

Electronic Supplementary Information

Visible Light-Induced Scission and Rapid Healing of Polyurethane Elastomers Based on Photoswitchable Hexaarylbiimidazole Units

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1. Experimental

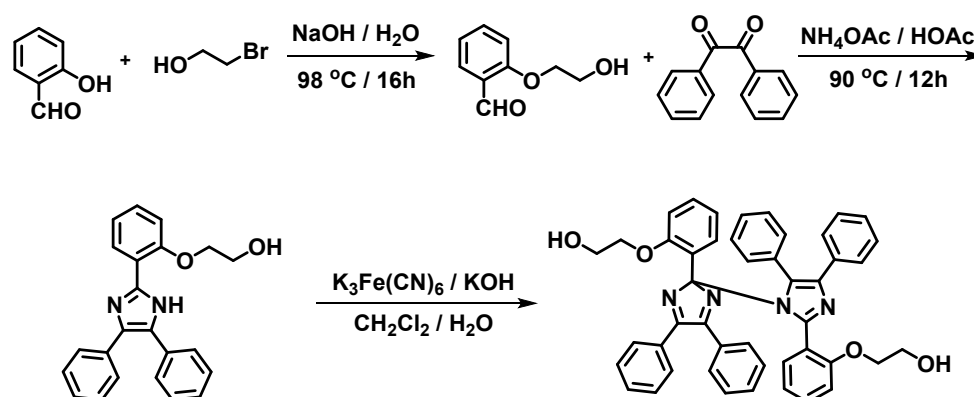
(1) Materials

Unless otherwise stated, all starting materials and reagents were obtained from commercial suppliers and used without further purification. Poly(tetramethylene ether glycol) (PTMG: $M_n = 1000$) was dried at 70°C under vacuum for 1 hours before use. Hexamethylene Diisocyanate (HDI) and ethylene glycol were also dried under vacuum for 1 hour before use. Anhydrous tetrahydrofuran (THF) was obtained from an Anhydrous Distillation System (SDS). All reactions were performed under N_2 atmosphere unless otherwise specified. The detailed synthetic procedures and characterizations of photoswitchable monomer 2-glycol-HABI were shown in **Scheme S1**.

(2) Instrumentation

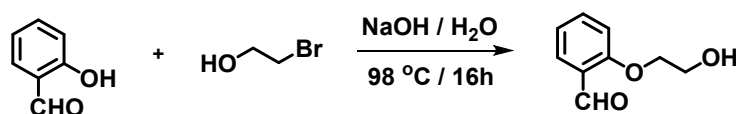
NMR spectra (1H and ^{13}C) were obtained using a 600 M Bruker AV600 with an internal standard of tetramethylsilane. Mass spectra were obtained through the Agilent 1100 LC/MSD Trap. UV-visible absorbance measurements were taken using an UV-Visible Spectrophotometer (UV-3600) from Shimadzu between 300 nm and 800 nm. Optical images were captured using Digital Single Lens Reflex (NIKON D90). The EPR tests were performed on a Bruker EPR A300 machine (X band). IR spectra were recorded using VERTEX 70. Glass transition temperature of HABI-PU was determined using differential scanning calorimetry (DSC) (-40-50 °C, 10 °C/min) performed on a Diamond DSC. The stress-strain measurements and stress relaxation measurements were performed on an Instron E1000 system (EHF-UV100k2-040-1A) from Shimadzu, and the GPC measurements were recorded using the PL-GPC 50 system from A Varian, Inc. Company. The 405 nm irradiation was operated with the laser (light power: 100 mW).

(3) Synthesis



Scheme S1. Synthetic routes of 2-glycol-HABI.

Synthesis of 2-(2-hydroxyethoxy)benzaldehyde



In a two-neck bottom flask, a solution of sodium hydroxide (4.92g, 0.123mol) in water (120ml) was formed. With stirring, salicylaldehyde (10g, 0.082mmol) and 2-bromine-ethanol

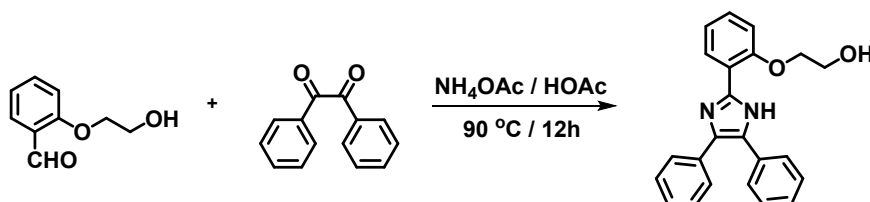
(12.25 g, 0.098mol) were added dropwise, the mixture heated to 98 °C under a nitrogen atmosphere. and the reaction held at 98 °C for 16 hours. After cooling to room temperature, a solution of sodium hydroxide in water (50ml) was added until the mixture is strongly alkaline (PH=10). The liquid was decanted and extracted with dichloromethane. After drying the dichloromethane layer over sodium sulfate, stripping and concentrating, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1/4, v/v) and dried in vacuo to give 2-(2-hydroxyethoxy)benzaldehyde as a brownish yellow oily liquid (7.8 g, 57.3 % yield).

¹H NMR (600 MHz, DMSO) δ (ppm): 10.46 (s, 1H), 7.69 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.66-7.59 (m, 1H), 7.21 (d, $J = 8.5$ Hz, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 4.98 (t, $J = 5.8$ Hz, 1H), 4.15 (t, $J = 4.8$ Hz, 2H), 3.78 (dd, $J = 10.0, 5.3$ Hz, 2H).

¹³C NMR (151 MHz, DMSO) δ (ppm): 190.19, 161.70, 136.75, 127.75, 124.88, 121.04, 114.03, 70.97, 59.98.

LC-MS (APCI): calculated 166.2, and found 167.1. The molecular weight of 2-(2-hydroxyethoxy)benzaldehyde shown in the mass spectrum is consistent with the molecular weight of the molecule we designed (Fig. S14).

Synthesis of 2-glycol-TPI



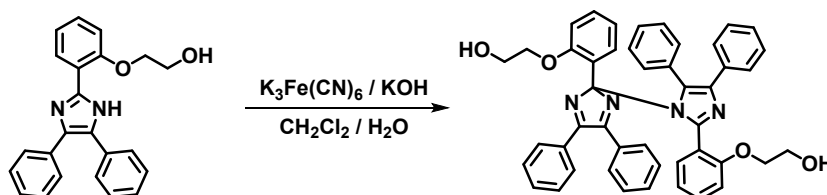
Into a two-neck flask, benzil (7.57 g, 0.036 mol), 2-(2-hydroxyethoxy)benzaldehyde (5 g, 0.03 mol) and ammonium acetate (23 g, 0.3 mol) were dispersed in acetic acid (80 ml). The mixture was stirred and heated to 90 °C for 12 h. After the reaction was finished, the organic was added into brine dropwise and then neutralized by aqueous sodium hydroxide solution. The white precipitate was filtered, washed with water and then toluene to remove the excess benzil. The remaining solid was further dried in vacuum at 65 °C for 12 h. Finally, 8.7 g white powder was obtained, yield 81%.

¹H NMR (600 MHz, DMSO) δ (ppm): 11.95 (s, 1H), 8.12 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.56 (d, $J = 7.4$ Hz, 2H), 7.49 (d, $J = 7.4$ Hz, 2H), 7.39 (ddd, $J = 15.6, 11.2, 4.5$ Hz, 3H), 7.33 (t, $J = 7.2$ Hz, 3H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.11 (t, $J = 7.5$ Hz, 1H), 5.54 (s, 1H), 4.33-4.18 (m, 2H), 3.85 (s, 2H).

¹³C NMR (151 MHz, DMSO) δ (ppm): 155.77, 143.75, 130.16, 128.93, 128.79, 128.02, 127.53, 122.03, 119.95, 115.05, 71.24, 59.92, 40.42, 1.63.

LC-MS (APCI): calculated 356.4, and found 356.9. The molecular weight of 2-glycol-TPI shown in the mass spectrum is consistent with the molecular weight of the molecule we designed (Fig. S15).

