

**Highly Stretchable, Tough, Healable and Mechanoresponsive Polyurethane Elastomers for
Flexible Capacitor Applications**

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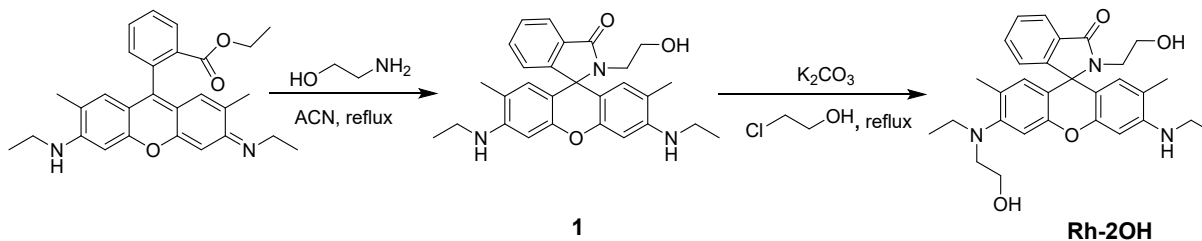
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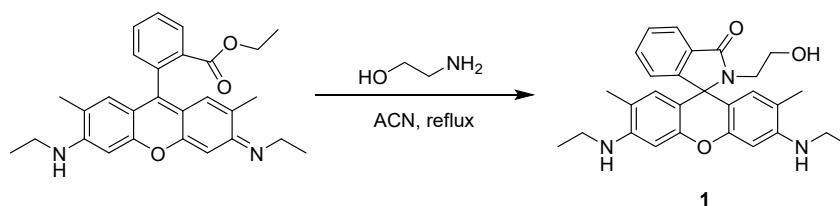
Keywords: Stimuli responsive elastomer, healable polyurethane, Diels-Alder reaction,
mechanochromic, Shape-memory, flexible capacitor.

1 Synthetic schemes:

1-1. Synthetic scheme of dihydroxy rhodamine 6G derivative:

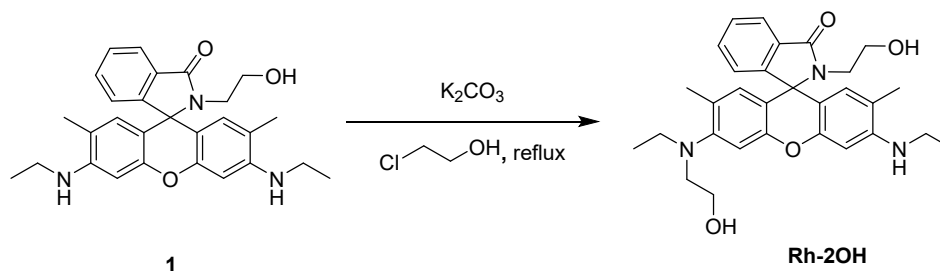


1-1-1. Synthesis of compound **1**:



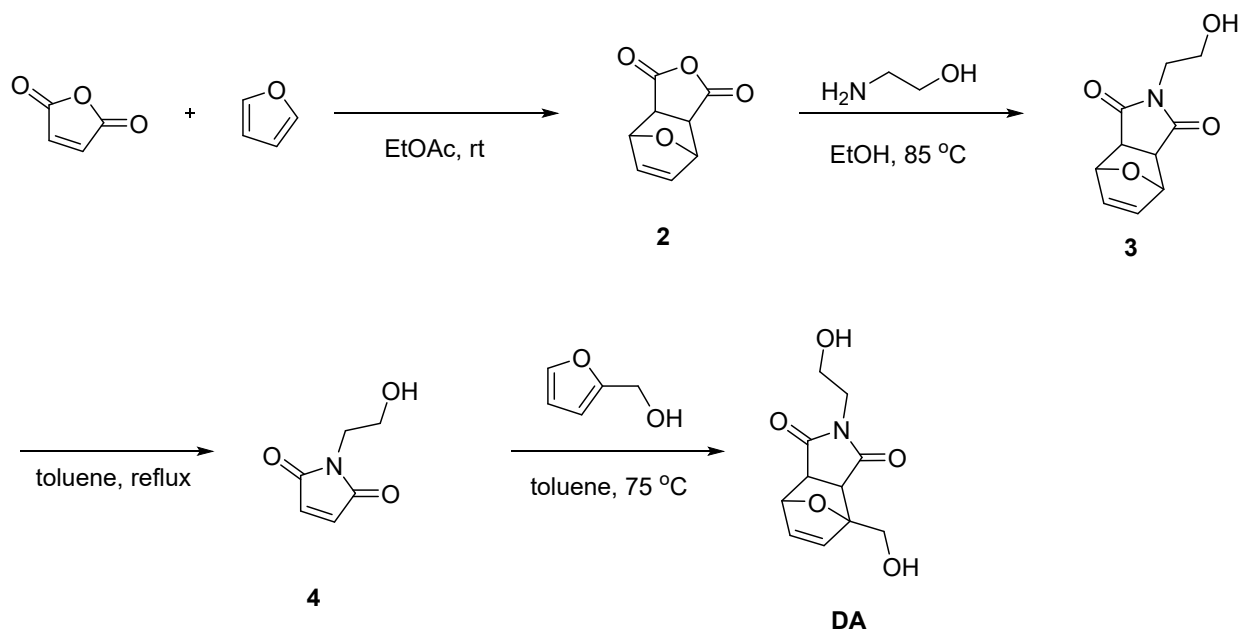
Synthesis of compound **1:** First, rhodamine 6G (2.00 g, 4.18 mmol) and ethanolamine (0.76 mL, 12.53 mmol) were dissolved in 30 mL acetonitrile. The solution was refluxed under N₂ atmosphere for 2 hrs. The deep red solution gradually became heterogeneous and lost its deep color. Then, the solution was cooled to room temperature and the solid was filtered out. Finally, this solid was washed with water for several times, and dried under vacuum to get compound **1** as a pink powder (1.61 g, yield: 84%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 7.94-7.90 (m, 1H), 7.47-7.41 (m, 2H), 7.05-7.00 (m, 1H), 6.34 (s, 2H), 6.27 (d, *J* = 0.8 Hz, 2H), 4.18 (s, 1H), 3.54 (s, 2H), 3.43 (t, *J* = 4.8 Hz, 2H), 3.26-3.18 (m, 6H), 1.91 (s, 6H), 1.31 (t, *J* = 7.2 Hz, 6H).

1-1-2. Synthesis of compound Rh-2OH:

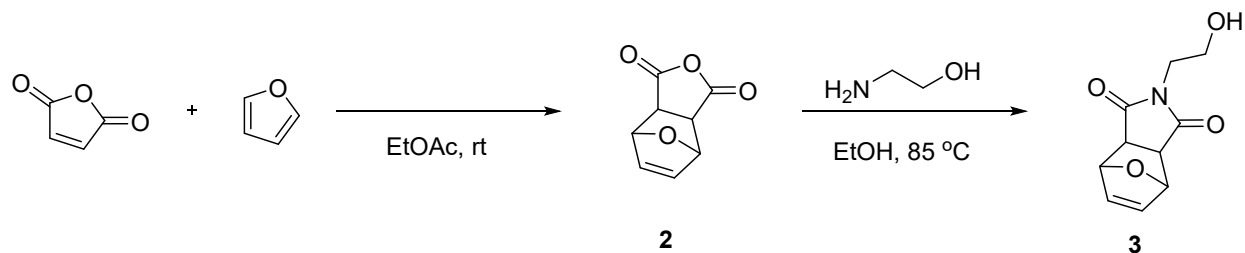


Synthesis of compound Rh-2OH: Compound **1** (1.00 g, 2.19 mmol) and K_2CO_3 (2.40 g, 17.48 mmol) in 20 mL ethylene chlorohydrin were refluxed for 2 hrs at 100 °C. The excessive ethylene chlorohydrin was evaporated using rotary evaporation. Then, the crude product was further purified on aluminum oxide using a column chromatography with a mixed solvent (CH_2Cl_2 /methanol = 100:1) to obtain compound **Rh-2OH** as a pink powder (0.72 g, yield: 65%). 1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.94-7.88 (m, 1H), 7.47-7.42 (m, 2H), 7.03-6.99 (m, 1H), 6.89 (s, 1H), 6.45-6.41 (m, 1H), 6.33-6.30 (m, 1H), 6.28-6.23 (m, 1H), 3.59 (t, $J = 5.6$ Hz, 1H), 3.42-3.33 (m, 2H), 3.28-3.15 (m, 6H), 3.04-2.95 (m, 2H), 2.06 (s, 3H), 1.89 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.00 (t, $J = 6.8$ Hz, 3H). ^{13}C -NMR (125 MHz, $CDCl_3$, δ ppm): 170.11, 153.58, 151.54, 150.72, 150.51, 147.83, 133.02, 130.30, 130.00, 129.54, 128.53, 128.06, 123.92, 123.17, 118.57, 113.70, 110.42, 104.83, 96.56, 65.76, 63.90, 62.14, 59.17, 53.87, 48.32, 44.59, 38.41, 17.92, 16.83, 14.74, 11.78. HRMS (ESI⁺) $[M+H]^+$: calcd. for $C_{30}H_{36}N_3O_4$ 502.2700, found 502.2701.

