Electronic Supplementary Information

Flexible and Voltage-Switchable Polymer Velcro Constructed by Host−Guest Recognition Between Poly(ionic liquid) Strips

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1. Materials

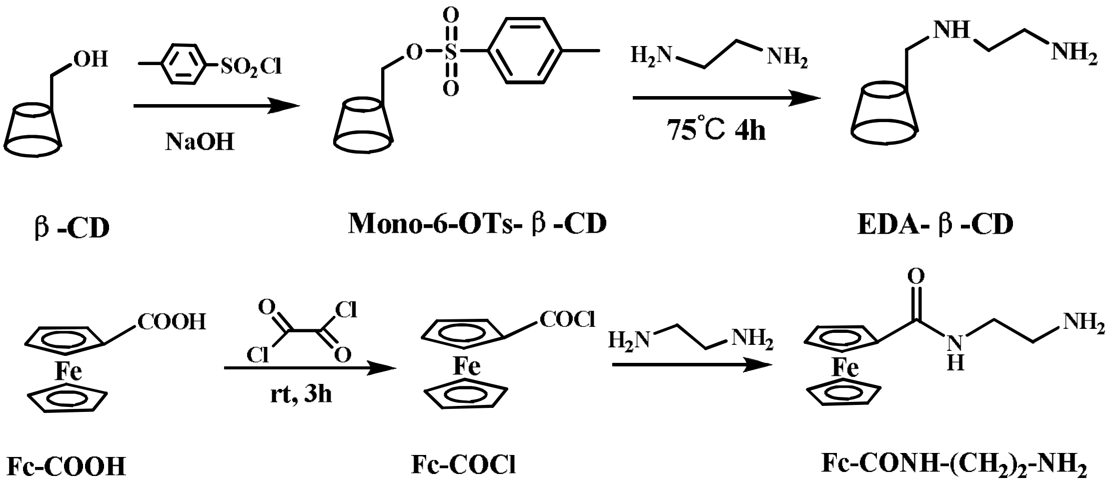
β-Cyclodextrin (β-CD), p-toluenesulfonyl chloride (p-TsCl), oxalyl chloride, benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) benzoinisobutyl ether, ethylenediamine (EDA), triethylamine, 1-bromoheptane, and ferrocenecarboxylic acid were purchased from Shanghai Chemical Reagents Co. (Shanghai, China). Acrylic acid, acrylonitrile, divinylbenzene and vinylimidazole were purchased from Acros and passed through a column of neutral alumina to remove the stabilizers before use. 1-vinyl-3-heptylimidazolium bromide [VHHm][Br] was synthesized as reported in the literature.[1] Mono-6-OTs-β-CD used in this work was synthesized according to the method reported in the literature.[2] All other reagents were analytic grade and used as received without further purification. Deionized water was used throughout all the experiments.

2. Characterization

^{1}HNMR measurements were conducted on UNITY INOVA 400MHz spectrometer at room temperature using d_6-DMSO and D_2O as the solvent. Infrared spectroscopy experiment was preformed on a Specode 75 model using KBr as the sample holder. Energy-dispersive X-ray (EDX) spectroscopy measurements were performed with the spectrometer attached on the Hitachi Model S-4700 field-emission SEM system. Elemental analysis was performed using EA1110 CHNO-S Elemental Analyzer. The wettability of the membranes was examined by static contact angle measurements (Drop Shape Analysis System DSA10, KRUESS, Germany). Droplets (1.0 μL) of pure water were placed randomly over the surface. The lap shear adhesion strength of the supramolecular velcro was measured by using an Instron 3365 at 25 ^{o}C at a crosshead speed of 1 mm min^{-1}. The adhesion strength (in pascals, Pa=Nm^{-2}) was determined by dividing the load (N) corresponding to the breaking points by an adhesion area (m^{2}). The electrochemical redox reaction of PIL-Fc membrane was performed on a CHI660c electrochemical workstation with a two-electrode system. PIL-Fc membrane and Pt wire were used as the working and counter electrode, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed using an XPS-7000 spectrometer (Rigaku) equipped with a Mg KaX-ray source.

3. Synthesis of host polymer

Scheme S1. Synthetic procedure for EDA-β-CD and Fc-CONH-$(CH_2)_2$-NH_2.