Synthesis of 2-glycol-HABI



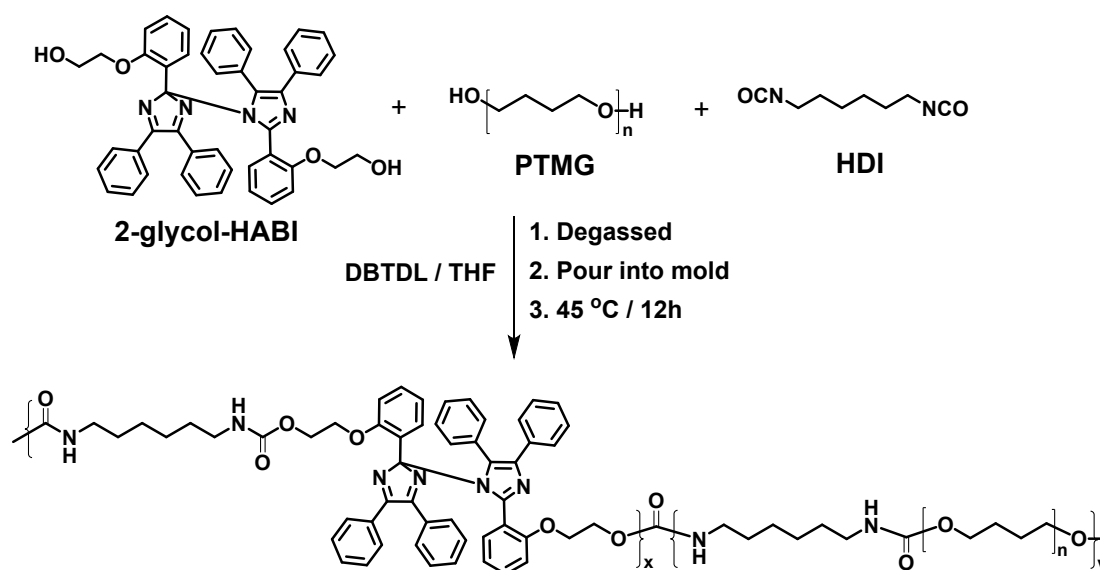
Into a 250 ml flask equipped with constant pressure funnel ($V_{\max} = 50$ ml) and covered by aluminum foil, 2-glycol-TPI (2 g, 0.0056 mol) was dissolved in dichloromethane (60 ml). $K_3Fe(CN)_6$ (9.22 g, 0.028 mol) and KOH (3.14 g, 0.056 mol) were dissolved in deionized water (30 ml) completely and then transferred to the constant pressure funnel. This aqueous solution was added dropwise and the mixture was vigorously stirred for 8 h. The reaction was monitored by TLC plate until all the starting materials were consumed. After the reaction was finished, the organic layer was collected, evaporated under reduced pressure and the residue was further purified by column chromatography on silica gel (eluent, ethyl acetate:Hexane = 4:1, v/v). Finally, 1.7 g saffron yellow powder was obtained, yield 85%.

1H NMR (600 MHz, DMSO) δ (ppm): 7.65-7.55 (m, 2H), 7.51-7.40 (m, 5H), 7.24 (dd, $J = 31.2, 23.9$ Hz, 9H), 7.12 (t, $J = 7.5$ Hz, 3H), 7.09-7.01 (m, 3H), 6.95 (s, 2H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.79 (d, $J = 8.2$ Hz, 1H), 6.69 (d, $J = 7.8$ Hz, 1H), 6.36 (t, $J = 7.6$ Hz, 1H), 4.85 (s, 1H), 4.63 (t, $J = 5.3$ Hz, 1H), 4.05 (s, 1H), 3.88 (d, $J = 63.6$ Hz, 4H), 3.65 (d, $J = 5.1$ Hz, 2H), 3.36 (s, 1H).

^{13}C NMR (151 MHz, DMSO) δ (ppm): 157.94, 157.07, 144.99, 137.06, 135.19, 132.49, 132.17, 130.80, 130.19, 130.07, 129.49, 128.83, 128.33, 128.27, 128.23, 126.71, 126.54, 126.38, 125.38, 120.74, 120.00, 113.35, 111.17, 71.39, 70.50, 60.02, 59.76.

LC-MS (APCI): calculated 710.8, and found 710.9. The molecular weight of 2-glycol-HABI shown in the mass spectrum is consistent with the molecular weight of the molecule we designed (Fig. S16).

Synthesis of linear HABI-PU polyurethane



Scheme S2. The chemical structure and synthetic routes of HABI-PU.

The chemical structure and synthetic routes of HABI-PU were shown in **Scheme S2**. Poly(tetramethylene ether glycol) (PTMG₁₀₀₀) (3.8 g, 3.8 mmol, 12.5 equiv) were dissolved in 5 ml anhydrous tetrahydrofuran (THF) to form solution A. Dihydroxy functionalized HABI (2-glycol-HABI) (216 mg, 0.304 mmol, 1 equiv) was dissolved in 5 ml anhydrous THF to form solution B. Solution A and B were mixed and the mixture was stirred at room temperature for 15 min. Hexamethylene diisocyanate (HDI) (0.69 g, 4.1 mmol, 13.5 equiv) was added into the mixture and the mixture was stirred at room temperature for another 15min. The mixture was heated and stirred at 35 °C under vacuum to remove THF, degassed,

and poured into a Teflon mold. The mold was kept in an N₂-purged oven at 45 °C for 12 h. The final samples were removed from the mold and kept under ambient conditions for 12 hours before testing. For the choice of anhydrous THF solvent, butyltin dilaurate catalyst (DBTDL), and oligomeric glycol PTMG, we draw on the experience of the reported literature with appropriate modifications¹.

(4) GPC tests

With stirring, HABI-PU (4 mg) is first completely dissolved in tetrahydrofuran (4 mL) over 24 hours, and then be divided equally for 2 equal parts. One part is tested on GPC before and after 405 nm exposure, while the second one in which 2 mg HABI monomer was added and then running the GPC before and after 405 nm exposure.

(5) Mechanical tests

Static tensile tests in Fig. 2f were carried out at room temperature at speed of 2 mm/min. First, stretch test was performed on the initial dumbbell-shaped HABI-PU sample (3.6 cm × 0.38 cm × 0.22 cm) to 100% strain. The width of the dumbbell-shaped HABI-PU is the middle width of the sample. The sample was then released to rebound to the initial length, the tensile test was carried out again to the same sample, which was irradiated continuously with the 405 nm laser during the testing. Other static tensile tests and the loading-unloading tests were also performed at room temperature at speed of 2 mm/min.

