SUPPORTING INFORMATION

High efficiency bionic self-healing flexible waterborne polyurethane elastic film based on cyclodextrin-ferrocene host-guest interaction

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Synthesis and characterization of Fc-diol

Scheme 1 showed the synthesis process of Fc-diol. First, the carboxyl group of FcA was chlorinated with OC to obtain ferrocenyl chloride. Subsequently, ferrocene formyl chloride reacted further with AMPD to generate Fc-diol. The effective functionalization of Fc was demonstrated by different characterization methods. FTIR spectra of FcA, AMPD and Fc-diol were shown in **Figure S1**. The stretching vibration of -OH and -NH- were observed near 3246 cm^{-1} from FTIR spectra of Fc-diol. The peak at 1472 cm^{-1} and 1391 cm^{-1} were ascribed to -OH or -NH- bending vibration, respectively. The absorption peaks at 3109~3009 cm^{-1} and 827 cm^{-1} were the stretching and bending vibration of C-H bond on ferrocene cyclopentadienyl rings, respectively. The stretching vibration of C-C on ferrocene rings were observed at 1159 cm^{-1}, and the stretching vibration of Cp-Fe had two spikes at 509 cm^{-1} and 486 cm^{-1}. The peak at 1287 cm^{-1} and 1030 cm^{-1} were attributed to the stretching vibration of C-N and C-O bond, respectively. It can be seen from the spectrum that the wavenumber and shape of these characteristic absorption peaks are roughly similar to the corresponding groups on AMPD and FcA. ^{1}H-NMR spectra of Fc-diol were shown in **Figure S2**. The sharp signal observed at 6.66 ppm was the proton peak imide group. The signal observed at 4.94 ppm were attributed to the proton on hydroxyl (-OH). The chemical shifts at 4.77 ppm and 4.34 ppm were assigned to protons (-CH) on mono-substituted ferrocene ring, respectively. Peaks at 4.19 ppm corresponded to protons (-CH) on another ferrocene ring. The peaks at 3.63-3.57 ppm and 3.54-3.47 ppm were assigned to the protons on methylene ($-CH_2-$), respectively. The signals were observed at 1.25 ppm corresponded to methyl group ($-CH_3$). FT-IR and ^{1}H-NMR spectra analysis results demonstrated that the dihydroxylation of FcA was completed. Fc-diol was synthesized successfully by **Scheme 1.**

Preparation of self-healing flexible conductive film (WPU-Fc/CD/Ag)

Micron-sized silver powder was added to WPU-Fc/CD 2:1 emulsion (30 wt.% of silver powder) and uniformly dispersed under high-speed stirring (1200 rpm) for 1 h.

The mixture was continued to disperse by ultrasound for further application. WPU-Fc/CD 2:1 emulsion was poured into a rectangular mold. It was dried at 60 °C for 3 h after standing horizontally at room temperature for 12 h to form self-healing substrate. Subsequently, the prepared conductive paste was painted on the substrate and dried at 60 °C for 1 h. After that, another layer of WPU-Fc/CD 2:1 emulsion was drop-casted onto the conductive thin layer and dried at 60 °C for 3 h. The self-healing flexible conductive film (WPU-Fc/CD/Ag) was obtained after demolding.

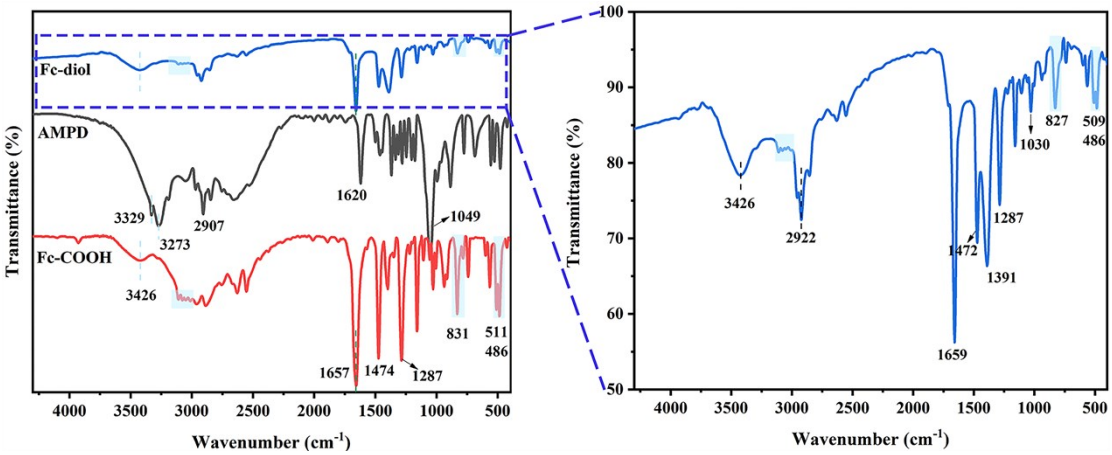

Figure S1. FTIR curves of Fc-COOH, AMPD and Fc-diol.