1-2. Synthetic scheme of Diels–Alder derivative (DA):



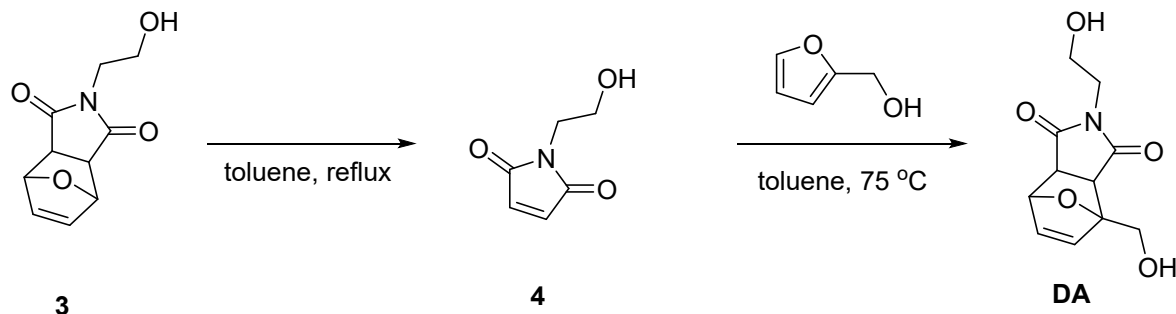
1-2-1. Synthesis of compounds 2 and 3:



Synthesis of compound 2: In a round bottomed flask, maleic anhydride (20.00 g, 203.99 mmol) was dissolved in ethyl acetate, followed by the addition of furan (13.90 g, 203.99 mmol). After 24 hrs reaction at room temperature under magnetic stirring, a white solid powder was precipitated. The precipitate was collected via suction filtration, washed with diethyl ether and dried under vacuum to obtain compound **2** (28.80 g, yield: 65%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm): 6.58 (t, $J = 1.2$ Hz, 2H), t, $J = 0.8$ Hz, 2H), 3.17 (s, 2H).

Synthesis of compound 3: Compound **2** (10.00 g, 60.19 mmol) and ethanol were mixed in a round-bottomed flask using magnetic stirring. A solution of ethanolamine (5.52 g, 90.29 mmol) in ethanol was added dropwise to the former mixture in an ice bath condition. Then, the clear solution was refluxed for 24 hrs at 65 °C. Next, the solution was kept inside a freezer to obtain the slight yellow powder due to crystallization. Finally, the crystal was filtered out, washed with diethyl ether and dried under vacuum to obtain compound **3** as a pale yellow powder (8.18 g, yield: 65%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ ppm): 6.50 (t, $J = 1.2$ Hz, 2H), 5.26 (t, $J = 0.8$ Hz, 2H), 3.74-3.71 (3, 2H), 3.67-3.64 (m, 2H), 2.87 (s, 2H), 2.48 (s, 1H).

1-2-2. Synthesis of compounds 4 and DA:



Synthesis of compound 4: Compound **3** (1.55 g, 7.41 mmol) was refluxed in toluene for 24 hrs, then the resulting solution was put into a freezer to precipitate the white powder. The product was filtered out, washed with diethyl ether and dried under vacuum to yield compound **5** as a white solid (0.85 g, yield: 81%). ¹H NMR (400 MHz, CDCl₃, δ ppm): 6.73 (s, 2H), 3.78-3.76 (m, 2H), 3.73-3.71 (m, 2H), 2.37 (s, 1H).

Synthesis of compound DA: Compound **4** (0.85 g, 6.02 mmol) was dissolved in 20 mL toluene, and then furfuryl alcohol (0.6 g, 6.12 mmol) was added to the former solution. After the mixture was stirred under magnetic stirring at 75 °C for 24 hrs, a white solid was precipitated as a product. The precipitate was filtered out, washed with diethyl ether and dried under vacuum to obtain compound **DA** as a white solid (1.3 g, yield: 90%). ¹H NMR (400 MHz, *d*₆-DMSO, δ ppm): 6.53-6.48 (m, 2H), 5.06-5.02 (m, 2H), 5.01-5.04 (m, 2H), 4.85 (d, *J* = 6.4 Hz, 1H), 4.04-4.00 (m, 1H), 3.68-3.65 (m, 1H), 3.40 (t, *J* = 4.4 Hz, 4H), 3.02 (d, *J* = 6.4 Hz, 1H), 2.86 (d, *J* = 6.4 Hz, 1H). ¹³C-NMR (125 MHz, *d*₆-DMSO, δ ppm): 176.72, 175.24, 138.24, 136.71, 91.82, 80.39, 59.14, 57.48, 50.15, 47.98, 40.75. HRMS (ESI⁺) [M+H]⁺: calcd. for C₁₁H₁₄NO₅ 240.0866, found 240.0865.

2 Experimental Section

Materials: Chemicals were commercially bought from Alfa Aesar, Combi Blocks, TCI and Sigma-Aldrich and used without further purification. All solvents were reagent grade, which were dried and distilled prior to use as a standard procedure. The list of chemicals and solvents are itemized in Tables S1 & S2 in the Supporting Information.

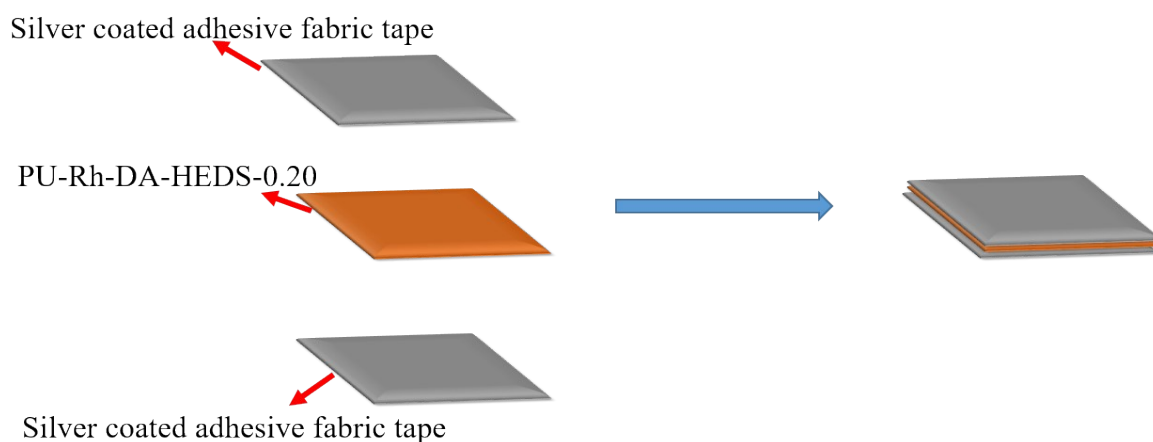
Compound Synthesis and Purification: The detailed synthetic procedures of intermediate materials are listed as Figs. S1-S11 in the Supporting Information. The molecular structures were characterized using ¹H NMR, ¹³C NMR and high-resolution ESI mass spectrometry.

Preparation of PU-Rh-DA-HEDS-i: The syntheses of the elastomeric films were done via the following procedures. For example, PU-Rh-DA-HEDS-0.20 film was prepared as follows: First, Rh-2OH (20.0 mg, 0.04 mmol), PEG (844.8 mg, 2.82 mmol), HEDS (108.6 mg, 0.70 mmol), DA (47.8 mg, 0.20 mmol) and DBTDL (1 drop) were dissolved in dry THF (16 mL), and the solution was refluxed under N₂ atmosphere for 15 min. Then, HDI (807.3 mg, 4.80 mmol) was added slowly and allowed them to react continuously for 1 hour. Next, TEA (83.6 mg, 0.56 mmol) was added to the solution and reacted for another 20 min. Finally, mechanochromic PU films were obtained by pouring the solution into a specified Teflon mold and dried in an oven at 70 °C for 24 h to evaporate the solvent. The compositions of the polymers for various elastomeric films are listed in Table S3 in the Supporting Information.

Mechanical Tests: All stress-strain measurements were carried out by using an MTS Tytron 250 tensile system at 60 mm/min strain rate. The polymer films were cut into a rectangular shape with the following dimension: 15 mm (length) × 2 mm (width) × 0.5 mm (thickness).

Assembly and measurement procedure of capacitors: Flexible capacitors were fabricated using silver coated adhesive fabric tapes and PU-Rh-DA-HEDS-0.20 as electrodes and dielectric layers, respectively. Schematic S1 illustrates the assembly procedures of flexible capacitors. The PU-Rh-DA-HEDS-0.20 film was sandwiched between the silver coated adhesive fabric tapes followed by mechanically pressing using hand to improve the adhesion between the electrodes and dielectric layers. Capacitance and dielectric measurements were carried out by a broadband dielectric spectrometer (Alpha and Beta Analyzer, Novocontrol Technology,

Germany). The samples were sandwiched between two adhesive conductive films as capacitors for capacitance and dielectric measurements. Capacitance vs. voltage measurements were proceeded in the voltage range of -1 to 1V at frequencies 1 and 1KHz. Frequency-dependent capacitance and dielectric properties were measured in the frequency range of 1-1MHz.



Schematic S1: Assembly procedure of capacitors.

Other performed characterizations: Nuclear Magnetic Resonance (NMR) spectra were acquired on Agilent 400 NMR and Bruker 500 NMR 1-D (^1H , ^{13}C) at a frequency of 400 or 500 MHz for ^1H and 125 MHz for ^{13}C . A high-resolution mass spectrometer (HRMS) was operated by a Bruker-Impact HD spectrometer (ESI mode). A fluorescence spectrophotometer (Model: HITACHI F-4500) was used for PL measurements. Fourier transform infrared spectroscopy (FTIR) was measured from 4000 to 400 cm^{-1} using PerkinElmer spectrum 100 at room temperature. The thermal stability was measured using thermo-gravimetric analysis (TGA) (TA instruments Q500, heating rate = 10 $^{\circ}\text{C min}^{-1}$). The Raman spectra were acquired using Horiba Jobin Yvon Labram HR 800 Raman spectroscopy with 514.5 nm Ar laser. The thermal properties were measured

using the Pyris™ Diamond DSC-PerkinElmer (heating/cooling rate=10 °C/min). The high-resolution small angle XRD data were obtained from beamline TLS 23A at National Synchrotron Radiation Research Center (NSRRC), Taiwan ($\lambda=1.02108$ Å). The temperature-dependant oscillatory rheological experiments were performed using DISCOVERY HR-1 hybrid rheometer (TA Instruments) having a 20 mm diameter plate geometry.

