Supporting Information

A reversible underwater glue based on photo- and thermo-responsive dynamic covalent bonds

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1. General Information

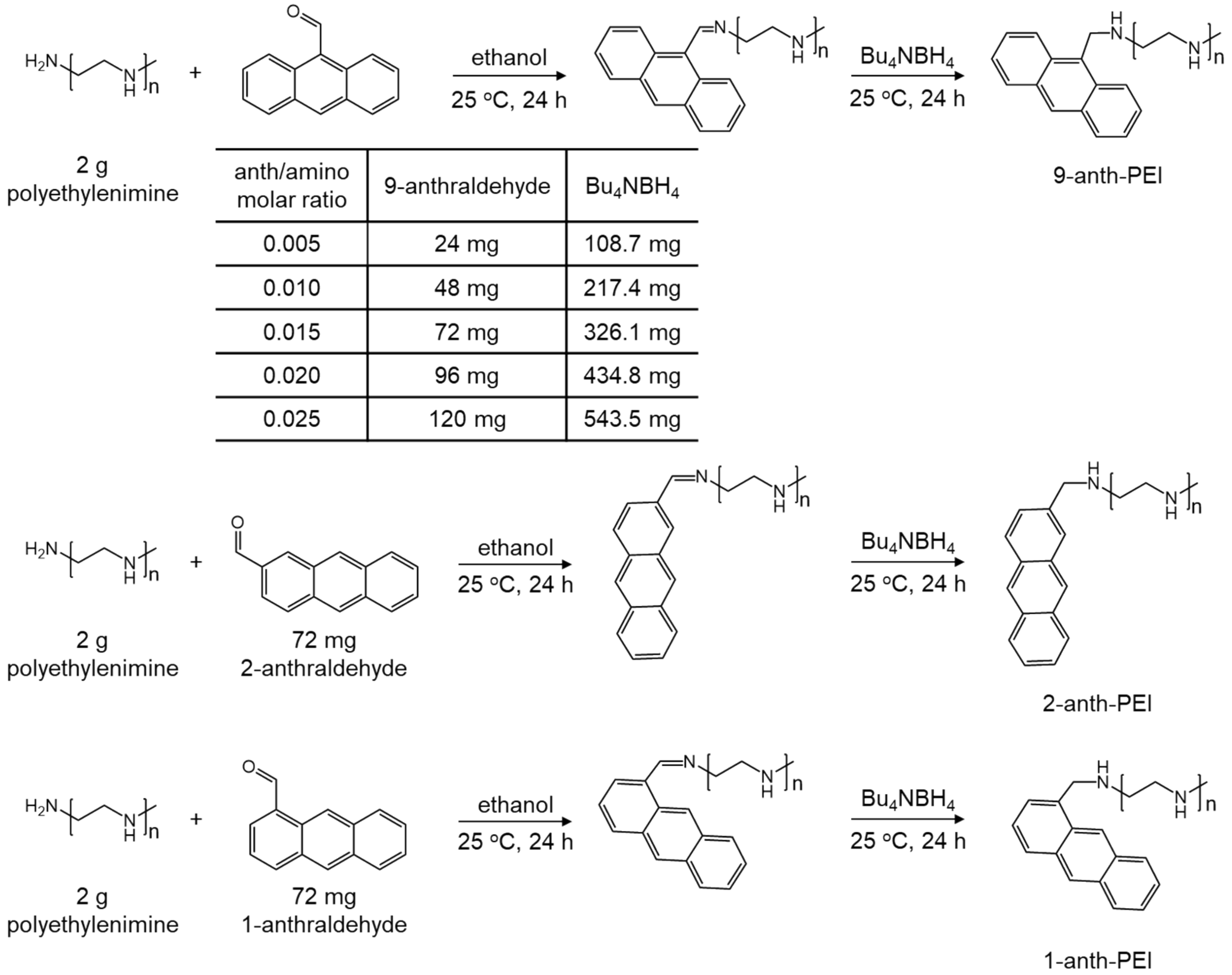
^1H NMR spectra were recorded on 400 MHz instruments (Bruker), and are internally referenced to residual portion solvent signals (for D_2O, referenced at 4.79 ppm[1]). UV-vis absorption spectra were recorded on a UV2600 spectrometer (Shimadzu). The sessile water droplet contact angle (CA) measurement was conducted using an OCA 20 system (DataPhysics) at ambient temperature. Scanning electron microscope images were obtained on a JSM-6701F field emission scanning electron microscope (FE-SEM) at 5 - 10 kV (JEOL). The macroscopic adhesion was measured using an M5-2 dynamometer (Mark-10 Corporation). The glue was imaged by a LSM710 confocal fluorescence microscopy (Zeiss). Zeta potentials of various modified substrate surfaces were measured by a zeta potential analyzer (Malvern). Rheological properties were measured on a physica MCR-301 rheometer (Anton Paar).

All reactions were carried out using oven-dried glassware. Poly(ethylenimine) solution (analytical standard, 50% (w/v) in H_2O, MW = 750 kDa) and tetrabutylammonium borohydride (98%) were purchased from Sigma-Aldrich. 9-Anthraldehyde (99%) was purchased from J&K scientific. 1-Anthraldehyde and 2-Anthraldehyde were prepared according to literature methods[2-4]. Commercially available solvents were used as received without further purification. Other chemical reagents were purchased from Acros, Energy Chemicals, J&K, Aladdin, and Alfa Aesar, and were used as received.

