SUPPORTING INFORMATION

Disulfide bonds and Diel-Alder Reaction Bonds Hybrid Polymers with High Stretchability, Transparency, Recyclability, and Intrinsic Dual-Healability for Skin-like Tactile Sensing

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Section S1. Experimental Details of Oligomer and Monomers

Preparation of PPG-DF: **PPG-DIO** (average M_n ~2,300, isocyanate ~3.6 wt.%) 11.5 g (5.02 mmol) is dissolved in 30 mL dry THF, then injected furfurylamine 1 mL (10.04 mmol, d = 1.01 g/cm^3) slowly at anhydrous environment. It was stirred at R.T. for 24 hours, then remove the THF by rotavapor. Finally, get **PPG-DF**, 11.6 g, light yellow viscosity colloid. The yield is about 92 %. (^{1}H-NMR: **Fig. S2**)

Preparation of CYS:[1] (1) cystamine dihydrochloride (4.0 g, 17.76 mmol) is dissolved in 40ml methanol, added KOH (2.2 g, 39.21 mmol), then stir for 24h at R.T. under dark. Filtering out the salt solid, removing methanol by rotavapor, then taking out cystamine by dichloromethane. Get intermediate, 2.46 g cystamine (yellow liquid, yield about 91%). (2) maleic anhydride (3.17 g, 32.31 mmol) is dissolved in 10 mL THF, then it was added to cystamine. The solution was heated to 105 °C, 5 min, then refluxed at 90 °C, 30 min. The catalyst solution, $Ni(OAc)_2.4H_2O$ (40 mg, 0.016 mmol) was dissolved in 6 mL Ac_2O and 1 drop triethylamine, was added to previous solution, then refluxed at 90 °C, 30min. Cooling down the solution to R.T., then pour in 200 g ice. Take out the precipitate, wash by 500 mL DI water. Purify it by column chromatography (EA: Hex = 1:1). Get **CYS**, 1.8g white powder, the yield is about 36 %. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ=2.90 (t, 4H), δ=3.83 (t, 4H), δ=6.70 (s, 4H) (**Fig. S3**)

Preparation of HEX:[2] Mixing 1,6-diaminohexane (5.8 g, 50 mmol), maleic anhydride and 30 mL dry DMF at anhydrous environment. Reacting at 105 °C, 5min, then 90 °C, 30 min. The catalyst solution, $Ni(OAc)_2.4H_2O$ (125 mg, 0.5 mmol) was dissolved in 20 mL Ac_2O and 1.2 mL triethylamine, was added to previous solution, then refluxed at 90 °C, 30 min. Cooling down the solution to R.T., then pour in 400 g ice. Take out the precipitate, wash by 500 mL DI water. Purify it by column chromatography (EA: Hex = 1:1), then recrystallization (EA and $CHCl_3$). Get **HEX**, 6.5g white powder, the yield is about 47%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ=1.25 (m, 4H), δ=1.52 (m, 4H), δ=6.64 (s, 4H) (**Fig. S4**)

Section S2. Experimental Details of Polymers

Fabrication of Tension Test Samples (ISO-37): Dissolving 1.5 mmol PPG-DF and 1.5 mmol linkers (CYS, HEX and DPM) by 5 mL THF. Then, removed solvent at 110 °C for 1h and curing at 60 °C for 12 h. After cooling down and demoulding, cut the polymer films to dumbbell shape with ISO-37 type-4.

Fabrication of Self-Healing Devices: We made a polymer thin film on the glass by spray coating. It is spray solution (0.3 mmol PPG-DF + 0.3mmol linker in 1 mL THF) on the glass (area: 2 cm × 5 cm) on the hot plate at 80 °C, then polymerizing on hot plate at 60 °C for 12 h.

Fabrication of Lap Shear Test Samples (ASTM D1002): Heating the steel substrate (W: 25.4 mm × L: 127 mm) to 80 °C, then spraying solution (0.3 mmol PPG-DF + 0.3 mmol linker in 1 mL THF) on 6 steel sheet (detail in the standard: ASTM D1002). Then, polymerizing samples in oven at 60 °C for 12 h, average thin film thickness is about 50 μm. Finally, combining two samples to adhesive in different conditions.

