Supporting Information

Stabilization of catechol-boronic ester bonds for underwater self-healing and recycling of lipophilic bulk polymer in wider pH range

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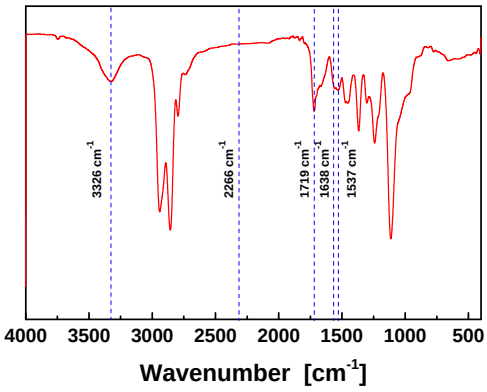


Figure S1. FTIR spectrum of HBPU-DMPA-B[DOPA]$_2$/TEA

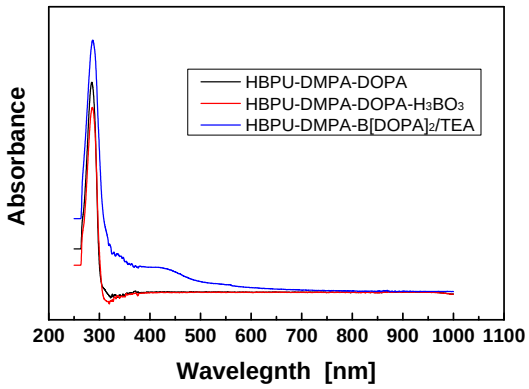


Figure S2. UV-vis spectrum of HBPU-DMPA-B[DOPA]$_2$/TEA in comparison with those of the controls (solvent: DMF). All polymers were tested immediately after the reaction.

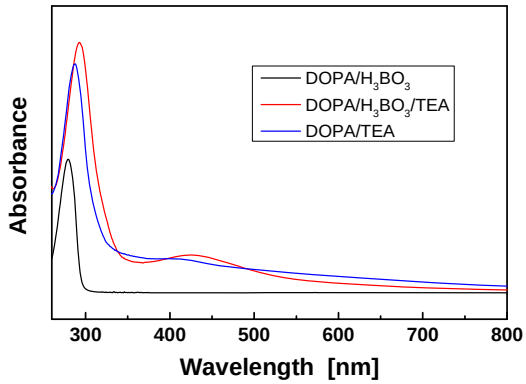


Figure S3. UV-vis spectra of ligand compounds of DOPA and boric acid in different conditions (n_{DOPA} : $n_{boric\ acid}$ = 2 : 1).

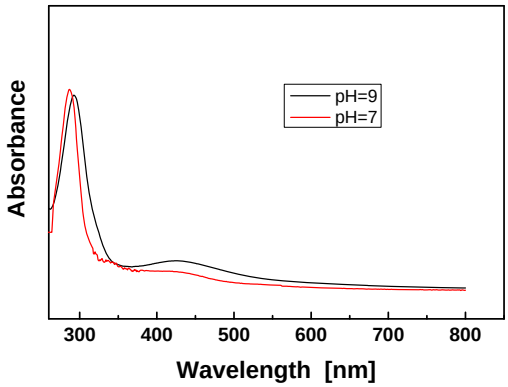
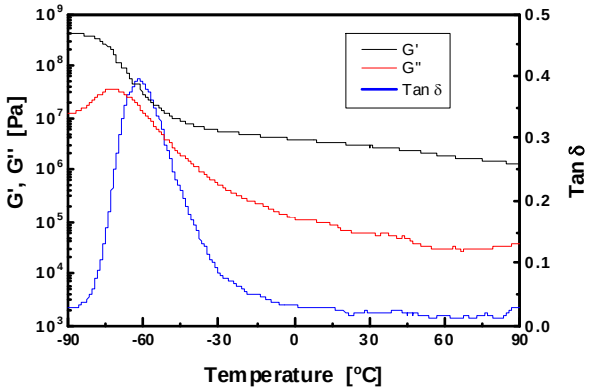
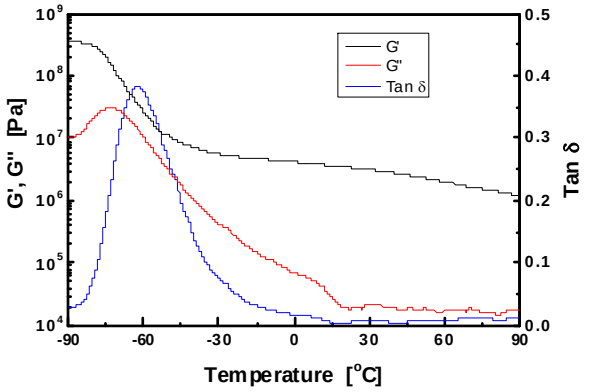