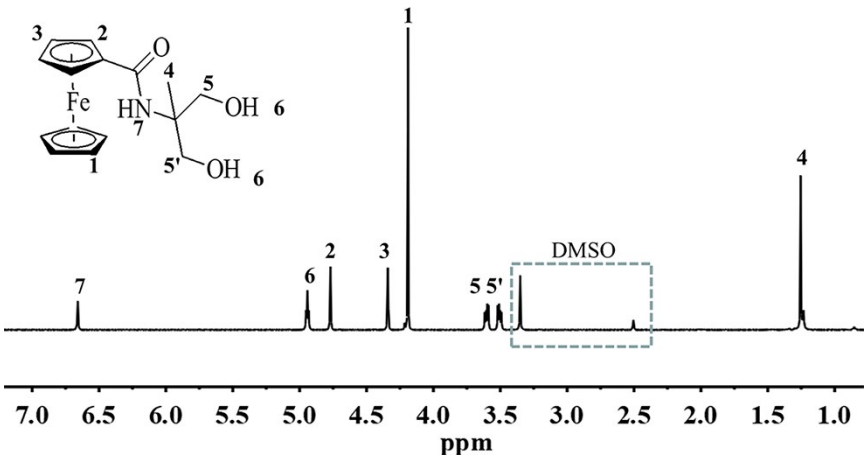

Figure S2. ^{1}H NMR spectrum of Fc-diol.

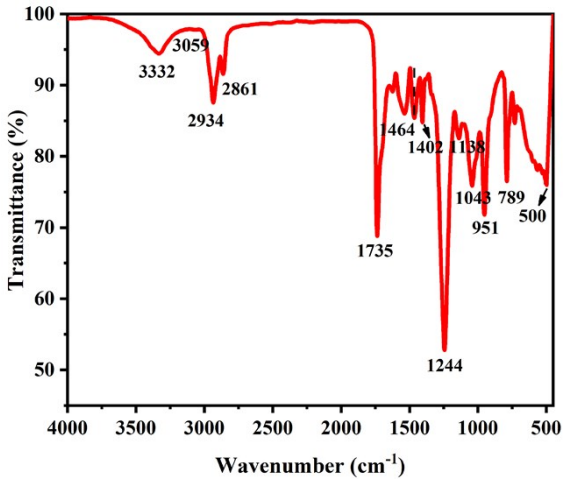

Figure S3. FTIR spectrum of thinner WPU-Fc/CD 2:1 film (film thickness: 40 μm).

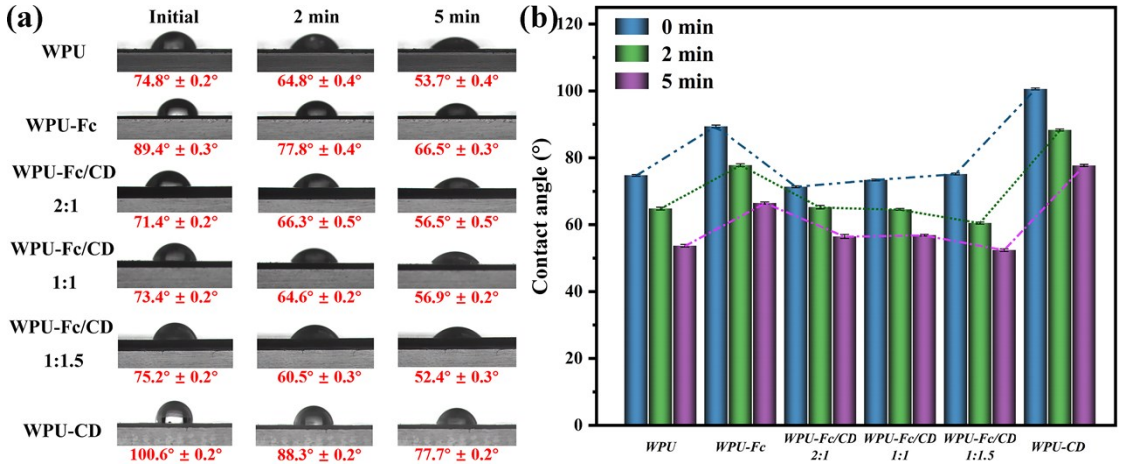

Figure S4. Images (a) and data bar charts (b) of contact angle of WPU, WPU-Fc, WPU-Fc/CD 2:1, WPU-Fc/CD 1:1, WPU-Fc/CD 1:1.5 and WPU-CD in different periods.