2. Synthesis of anth-PEI glues

In a 50-mL round-bottom flask equipped with a stirbar, polyethylenimine (2.00 g, 50% aqueous solution, containing ca. 23.3 mmol amino groups) was dissolved in ethanol (10 mL) at 25 ^{o}C in air. Then, 9-arthraldehyde (72.0 mg, 0.350 mmol, molar ratio of anthracenyl to amino groups = 0.015) was added. The flask was capped with a rubber septum, and the reaction mixture was stirred for 24 h at 25 ^{o}C before the addition of tetrabutylammonium borohydride (108 mg, 0.420 mmol). The resulting reaction mixture was stirred for another 24 h at 25 ^{o}C, and then concentrated using a rotary evaporator under reduced pressured to afford a light-yellow viscous liquid (approx. 1.43 g). The glue can be stored for at least one week at 4 ^{o}C in the absence of light.

Glues incorporating different anthracenyl/amino group ratios or using different regioisomers of anthraldehyde were prepared in analogy to the above procedure.



anth/amino molar ratio	9-anthraldehyde	Bu_4NBH_4
0.005	24 mg	108.7 mg
0.010	48 mg	217.4 mg
0.015	72 mg	326.1 mg
0.020	96 mg	434.8 mg
0.025	120 mg	543.5 mg

Fig. S1 Synthetic routes of anth-PEI glues of different anthracenyl incorporation ratios and anthracenyl regioisomers.

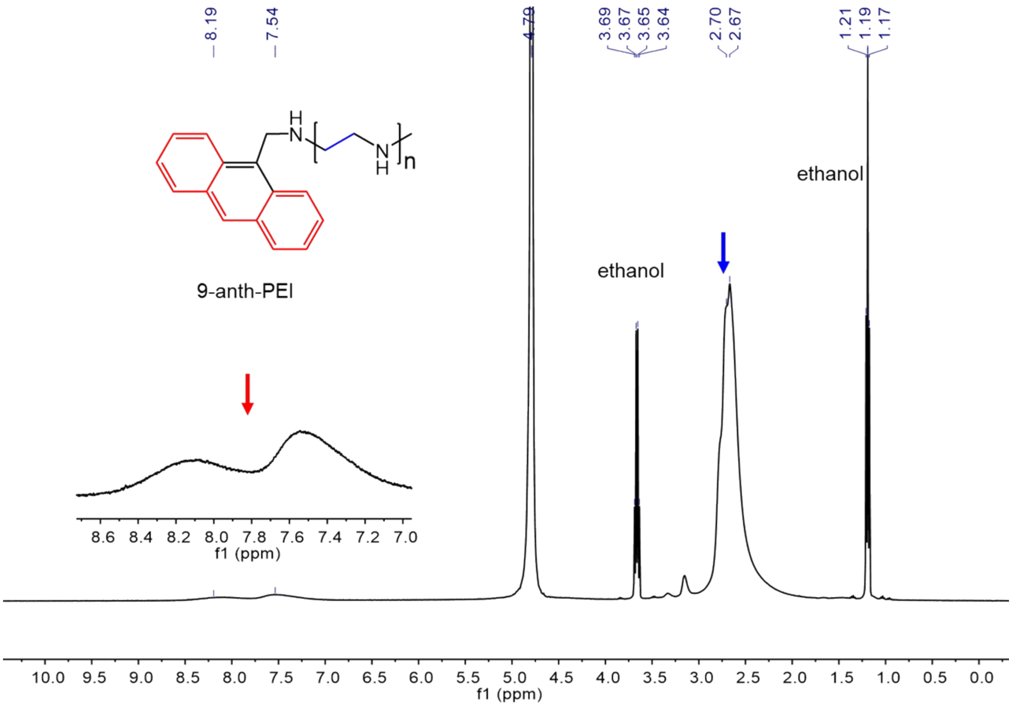


Fig. S2 ^{1}H NMR spectrum of the representative 9-anth-PEI glue. The peaks in the 7.0-8.6 ppm region are assigned to 9-anthracenyl and the peaks in the 2.0-3.0 ppm region are assigned to polyethylenimine, confirming the successful incorporation of 9-anthracenyl into polyethylenimine (It should be noted that the 9-anth-PEI glue sample was dialyzed in water for two days in the absence of light prior to NMR characterization). Compared to PEI proton peaks, the anthracene peaks appeared to be much broader because the anthracene groups would be aggregated by hydrophobic and pi-pi interactions in D$_2$O.