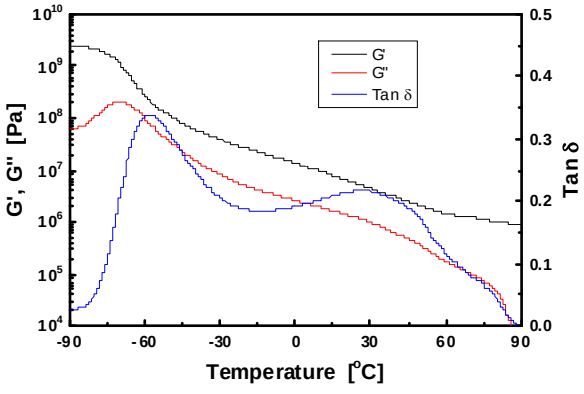
Figure S4. UV-vis spectra of HBPU-DMPA-B[DOPA]$_2$/TEA that had been immersed in water of different pH values at 25 °C for two months (solvent: DMF).



(a)



(b)



(c)

Figure S5. Temperature dependences of storage modulus, loss modulus and tan δ of HBPU-DMPA-B[DOPA]$_2$/TEA. pH: (a) 9, (b) 7 and (c) 4.

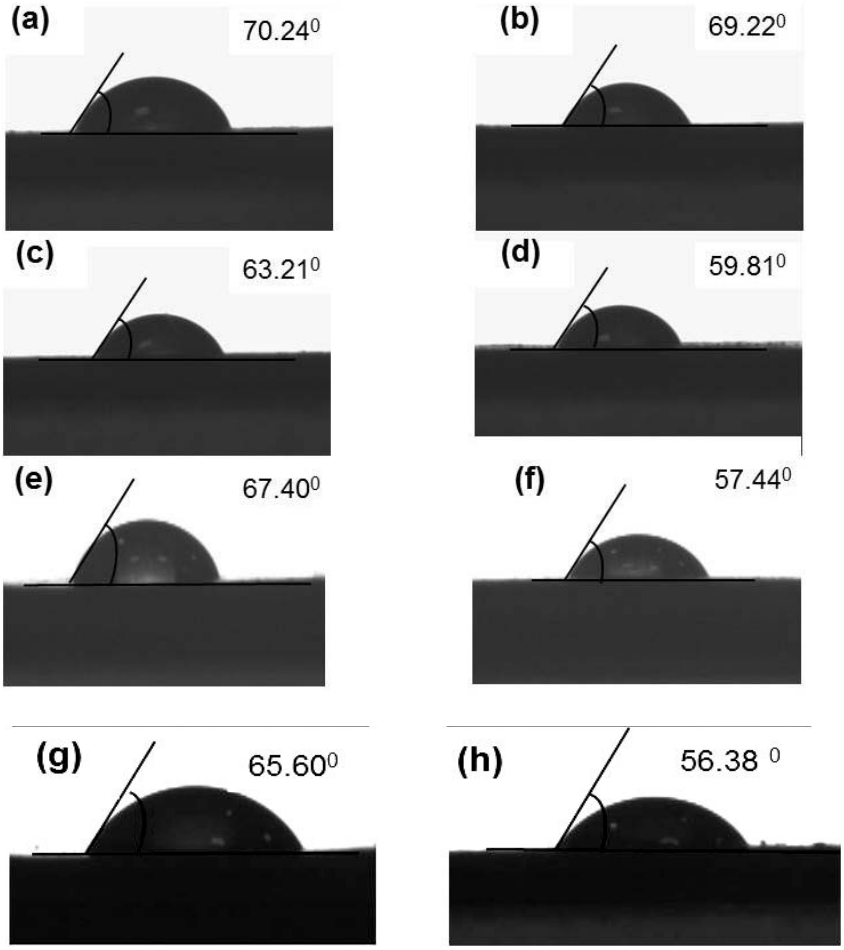


Figure S6. Water contact angles of (a) molded surface of HBPU-B[DOPA]$_2$/TEA, (b) cut surface of HBPU-B[DOPA]$_2$/TEA, (c) molded surface of HBPU-DMPA-B[DOPA]$_2$/TEA, (d) cut surface of HBPU-DMPA-B[DOPA]$_2$/TEA, (e) molded surface of HBPU-DMPA-DOPA, (f) cut