3.1 Synthesis of mono-6-deoxy-6-ethylenediamine-β-CD (EDA-β-CD) (see scheme S1)

EDA-β-CD was sythesized according to the method reported.[3] Mono-6-OTs-β-CD (2.0 g, 1.7 mmol) reacted with excess amount of EDA (14 ml, 0.200 mol) at 75 ^{o}C for 4 h. The mixture was cooled to room temperature after the reaction was completed, and then cold acetone was added to obtain the precipitate, which was repeatedly dissolved in water-methanol (1:1, v:v) mixture and poured into acetone several times for the removal of unreacted EDA. The obtained compound was dried at 50 °C in a vacuum oven before the characterization. ^{1}H NMR (d_6-DMSO): δ5.67 (2H,-NH_2) δ4.83(7H, C(1)–H), δ3.69–3.56 (28H, C(3)–H,C(6)–H,C(5)–H), δ3.40–3.27 (14H; C(2)–H, C(4)–H), 2.89 (2H, –CH_2NH–β-CD) δ1.09 (1H,-NH-).

3.2 Synthesis of Fc-CONH-$(CH_2)_2$-NH_2 (see scheme S1)

Synthesis of Fc-CONH-$(CH_2)_2$-NH_2 was performed follow the method reported in the literature.[4] To a solution of ferrocenecarboxylic acid (1.00 g, 4.3 mmol) dissolved in 60 ml of dichloromethane (DCM), oxalyl chloride (1 ml, 11.6 mmol) was added dropwise. The mixture was stirred for 3 h at room temperature. After the evaporation of the solvent, the obtained red solid was dissolved in 30 ml DCM. Then ethylenediamine (3 ml, 38.5 mmol) dissolved in 30 ml DCM was added dropwise to ferrocenecarboxyl chloride solution. The mixture was stirred at room temperature for 24 h. The resultant mixture was washed with 40 ml KOH solution (10 wt%), and collected the DCM layer. After the evaporation of the solvent, the orange solid was obtained, which was further washed with 150 ml of solvent mixture (hexane: ethylacetate (9:1, v:v)). The collected yellow powder was dried at 50 °C to obtain Fc-CONH-$(CH_2)_2$-NH_2. ^{1}HNMR (D_2O): δ 2.83 (2 H, t, Fc-CONH-CH_2-CH_2- NH_2), 3.38(2 H, t, Fc-CONH-CH_2-CH_2-NH_2), 4.25 (5 H, s, Cp), 4.51 (2 H, t, Cp), 4.72 (2 H, t, Cp). Elemental analysis Calcd.: C, 58.82; H, 5.88; N, 10.29. Found: C, 58.73; H, 5.71; N,10.14.

3.3 Preparation of PIL membranes

A mixture containing acrylic acid (54 wt%), acrylonitrile (20 wt%), [VHHm][Br] (26 wt%), divinylbenzene (8 wt % of the formulation based on the monomer weight), and 1 wt % of benzoin ethyl ether (photo-initiator) was stirred and ultrasonicated to obtain a homogeneous solution, which was then cast into a glass mold and photo-crosslinked by irradiation with UV light of 250 nm wavelength at room temperature.[5] The cross-linked PIL membranes were stored in a desiccator before surface modification.

3.4 Preparation of PIL-β-CD and PIL-Fc membranes

PIL-β-CD and PIL-Fc membranes were prepared via the surface functionalization of PIL membranes with β-CD and Fc moieties, respectively. The prepared PIL membrane (containing acrylic acid unit 0.120 mol) was immersed in N,N-dimethylformamide (DMF) solution in which PyBOP (0.06 mol) and Et_3N (0.06 mol)was added. The mixture was stirred at room temperature for 2 h, and then EDA-β-CD or Fc-CONH-$(CH_2)_2$-NH_2 (0.06 mol) was added, respectively. After the reaction was gently stirred at room temperature for another 12 h, the surface functionzalized PIL-β-CD and PIL-Fc membranes were thoroughly washed with ethanol and water and dried in a vacuum oven before the characterization.