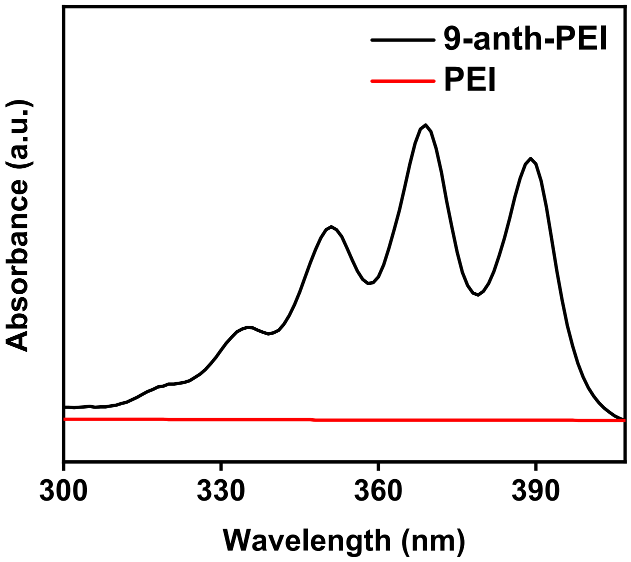


Fig. S3 The UV-Vis spectra of the representative 9-anth-PEI and PEI. The absorption bands at 335, 351, 369 and 389 nm are assigned to anthracene groups, further confirming the successful incorporation of anthracenyl moieties.

3. Tensile adhesion tests

Substrate plates (2 mm thick) were cut into dimensions of 2 cm × 1 cm, and then sonicated in acetone, ethanol, and water in sequence for 0.5 h. After that, the anth-PEI glue was applied to one submerged substrate plate and cross overlapped with another one, and then pressed with a preload for two minutes to prepare adhesion testing samples. These adhesion samples were directly irradiated by an LED blue light (Kessil® LED Light A160WE Tuna Blue) (I_s = 1.17 W/cm^2, $\lambda > 400$ nm) under water at 25 ^{o}C. Then the crosslinked adhesion samples were removed from water and measured immediately on a dynamometer with a crosshead speed of 20 mm/min. The maximum tensile force at joint failure divided by the overlap area provided the adhesion strength. At least 3 ~ 5 samples were measured and averaged data were reported. For measuring adhesion strength on different substrates, we used one piece of submerged quartz plate, and then pressing the quartz plate with another kind of substrate plate (metal, plastic, ceramic) with 10 kPa preload before irradiation. For measuring the adhesion strength after thermolysis, the crosslinked adhesion samples were sealed in a glass container under wet condition, and then placed in an oven. Finally, the adhesion strength was measured through the aforementioned methods.

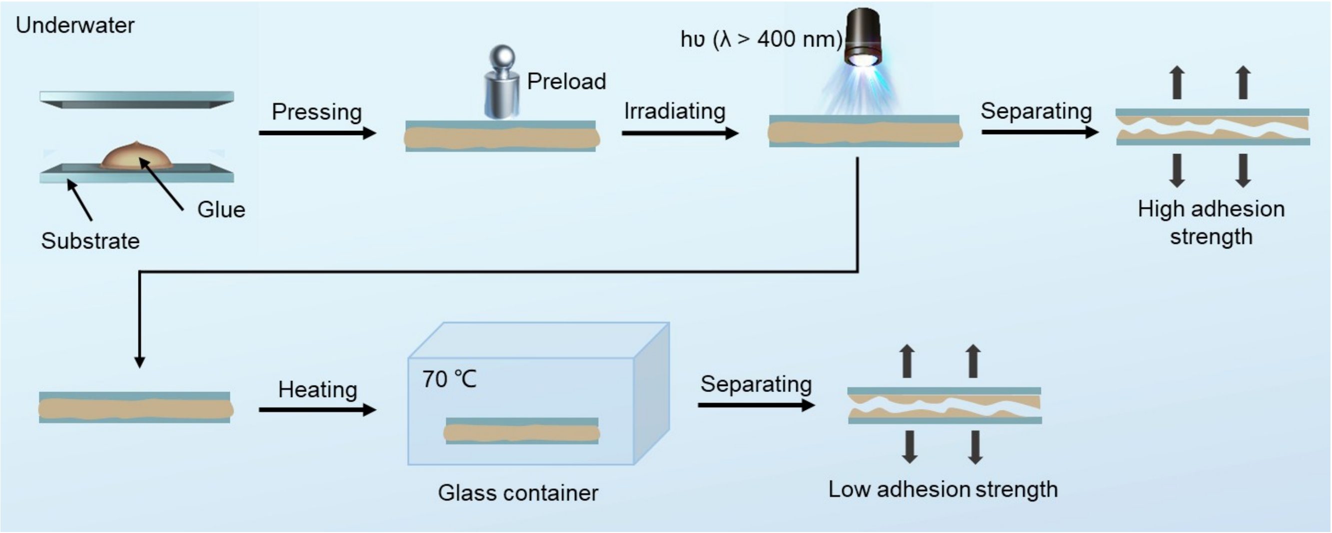


Fig. S4 The schematic process of testing sample preparation and adhesion strength measurements.