NMR Data of intermediate compounds:

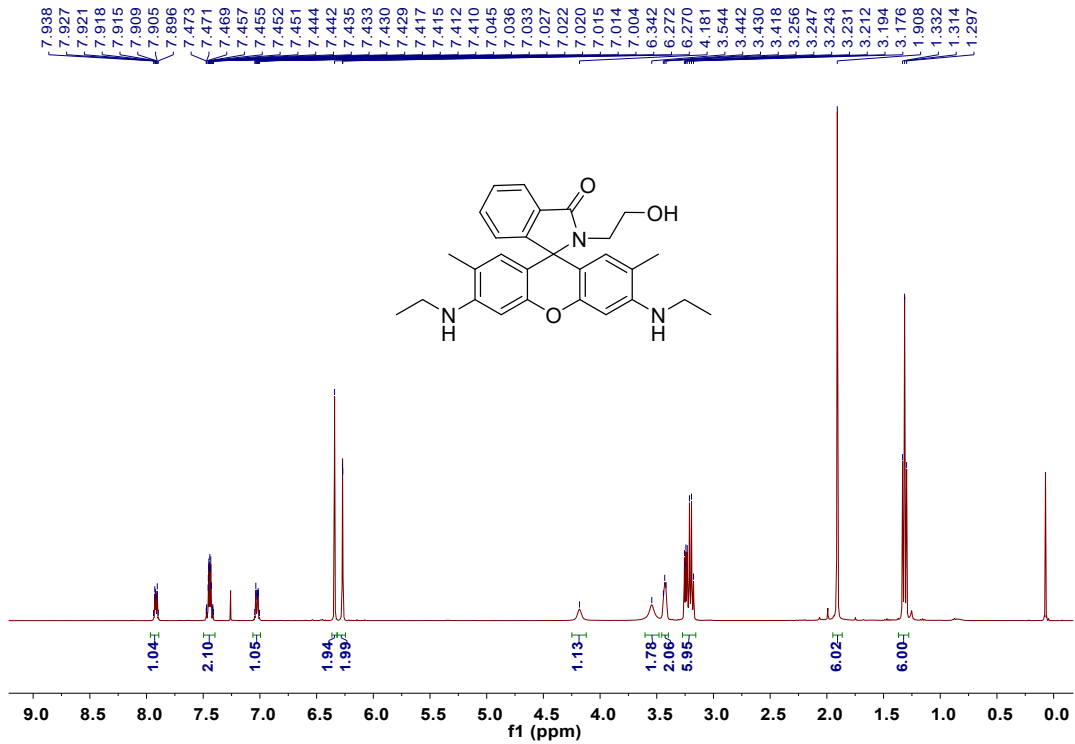


Figure S1. ¹H NMR spectrum (400 MHz, CDCl₃) of compound 1.

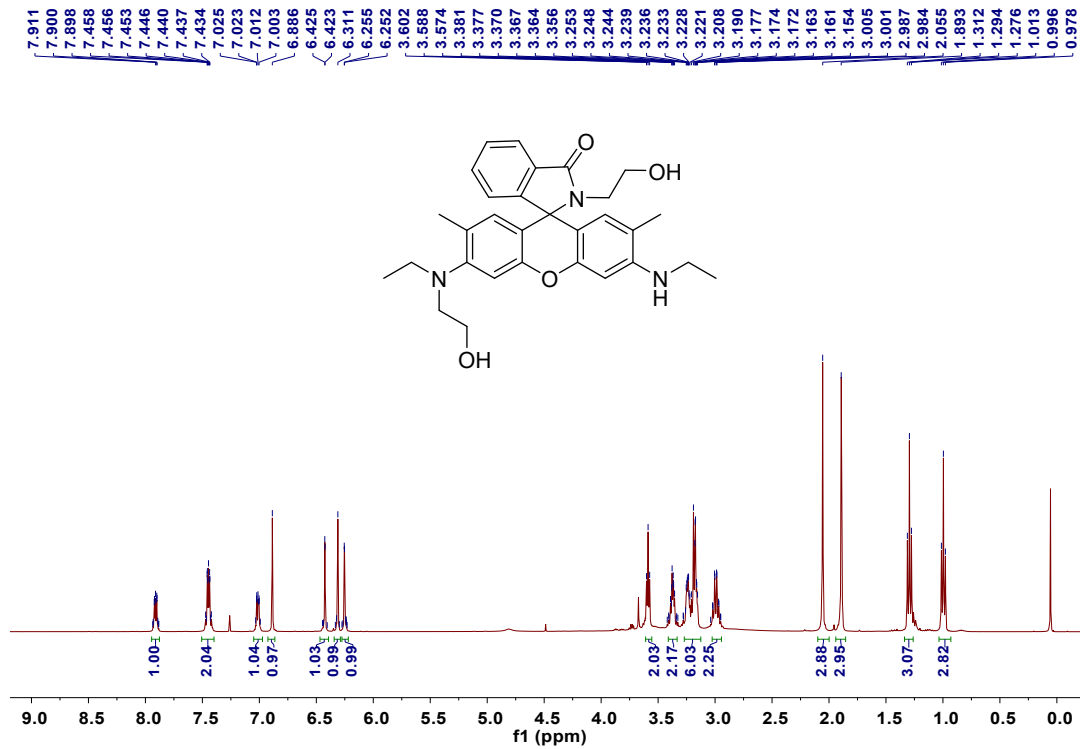


Figure S2. ¹H NMR spectrum (400 MHz, CDCl₃) of Rh-2OH.

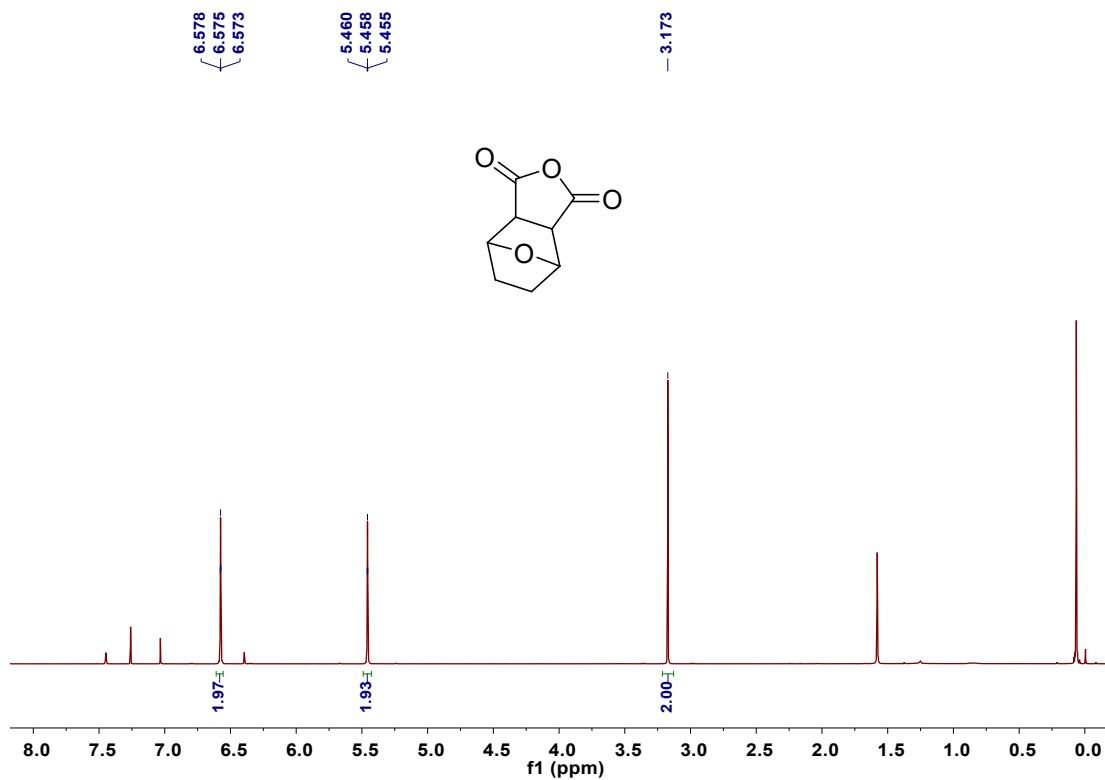


Figure S3. ^1H NMR spectrum (400 MHz, CDCl_3) of compound 2.