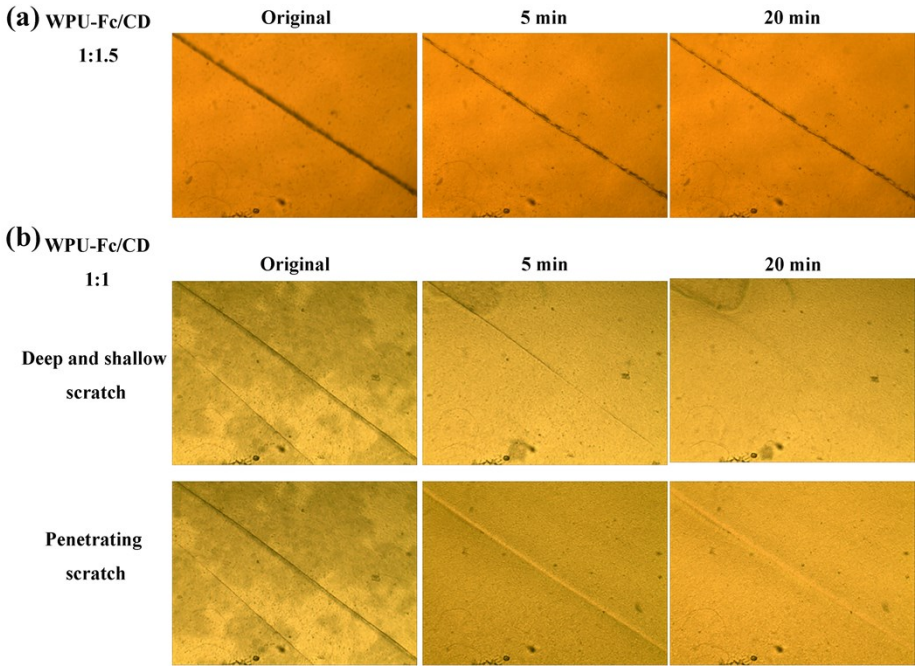

Figure S5. Optical microscope images of scratches on the WPU-Fc/CD 1:1.5 film before and after recovery at 120 ℃ for different times(a). The self-healing process images of WPU-Fc/CD 1:1 film with different degrees of damage at 120 ℃ for different times (b).