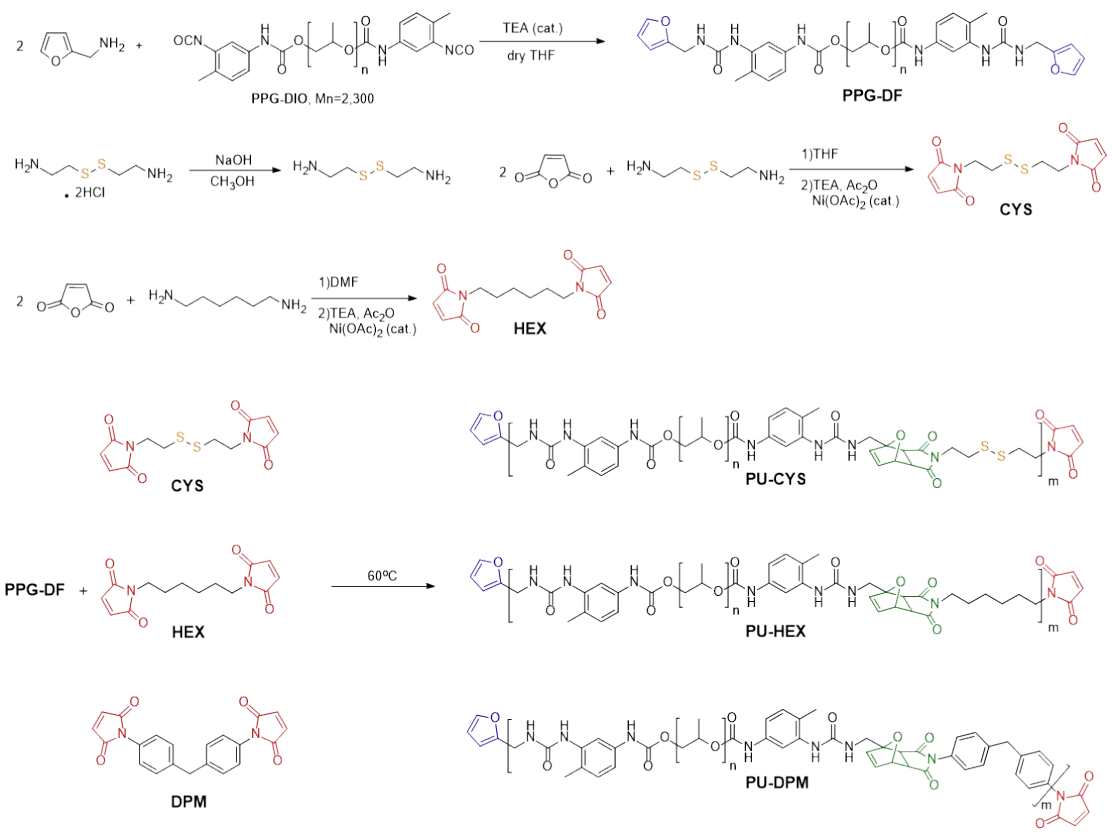

Fig. S1. Synthetic scheme of PU-CYS, PU-HEX and PU-DPM

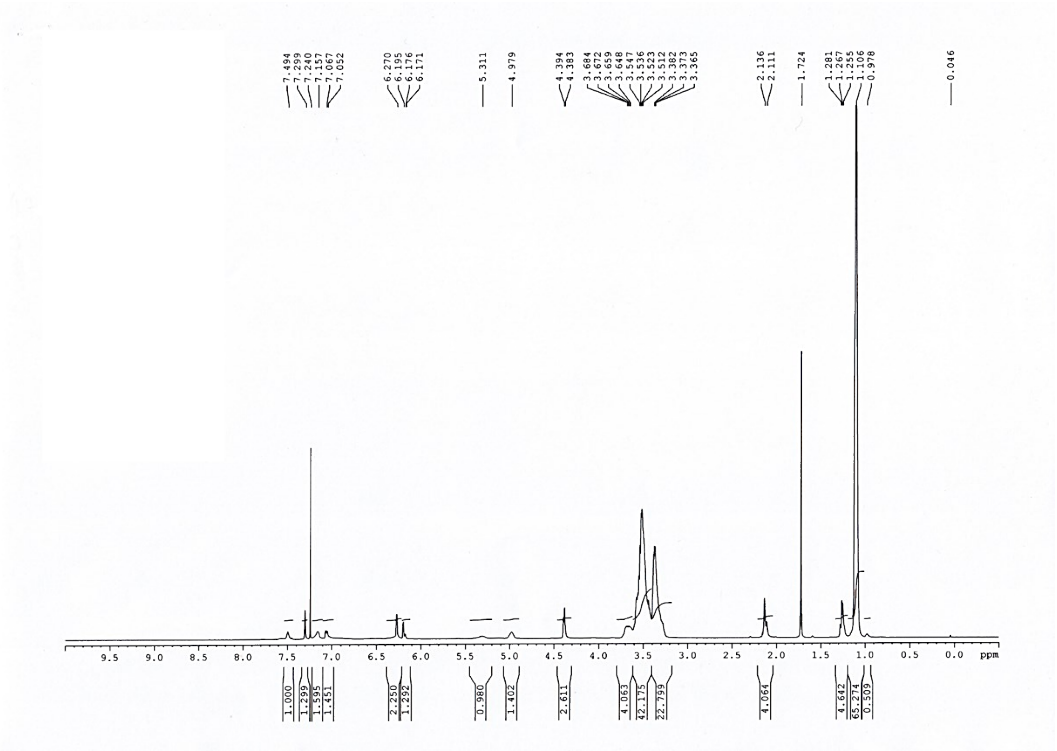

Fig. S2. 1H-NMR of compound **PPG-DF**