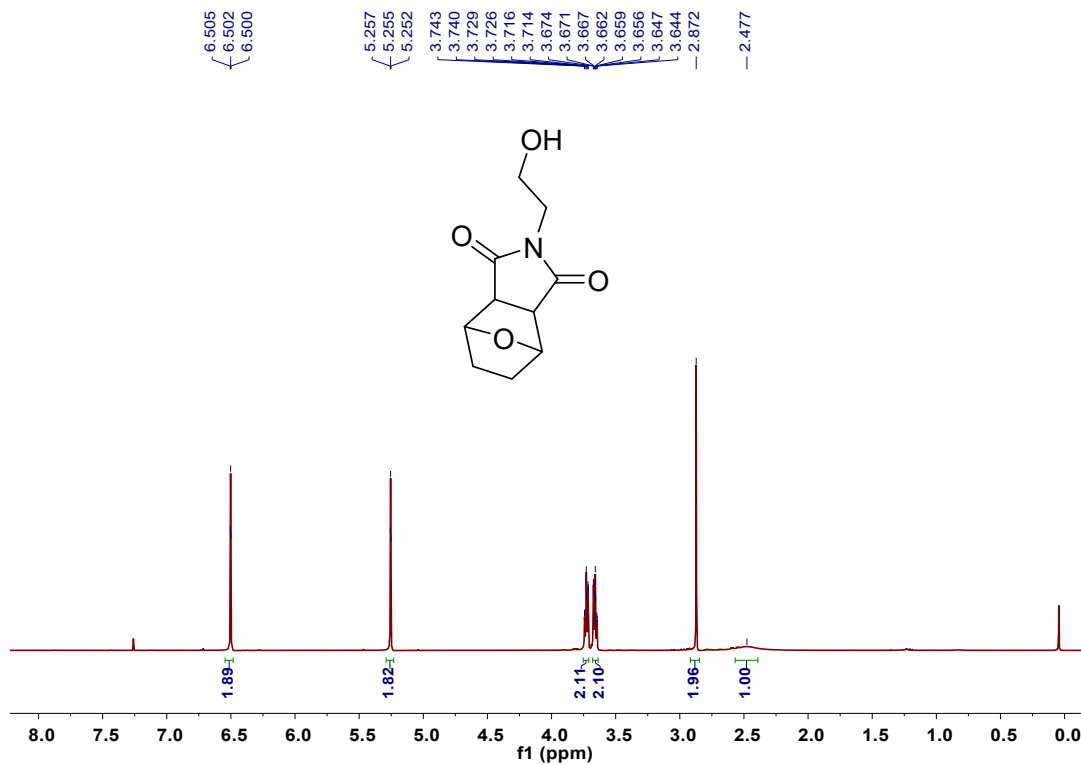


Figure S4. ^1H NMR spectrum (400 MHz, CDCl_3) of compound 3.

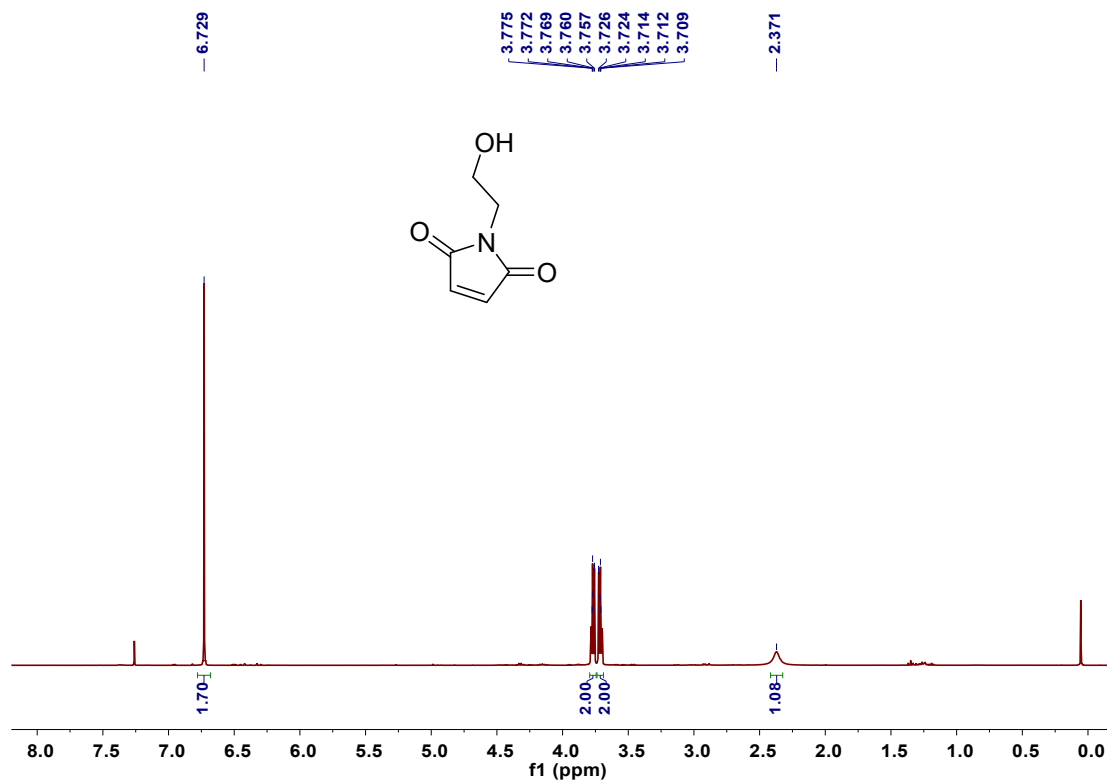


Figure S5. ^1H NMR spectrum (400 MHz, CDCl_3) of compound 4.

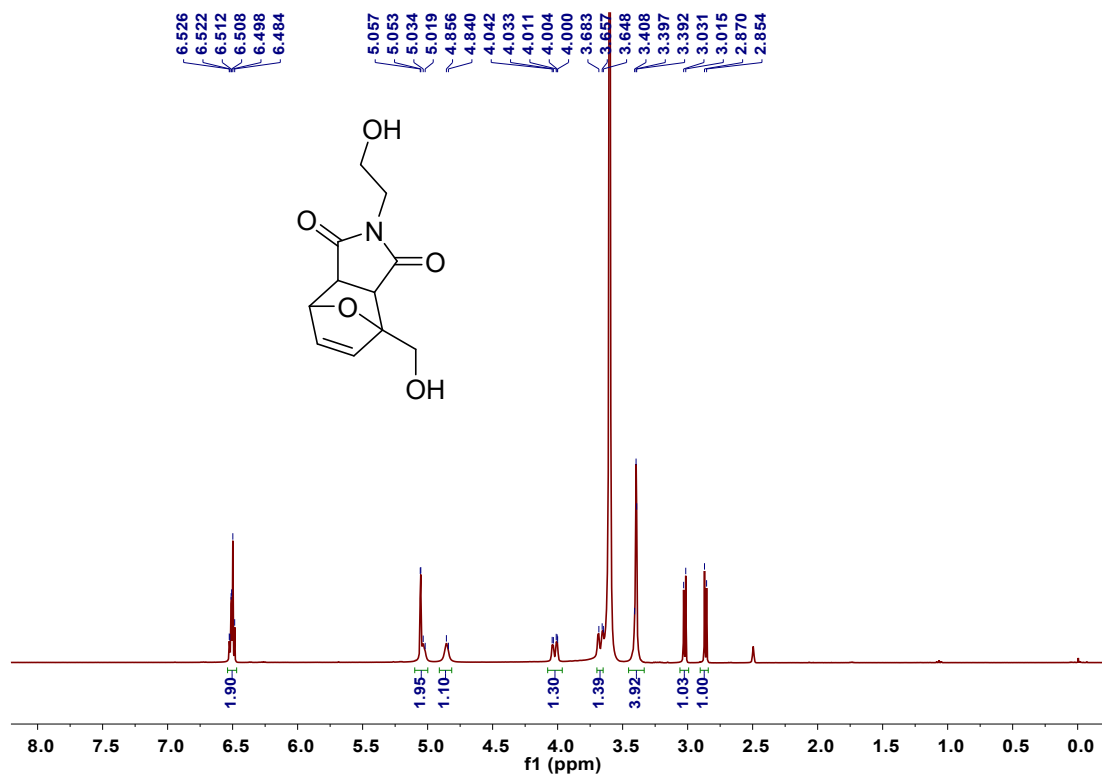


Figure S6. ^1H NMR spectrum (400 MHz, d_6 -DMSO) of compound DA.

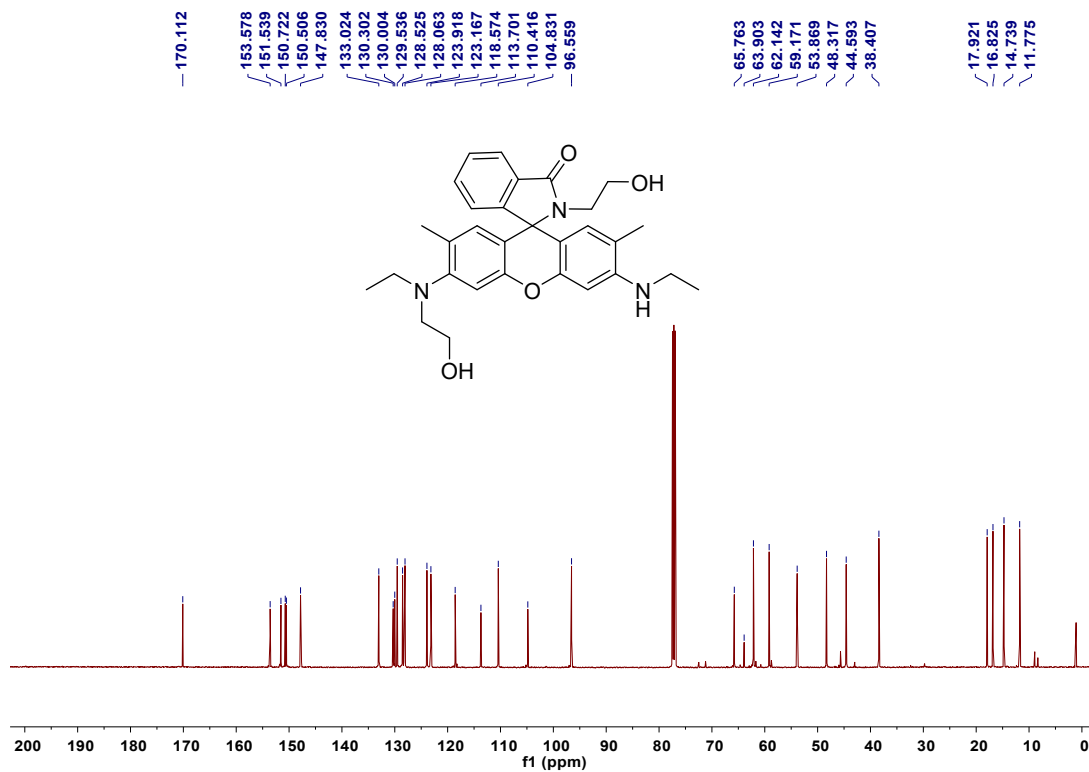


Figure S7. ^{13}C NMR spectrum (125 MHz, CDCl_3) of compound Rh-2OH.

