Supporting Information

Toughening Self-Healable and Recyclable PDMS Supramolecular Elastomer through

End-Capping Agent and Metallic Crosslinker

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Experimental Section

Mechanical property test

The mechanical properties (uniaxial tensile tests and cyclic tensile tests) of PUIP-Hac, PUIP-Hac-Alac, PUIP-Hac-AlOTf and PUIP-Hac-AlClO₄ films (measuring 3 cm x 1 cm x 0.5 mm) were evaluated at room temperature using a uniaxial tensile tester with a displacement rate of 100 mm/min. In the cyclic tensile test, there will be a one-minute interval between each cycle.

Density Functional Theory (DFT) Calculations

Computational models for each sample were constructed using density functional theory (DFT). All calculations were performed with Gaussian 16, and each structure was fully optimized geometrically at the B3LYP/6-31G(d) level.

The binding energy (E_b) of each metal salt cross-linker with PUIP-Hac was calculated as follows:

$$E_b = E_{(PUIP - Hac - Alx)} - E_{(PUIP - Hac)} - E_{(Metal salt)}$$

where $E_{(PUIP-Hac-Alx)}$, $E_{(PUIP-Hac)}$, and $E_{(Metal Salt)}$ represent the energies of metal salt crosslinker on PUIP-Hac complex system (PUIP-Hac-Alac, PUIP-Hac-AlOTf, and PUIP-Hac-AlClO₄), the PUIP-Hac polymer, and the metal salt cross-linker (Al(acac)₃, Al(OTf)₃, and Al(ClO₄)₃), respectively. A negative binding energy indicates the interaction is energetically favorable, suggesting stable complex formation.

Self-Healing test

In the self-healing experiment, elastomer films underwent cutting into two pieces using a razor blade, followed by rejoining and healing in a 50°C oven for different period of time (2, 4, 6, 8, and 12 h). Each sample underwent testing with at least three specimens. The self-healing efficiency is defined as follows:

 $Healing \ efficiency = \frac{Toughness_{healed}}{Toughness_{pristine}} \times 100\%$

Electrochemical tests

A three-electrode system was utilized to investigate the intrinsic electrochemical properties of the AgFK-PUIP-Hac-AlOTf electrodes using an electrochemical workstation (CHI6273E, CH Instruments). A free-standing electrode $(1 \times 1.5 \text{ cm}^2)$ served as the working electrode, while a platinum (Pt) wire and an Ag/AgCl electrode were employed as the counter and reference electrodes, respectively. A 0.5 M NaCl solution was used as the electrolyte. For cyclic voltammetry (CV) measurements, the electrochemical potential window was set between -0.5 V and 0.5 V (vs. Ag/AgCl). Electrochemical impedance spectroscopy (EIS) measurements were conducted at an initial potential of 0 V (vs. Ag/AgCl) with a 5 mV perturbation amplitude over a frequency range of 10^5 –10 Hz.

ECG measurement

ECG signals were recorded using a Tektronix TBS 2000B digital oscilloscope. The electrodes were placed with the positive electrode on the right arm and the negative and ground electrodes on the left arm of the subject. For comparison, gelled Ag/AgCl

electrodes (KendallTM H135SG) were used as commercial references for ECG signal acquisition.

Characterization

Fourier transform infrared (FT-IR) spectra were acquired using a NICOLET iS50 FT-IR spectrometer within the range of 400–4000 cm⁻¹ (32 scans, 4 cm⁻¹ resolution). Nuclear magnetic resonance (¹H NMR) spectra were obtained with a Bruker Avance 500 MHz NMR spectrometer, dissolving samples in chloroform-d. Gel permeation chromatography (GPC) was performed using a Hitachi Gel Permeation Chromatography and 5450 RI detector with polystyrene standards; the mobile phase was tetrahydrofuran (flow rate: 1.00 mL min⁻¹). Thermogravimetric analysis (TGA) was conducted using a TA Q600 instrument from 30–600 °C under nitrogen (heating rate: 10 °C min⁻¹). Optical microscope (OM) examinations utilized a WHITED WM-100 system. Ultraviolet-visible (UV-vis) spectra were recorded using a Shimadzu UV-1900 spectrophotometer. Tensile tests employed a QC-505M2F with a 100 N load cell. Samples (30 mm \times 10 mm \times 0.4 mm) were tested at a displacement rate of 100 mm min⁻¹. Dynamic mechanical performance of the samples was performed on a TA Instrument Q800 in the tension film mode. The measurements were performed from -140 to 60 °C with a heating rate of 3 °C/min and a frequency of 1 Hz.



Figure S1 Synthesis process of PUIP-Hac and PUIP-Hac-Alx. (x=ac, OTf and ClO₄)

Table S1 Molecular weight and polymer dispersity index (PDI) of the PUIP-Hac, PUIP-Hac-Alac, PUIP-Hac-AlOTf and PUIP-Hac-AlClO4.