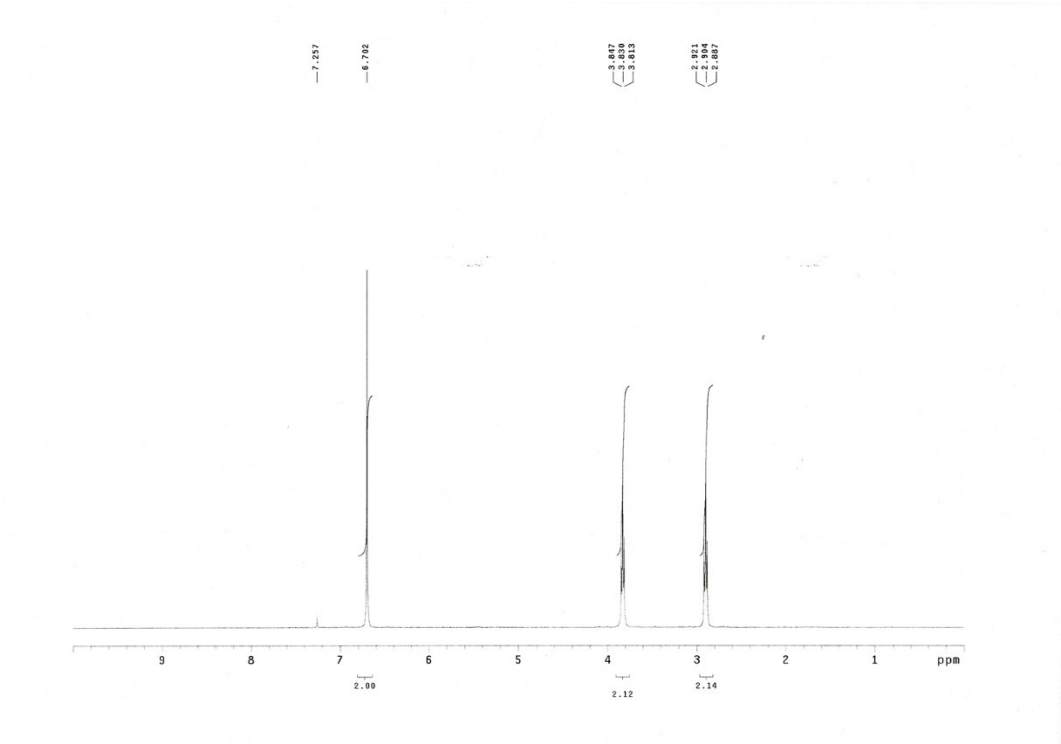

Fig. S3. 1H-NMR of **CYS**

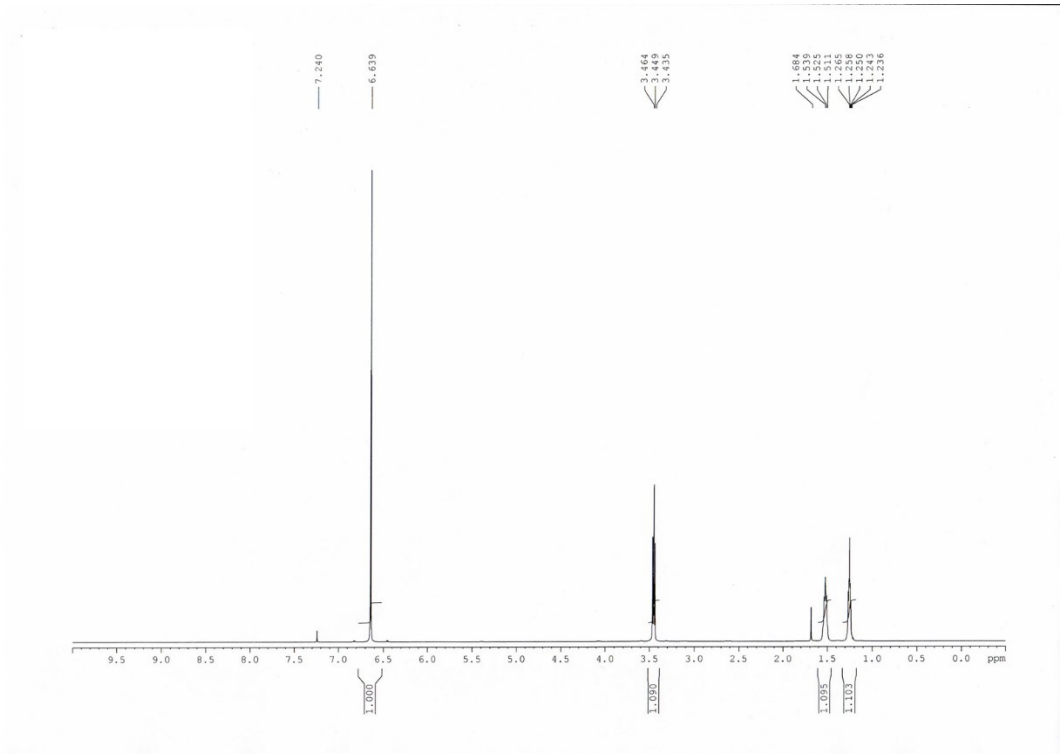

Fig. S4. 1H-NMR of **HEX**

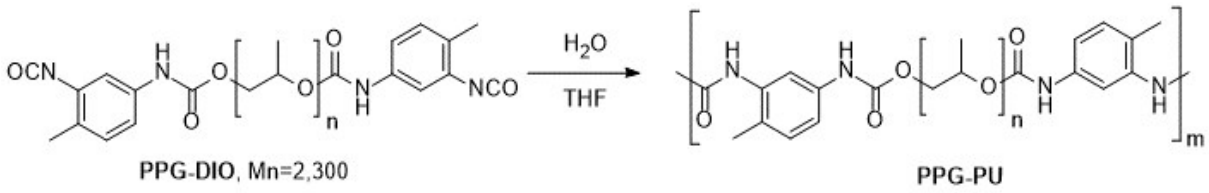