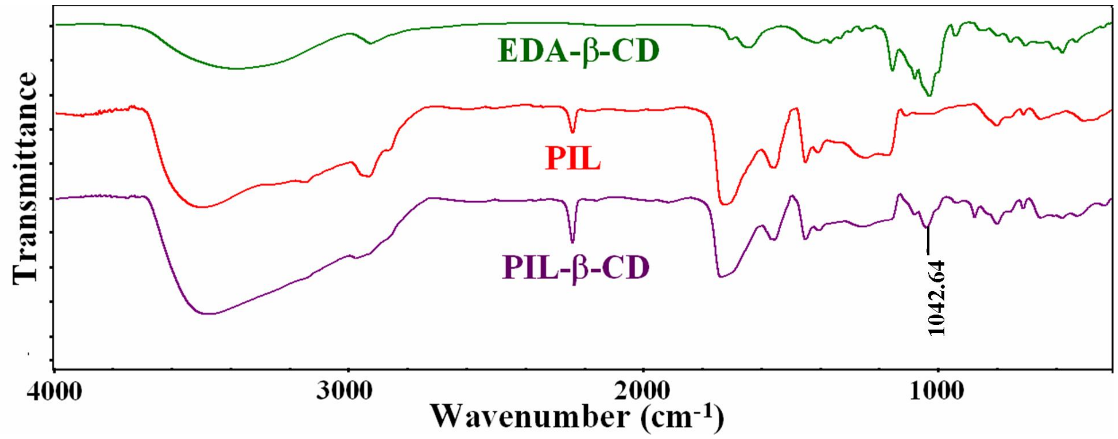


Fig S1. FT-IR spectra of EDA-β-CD (top), PIL (middle) and PIL-β-CD membranes (bottom).

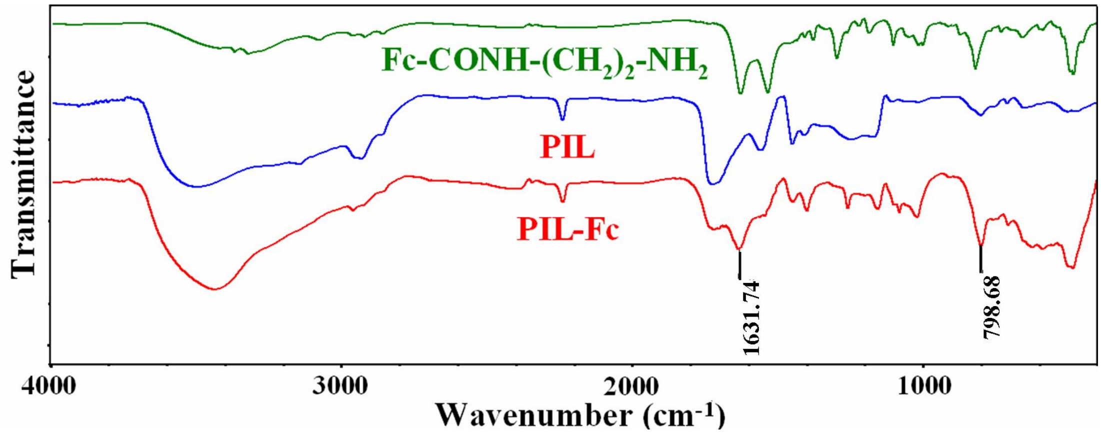


Fig S2. FT-IR spectra of Fc-CONH-$(CH_2)_2$-NH_2 (top), PIL (middle) and PIL-Fc membranes (bottom).

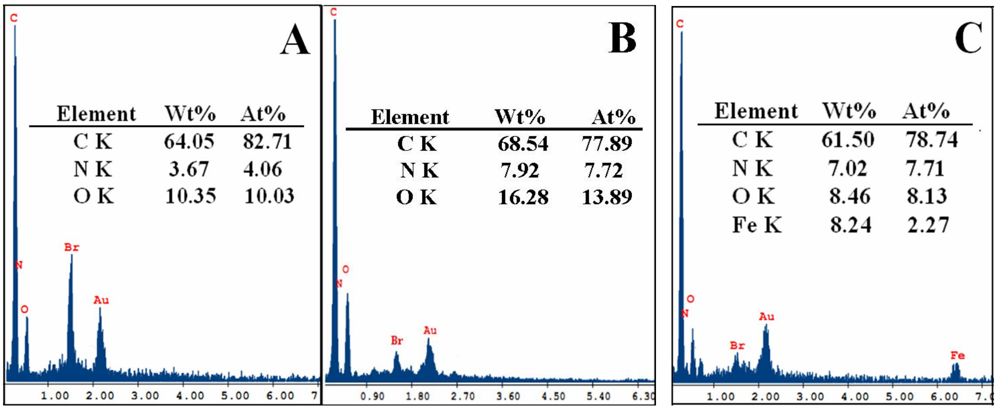


Fig S3. EDX spectra of (A)PIL, (B) PIL-CD and (B) PIL-Fc membranes.