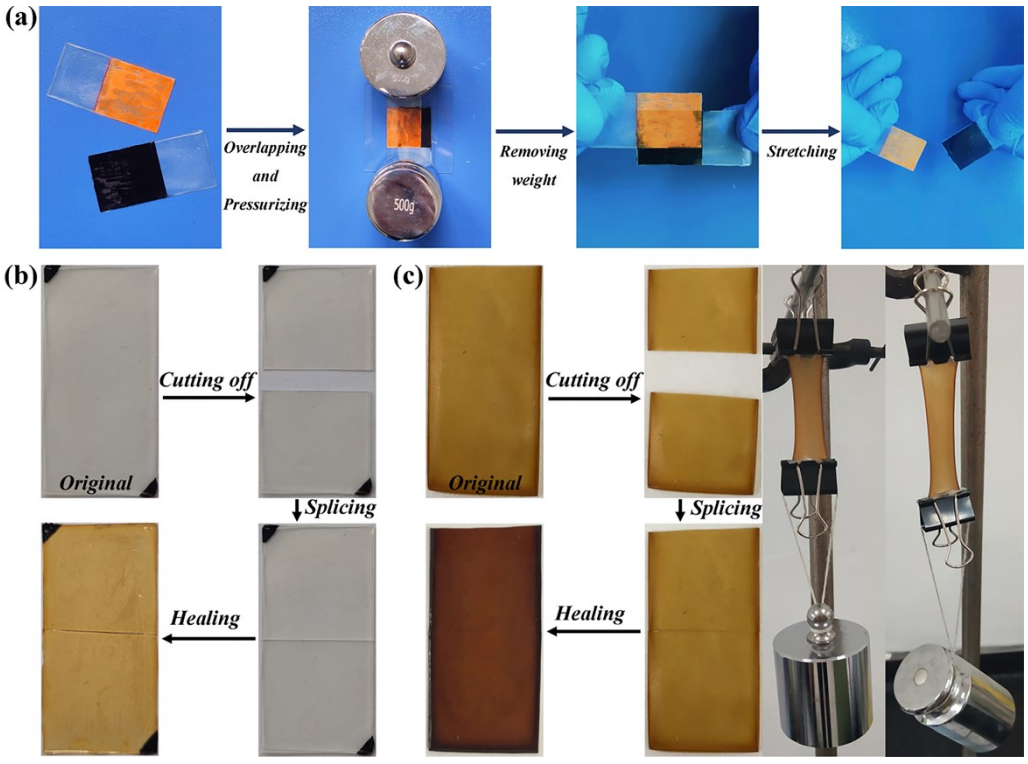

Figure S6. The evaluation process of the viscosity and fluidity of pure WPU film (a). Demonstration of the healing process and effect of WPU film (b). Schematic diagram of the healing process of WPU-Fc/CD 2:1 film and load test after self-heal (c).

To certify that the host-guest interaction is the key factor to endow WPU film with self-healing performance, the comparison of heal effects between WPU and WPU-Fc/CD 2:1 was implemented. Firstly, as shown in Figure S6a, Half of the two WPU films were painted orange and black, respectively. The colored parts were staggered and placed between the glass plates. Then it was pressurized with 1000 g weight for 2 days. After the weight was removed, the films were not deformed and could be easily separated without any signs of adhesion. The results showed that the sample film had no adhesion and fluidity at room temperature. Secondly, WPU film was cut off, and then the broken parts were rejoined together. The spliced sample was placed at 120 ℃ for 24 h. It could be observed that the damaged WPU film had not been repaired and the fracture mark was still obvious from Figure S6b. However, WPU-Fc/CD 2:1 could self-heal completely under the same conditions. And the healed film could bear the weight of 500g and 1000g successively, showing well mechanical properties (as shown in Figure S6c).

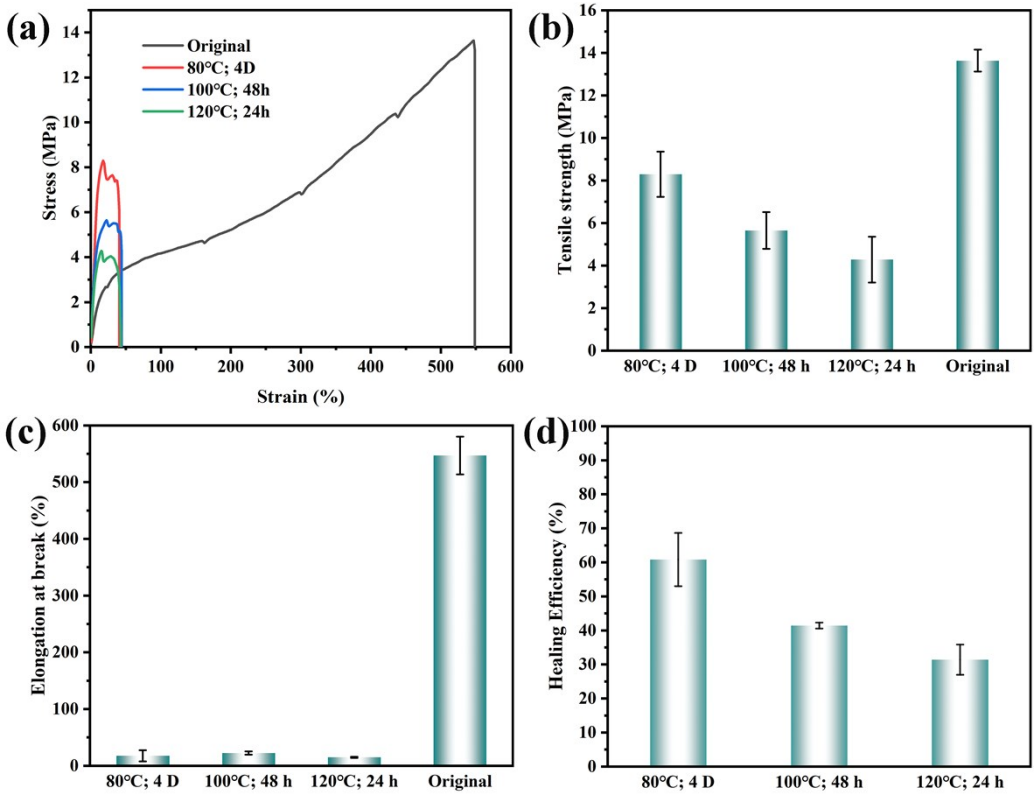

Figure S7. Mechanical properties (a, b, c) and self-healing efficiency (d) of WPU-Fc/CD 1:1 sample healed at 120 ℃ for various time.