surface of HBPU-DMPA-DOPA, (g) molded surface of HBPU-DMPA-phenethylamine, and (h) cut surface of HBPU-DMPA-phenethylamine. Here, HBPU-B[DOPA]$_2$/TEA serves as the reference material. The difference between HBPU-B[DOPA]$_2$/TEA and HBPU-DMPA-B[DOPA]$_2$/TEA lies in the fact that the former was not hydrophilically modified by DMPA.

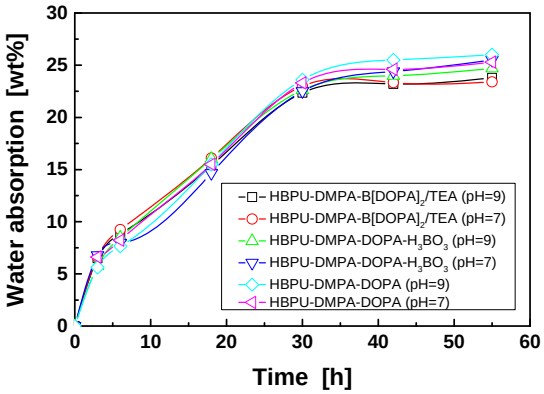
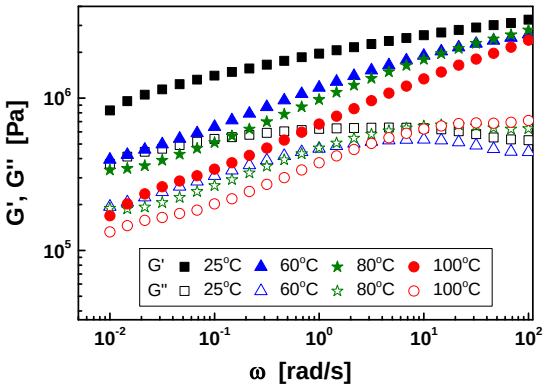
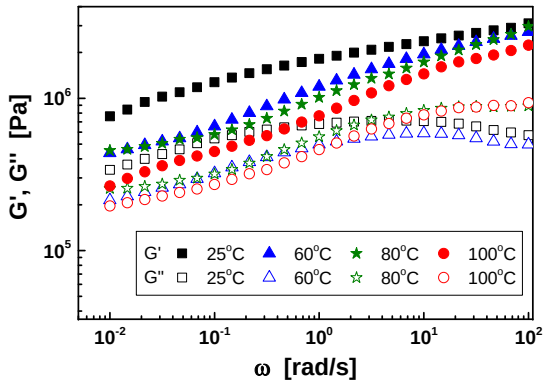


Figure S7. Time dependence of water absorption of HBPU-DMPA-B[DOPA]$_2$/TEA at 25 °C.

Figure S8. Dumbbell-shaped specimen for underwater tensile test. The scale bar represents 4 mm in length.