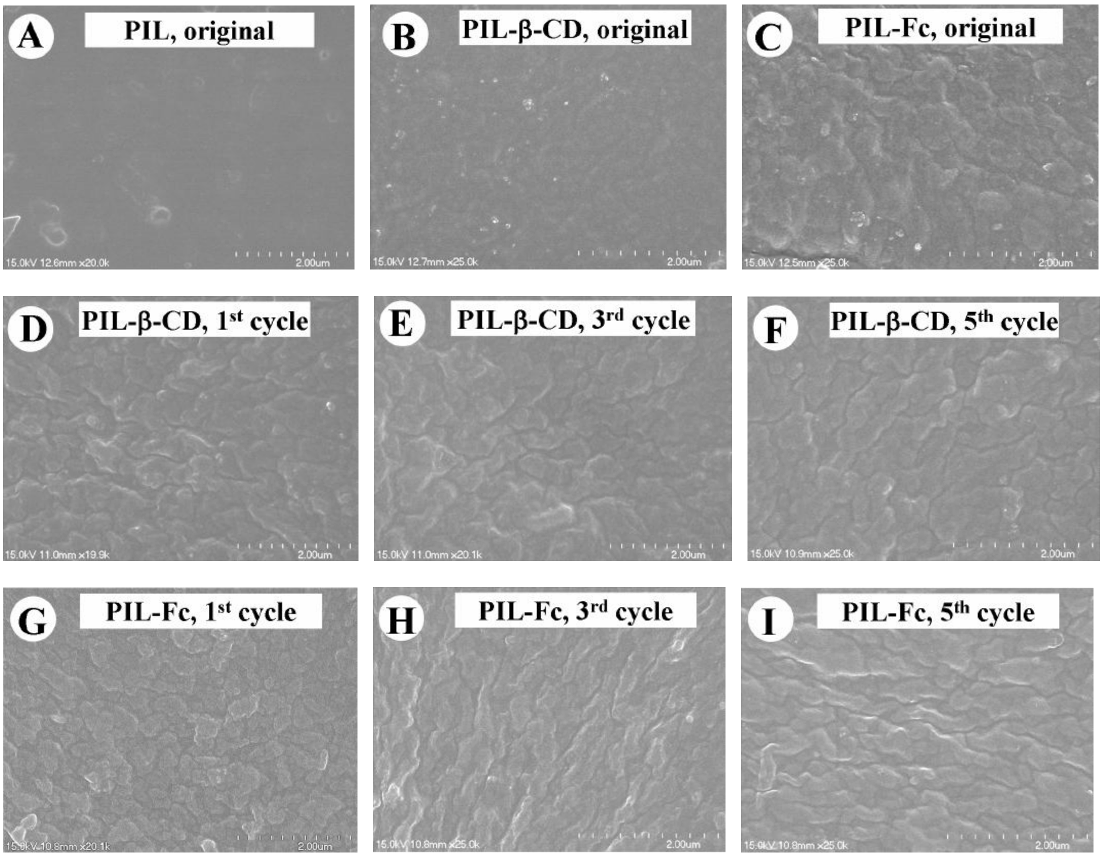


Fig S4. SEM images of the surfaces of A) PIL, B) PIL-β-CD and C) PIL-Fc membranes. D–F) Surfaces of PIL-β-CD membranes after various fastening and unfastening process cycles. G–H) Surfaces of PIL-Fc membranes after various fastening and unfastening process cycles.