2. Optical, Thermal and Mechanical Properties

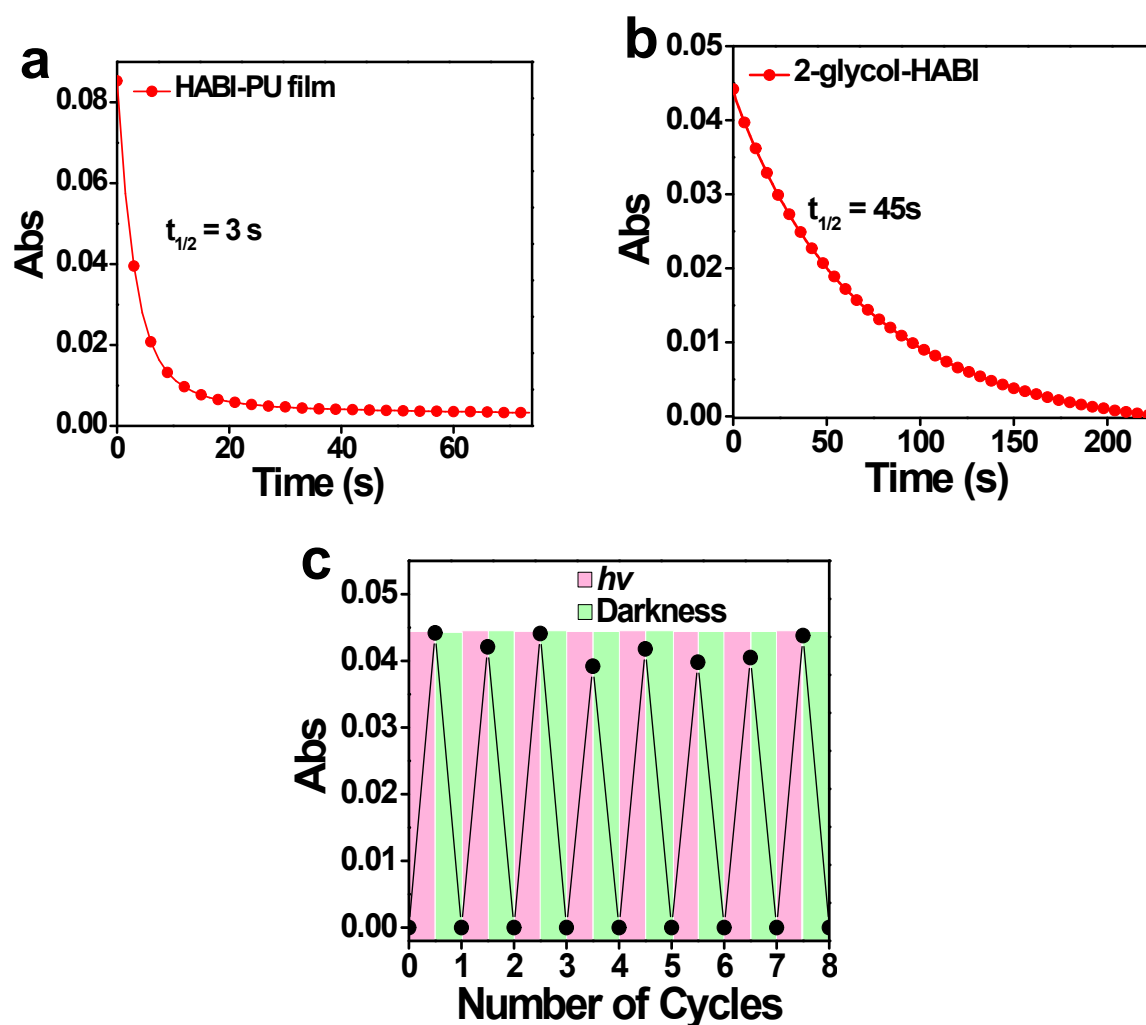


Fig. S1 (a) The fading kinetics of the colored HABI-PU film after 405 nm laser irradiation for 10 s. $t_{1/2}$ is the half-life time of the TPIRs absorbance in HABI-PU film. (b) The fading kinetics of the colored species in THF solution (5×10^{-5} mol/L) after 405 nm laser irradiation for 10 s. The half-life time ($t_{1/2}$) of the colored species is calculated to be 45 s. (c) Absorbance change measured at 610 nm of 2-glycol-HABI subjected to 405 nm irradiation and thermos-recover cycles. Pink areas: irradiation at 405 nm for 10 s. Green areas: after ceasing 405 nm laser. The photo-switching process can be reversibly performed more than 8 times without obvious degradation, indicating the great fatigue resistance, high reversibility and the sensitivity to 405 nm light irradiation.

Note S1. Discussion about Fig. S1

The half-life time ($t_{1/2}$) of the fading kinetics curve of the colored HABI-PU polymer film is shorter than that in the solution state after 405 nm irradiation, indicating the recombination rate of the TPIR free radicals in the polymer materials is faster. Generally, the molecules in the solution can move freely in the entire solution system. However, the movement of the molecules are limited in solid polymer, so that the divided TPIR free radicals can recombine faster in the initial stage.

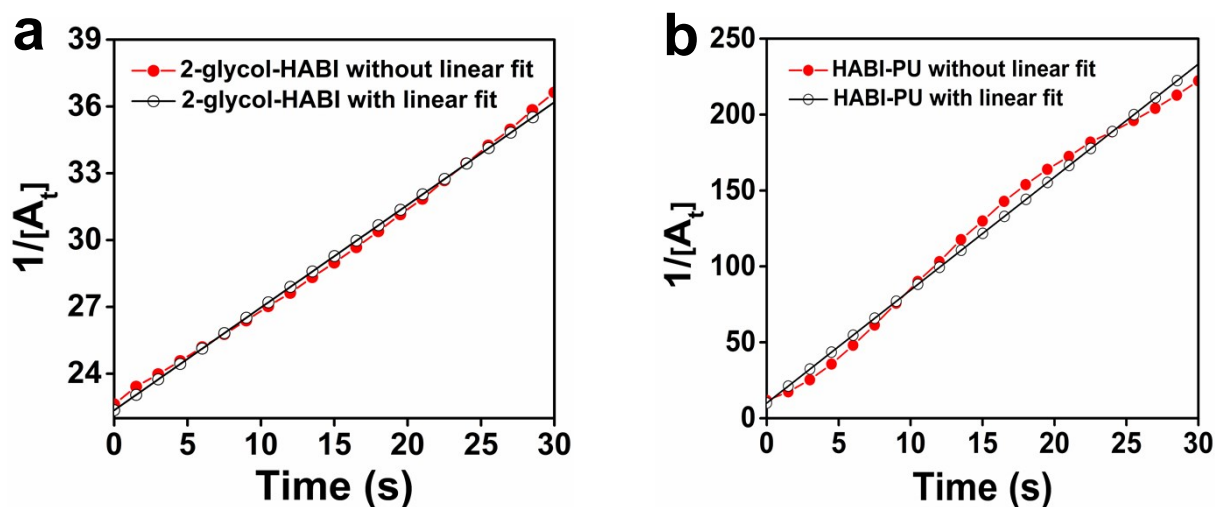


Fig. S2 (a) The plot of $1/[A_t] \sim t$ of 2-glycol-HABI in THF (5×10^{-5} mol/L) from Fig. S1b and its linear curve fitting. (b) The plot of $1/[A_t] \sim t$ of HABI-PU film (the molar percentage of 2-glycol-HABI is 3.7%) from Fig. S1a and its linear curve fitting. The results indicate the recombination processes of TPIRs in THF solution and HABI-PU polymer both are the second order reactions.

Note S2. Discussion about Fig. S2

The inverse of absorbance ($1/[A_t]$) of TPIRs in THF solution and HABI-PU polymer materials is linear with time in the first 30 s after removing 405 nm irradiation, indicating both the recombination processes of TPIRs in THF solution of 2-glycol-HABI and HABI-PU polymer materials are the second order reaction (Fig. S2).