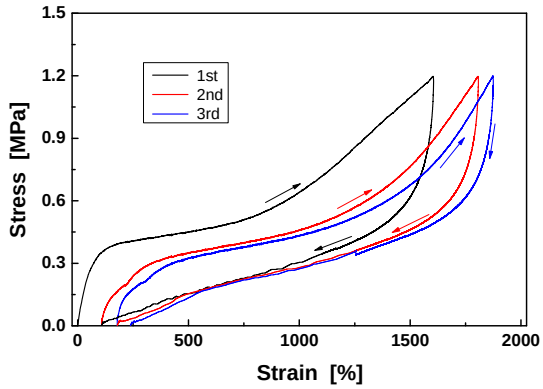


(a)

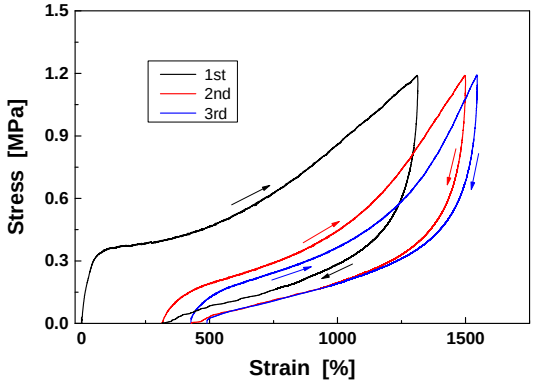


(b)

Figure S9. Storage shear modulus, G′, and loss shear modulus, G″, as a function of oscillatory frequency, ω, for HBPU-DMPA-DOPA. The samples are saturated by water at (a) pH=9 and (b) pH=7.



(a)



(b)

Figure S10. Tensile stress-strain curves recorded during cyclic loading and unloading tests of HBPU-DMPA-DOPA beyond the yield region at 25 °C. Arrows indicate directions of loading and unloading. The specimens are saturated by water at (a) pH=9 and (b) pH=7. Only cycles 1, 2 and 3 are shown for clarity (cycles 4 and 5 are not given). The cyclic tests were continuously conducted without resting between successive cycles.

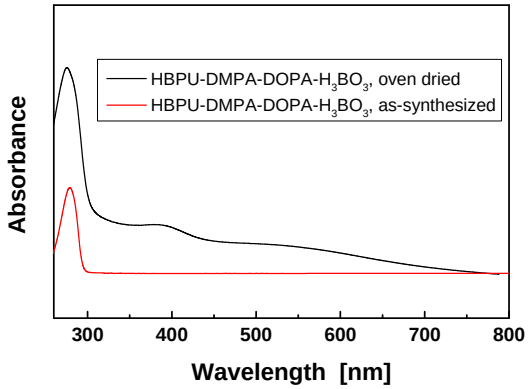


Figure S11. UV-vis spectra of as-synthesized and oven-dried HBPU-DMPA-DOPA-H_3BO_3 (solvent: DMF). Conditions for drying: 40 °C, 48 h, air. By comparing the two curves, it is seen that an absorption peak appears at around 400 nm after drying in oven as a result of oxidation of dopamine.