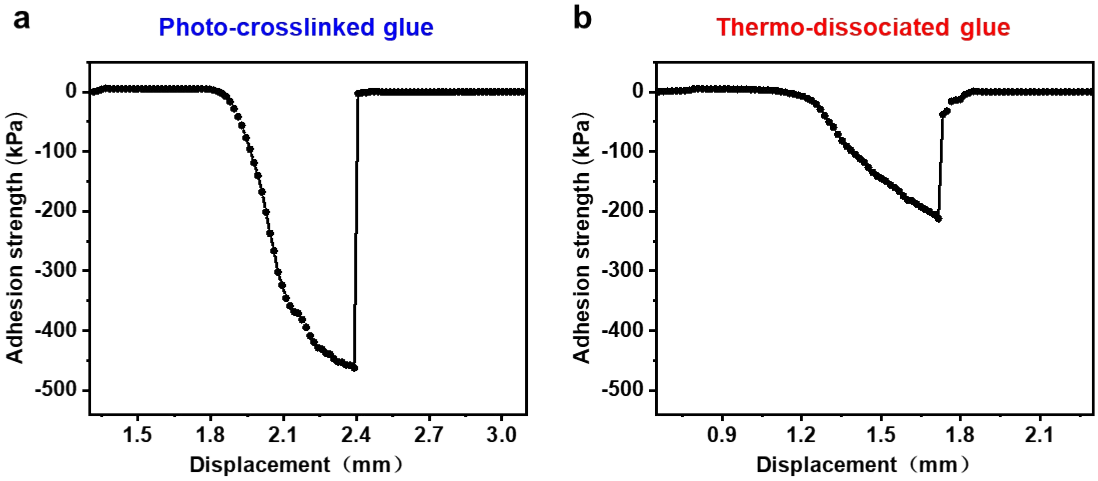


Fig. S5 The representative tensile measurement curves of the 9-anth-PEI glue with **a** high adhesion strength after irradiation for 1 min and **b** low adhesion strength after heating for 15 min at 70 °C.

4. Characterizations of the 9-anth-PEI glue

Time-dependent UV-Vis spectra of the 9-anth-PEI glue. UV-Vis spectra were employed to characterize the formation and dissociation process of dianthracene within the 9-anth-PEI glue under different irradiation time and thermolysis time. Anthracene characteristic absorption bands at 335, 351, 369 and 389 nm decreased with increasing irradiation time (Figure S6a). With regard to the thermolysis process, we observed the increase of free anthracene absorption profile between 330 and 400 nm within the crosslinked glue (under irradiation time of 1 min) with increasing thermolysis time (Figure S6b), indicating the successful thermolysis of anthracene dimers and regeneration of free anthracenyl groups. It can be seen only part of free anthracenyl groups can be regained because of some irreversible side reactions according to the increase of the absorbance profile between 290 and 310 nm. Therefore, the reversibility of the glue is mainly limited by the cleavage step (Figure S6c).

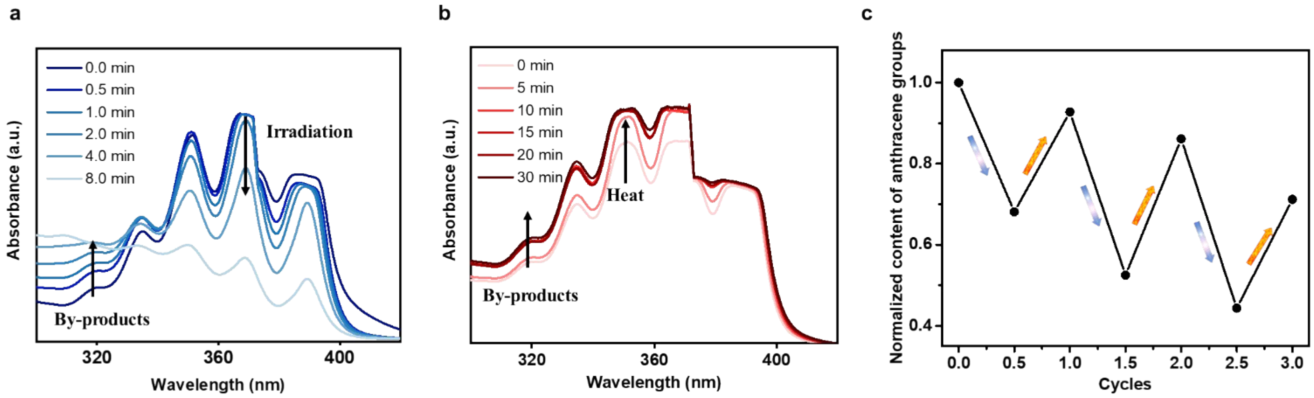


Fig. S6 Time-dependent UV-Vis spectra of dimerization and thermolysis process of the 9-anth-PEI glue under different conditions. **a** Anthracene absorption bands at 335, 351, 369 and 389 nm of the 9-anth-PEI glue decrease with increasing irradiation time. **b** Free anthracene absorption profile is increased within crosslinked glue after heating at 70 °C. **c** Remaining anthracene content in the 9-anth-PEI glue over repeatable cycles of visible light irradiation (1 min) and thermal dissociation (70 °C, 15 min). Anthracene content was estimated by calculating the area under the characteristic anthracene absorption bands between 340 and 400 nm.