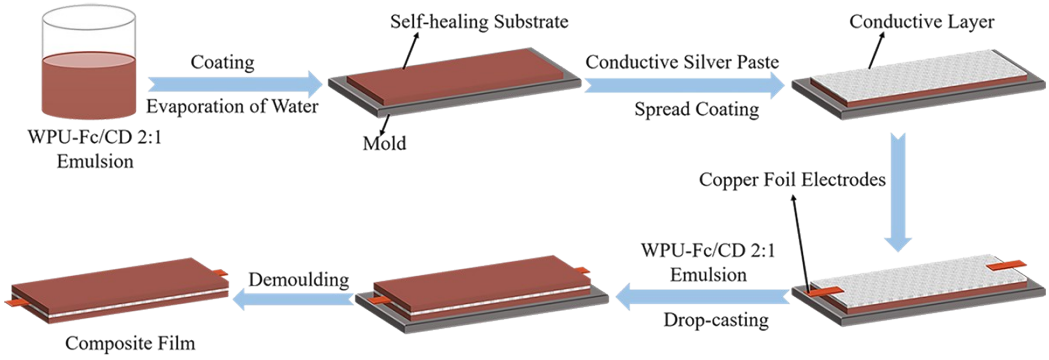

Figure S8. Demonstration of preparation of self-healing flexible conductive film.

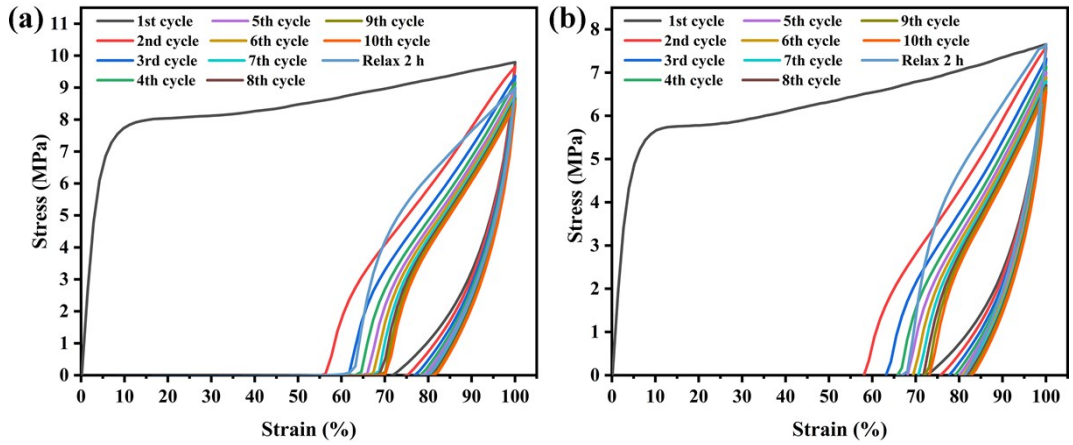

Figure S9. Repeated cyclic tensile curves of the original and healed WPU-Fc/CD 2:1 sample (a, b).

The results of repeated cyclic tensile test showed that the performance of the healed sample was greatly similar to that of the original sample. As shown in Figure S8. There was no waiting time between two consecutive cyclic tests for ten cycles. There was a large hysteresis loop in first cycle indicating a significant energy dissipation, owing to hydrogen bond, host-guest interaction and cross-linking structure could be destroyed during stretching. The energy dissipation in second cycle was much less than that in first cycle because the broken sacrificial bonds did not have enough time to restore to their original state during the limited time. The hysteresis loop slightly decreased with the increase of cycle in sequential test, indicating the continuous reorganization of sacrificial non-covalent bonds. When the sample was allowed to relax for 2 h at 25 °C and subjected to the 11th cyclic tensile, it showed a loading–unloading curve similar to that of the second cycle, indicating favorable elastic recovery of WPU-Fc/CD 2:1.

Table S1. The specific component of different samples.

Sample	PCDL (mmol)	HDI (mmol)	DMPA (mmol)	Fc-Diol (mmol)	Me-β-CD (mmol)	TEA (mmol)	EDA (mmol)	Fc:CD
WPU	10	40.99	24.16	/	/	24.80	7.00	/
WPU-Fc	10	46.28	24.16	4.26	/	24.80	7.82	1: 0
WPU-Fc/CD	10	55.50	24.16	4.26	2.13	24.80	7.82	2: 1
WPU-Fc/CD 1:1	10	64.77	24.16	4.26	4.26	24.80	7.82	1:1
WPU-Fc/CD 1:1.5	10	73.99	24.16	4.26	6.39	24.80	7.82	1: 1.5
WPU-CD	10	63.18	24.16	/	4.26	24.80	10.79	0: 1