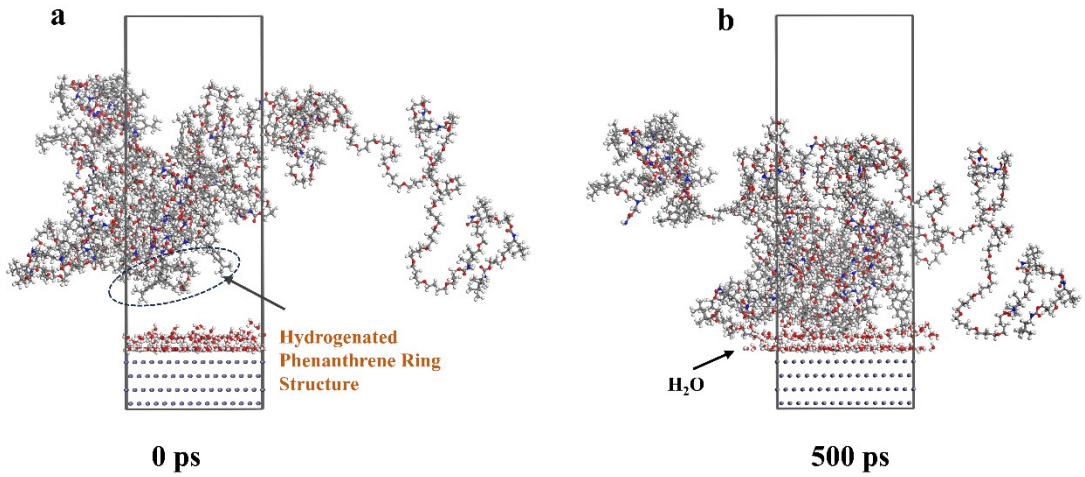
129 Figure S7. Underwater 180° peel test curves of DAP-PU on stainless steel substrate at different

130 times.



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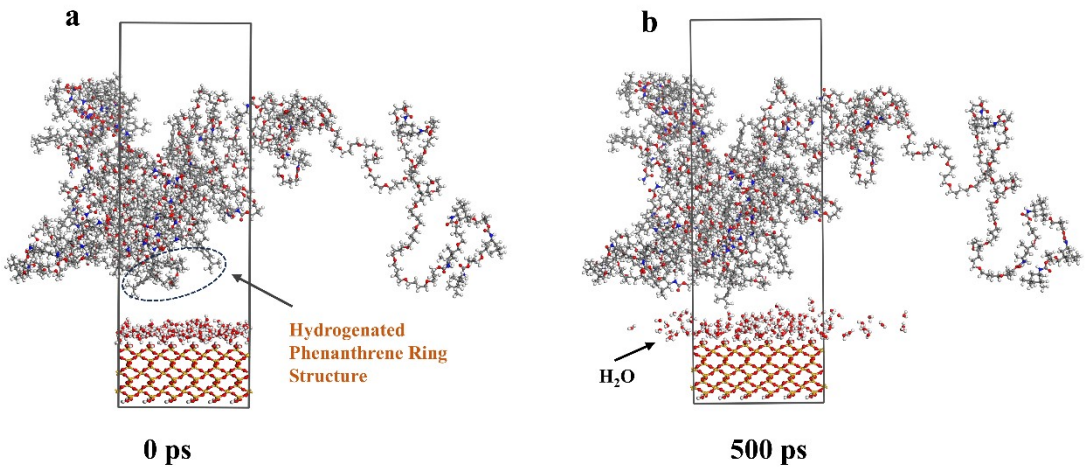
132 Figure S8. Conformational diagram of the DAP-PU layer on the iron surface with simulation time

133 in the presence of water.



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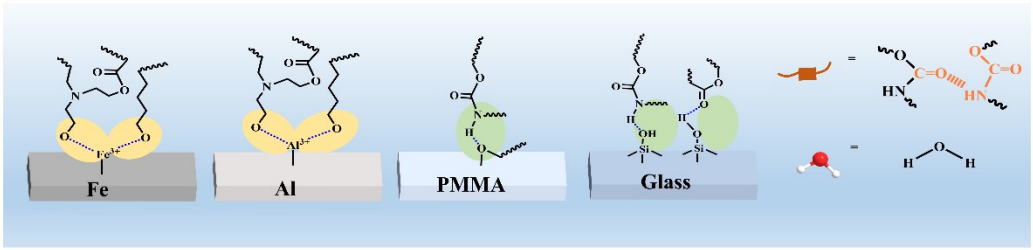
135 Figure S9. Conformational diagram of the DAP-PU layer on the glass (SiO_2) surface with simulation

136 time in the presence of water.



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138 Figure S10. The schematic diagram of the adhesion of DAP-PU on different substrates.

Video S1. DAP-PU adhesive's strong bonding ability to glass dish underwater。

Video S2. The bonded stainless steel plate can lifted with a weight of 50 kg and shaken several times without falling.

Video S3. DAP-PU adhesive immediately and repeatedly adheres to 200 g weights in underwater environments.