Sample Name	M _n	M_{w}	PDI
PUIP-Hac	21107	30730	1.45
PUIP-Hac-Alac	20422	28974	1.42
PUIP-Hac-AlOTf	15523	75347	4.85
PUIP-Hac-AlClO ₄	14861	75093	5.05

The molecular weight of PUIP-Hac-Alac is comparable to that of PUIP-Hac, while PUIP-Hac-AlOTf and PUIP-Hac-AlClO₄ exhibit higher molecular weights and broader molecular weight distributions. This phenomenon can be attributed to the differences in the coordination tendencies of aluminum ions, as discussed in the manuscript. In PUIP-Hac-Alac, the counter anion of the added metal salt Al(acac)₃ is identical to the end-capping agent Hacac. Due to steric hindrance, aluminum ions preferentially coordinate with acac⁻ anions, rather than facilitating extensive coordination crosslinking with the polymer chains. As a result, the molecular weight of PUIP-Hac-AlaClO₄, the introduction of aluminum ions promotes coordination-driven crosslinking within the polymer network, leading to an increase in molecular weight and a broader molecular weight distribution (higher PDI). This observation underscores the critical role of counter anions in modulating the metal-ligand coordination and the resulting polymer network structure.



Figure S2 Variable-temperature ¹H NMR sprectra of PUIP-Hac.



Figure S3 FT-IR spectra of PUIP-Hac and PUIP-Hac-Alac, AlOTf and AlClO4.

Table S2 X-ray photoelectron spectroscopy (XPS) data of PUIP-Hac-Alac, AlOTf andAlClO4.

Sample Name	Peak	Binding energy (eV)	Reference
Al 2p	Al-O	73.3	[58] [59]
Al 2p	Al-N	74.5	[00],[00]

Table S3 Summarized thermal decomposition temperature (T_d) of PUIP-Hac and PUIP-Hac-Alac, AlOTf and AlClO4.

Sample Name	$T_d(^{\circ}C)$
PUIP-Hac	278
PUIP-Hac-Alac	263
PUIP-Hac-AlOTf	264
PUIP-Hac-AlClO ₄	251



Figure S4 Dynamic mechanical analyzer (DMA) spectra of (a) PUIP-Hac, (b) PUIP-Hac-Alac, (c) PUIP-Hac-AlOTf, and (d) PUIP-Hac-AlClO₄.

Table S4 Glass transition temperature (Tg) of PUIP-Hac and PUIP-Hac-Alac, AlOTf and

Sample Name	T _g (°C)
PUIP-Hac	-104.16 ± 2.85
PUIP-Hac-Alac	-102.96 ± 3.05
PUIP-Hac-AlOTf	-109.90 ± 2.13
PUIP-Hac-AlClO ₄	-113.20 ± 2.82

AlClO₄.



Figure S5 Water contact angle test (WCA) of (a) bare glass, (b) PUIP-Hac, (c) PUIP-Hac-Alac, (d) PUIP-Hac-AlOTf, and (e) PUIP-Hac-AlClO₄.

Table S5 Summarized water contact angle of bare glass, PUIP-Hac, PUIP-Hac-Alac,PUIP-Hac-AlOTf, and PUIP-Hac-AlClO4.

Sample Name	Water Contact Angle (°)	
Blank (bare glass)	73.1 ± 0.57	
PUIP-Hac	107.08 ± 1.45	
PUIP-Hac-Alac	107.05 ± 1.31	
PUIP-Hac-AlOTf	105.59 ± 1.19	
PUIP-Hac-AlClO ₄	111.40 ± 0.94	

All results were obtained from experiments conducted at least three times for each sample.



Figure S6 Elemental mapping of the PUIP-Hac surface shows a uniform distribution of C,

Si, O, and N, indicating the homogeneity of hydrogen bonding throughout the polymer.





Figure S7 Elemental mapping of the PUIP-Hac-Alac surface shows a uniform distribution of C, Si, O, N, and Al indicating the homogeneity of hydrogen bonding and metal coordination throughout the polymer.





Figure S8 Elemental mapping of the PUIP-Hac-AlOTf surface shows a uniform distribution of C, Si, O, N, S, F, and Al indicating the homogeneity of hydrogen bonding and metal coordination throughout the polymer.



Figure S9 Elemental mapping of the PUIP-Hac-AlClO₄ surface shows a uniform distribution of C, Si, O, N, Cl, and Al indicating the homogeneity of hydrogen bonding and metal coordination throughout the polymer.