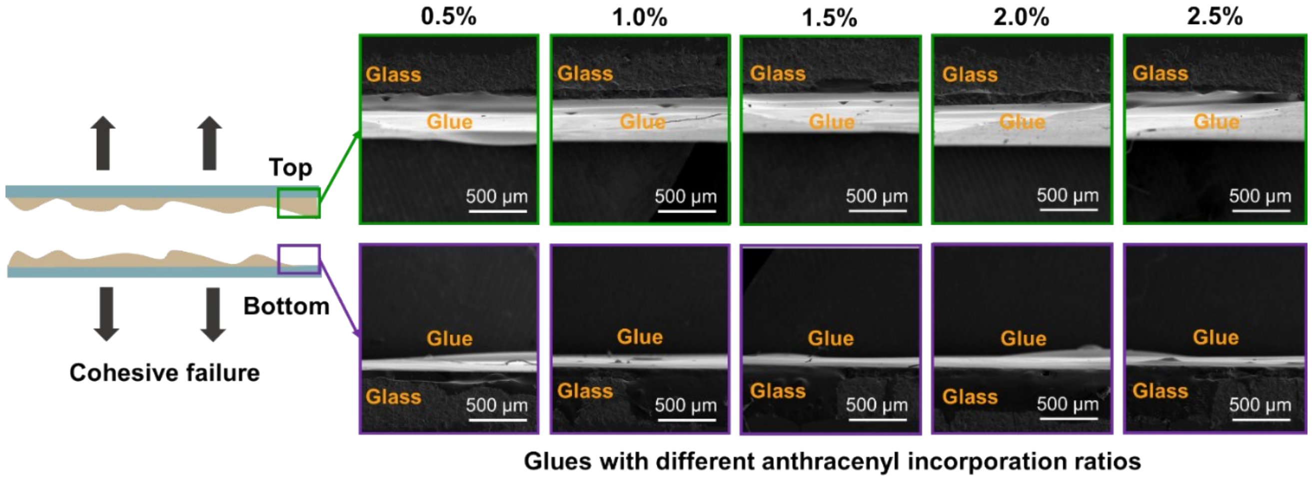


Fig. S7 The 9-anth-PEI glue with different anthracenyl incorporation ratios all fractured in bulk and maintained intact at the contact interface between the glue and substrate.

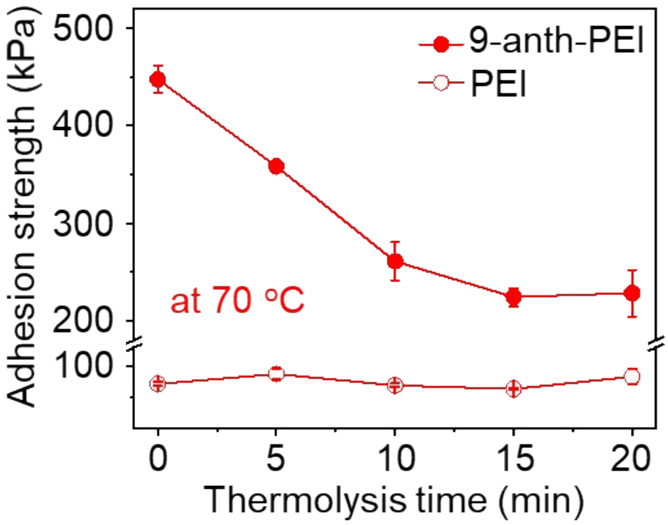


Fig. S8 Impact of thermolysis time on underwater adhesion strength. The adhesion strength of crosslinked 9-anth-PEI glue decreased with increasing thermolysis time and reached a minimum after heating for 15 min. While the adhesion strength of PEI showed little changed.

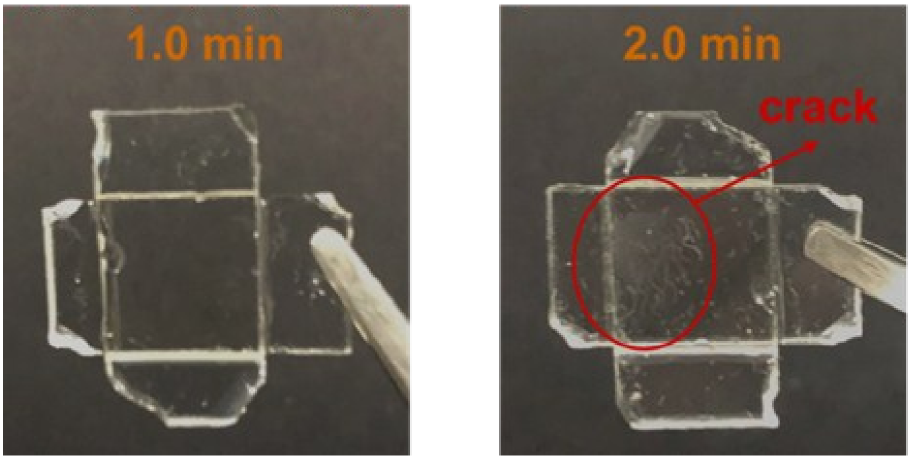


Fig. S9 Optical images of thermolytic 9-anth-PEI glue under different irradiation time. During the detachment process (70 °C for 15 min), some cracks appeared on the adhesion samples prepared under the irradiation time of 2 min. Therefore, we chose irradiation time of 1 min to achieve reversible underwater adhesion.