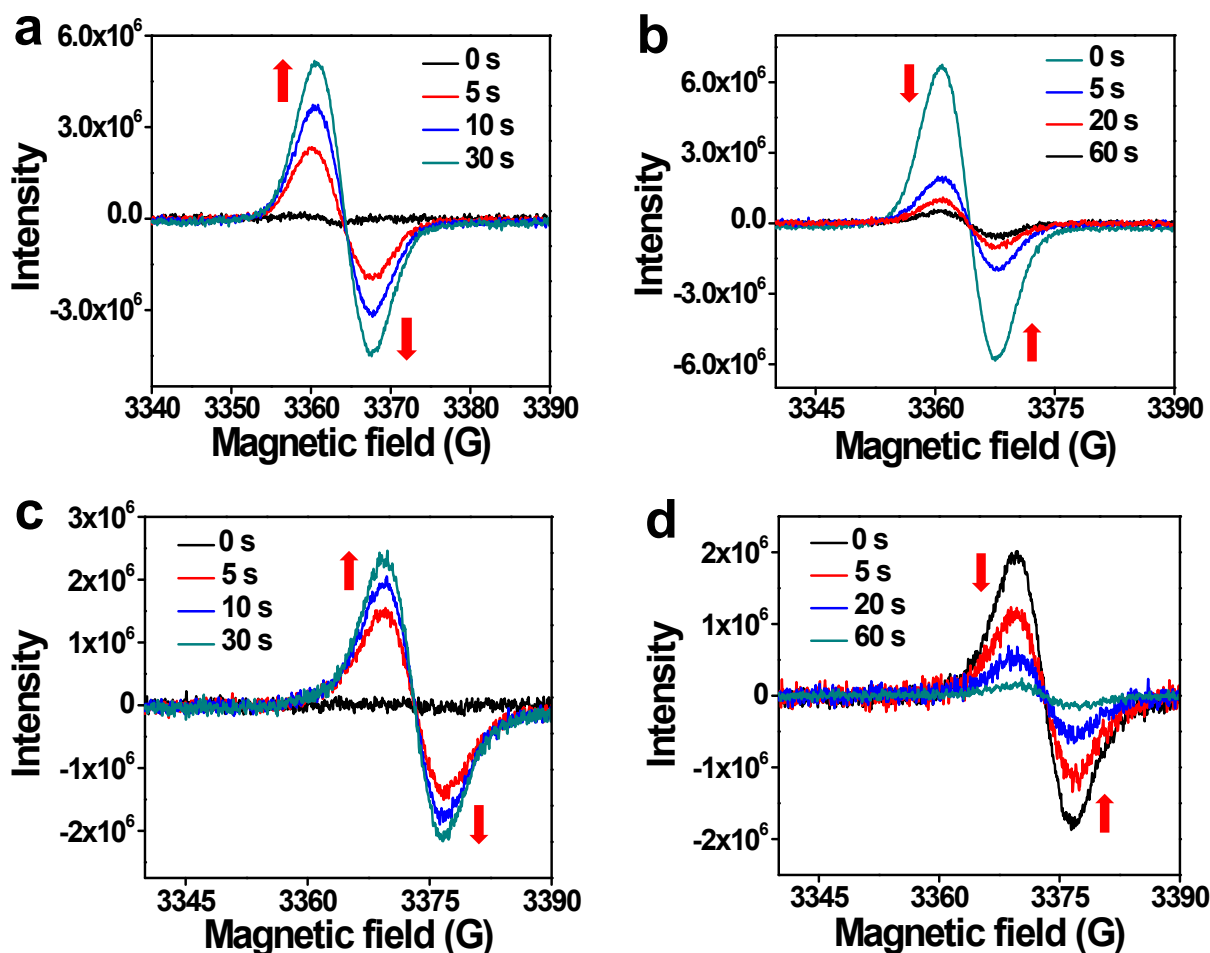


Fig. S3 Photo-induced EPR changes of HABI-PU materials and 2-glycol-HABI. (a) Photo-induced EPR changes of HABI-PU materials before (0 s) 405 nm irradiation and after 405 nm irradiation (325 mW/cm^2) with different time. (b) Spontaneously fading of the EPR spectra of HABI-PU materials for various waiting time after removing 405 nm irradiation. The molar percentage of 2-glycol-HABI unit in HABI-PU is 3.7%. (c) Photo-induced EPR changes of 2-glycol-HABI in THF solution (0.01 mol/L) upon 405 nm irradiation (325 mW/cm^2) for various time. (d) Spontaneously fading of the EPR spectra of 2-glycol-HABI in THF solution for various waiting time after removing 405 nm irradiation.

Note S3. Discussion about Fig. S3

EPR spectra before and after UV irradiation directly demonstrated the cleavage of the dynamic C-N bond in HABI to produce a pair of TPIRs. Fig. S3c shows the rapid increase in signal intensity of TPIRs after 405 nm irradiation for 5 s, indicating that 2-glycol-HABI is sensitive to 405 nm visible light. The g -tensor was measured to be 2.003, corresponded to the reported values for TPIR exactly.^{2, 3} After 2-glycol-HABI in THF was illuminated for one minute with 405 nm light, and then terminating UV irradiation, the generated TPIRs would recouple with each other, resulting in a fast decrease of the relative signal intensity (Fig. S3d). The EPR spectra of HABI-PU elastomers before and after UV irradiation show the same trend as 2-glycol-HABI in THF solution. In addition, after HABI-PU materials was illuminated for one minute with 405 nm light, the signal intensity decreased rapidly especially in the first 5 s after terminating irradiation (Fig. S3b), further indicating that the TPIRs in HABI-PU polymers has a very fast recombination speed.

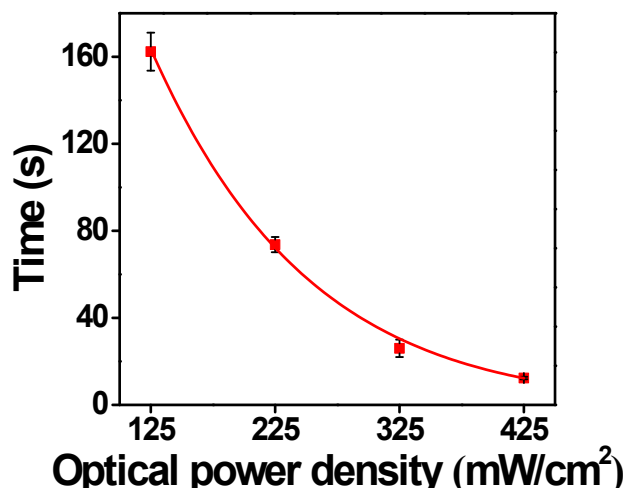


Fig. S4 Dependence of fracture time on optical power density when loading mass is 100 g. Error bars, standard deviation for 3 measurements.

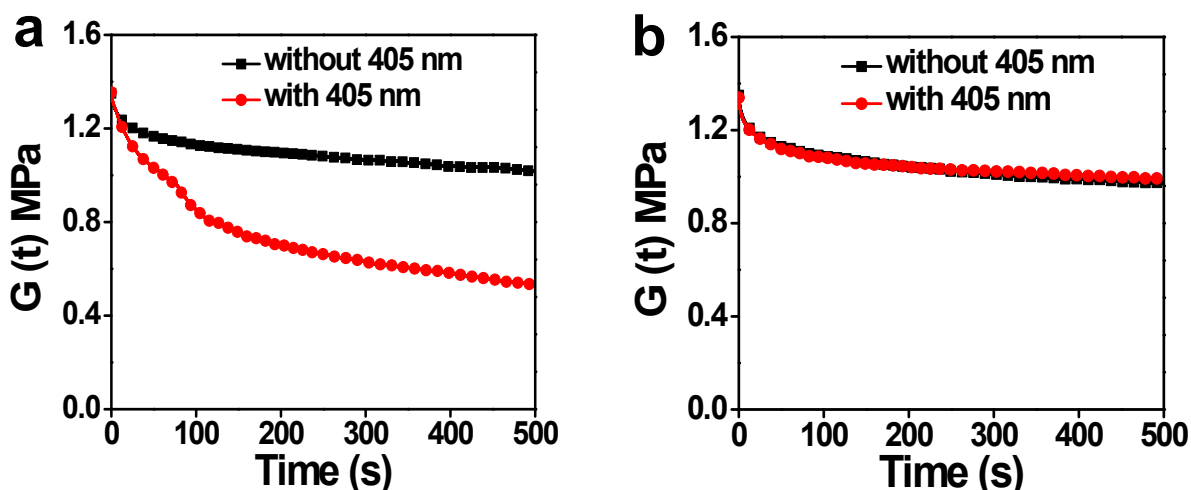


Fig. S5 (a) Stress relaxation modulus $[G(t)]$ of the HABI-PU samples with or without 405 nm irradiation. (b) Stress relaxation modulus $[G(t)]$ of PU control samples with or without 405 nm irradiation. The applied strain in these tests are 100%.

Note S4. Discussion about Fig. S5

To further elucidate the importance of dynamic covalent bonds in HABI from the view of rheology, stress relaxation tests were performed to demonstrate the distinction on chain mobility of the HABI-PU and PU control samples with/without 405 nm irradiation. Both of the HABI-PU or PU control samples have almost the similar attenuation of $G(t)$ without 405 nm irradiation, which is about 0.33 MPa and 0.38 MPa respectively. It indicates that the polymer chains of the matrix material in original HABI-PU and PU control sample themselves have a certain mobility. The mobility of the polymer chain is beneficial to photo-induced self-healing.⁴ As expected, the $G(t)$ attenuation of PU control sample is about 0.35 MPa upon 405 nm irradiation, which is almost unchanged, whilst that of HABI-PU under 405 nm irradiation is 0.82 MPa. It indicates that the chain mobility of HABI-PU materials containing dynamic HABI joints has been greatly improved upon 405 nm irradiation. Thus,

HABI-PU materials obtain better chain mobility under illumination because of the photo-induced scission of long polymer chains based on the cleavage of dynamic covalent C-N bonds in HABI, which is the key mechanism to photo-induced healing.