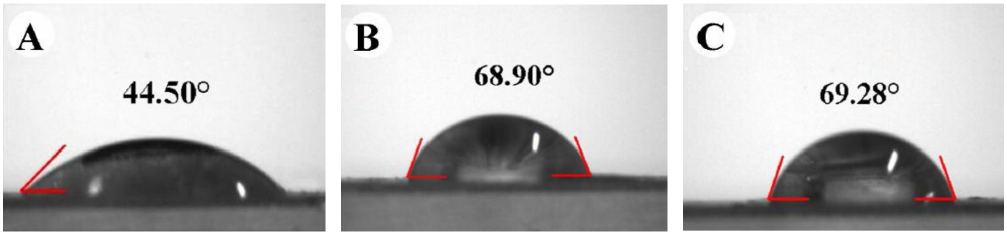


Fig S5. Contact angle of A)PIL, B）PIL-β-CD and C) PIL-Fc membranes measured by ellipsometry with water droplets on the membrane surfaces.

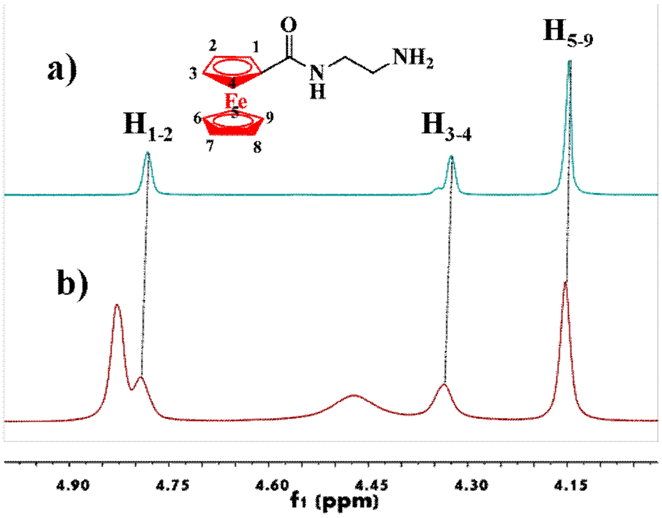


Fig S6. Partial ^{1}H NMR spectra for (a) pure Fc-CONH-$(CH_2)_2$-NH_2 and (b) EDA-β-CD/Fc-CONH-$(CH_2)_2$-NH_2 (1:1 molar ratio). Downfield shifts of $H_{1\text{-}2}$, $H_{3\text{–}4}$, and $H_{5\text{–}9}$ indicating the interaction of EDA-β-CD with Fc group. The samples were dissolved in d_6-DMSO.

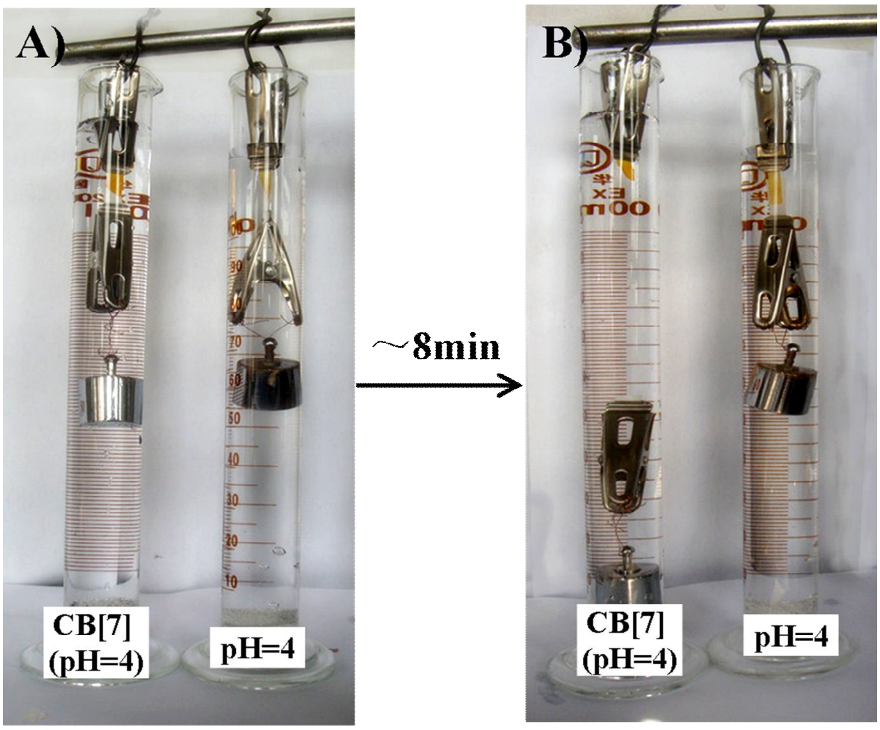


Fig S7. Characterization details of the polymer velcros (A) holding a 100 g weight in cucurbit[7]uril (15 mM) solution (pH=4) and pure aqueous solutions (pH=4), respectively. (B) The detachability of the polymer velcro in the cucurbit[7]uril aqueous solution.