Sample Name	Stress (MPa)	Strain (%)	Modulus (MPa)	Toughness (MJm ⁻³)
PUIP-Hac	1.03 ± 0.18	507 ± 16	1.15 ± 0.32	3.41 ± 1.0
PUIP-Hac-Alac	1.62 ± 0.27	300 ± 81	3.41 ± 1.32	3.83 ± 0.8
PUIP-Hac-AlOTf	4.36 ± 0.03	1352 ± 110	6.89 ± 1.49	48.73 ± 2.6
PUIP-Hac-AlClO ₄	4.44 ± 0.32	712 ± 111	8.38 ± 0.61	26.15 ± 6.0
AlOTf and AlClO ₄ .				

Table S6 Summary of the mechanical properties of the PUIP-Hac and PUIP-Hac-Alac,

Using a uniaxial tensile tester with a rate of 100 mm/min. All results were obtained from experiments conducted at least three times for each sample.



Fig S10 Cyclic loading/unloading curves of (a) PUIP-Hac, (b) PUIP-Hac-Alac, (c) PUIP-Hac-AlOTf, and (d) PUIP-Hac-AlClO₄ with 50%, 100%, 150%, 200% and 250% tensile strains and there was no waiting time between two cyclic tensile tests.

48	PDMS-TDI-Al	1700	2.6	14.7	90.0
61	LP2-SS-HP	224	8.6	16.3	95.3
62	PDMS-U/PDMS-C _{0.3} /Zn ²⁺	776	4	16	98
63	PDMS-2	410	3.65	10.04	96
64	PDMS/CNTs 2.0 -2S	1420	1.1	5	95
65	SiR-SN 0.1/1	931	0.2	1.16	86
66	SF-PUU	1000	4.18	27.7	100
This	PUIP-Hac-AlOTf	1353	136	19 72	05.3
Work		1332	4.30	40./3	75.5

 Table S7 Summarized mechanical properties of recently published self-healing PDMS

polymers.



Fig S11 Optical microscope images of scratch tests conducted under room temperature after 1 day. (a) PUIP-Hac (b) PUIP-Hac-Alac (c) PUIP-Hac-AlOTf, and (d) PUIP-Hac-AlClO₄.



Fig S12 Fracture tests conducted under 50°C after 12h. (a) PUIP-Hac (b) PUIP-Hac-Alac (c) PUIP-Hac-AlOTf, and (d) PUIP-Hac-AlClO₄.



Fig S13 Stress relaxation curve of (a) PUIP-Hac, (b) PUIP-Hac-Alac, (c) PUIP-Hac-AlOTf and PUIP-Hac-AlClO₄ elastomers.

The relaxation stress declined more rapidly as the temperature increased, as reflected in the characteristic relaxation time (τ), which is defined as the time required for the stress to decrease to 1/e of its initial value. The relationship between relaxation time and temperature follows the Arrhenius equation, allowing the activation energy (Ea) to be determined from the fitted data. The activation energy (Ea) is calculated using the following equation:

$$ln(\tau) = \frac{E_{\rm a}}{RT} + ln(\tau_0)$$

where τ represents the relaxation time, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (K).

Ref.	Name	Strain (%)	Stress (MPa)	Temperature (°C)	Healing Time (h)
33	Zn(Hbimcp) ₂ -PDMS	2400	2.3	r.t	48
40	Fe-Hpdca-PDMS	1800	0.225	r.t	48
41	PDMS-SS-IP-BNB	1300	0.1	r.t	2
44	CHZ-PDMS	1730	2	70	24
45	PDMS-MPU _{0.4} -IU _{0.6}	1600	1.6	r.t	48
47	PDMS-DAP@Fe-1/3	1475	2.81	70	48
48	PDMS-TDI-A1	1700	2.6	r.t	36
62	$PDMS\text{-}U/PDMS\text{-}C_{0.3}/Zn^{2+}$	776	4	60	8
66	SF-PUU	1000	4.18	60	48
67	PDMSOH ₁ -DTB _{0.5}	670	2.9	60	0.5
68	P3K-SS-IP	507	1.97	r.t	24
69	PDMS-PUa-TFB 0.1	890	3	r.t	36
70	PDMS-MDI _{0.3} -IPDI _{0.7}	785	10.5	60	24
71	U-PDMS-SP4	528	0.21	r.t	16
72	SH PDMS	450	0.075	r.t	24
This Work	PUIP-Hac-AlOTf	1352	4.36	50	12

Table S8 Summarized self-healing ability and mechanical properties with previouslyreported robust self-healing PDMS elastomers.



Fig S14 The FT-IR spectra of the pristine and recycled PUIP-Hac-AlOTF



Fig S15 Electrochemical properties of AgFK-PUIP-Hac-AlOTf. (a) Cyclic voltammograms curves recorded at 1^{st} and 2^{nd} cycles. (b) Cyclic voltammograms recorded at different scan rates using a three-electrode configuration. (c) Electrochemical impedance spectra (EIS) of the electrodes measured in a three-electrode setup at open-circuit potential with an amplitude of 5 mV, over a frequency range from 10^{5} Hz to 10 Hz, in a 0.5 M NaCl electrolyte.