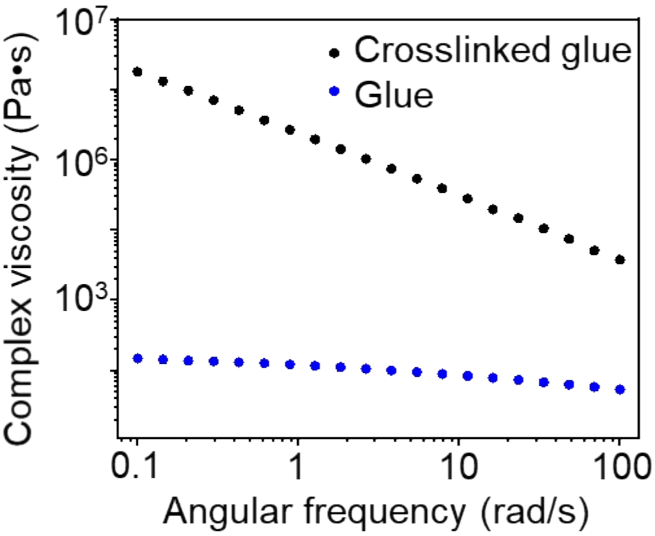


Fig. S10 Complex viscosity of 9-anth-PEI glue and crosslinked 9-anth-PEI glue. The viscosity of the crosslinked glue is higher than the glue without irradiation.

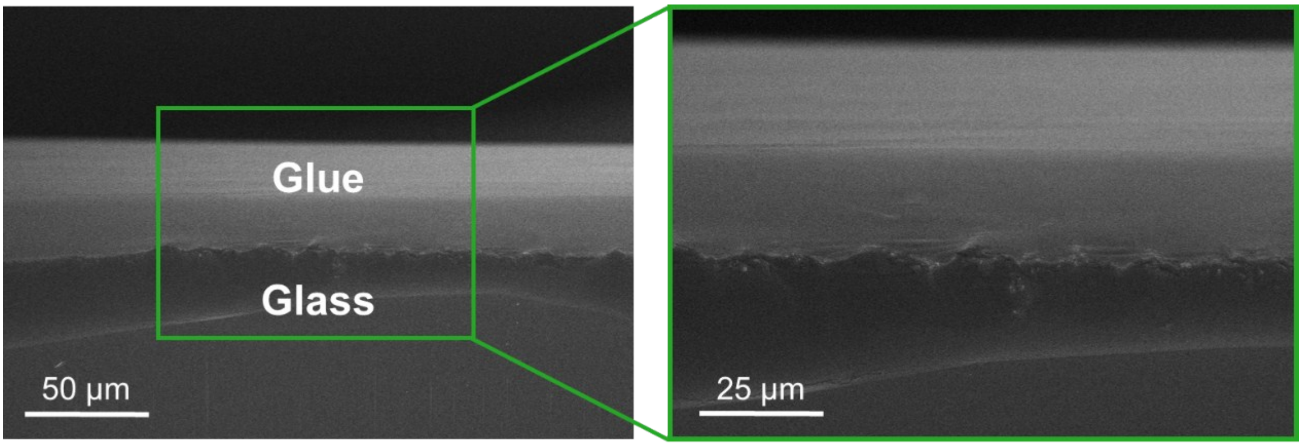


Fig. S11 SEM images of the 9-anth-PEI glue coated surfaces. The crosslinked 9-anth-PEI glue contacted the substrate surfaces closely to maximize interfacial adhesive area.

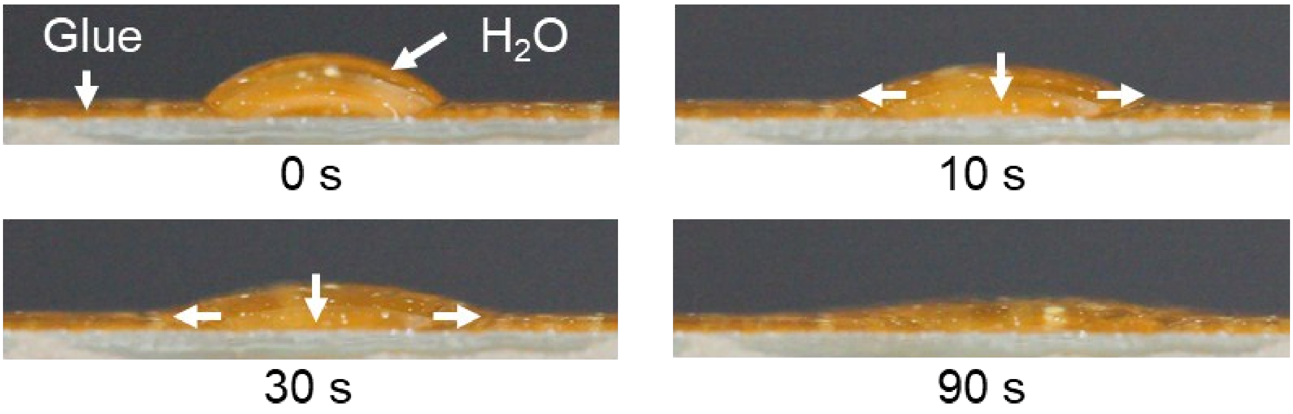


Fig. S12 The water absorption process of the 9-anth-PEI glue. A water droplet could be absorbed into a thin layer of glue-coating gradually.