Meanwhile, above stress relaxation tests also proved the scission of polymer chains under 405 nm irradiation. Polymer backbones containing HABI joints (HABI-PU) will break up into discontinuous shorter chains with lower molecular weight on accounts of the dissociation of dynamic C-N bond in HABI units upon light irradiation, resulting in the greater attenuation of stress relaxation modulus $[G(t)]$ of the HABI-PU samples with 405 nm irradiation. With the prolonged irradiation time, a large number of polymer chains will be broken, molecular-level photo-induced scission could be manifested as the macroscopic decreasing of the mechanical performance of the HABI-PU materials once the amount of dissociation of the C-N covalent bonds in HABI-PU reaches a certain degree. Macroscopically, the HABI-PU elastomers will undergo plastic deformation or even fracture when loading a certain weight. In addition, the molar equivalent ratio of the dihydroxy functionalized HABI molecule to poly(tetramethylene ether glycol) (PTMG1000) is 1:12.5, in the process of the polymerization with hexamethylene diisocyanate (HDI), theoretically, the short chain formed by 12.5 PTMG units will be alternately connected with one HABI unit to form the long polymer chain with high molecular weight. That is, lots of HABI joints exist in long polymer chains. In HABI-PU polyurethane materials, the depolymerization of long chains into short chains occurs under irradiation due to the existence of dynamic C-N covalent bonds in HABI joints, thereby weakening the mechanical strength of HABI-PU materials. It is the key mechanism to photo-induced plastic deformation and photo-induced scission when loading a certain weight.

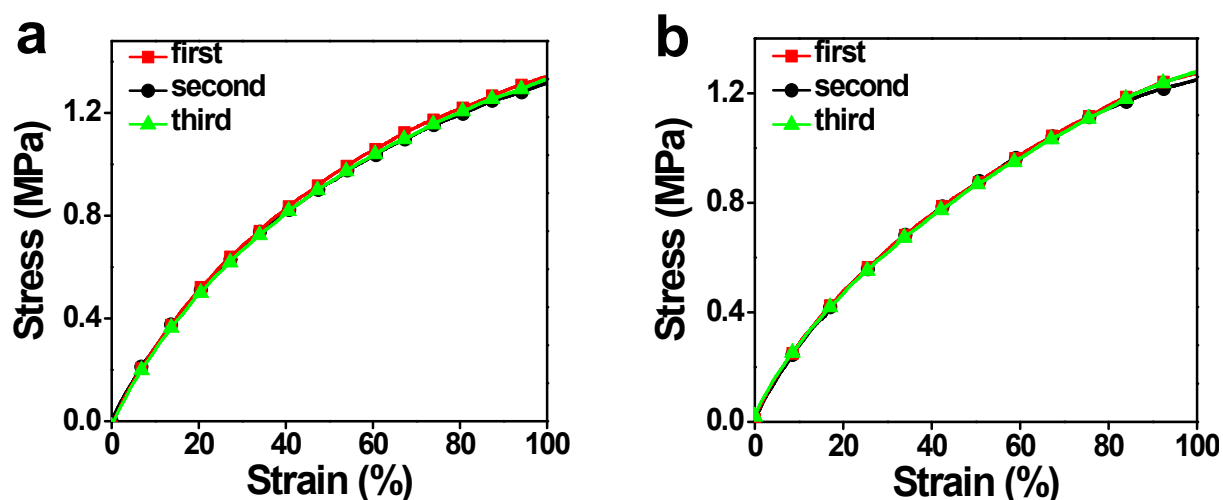


Fig. S6 (a) Static tensile test within 100% strain of the same pristine HABI-PU sample was performed for three times without 405 nm irradiation. (b) Static tensile test within 100% strain of the same HABI-PU sample after healing for 30 s under 405 nm at room temperature followed by putting it in the dark for 6 h was performed for three times without 405 nm irradiation.

Note S5. Discussion about Fig. S6

Static tensile tests were carried out on the same original sample for three times repeatedly. The mechanical strength does not decrease significantly within 100% strain (Fig. S6a), indicating that the pristine HABI-PU samples possess excellent elasticity before 405 nm irradiation.

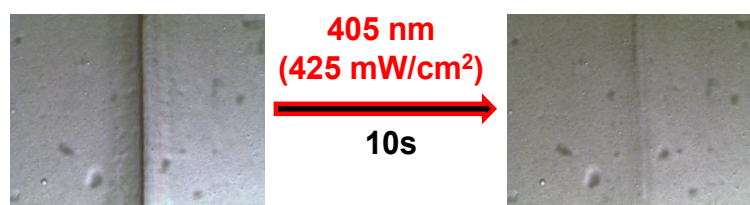


Fig. S7 Optical microscope images of photo-induced healing behaviors of scratched HABI-PU films under 405 nm laser (425 mW/cm²) irradiation at room temperature for 10s.

Note S6. Discussion about Fig. S7

As the extinction coefficient of the 2-glycol-HABI moieties at approximately 405 nm is about 220 L mol⁻¹ cm⁻¹ and more than 99 % of the incident photons are absorbed by the surface with a thickness of more than 0.19 cm. However, the thickness of the dumbbell-shaped HABI-PU strip samples are 0.22 cm. Therefore, light cannot penetrate through the strips completely, resulting in the materials become more dynamic on top surface towards the light source, and less dynamic on the bottom. This is one reason why the healing time required for the healing of the HABI-PU film is less than that of the dumbbell-shaped bulk materials. The thickness of the HABI-PU film is 1 mm, 405 nm light can penetrate through the polymer film well and activate the dynamic C-N covalent bonds at different depth of the scratches, promoting the rapid photo-induced healing.

The relevant calculation is as follow: Extinction coefficient $\epsilon = A/cb$, Where A is the absorbance at 405 nm, about 0.011 in UV-vis spectra (Fig. 1c); c is the molar concentration of 2-glycol-HABI in THF solution, it is 5×10^{-5} mol/L; b is the optical path length in the quartz cuvette, i.e., 1 cm. The extinction coefficient at 405 nm was calculated to be 220 L mol⁻¹ cm⁻¹. For the HABI-PU polyurethane sample, if we defined the depth of light penetration where 99.9 % of the incident light were absorbed (A is 3), we can calculate the depth of light penetration $b = A/c\epsilon = 0.19$ cm. (The molar concentration of 2-glycol-HABI in HABI-PU, $c = 0.072$ mol/L; $\epsilon = 220$ L mol⁻¹ cm⁻¹)”

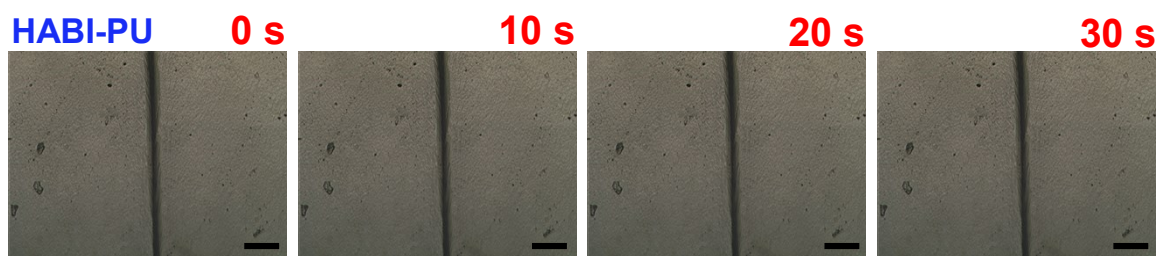


Fig. S8 Optical microscope images of photo-induced healing behaviors of scratched HABI-PU films without 405 nm laser irradiation (325 mW/cm^2) at room temperature for 30 s. Scale bars are 0.1 mm.

Note S7. Discussion about Fig. S8

Compared to the optical microscope images of scratched HABI-PU films healed under 405 nm laser irradiation at room temperature for 30 s (Fig. 3a), the scratches of the control sample without 405 nm irradiation remains evident after healing for 30 s at room temperature, further confirming that the healing ability of HABI-PU stems from the photo-induced re-formation of C-N bonds of dynamic HABI linkages across the damaged interface.