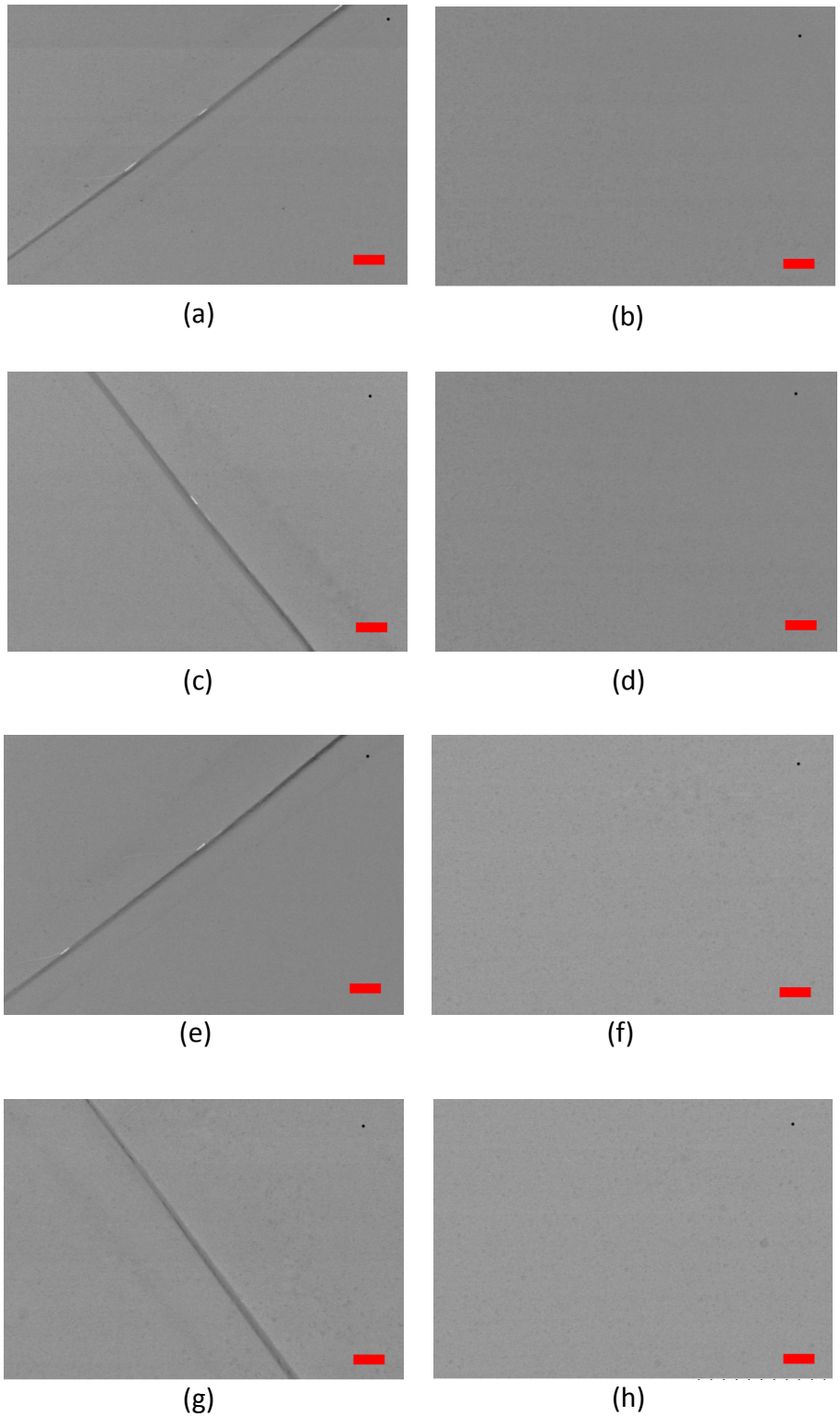