5. Modifications of functional molecules on substrate surfaces

Surface charge and hydrophilicity could be tuned by chemically grafting functional molecules. Firstly, these quartz plates were sonicated in acetone, ethanol and water in sequence for 0.5 h, then treated with O_2 plasma for 300 s at 150 W. After that, $HCl/H_2O_2/H_2O$ (v/v/v = 1:1:4) mixture solution was used to treat these substrates for 30 min to obtain hydrophilic substrates (-OH). Hydrophobic (-F) substrates were obtained by subsequently silanizing hydrophilic substrates (-OH) with trimethoxy(1H,1H,2H,2H-heptadecafluorodecyl)silane evaporation in a decompression (≈ 0.2 atm) environment at 80 ^{o}C for 12 h. To get charged substrate surfaces, 4% (v/v) 3-mercaptopropyltriethoxysilane solution in ethanol was used to treat the hydrophilic substrates (-OH) for 12 h (25 ^{o}C) to get sulfydryl surfaces (-SH). After that, these substrates (-SH) were sequentially washed with ethanol and DMSO. Later, charged substrates could be readily prepared by further soaking these sulfydryl surfaces with different functional molecule solution for 12 h (25 ^{o}C), including acryloyloxyethyltrimethyl ammonium chloride (2 mM in 4:1 volume ratio of ethanol and triethylamine) for positively charges ($-NH_3^+$) and H_2O_2/CH_3COOH (v/v=1:1) for negatively charges ($-SO_3^-$). To obtain substrate surfaces with carboxyl groups (-COOH), 4% (v/v) 3-glycidoxypropyltrimethoxysilane solution in ethanol was used to treat the hydrophilic substrates (-OH) for 12 h (25 ^{o}C), then these substrates were treated with 3-mercaptopropionic acid (2 mM in 4:1 volume ratio of ethanol and triethylamine) for another 12 h (25 °C) to modify carboxyl (-COOH) groups for negative charges. Finally, these substrates were washed with phosphate buffer solution to remove excess functional molecules and stored in PBS solution for 30 min.