Fig. S5. Synthetic scheme of PPG-PU

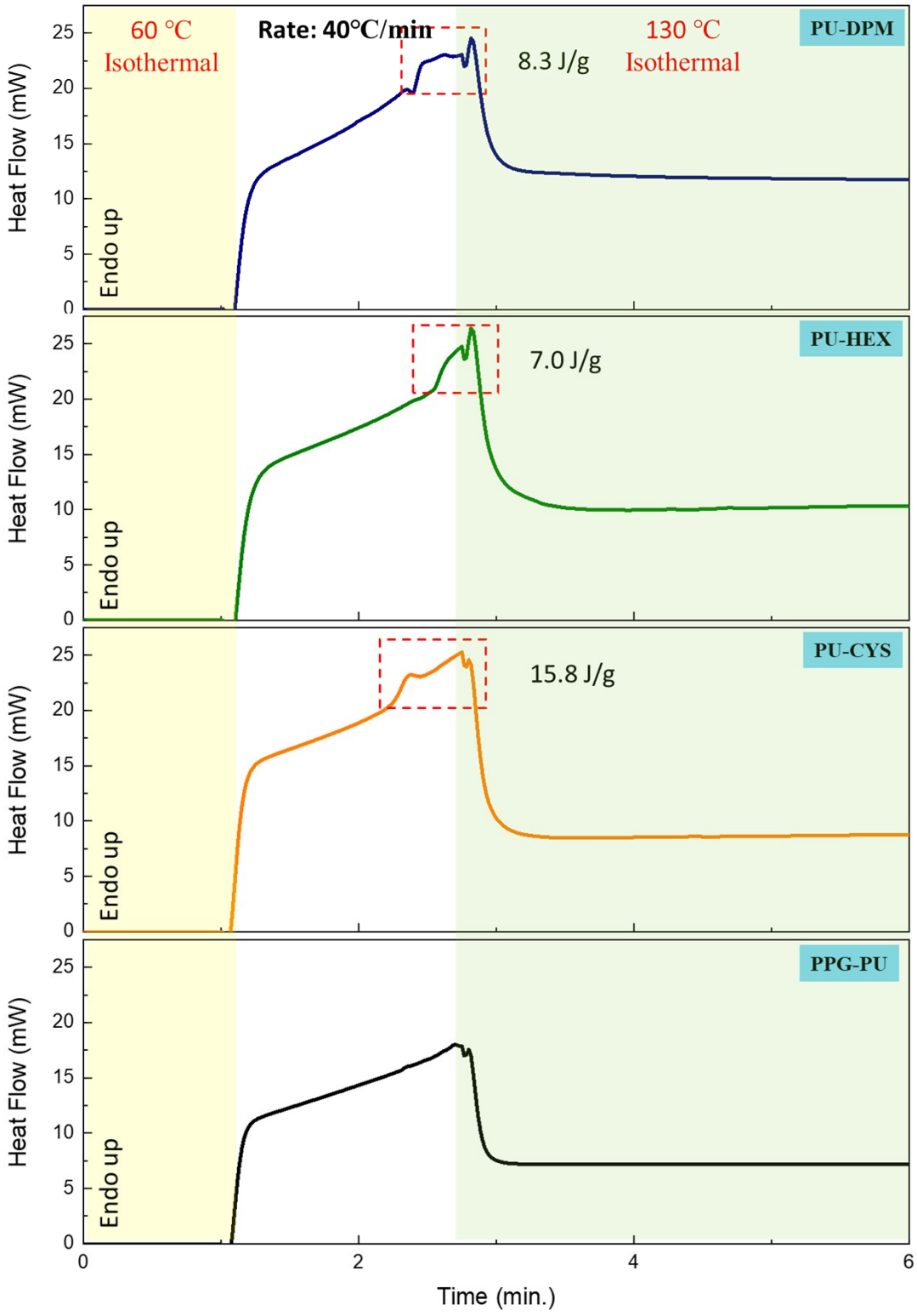

Fig. S6. Isothermal DSC analysis of PU-DPM, PU-HEX, PU-CYS and PPG-PU

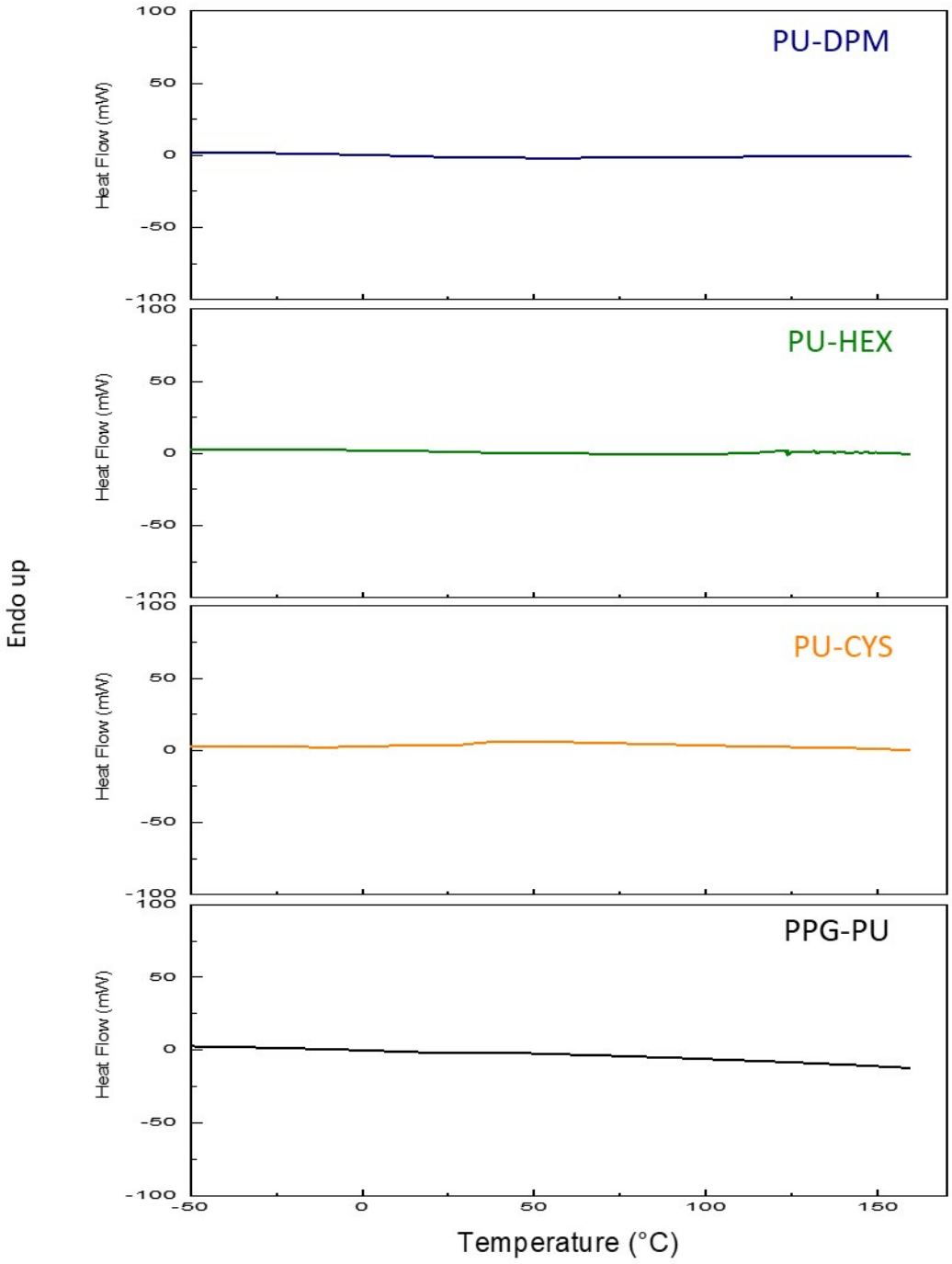