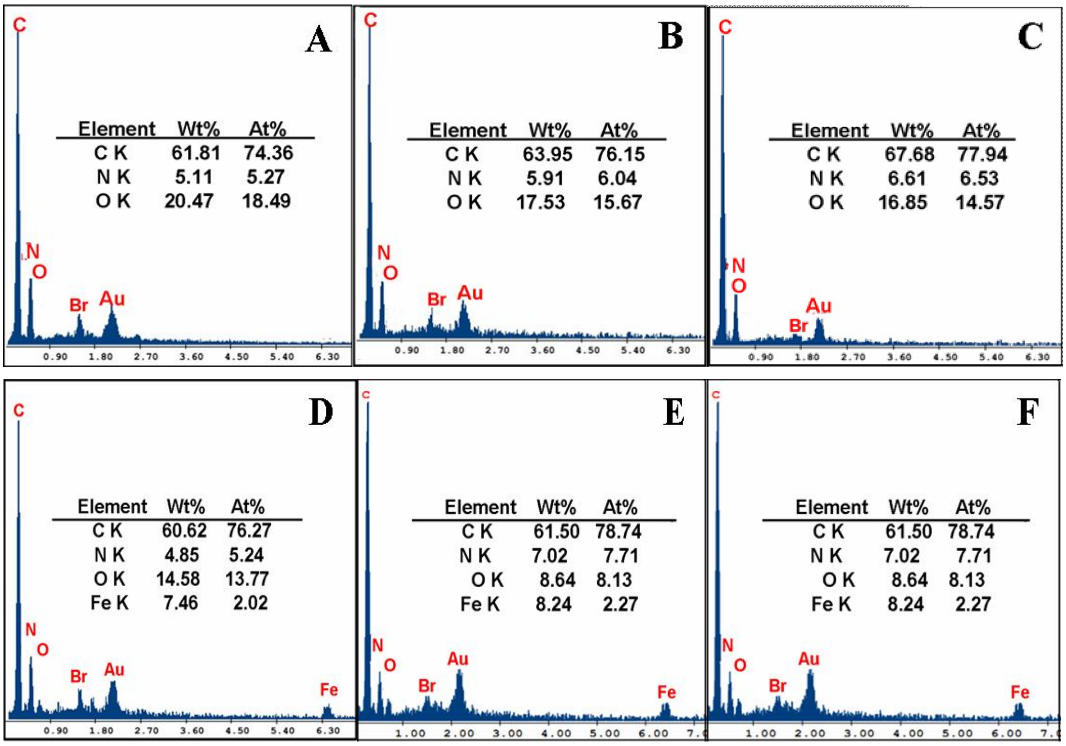


Fig S8. EDX spectra of PIL-CD (A-C) and PIL-Fc (D-F) membranes with various surface grafting degree of β-CD and Fc moieties. The surface grafting degree of β-CD is about 21.3%, 15.0%, 12.3.% for A to C, while the grafting degree of Fc is about 13.5% , 19.0%, 23.4% for D to F, respectively.

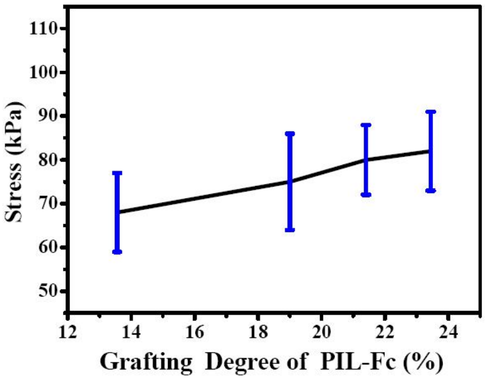


Fig S9. The adhesion strength of polymeric velcros tuned by varying the grafting degree of Fc moiety onto the surface of PIL-Fc membrane. The grafting degree of β-CD is ~15 % for PIL-β-CD membrane.