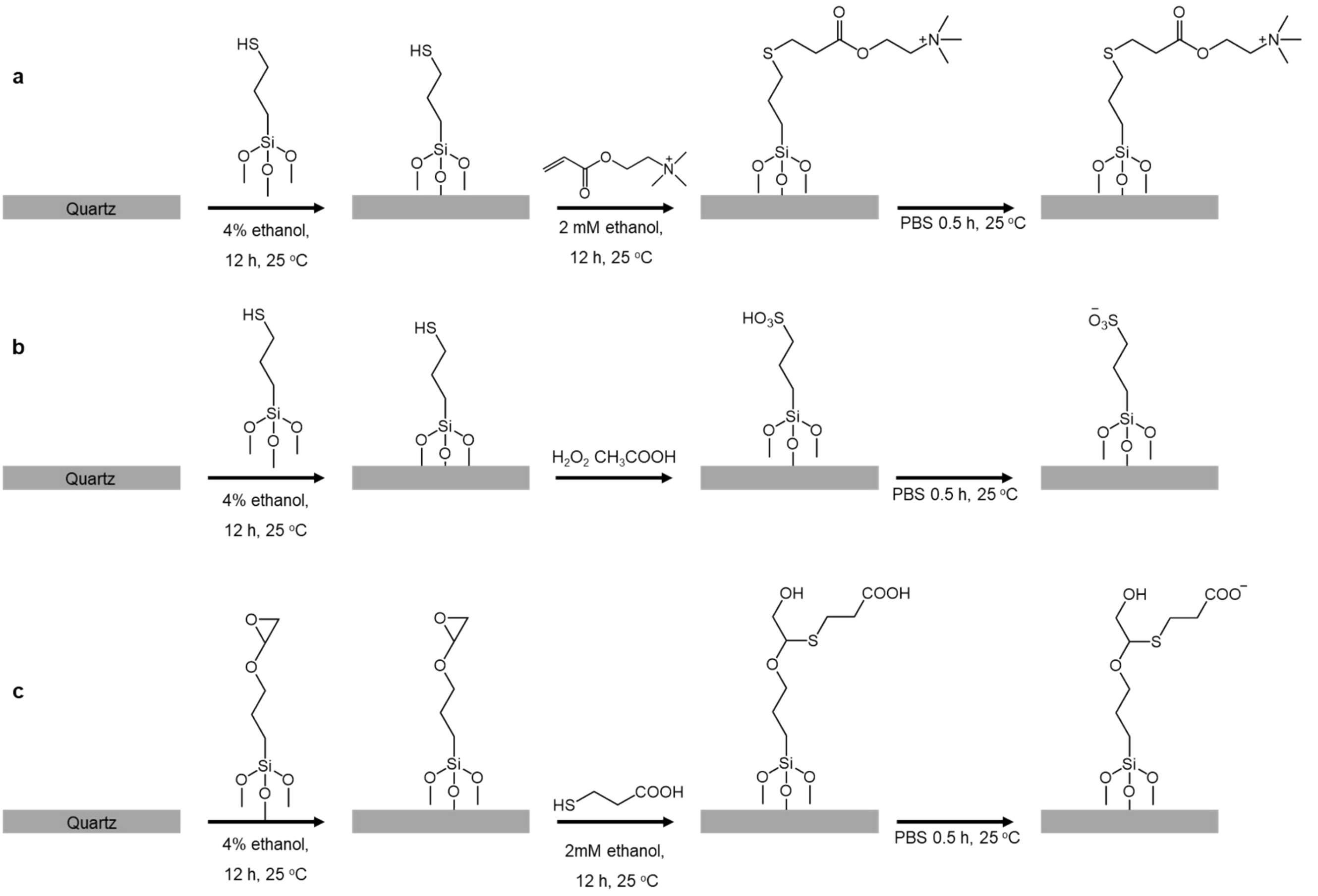


Fig. S13 The chemical modification process of quartz surfaces with different functional molecules, providing **a** positively or **b, c** negatively charged surfaces.

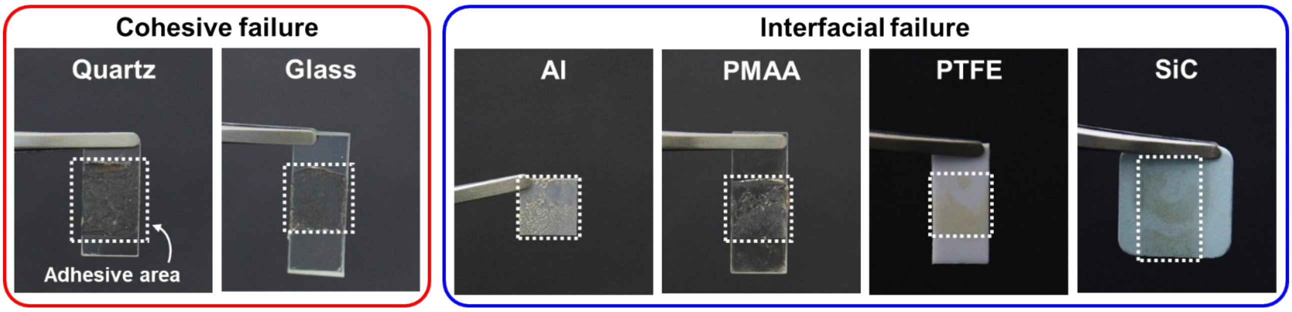


Fig. S14 The failure modes of the glue on different substrates. The cohesive failure occurred on quartz and glass surfaces, and interfacial failure appeared on aluminum, PMMA, PTFE and SiC surfaces.

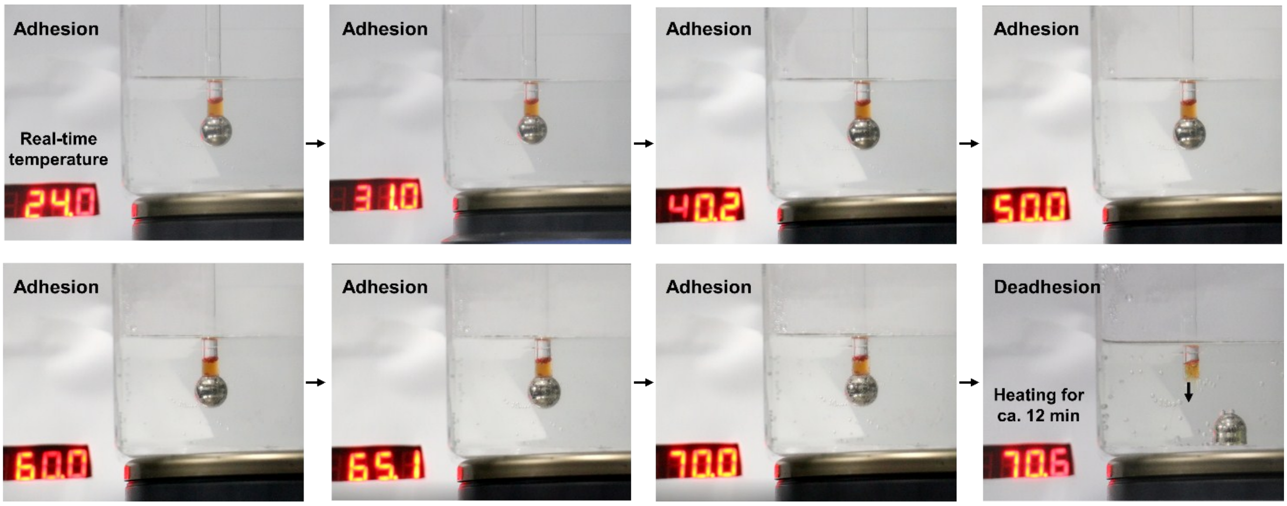


Fig. S15 The releasing process of a steel ball. When rising the temperature from 25 °C to 70 °C at a rate of around 5 °C/min, the steel ball can be further released after heating for ca. 12 min at ca. 70 °C in the bath.

References

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