Fig. S7. Large range DSC analysis of PU-DPM, PU-HEX, PU-CYS and PPG-PU

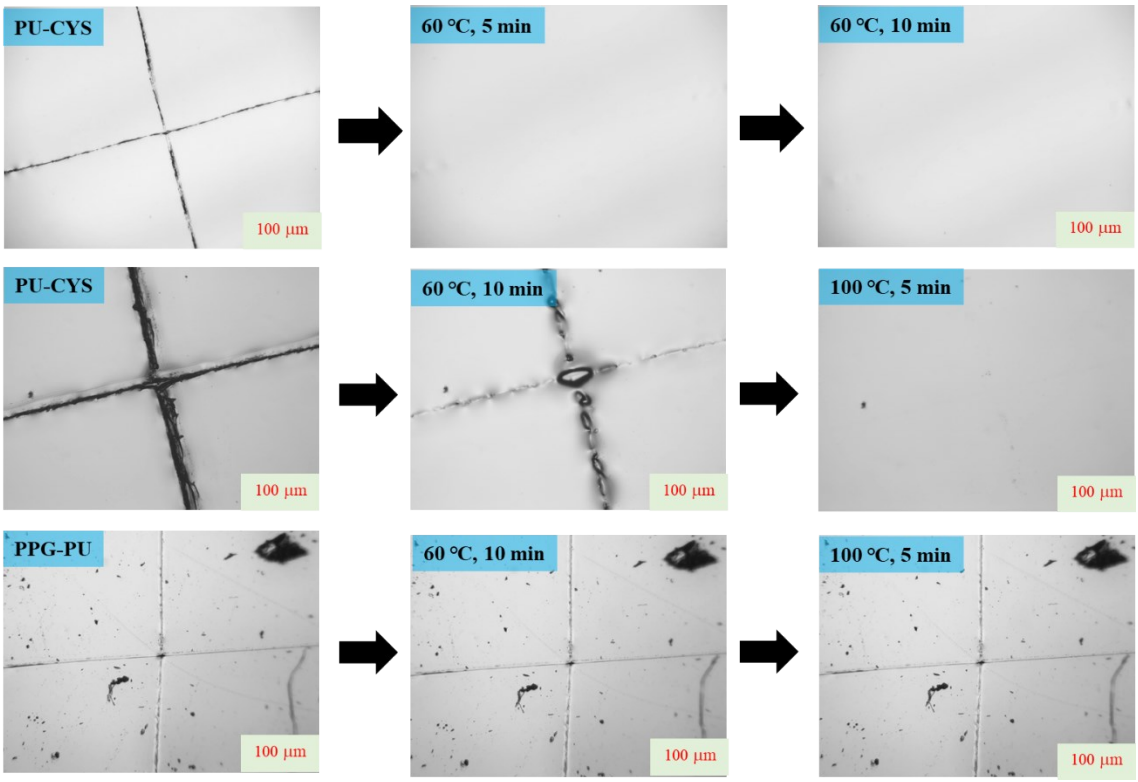

Fig. S8. Optical microscope images demonstrating the