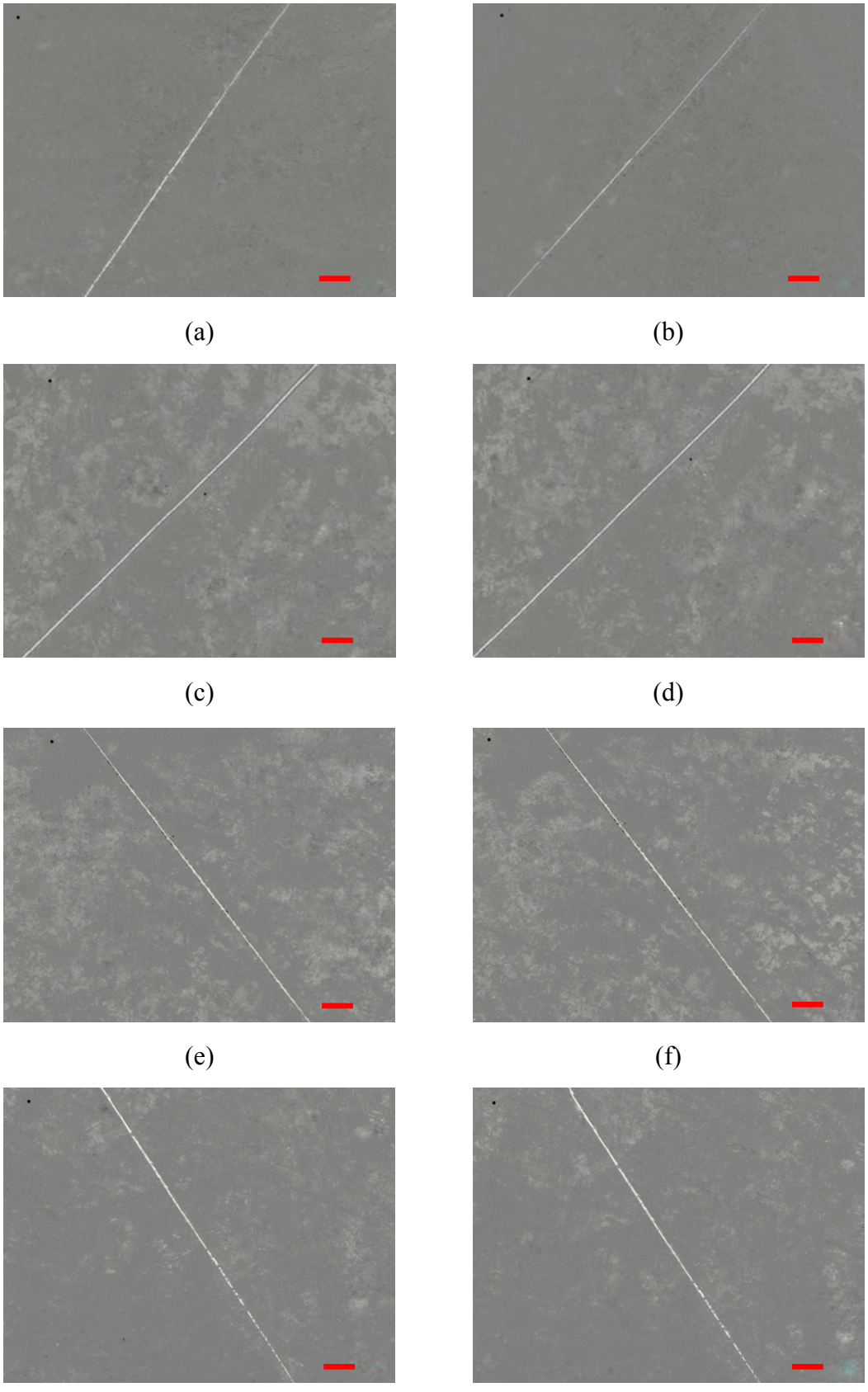