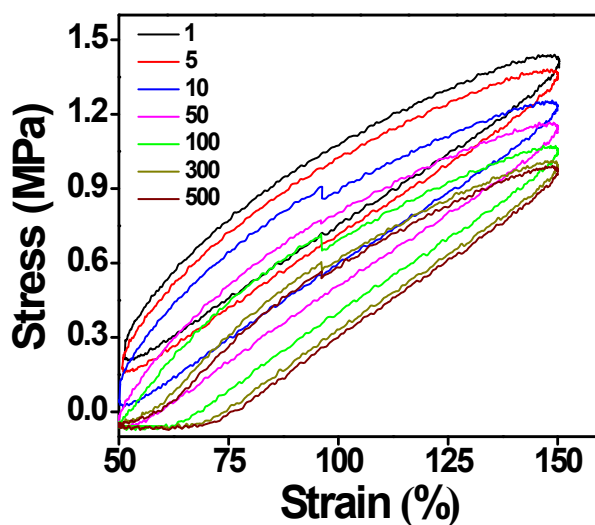


Fig. S9 The loading-unloading cycles from 50% strain to 150% strain of the pristine HABI-PU elastomer in 500 continuous cycles at 1Hz.

Table S1. Healing times of selected solvent-free polymer films with scratches.

Material for self-healing	Healing system	Conditions for self-healing	Healing times of the solvent-free polymer films with scratch	References
Thermoplastic polyurethane	Disulfides	At 25 °C	2 h	<i>ACS. Appl. Mater. Inter.</i> 2019 , <i>11</i> , 23623.
Triblock copolymers elastomer	Hydrogen bonds interactions	At 50 °C	3 h	<i>Science</i> 2014 , <i>344</i> , 591.
Polyurethane	Hierarchical hydrogen bonds	At 90 °C	5 min	<i>Chem. Commun.</i> 2015 , <i>51</i> , 13058
Polyurethane	Diarylbibenzofuranone (DABBF)	At 50 °C	12 h	<i>Chem. Commun.</i> 2016 , <i>52</i> , 13068
Supramolecular polyurethane	π - π stacking and hydrogen bonding interactions	At 45 °C	2 h	<i>Adv. Mater.</i> 2018 , <i>30</i> , 1704407
Metallosupramolecular polymer	Metal-ligand motifs	Under 320-390 nm irradiation (950 mW/cm ²)	1 min	<i>Nature</i> 2011 , <i>472</i> , 334-337.
Crosslinked Polyurethane	polyurethane networks based on oxetane-substituted derivative of chitosan	302 nm UV light (120W UV lamp)	30 min	<i>Science</i> 2009 , <i>323</i> , 1458-1460.
Linear polyurethane	Hexaarylbiimidazole (HABI)	Visible light with 405-nm (425 mW/cm ²)	10 s	Our work

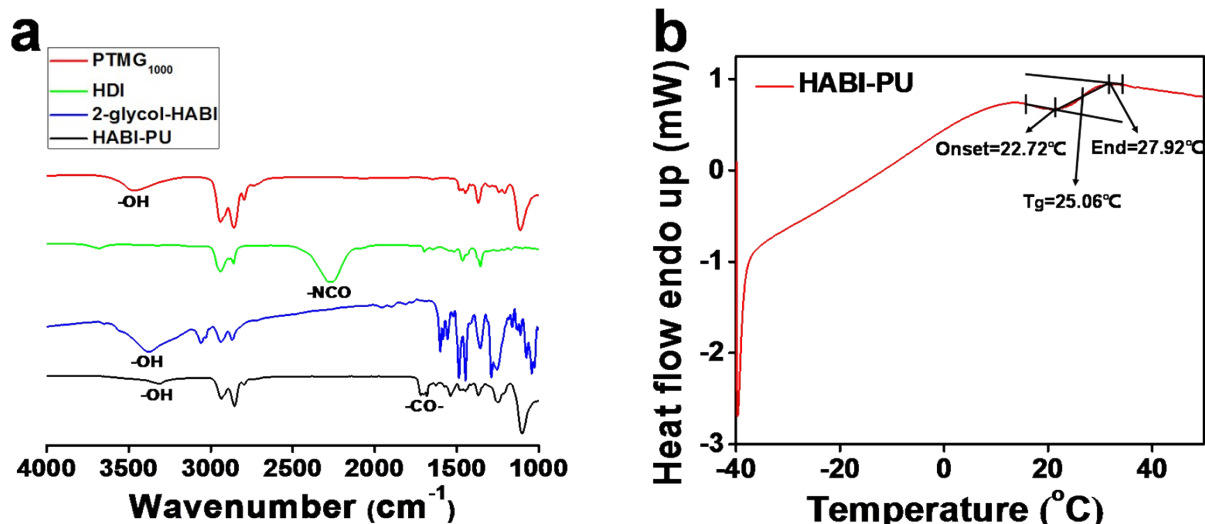


Fig. S10 (a) IR spectra of PTMG₁₀₀₀, HDI, 2-glycol-HABI and HABI-PU. (b) DSC curve of HABI-PU, showing T_g around 25.06 °C.

Note S8. Discussion about Fig. S10

The glass transition temperature (T_g) is the transition temperature between the glassy and highly elastic state of the amorphous polymer materials. Below the T_g, polymer materials are in glassy state and the movement of the molecular chains inside the polymer materials is limited, which is not beneficial to self-healing process behaviors based on polymer molecular chain movement. Above the T_g, polymer materials are in a highly elastic state, the movement of the molecular chain inside the polymer materials is no longer restricted. Hence the movement of the molecular chain is conducive to the self-healing of the polymer. The glass transition temperature of the linear HABI-PU materials is about 25.06 °C (Fig. S10b). The room temperature for the photo-induced self-healing experiments is about 28 °C, which is above the T_g. On the other hand, glass transition is a process that occurs at slightly lower temperature than T_g. Polymer materials starts glassy state transition below T_g. Therefore, for this experiment, room temperature is conducive to photo-induced healing process. The movement of the molecular chains inside the HABI-PU polymer materials is not strongly restricted at present experiment condition.