healing process of PU-CYS and PPG-PU at 60 °C and 100 °C

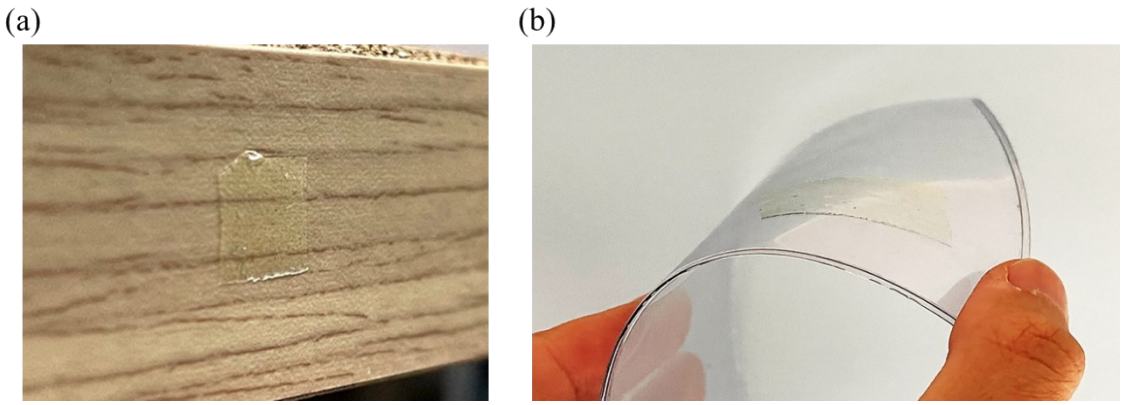

Fig. S9. Photo images of the adhesion of PU-CYS on (a) a wooden surface and on (b) a bent PET substrate.