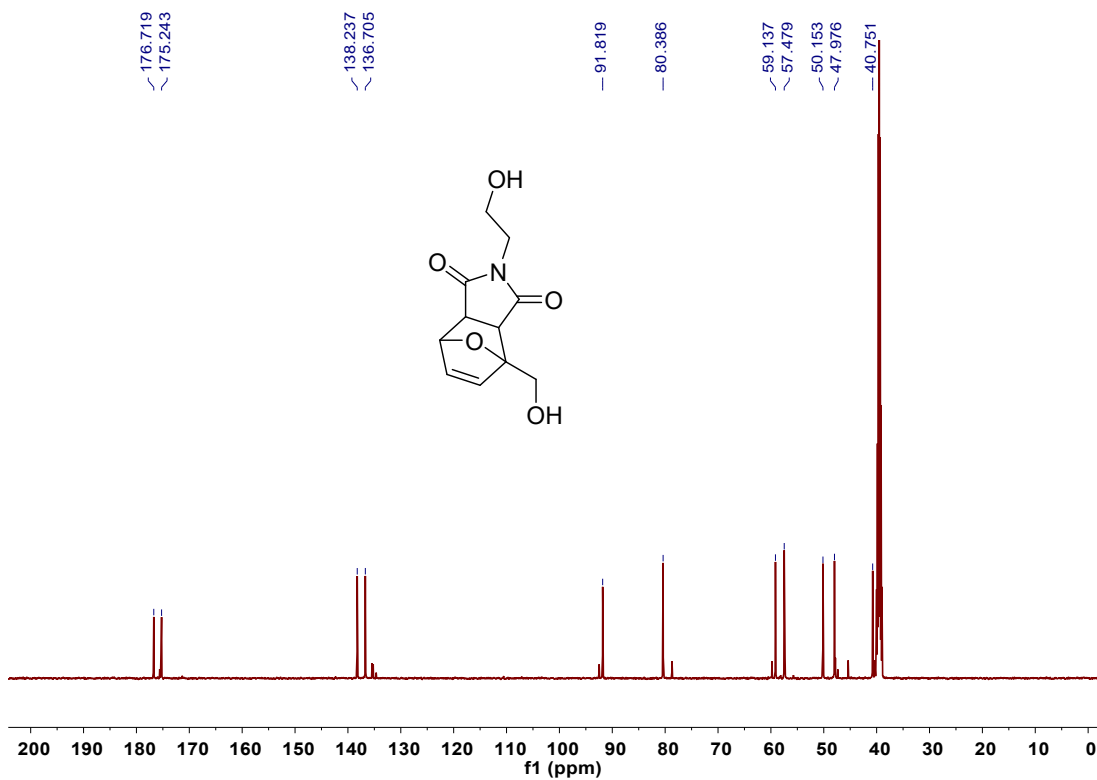


Figure S8. ^{13}C NMR spectrum (125 MHz, d_6 -DMSO) of compound DA.

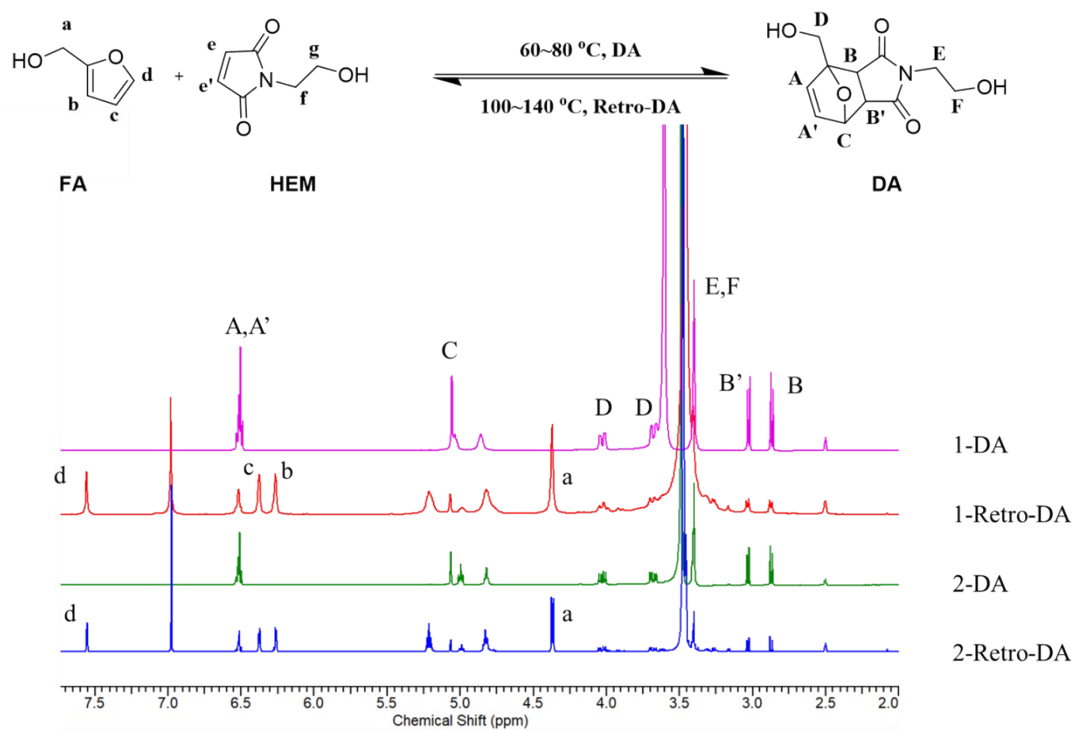


Figure S9. ¹H NMR spectra (500 MHz, *d*₆-DMSO) of reversible **DA** and **retro-DA**.

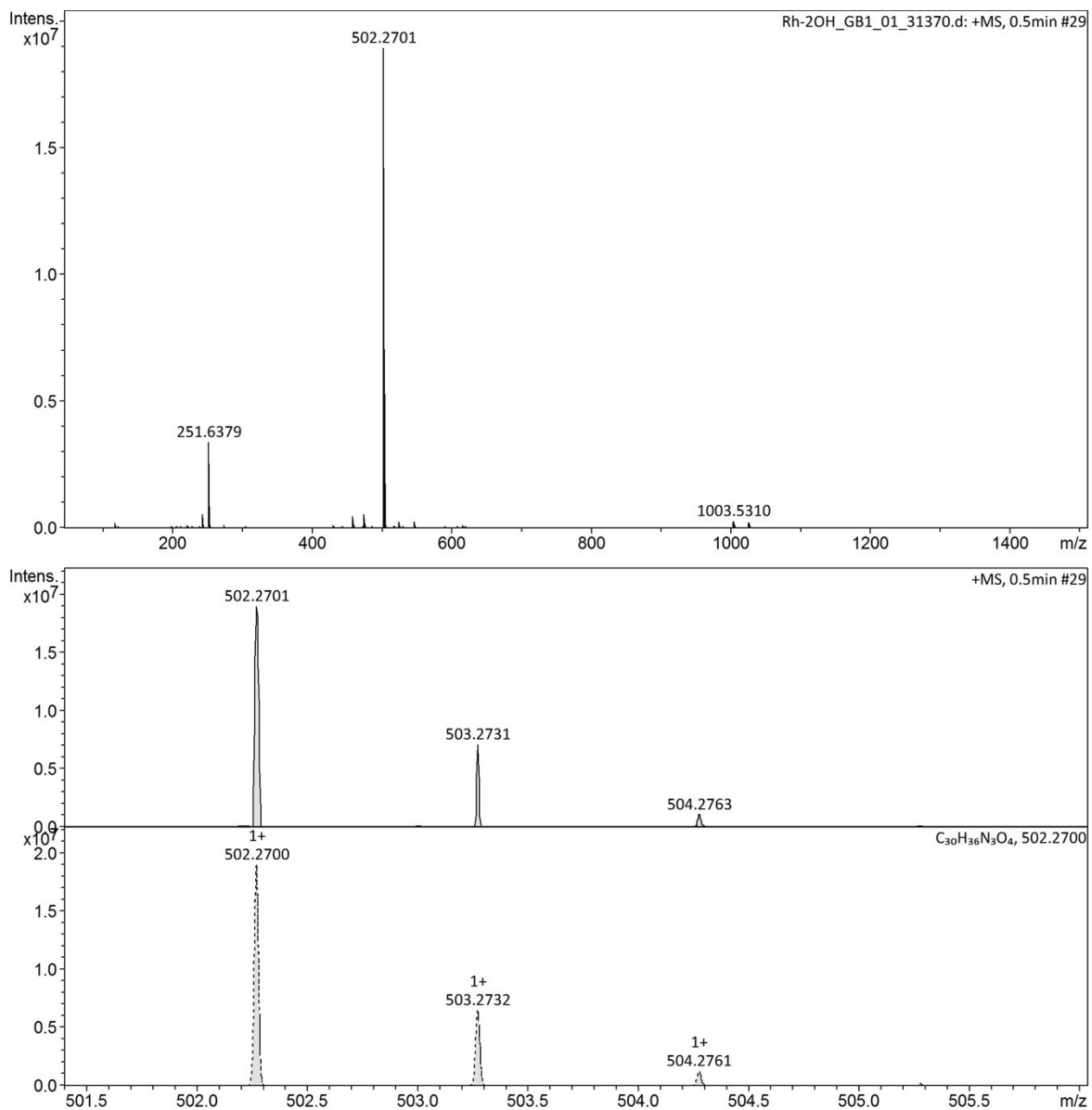


Figure S10. HRMS-ESI spectra of Rh-2OH.