Figure S12. SEM photos showing self-healing of razor cuts on HBPU-DMPA-B[DOPA]$_2$/TEA. The scale bars represent 50 μm in length. Both the cutting and healing were conducted in waters of (a-d) pH = 9 and (e-h) pH = 7 at 25 °C. Healing time: 24 h. (a, e) The first cut. (b, f) Effect of the first healing. (c, g) The second cut. (d, h) Effect of the second healing.



(a) (b) (c) (d) (e) (f) (g) (h)

Figure S13. Optical images showing self-healing of razor cuts on (a-d)

HBPU-DMPA-DOPA-H_3BO_3 and (e-h) HBPU-DMPA-DOPA. The scale bars represent 50 μm in length. Both the cutting and healing are conducted in waters of (a, b, e, f) pH = 9 and (c, d, g, h) pH = 7 at 25 °C. Healing time: 24 h. (a, c, e, g) The cutting mark. (b, d, f, h) Effect of healing.

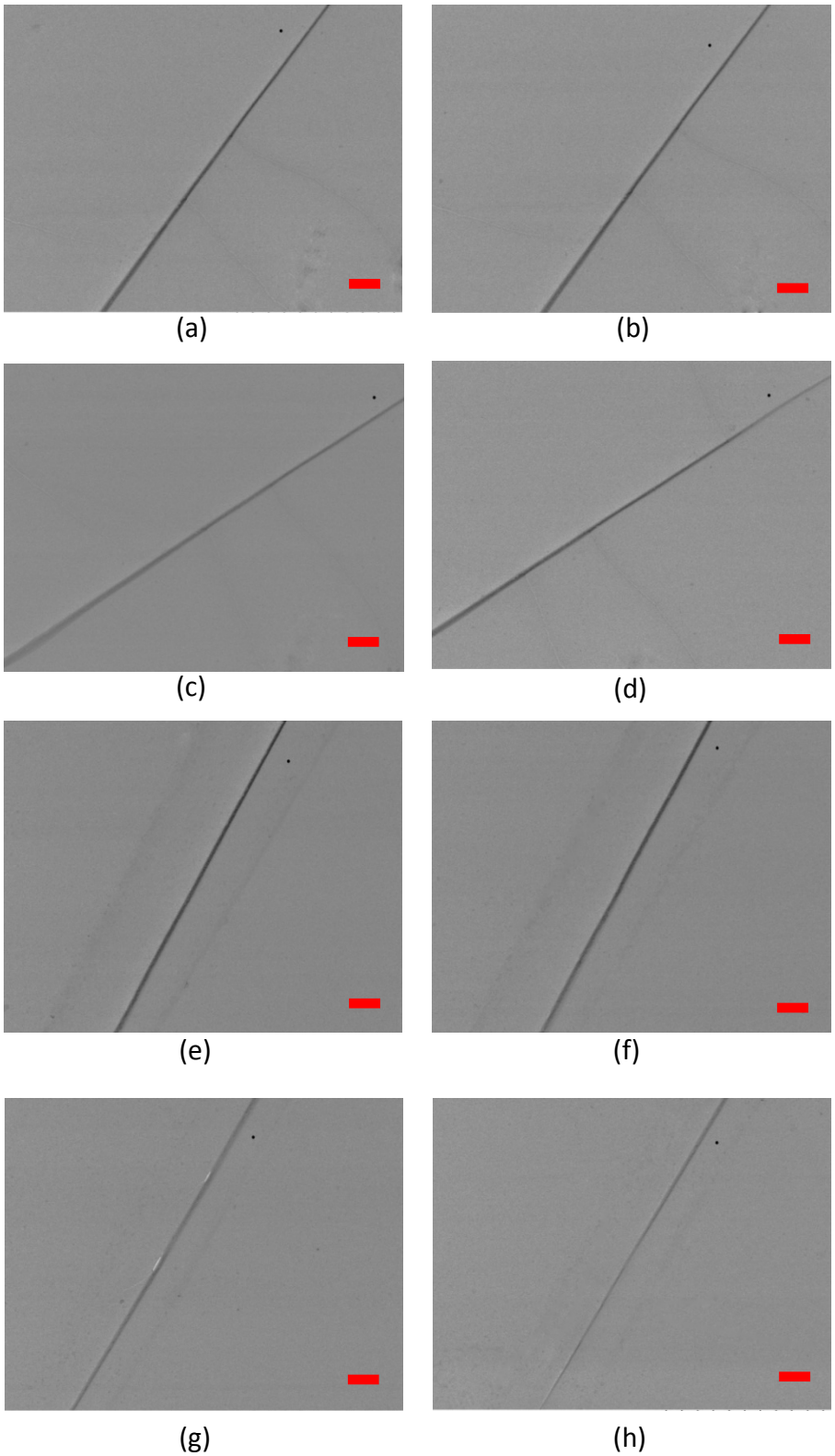


Figure S14. SEM photos showing self-healing of razor cuts on (a-d) HBPU-DMPA-DOPA-H_3BO_3 and (e-h) HBPU-DMPA-DOPA. The scale bars represent 50 μm in length. Both the cutting and healing are conducted in waters of (a, b, e, f) pH = 9 and (c, d, g, h) pH = 7 at 25 °C. Healing time: 24 h. (a, c, e, g) The cutting mark. (b, d, f, h) Effect of healing.