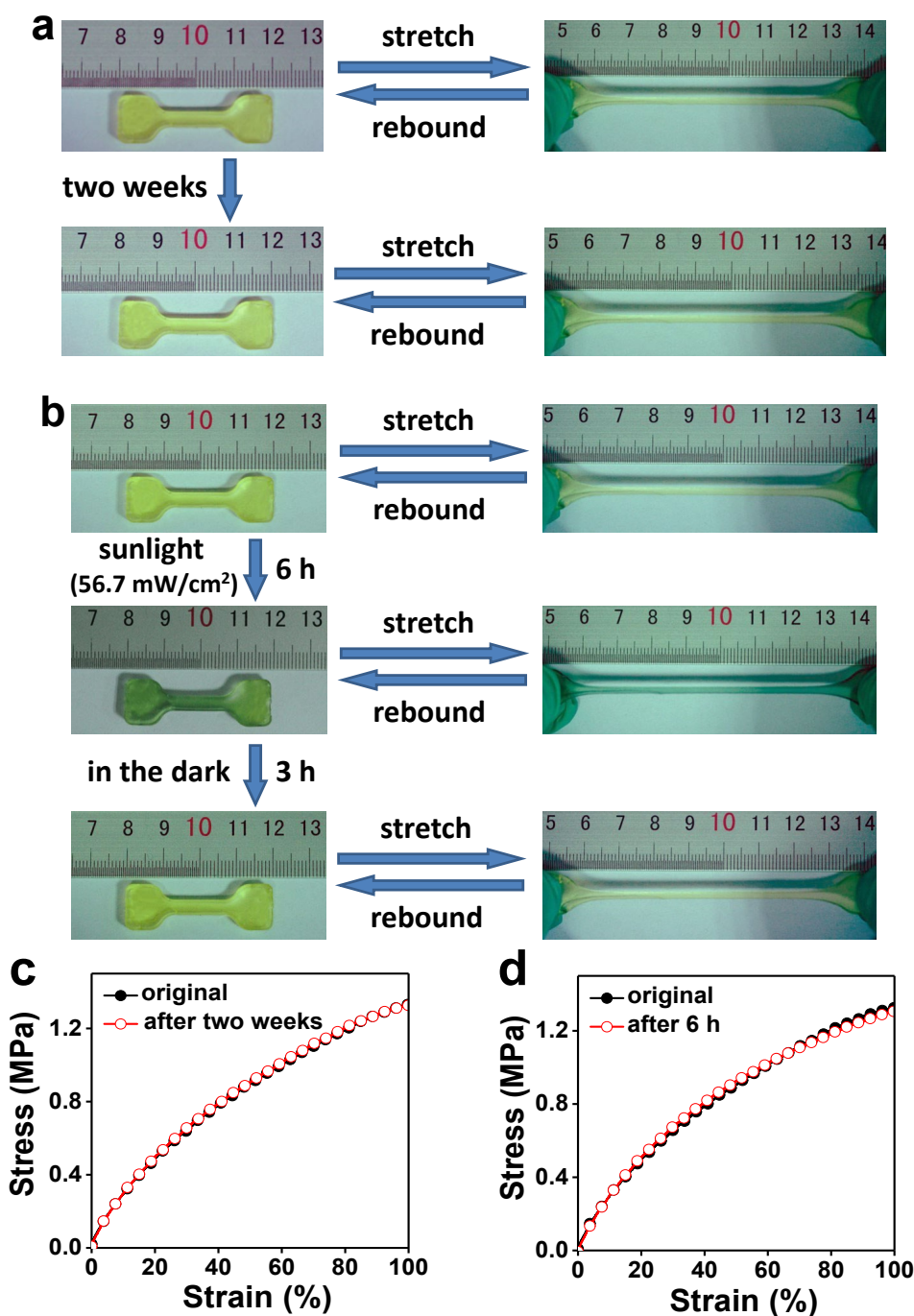


Fig. S11 The characterization about the stability of HABI-PU elastomer materials. (a) The as-prepared HABI-PU sample could be stretched to about 7 cm from the initial length of 2 cm (the length is the actual length that's being stretched). The stretched HABI-PU will finally rebound to original length when the same original sample being placed at room temperature and exposed in the air for two weeks. (b) The as-prepared HABI-PU sample could be stretched to 7 cm from the initial length of 2 cm. The stretched HABI-PU will finally rebound to original length when placed at the sunlight (56.7 mW/cm²) for 6 h on a typical sunny day. After standing in the dark for 3 h, the mechanical toughness of the material is still as good as that of the initial sample. (c) Static tensile tests within 100% strain of the original HABI-PU sample and the same sample after being placed at the room temperature and exposed in the air for two weeks. (d) Static tensile tests within 100% strain of the original HABI-PU sample and the same sample after being placed at the sunlight for 6 h followed by standing in the dark for 3 h.

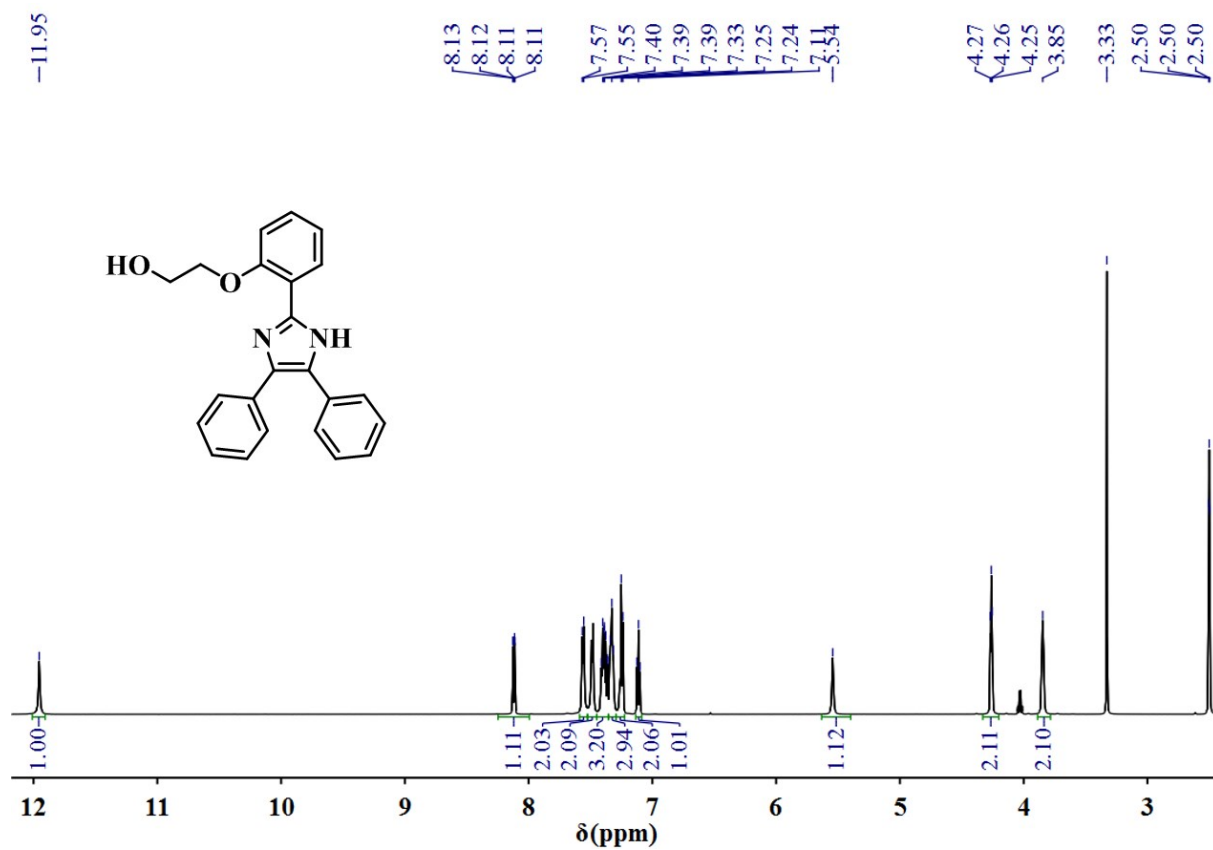
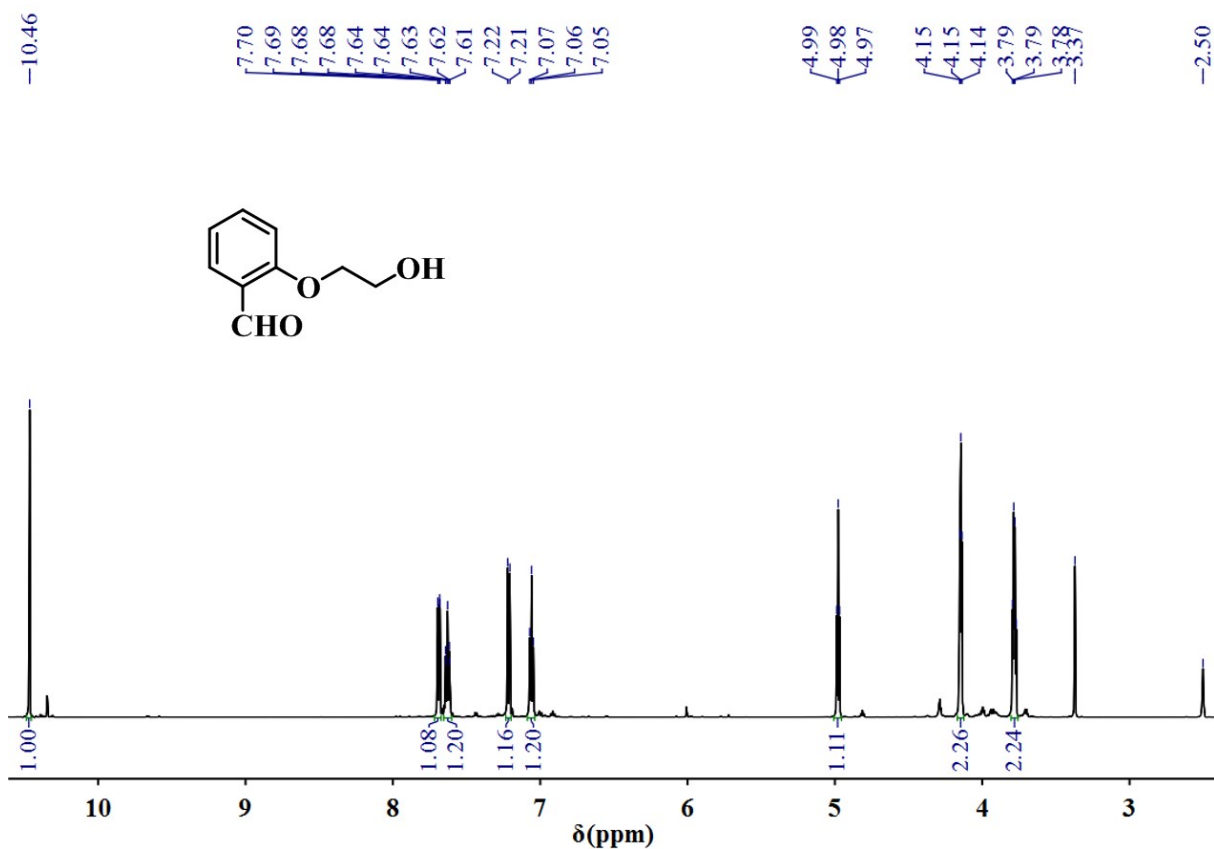
Note S9. Discussion about Fig. S11