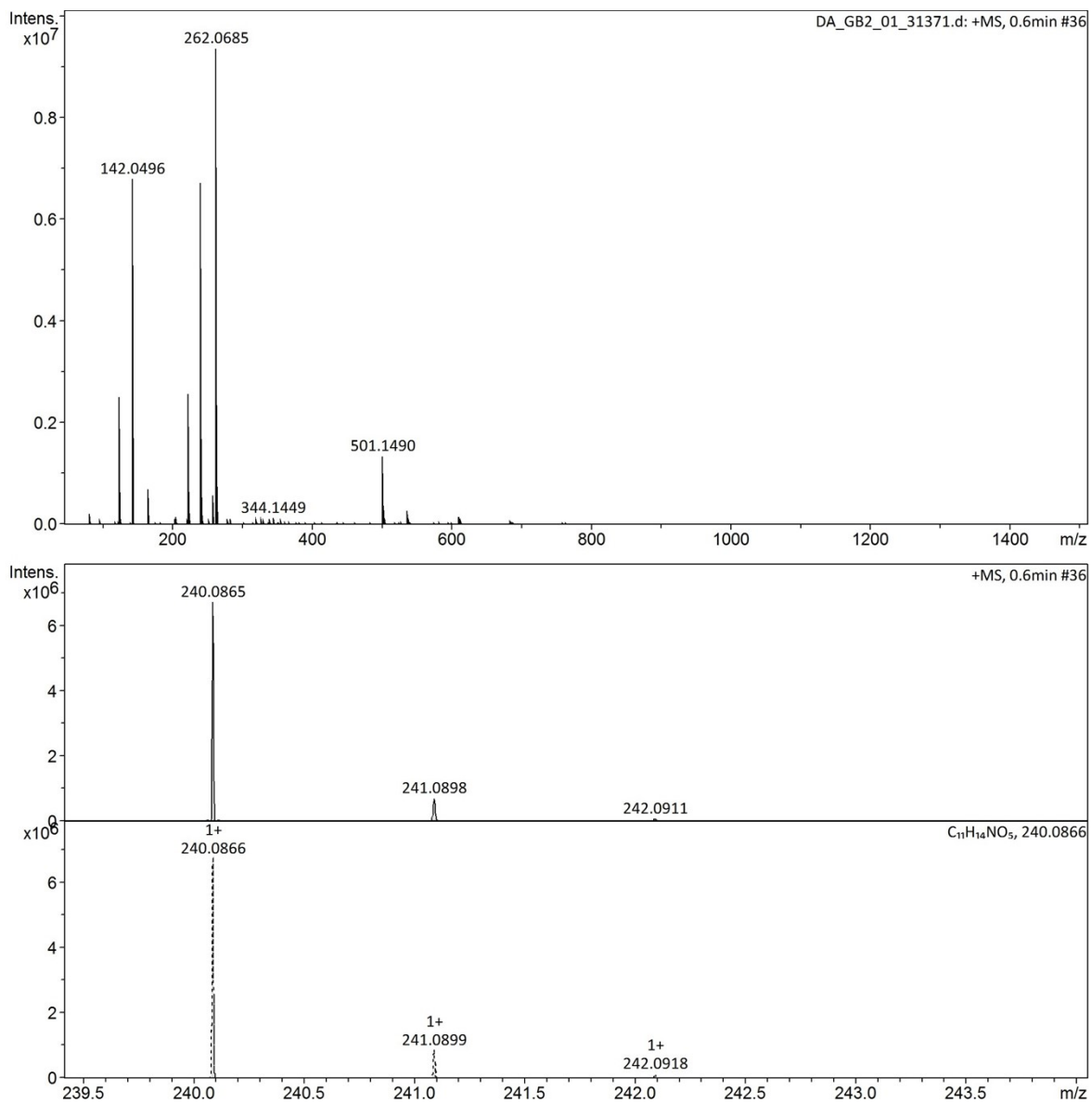


Figure S11. HRMS-ESI spectra of DA.

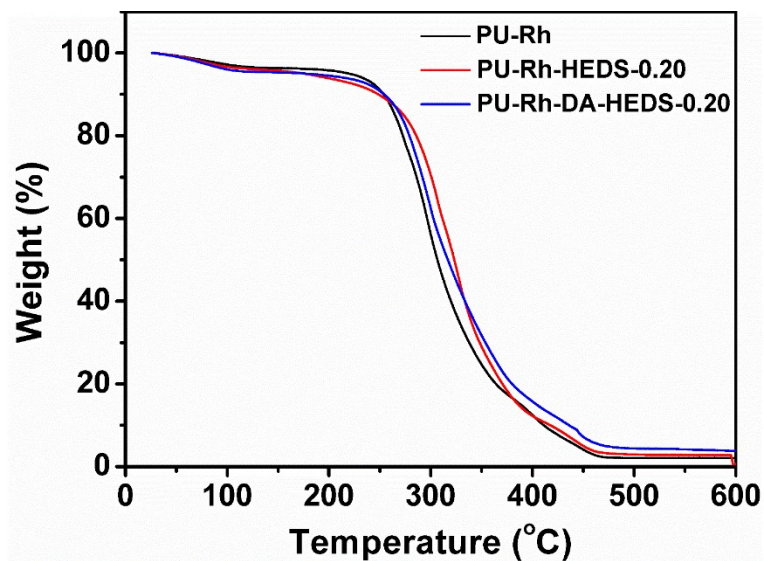


Figure S12. Thermogravimetric analysis (TGA) curves of various PU films.

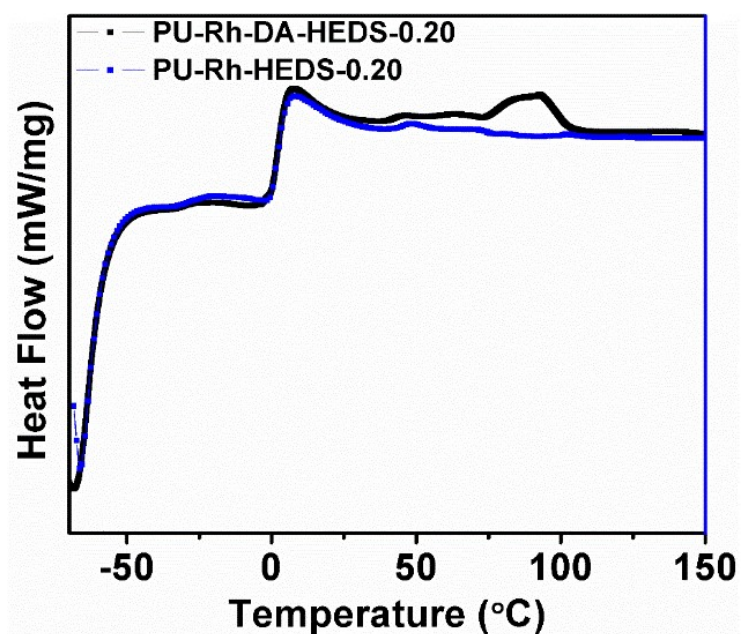


Figure S13. Differential scanning calorimetry (DSC) curves of PU films (PU-Rh-DA-HEDS-0.20 and PU-Rh-HEDS-0.20).

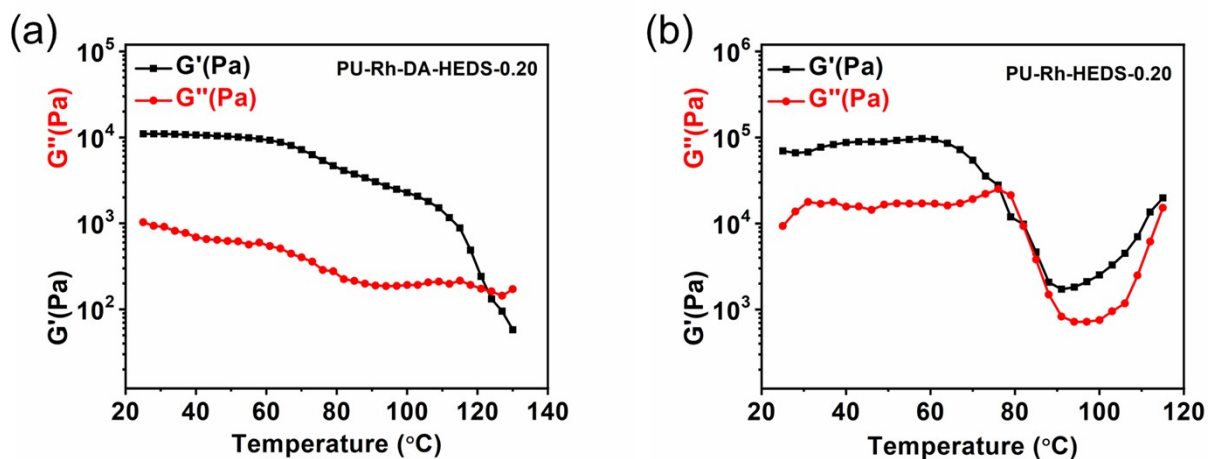


Figure S14. Temperature-dependent rheology curves of PU films (PU-Rh-DA-HEDS-0.20 and PU-Rh-HEDS-0.20).