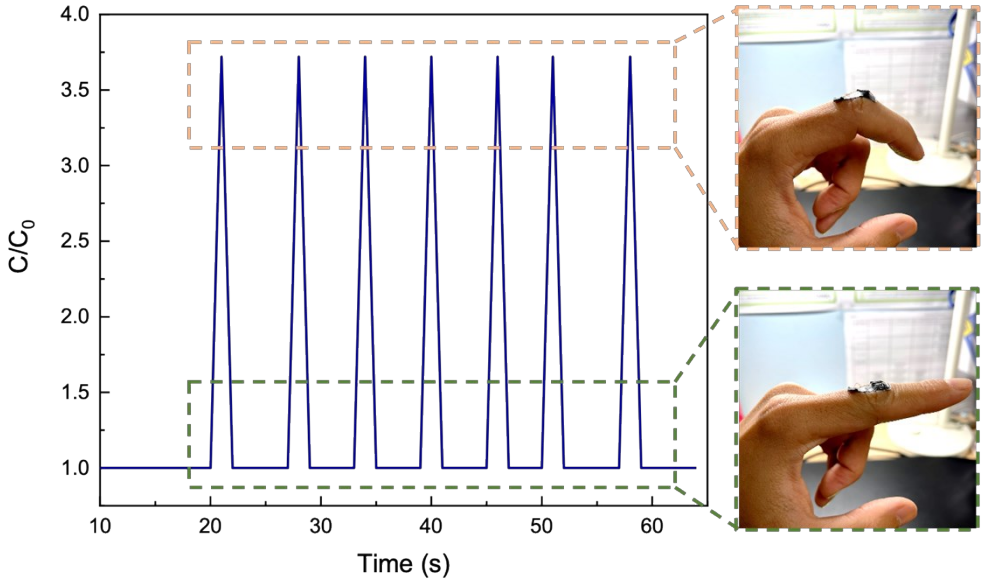

Fig. S10. Responses of PU-CYS-based human motion sensor to cyclic motions with finger bending and recovering.