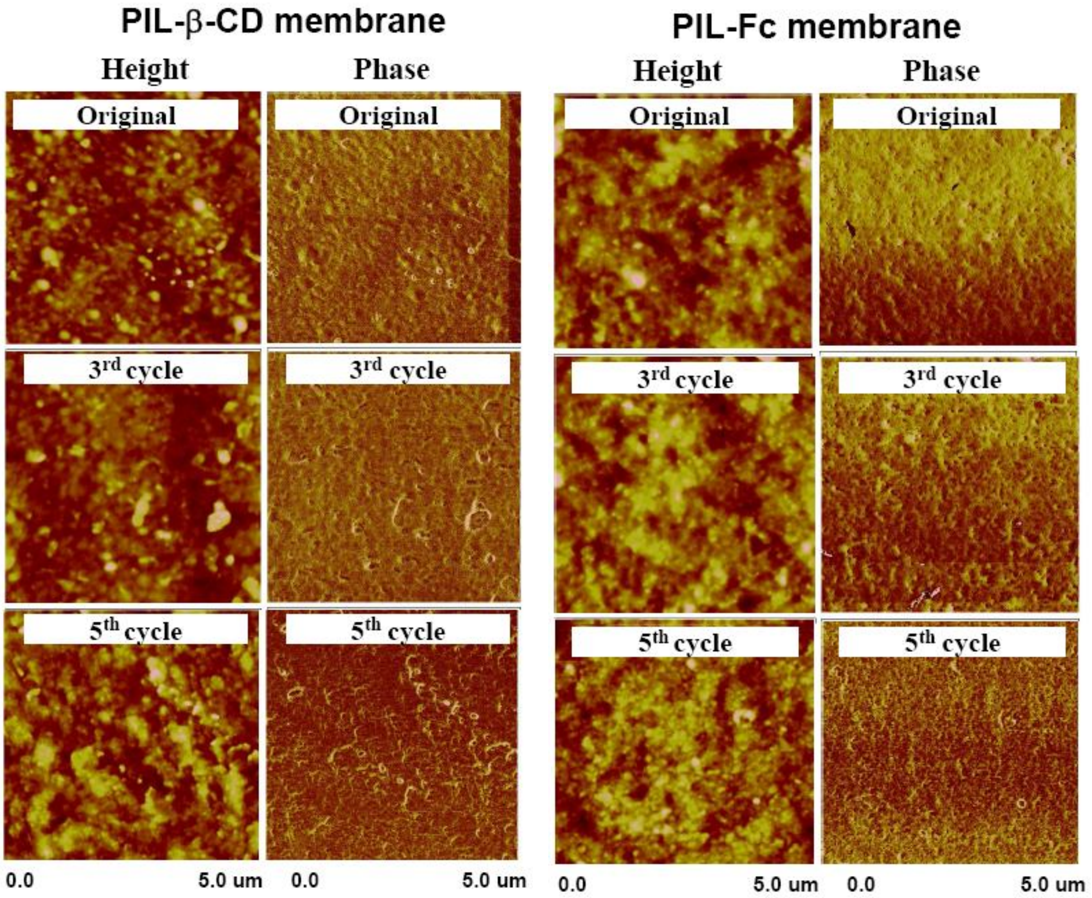


Fig S10. Phase-lag atomic force microscopy (AFM) of height (A) and phase (A’) images of PIL-β-CD membranes; and height (B) and phase (B’) images of PIL-Fc membranes, after various fastening and unfastening process cycles.