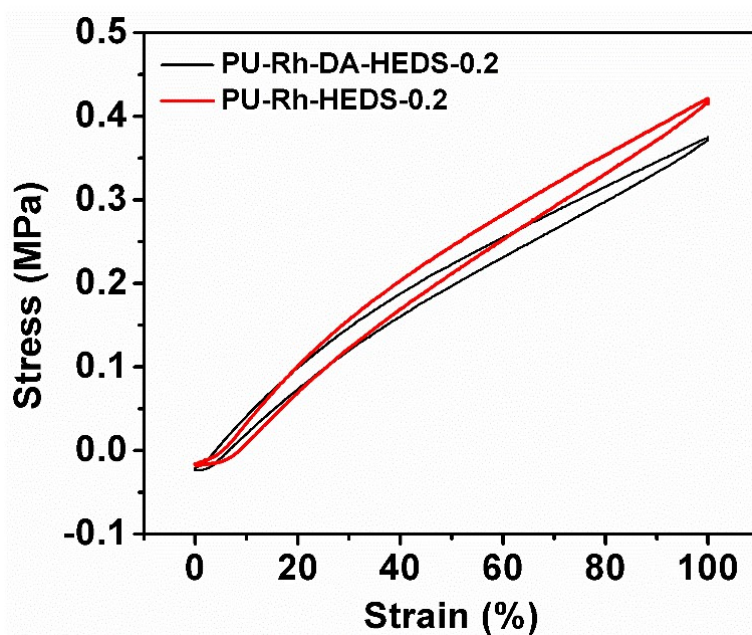


Figure S15. Cyclic tensile curves of PU-Rh-DA-HEDS-0.2 and PU-Rh-HEDS-0.2 films.

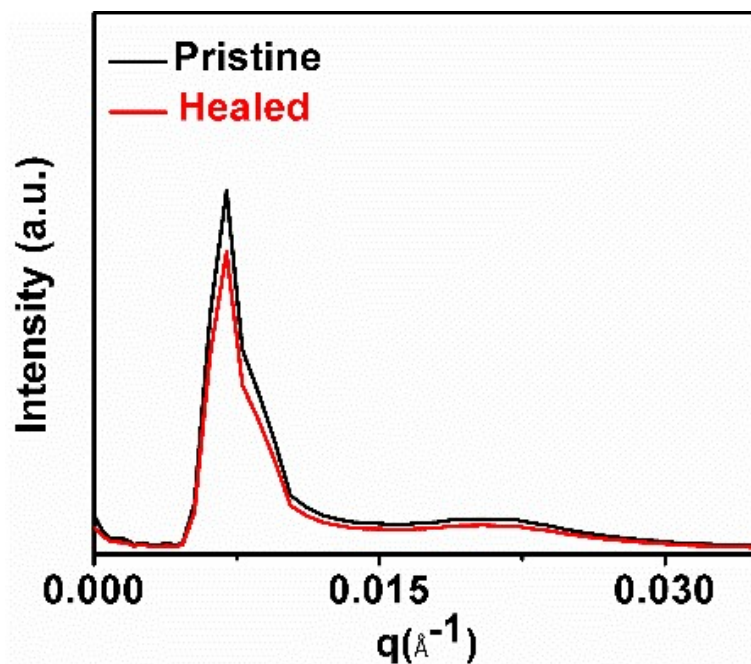


Figure S16. SAXS spectra of PU-Rh-DA-HEDS-0.20 film before and after healing.

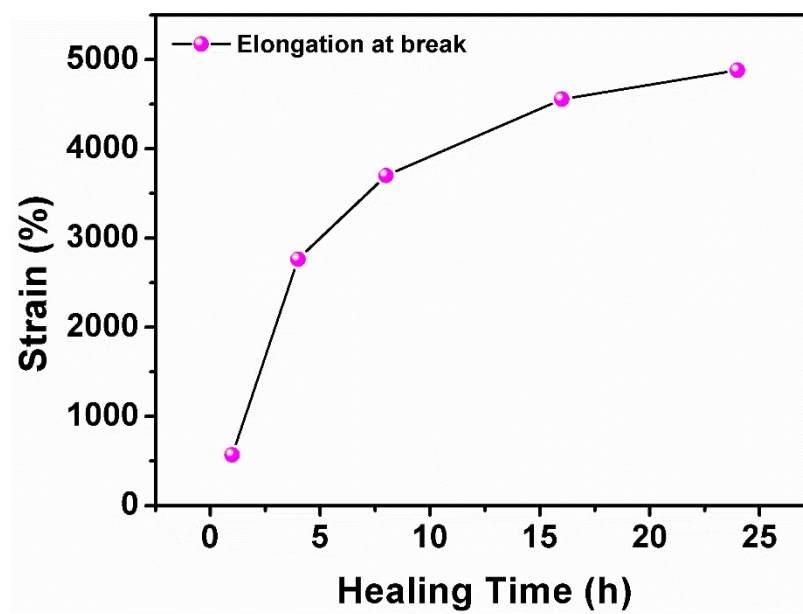


Figure S17. Strain curves of PU-Rh-DA-HEDS-0.20 film at different healing time intervals.

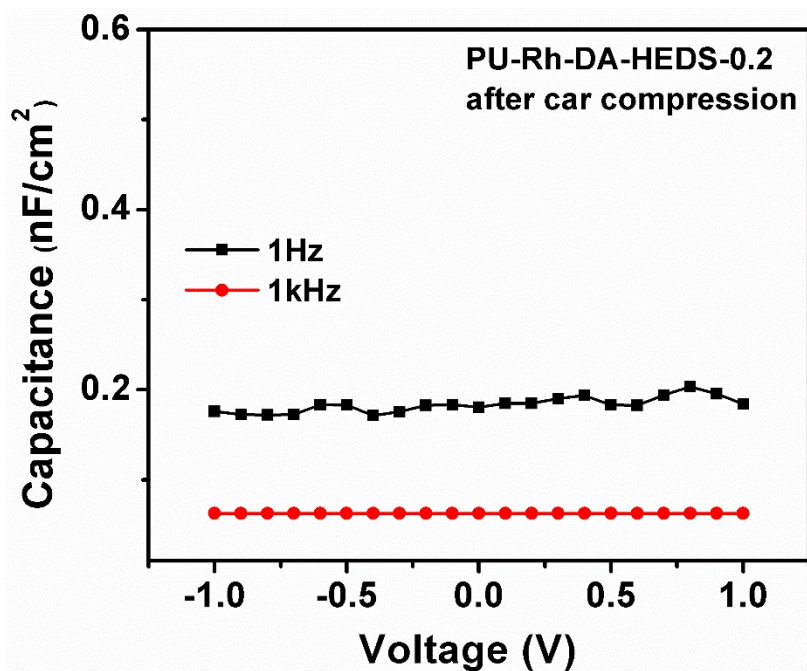


Figure S18. Voltage-dependent capacitance measurements of PU-Rh-DA-HEDS-0.20 film after car compression at low (1 Hz) and high (1 KHz) frequencies.

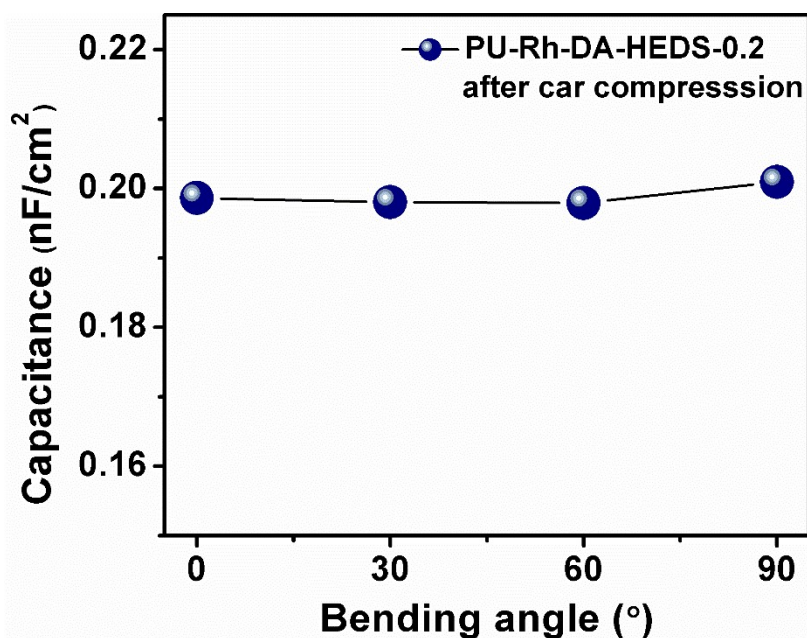


Figure S19. Capacitance measurements (at 1 Hz and 100 mV) of PU-Rh-DA-HEDS-0.20 film after car compression at different bending angles (0, 30, 60 and 90°).