Table S1 The tensile strength, tensile strain, transparency, adhesion and healing ratio of PU-CYS, and comparison with state-of-the-art self-healing materials.

	Tensile Stress (MPa)	Tensile Strain (%)	Transparency (%)	Adhesion (MPa)	Recycling or healing efficiency (%)
Adv. Mater. **2018**, 30 (38), 1802556.	25	1600	99	-	85
Science **2018,** *359* (6371), 72-76.	45	393	-	-	99+
ACS Appl. Mater. Interfaces **2019**, 11 (8), 7755-7763.	0.06	4000	-	0.046	96
J. Mater. Sci. **2019**, 54 (7), 5472-5483.	1.09	64	-	-	93
Adv. Mater. **2019,** 31 (23), 1901402.	14.8	1200	-	-	93
Nat. Commun **2019,** *10*, 1-8.	35.9	805	-	-	99+
New J. Chem. **2020,** *44* (21), 8977-8985.	0.09	515	-	-	88
Nat. Mater. **2020**, 19(11), 1230-1235..	23	200	-	-	99+
Nat. Mater. ***2020****, 19 (2), 182-188.*	1.06	906	94	-	91
PU-CYS (Our Work)	4.63	1092	97	2.54	92

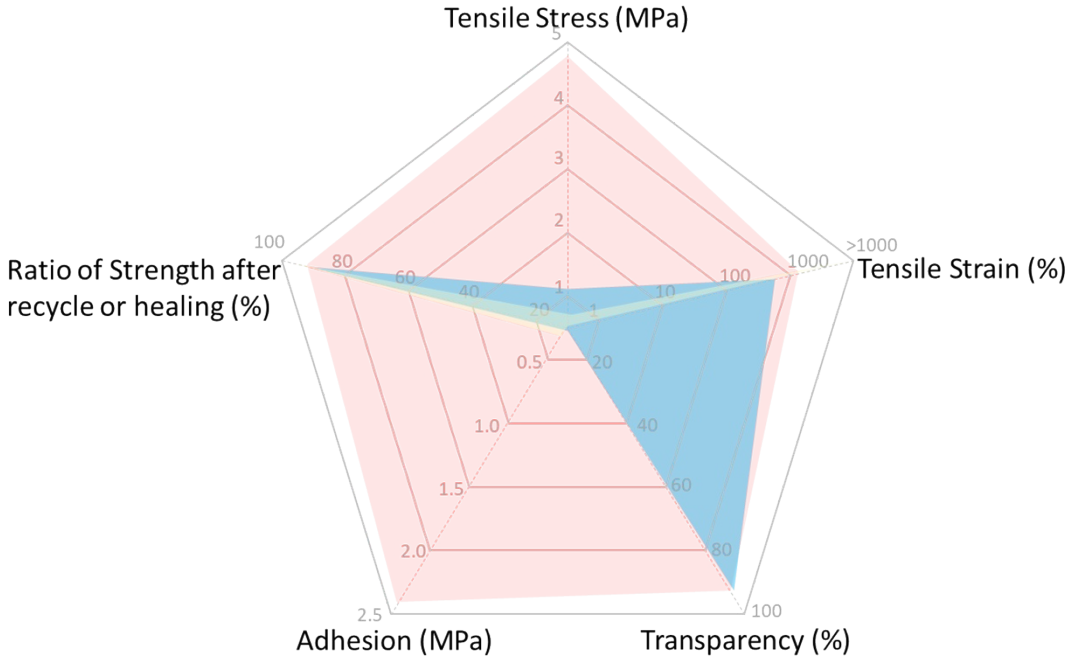

Fig. S11. The radar plot of PU-CYS is compared to that of state-of-the-art self-healing materials that use different chemistries.

Reference

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2. C. C. Xiao, Y. Zhu, J. D. Chen and S. M. Zhang, *Polymer*, 2017, **110**, 74-79.