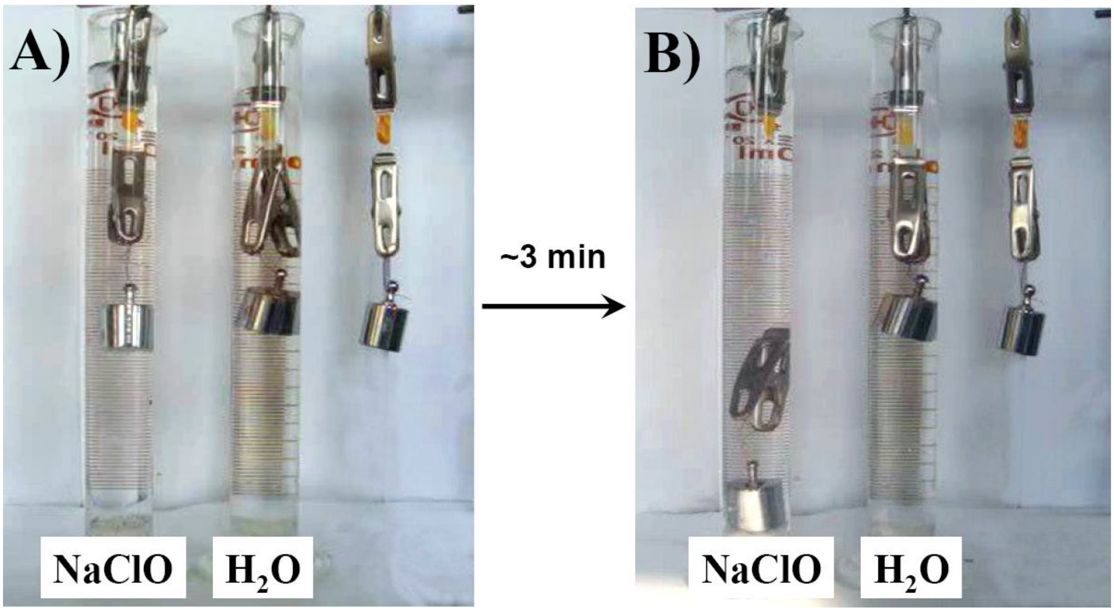


Fig S11. Characterization details of the polymer velcros (A) holding a 100 g weight in NaClO (5 mM), and pure aqueous solutions, and in air, respectively. (B) The detachability of the polymer velcro in the NaClO aqueous solution.

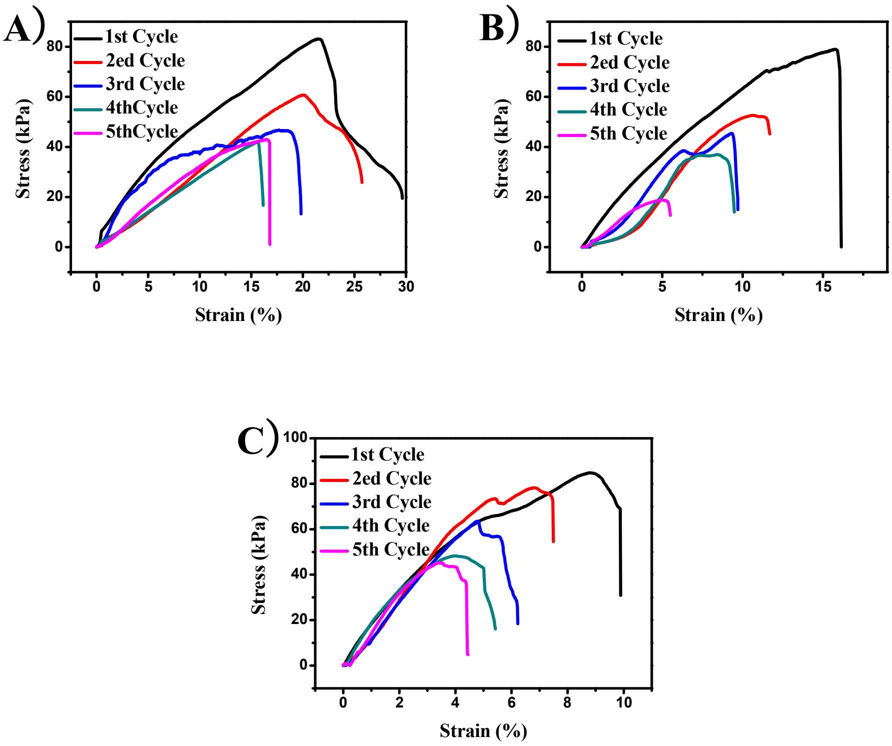


Fig S12. Loading curves for PIL-β-CD/PIL-Fc supramolecular Velcro via (A) mechanical, (B) chemical, and (C) electrochemical means.

References

1. J. Guo, L. Qiu, Z. Deng, F. Yan, *Polym. Chem.* 2013, **4**, 1309-1312.
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