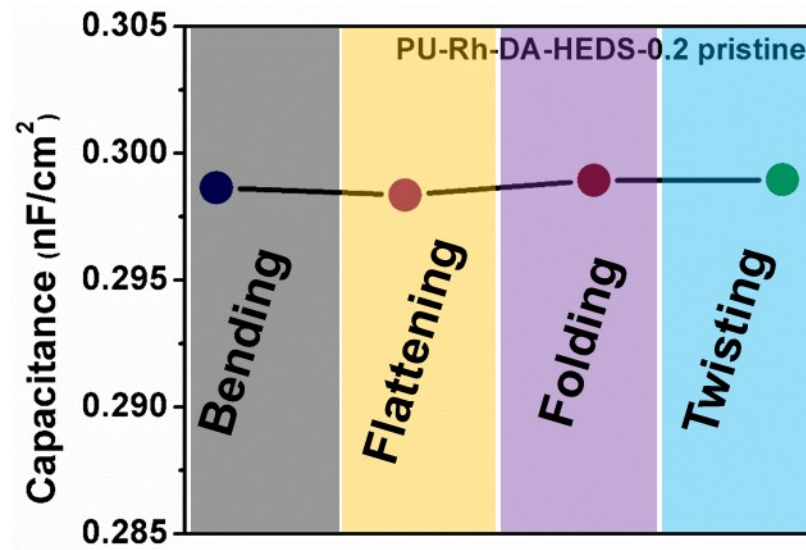


Figure S20. Capacitance measurements (at 1 Hz and 100 mV) of PU-Rh-DA-HEDS-0.20 film under different deformations (bending, flattening, folding and twisting).

Table S1. Chemical list.

Chemical Name	Amount	Company
Rhodamine 6G	50 g	Alfa Aesar
Ethanolamine	100 mL	Sigma-Aldrich
Sodium sulfate	500 g	SHOWA
Potassium carbonate	500g	SHOWA
Ethylene chlorohydrin	2.5 L	Alfa Aesar
Maleic anhydride	500 g	Alfa Aesar
Furan	500 mL	Acros
Furfuryl alcohol	500 mL	Alfa Aesar
Polyethylene glycol (PEG)	1 L	Acros
Triethanolamine (TEA)	1 L	Sigma-Aldrich
Hexamethylene diisocyanate (HDI)	1 L	TCI
Dibutyltin dilaurate (DBTDL)	100g	Alfa Aesar

Table S2. Solvents list.

Solvent Name	Amount	Brand
Acetone	20 L	GRAND
Dichloromethane (DCM)	20 L	TEDIA
Ethyl acetate (EtOAc)	20 L	GRAND
Ethyl ether	20 L	MACRON
n-Hexane	20 L	GRAND
Tetrahydrofuran (THF)	20 L	ECHO
Acetonitrile (ACN)	4 L	AENOCORE
Acetone	4L	ECHO
Ethanol (EtOH)	4 L	TEDIA
Methanol (MeOH)	4 L	J. T. Baler
Tetrahydrofuran (THF)	4 L	MACRON
Dimethyl sulfoxide (DMSO)	4 L	ECHO
Toluene	4 L	TEDIA
Pentane	4L	TEDIA
Isopropyl alcohol	4L	TEDIA
Triethylamine (TEA)	1 L	TEDIA
Sulfuric acid	1L	Sigma-Aldrich
d-Chloroform	100mL	Sigma-Aldrich
d ₆ -Dimethyl sulfoxide	25mL	Sigma-Aldrich

Table S3. Polyurethane films with different percentages of components.

Sample Name	Rh		PEG		HDI		HEDS		TEA		DA	
	mg	mmol	mg	mmol	mg	mmol	mg	mmol	mg	mmol	mg	mmol
PU-Rh	20	0.04	1068.0	3.56	807.3	4.80	0	0	83.6	0.56	0	0
PU-Rh-HEDS-1.00	20	0.04	0	0	807.3	4.80	549.1	3.56	83.6	0.56	0	0
PU-Rh-HEDS-0.50	20	0.04	534.0	1.78	807.3	4.80	274.5	1.78	83.6	0.56	0	0
PU-Rh-HEDS-0.33	20	0.04	712.8	2.38	807.3	4.80	182.6	1.18	83.6	0.56	0	0
PU-Rh-HEDS-0.25	20	0.04	801.0	2.67	807.3	4.80	137.3	0.89	83.6	0.56	0	0
PU-Rh-HEDS-0.20	20	0.04	854.4	2.85	807.3	4.80	109.8	0.71	83.6	0.56	0	0
PU-Rh-DA-HEDS-0.20	20	0.04	844.8	2.82	807.3	4.80	108.6	0.70	83.6	0.56	47.8	0.20

Table S4. Mechanical strengths of different polymers.

Sample Name	Breaking Stress (MPa)	Breaking Strain (%)
PU-Rh	-	-
PU-Rh-HEDS-1.00	Powder	
PU-Rh-HEDS-0.50	12.8	3039 ± 50
PU-Rh-HEDS-0.33	11.8	3525 ± 82
PU-Rh-HEDS-0.25	9.4	5168 ± 23
PU-Rh-HEDS-0.20	8.8	5533 ± 17
PU-Rh-DA-HEDS-0.20	8.7	5560 ± 84

Table S5. Mechanical properties of PU-Rh-HEDS-DA-0.2 and most recently reported healable PU-Based elastomers

Reference Number	Max Tensile Strength (MPa)	Max Tensile Strain	Toughness (MJ/m ³)	Thickness (mm)
1	57.4	3000%	228	0.8-1
2	53.3	1272%	129	N/A
3	24.0	1900%	176	≈0.4
4	9.4	2340%	75	>0.6
5	20.0	172%	N/A	1
6	7.0	900%	27	0.3
7	58.0	2200%	364	0.4
8	75.6	1520%	390	0.75
9	17.4	500%	47.8	1
10	30.0	1500%	125	0.8-1
11	29.0	1750%	122	1
12	42.5	450%	76	1
13	10.3	596.2%	37.8	N/A
14	13	1500%	110	0.2-0.3
15	15.8	1360%	127.8	0.5
PU-Rh-DA-HEDS-0.2 (This Work)	>8.7	>5500%	324	0.5

N/A: Not available.

Table S6. Tensile properties and healing efficiencies of different elastomers.

Sample Name	Resilience (MJ/m ³)	Breaking Strain before Healing (%)	Breaking Strain after Healing (%)	Healing Efficiency (%)
PU-Rh	0.3 till 27%	>6000	2473	<40
PU-Rh-HEDS-0.20	5.6 up to 330%	5533	4366	79
PU-Rh-DA-HEDS-0.20	2.5 up to 305%	5560	4838	87

References:

- 1 X. Chen, Q. Zhong, C. Cui, L. Ma, S. Liu, Q. Zhang, Y. Wu, L. An, Y. Cheng, S. Ye, X. Chen, Z. Dong, Q. Chen and Y. Zhang, *ACS Appl. Mater. Interfaces*, 2020, **12**, 30847–30855.
- 2 Z. Liu, W. Guo, W. Wang, Z. Guo, L. Yao, Y. Xue, Q. Liu and Q. Zhang, *ACS Appl. Mater. Interfaces*, 2022, **14**, 6016–6027.
- 3 W. B. Ying, G. Wang, Z. Kong, C. K. Yao, Y. Wang, H. Hu, F. Li, C. Chen, Y. Tian, J. Zhang, R. Zhang and J. Zhu, *Adv. Funct. Mater.*, 2021, **31**, 2009869.
- 4 M. W. M. Tan, G. Thangavel and P. S. Lee, *Adv Funct Materials*, 2021, **31**, 2103097.
- 5 J. Wu, L. Cai and D. A. Weitz, *Adv. Mater.*, 2017, **29**, 1702616.
- 6 S.-M. Kim, H. Jeon, S.-H. Shin, S.-A. Park, J. Jegal, S. Y. Hwang, D. X. Oh and J. Park, *Adv. Mater.*, 2018, **30**, 1705145.
- 7 X. Wang, S. Zhan, Z. Lu, J. Li, X. Yang, Y. Qiao, Y. Men and J. Sun, *Adv. Mater.*, 2020, **32**, 2005759.
- 8 Z. Li, Y. Zhu, W. Niu, X. Yang, Z. Jiang, Z. Lu, X. Liu and J. Sun, *Adv. Mater.*, 2021, **33**, 2101498.
- 9 M. Xiao, Y. Yao, C. Fan, Z. Xu, Y. Liu, B. Liu, J. Li, X. Zhang, X. Jin, J. Yang, J. Yang and W. Liu, *Chemical Engineering Journal*, 2022, **433**, 133260.
- 10 X. Liu, X. Liu, W. Li, Y. Ru, Y. Li, A. Sun and L. Wei, *Chemical Engineering Journal*, 2021, **410**, 128300.
- 11 Y. Li, W. Li, A. Sun, M. Jing, X. Liu, L. Wei, K. Wu and Q. Fu, *Mater. Horiz.*, 2021, **8**, 267–275.
- 12 Y. Eom, S.-M. Kim, M. Lee, H. Jeon, J. Park, E. S. Lee, S. Y. Hwang, J. Park and D. X. Oh, *Nat Commun*, 2021, **12**, 621.
- 13 X. Zhu, W. Zheng, H. Zhao and L. Wang, *J. Mater. Chem. A*, 2021, **9**, 20737–20747.
- 14 P. Zhao, C. Yin, Y. Zhang, X. Chen, B. Yang, J. Xia and L. Bian, *J. Mater. Chem. A*, 2020, **8**, 12463–12471.
- 15 P. Si, F. Jiang, Q. S. Cheng, G. Rivers, H. Xie, A. K. K. Kyaw and B. Zhao, *J. Mater. Chem. A*, 2020, **8**, 25073–25084.