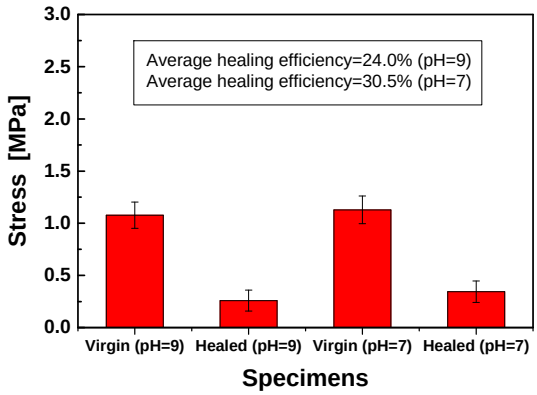


Figure S15. Tensile strengths of the virgin and healed HBPU-DMPA-DOPA specimens. Both the tensile tests and healing were conducted in water at 25 °C. Healing time: 24 h.

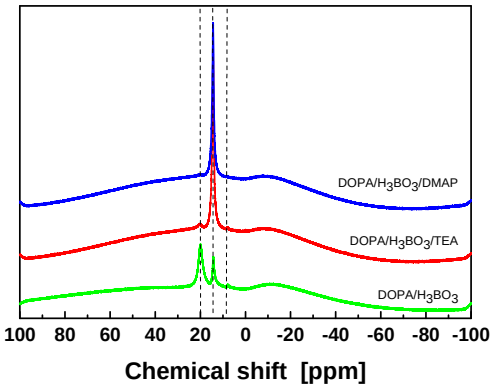


Figure S16. ^{11}B NMR spectra of the model compounds of DOPA and H_3BO_3 with and without alkaline regulator (TEA or DMAP). Prior to the measurements, dopamine hydrochloride was dissolved in deionized water and then H_3BO_3 was added with a feed molar ratio $n_{(DOPA)} : n_{(H_3BO_3)} = 2 : 1$ under stirring. Afterwards, TEA or DMAP was incorporated to tune the pH of the system to 9. It is seen from the spectrum of the

mixture of DOPA and H_3BO_3, The signals of boron appear at 20.0, 14.3 and 7.8 ppm, respectively. It means that esterification between DOPA and H_3BO_3 could not take place in the case of lower pH and boron has to exist in free form. When TEA is present, the peak at 14.3 ppm is greatly intensified, while that at 7.8 ppm is no longer visible and that at 20.0 ppm significantly diminishes. It means that DOPA and H_3BO_3 are allowed to produce stable borate ester under alkaline conditions (refer to He L, Fullenkamp D E, Rivera J G, et al., pH responsive self-healing hydrogels formed by boronate-catechol complexation, Chemical Communications, 2011, 47, 7497). Owing to the stronger electronic withdrawing ability of pyridine ring, moreover, DMAP could more effectively reduce electron density of borate ester as compared to the case with TEA. Only a single peak is detected at 14.3 ppm on the spectrum of the mixture of DOPA, H_3BO_3 and DMAP.

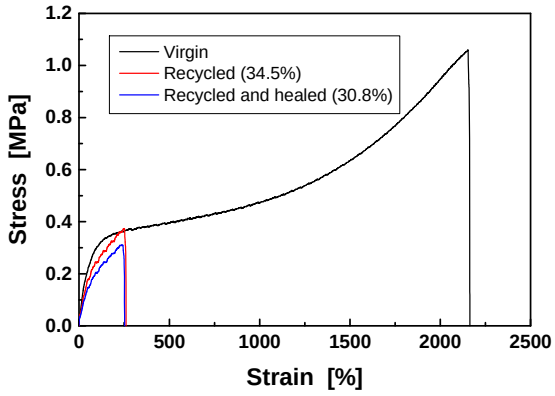


Figure S17. Recycling performance of HBPU-DMPA-DOPA. Reprocessing, tensile tests and healing were conducted in water of pH = 9 at 25 °C. Healing time: 24 h. The rate of strength restoration due to recycling (appearing in the parentheses behind the term "recycled" of the legend) is calculated from the ratio of tensile strength of the recycled specimen to that of the virgin one. Meanwhile, the self-healing efficiency (appearing in the parentheses behind the term "recycled and healed" of the legend) is estimated by the ratio of tensile strength of the healed recycled specimen to that of the virgin one.