As for the stability of HABI-PU materials under the natural environment, we think that HABI-PU materials will degrade more or less when exposed to air and sunlight for a very long time. Many other kinds of plastic and resin materials will also suffer the same problem, which is usually dependent on the nature of the polymer structure. HABI is one of the typical photochromic materials, which has widely applications in optical memory, anti-counterfeiting, imaging, optical display. Further, the photochromic reaction of HABI materials is highly reversible. In Fig. 1d in the main text, 8 times thermos-recover cycles of HABI-PU has already indicated that HABI-PU has a great fatigue resistance of photochromism. We thought the HABI-PU containing HABI is also relatively stable in exterior applications for long time service. In order to evaluate the long-term stability/utility of HABI-PU materials, we have tested a dumbbell-shaped HABI-PU sample after being placed on natural environment for two weeks (Figure S11a). The as-prepared HABI-PU sample could be stretched to about 7 cm from the initial length of 2 cm (the length is the actual length that's being stretched). The stretched HABI-PU will finally rebound to original length. After the same original sample being placed at room temperature and exposed in the air for two weeks, HABI-PU still can be stretched to the length where the initial sample could be stretched. Removing the tensile stress, the HABI-PU could rebound to its original length (Figure S11a). In addition, the static tensile experiment within 100 % strain for the HABI-PU specimen and the same specimen after standing at room temperature and exposed in the air for two weeks has been carried out (Figure S11c). It can be seen from the stress-strain curves that the mechanical toughness of the elastomer after standing at room temperature and exposed in the air for two weeks is still as good as that of the initial sample, further indicating HABI-PU materials has excellent long-term stability/utility.

Additionally, the sunlight could indeed activate dynamic chemistry of HABI in HABI-PU elastomers. As the color change shown in Figure S11b, HABI-PU exhibit a slight photochromic phenomenon under sunlight. However, this low degree of photochromism would not cripple significantly the mechanical strength or performance, after all, most of HABI in the HABI-PU are not dissociated into the radical TPIRs. Moreover, the dissociated radicals could undergo spontaneous annihilation upon encountering adjacent radicals without deterioration or massive dislocation rearrangement, thus would not affect the mechanical properties of the HABI-PU materials. In order to evaluate the long-term stability/utility of HABI-PU materials when used in the typical sunny day, we have tested a dumbbell-shaped HABI-PU sample after being placed at the sunlight environment for 6 h (Figure S11b). The as-prepared HABI-PU sample could be stretched to 7 cm from the initial length of 2 cm (the length is the actual length that's being stretched). The stretched HABI-PU will finally rebound to original length (Figure S11b). After being placed at the sunlight environment for 6 h, HABI-PU still can be stretched to the length where the initial sample could be stretched. Removing the tensile stress, the HABI-PU could rebound to its original length. In addition, after standing in the dark for another 3 h, the mechanical toughness of the material is still as good as that of the initial sample. The static tensile experiment within 100 % strain for the HABI-PU specimen and the same specimen after standing at the sunlight environment for 6 h followed by standing in the dark for 3 h has been carried out (Figure S11d). It can be seen from the stress-strain curves that the mechanical toughness of the elastomer after standing at the sunlight environment for 6 h followed by standing in the dark for 3 h is still as good as that of the initial sample, further indicating HABI-PU materials has excellent long-term stability/utility when used in the typical sunny day. Furthermore, it should be noted that these experiment about HABI-PU elastomers were conducted under 405 nm laser irradiation whose intensity is much higher than that of sunlight (only UV and short wavelength visible light make sense). Instead, the partially dynamic dissociated HABI could bring the ability of

automatically repair damages when exposure to sunlight if there are latent damages. Although the light intensity of sunlight (56.7 mW/cm^2) on a typical sunny day is not as strong as that of the 405 nm laser (325 mW/cm^2) used in the self-healing experiment. The condition of sunlight irradiation and outdoor temperature ($28 \text{ }^\circ\text{C}$) in some degree contributes to slow self-healing process of HABI-PU without obviously sacrifice of mechanical properties. Thus, the lifetime and reliability of the HABI-PU materials would be substantially upgraded as their structures and original properties are maintained after healing under sunlight irradiation on a typical sunny day.

3. NMR Spectra



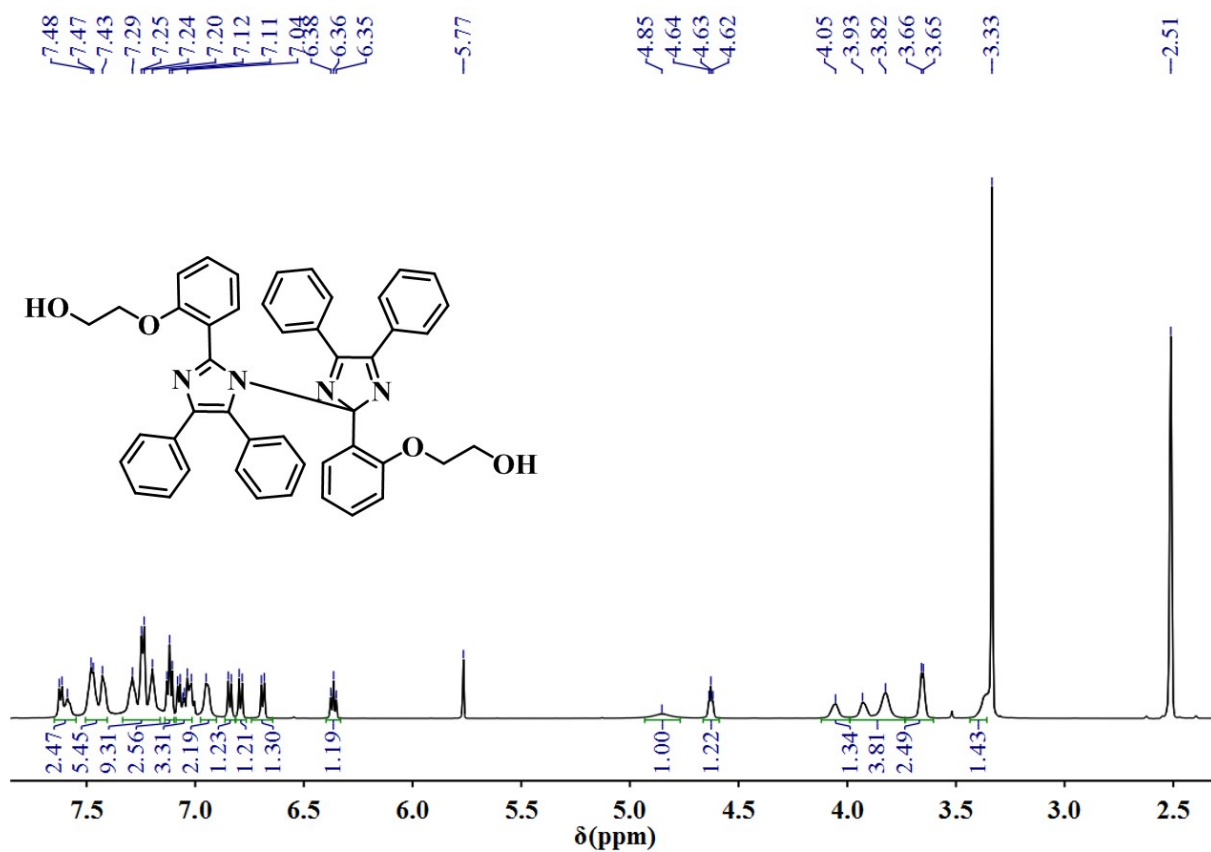
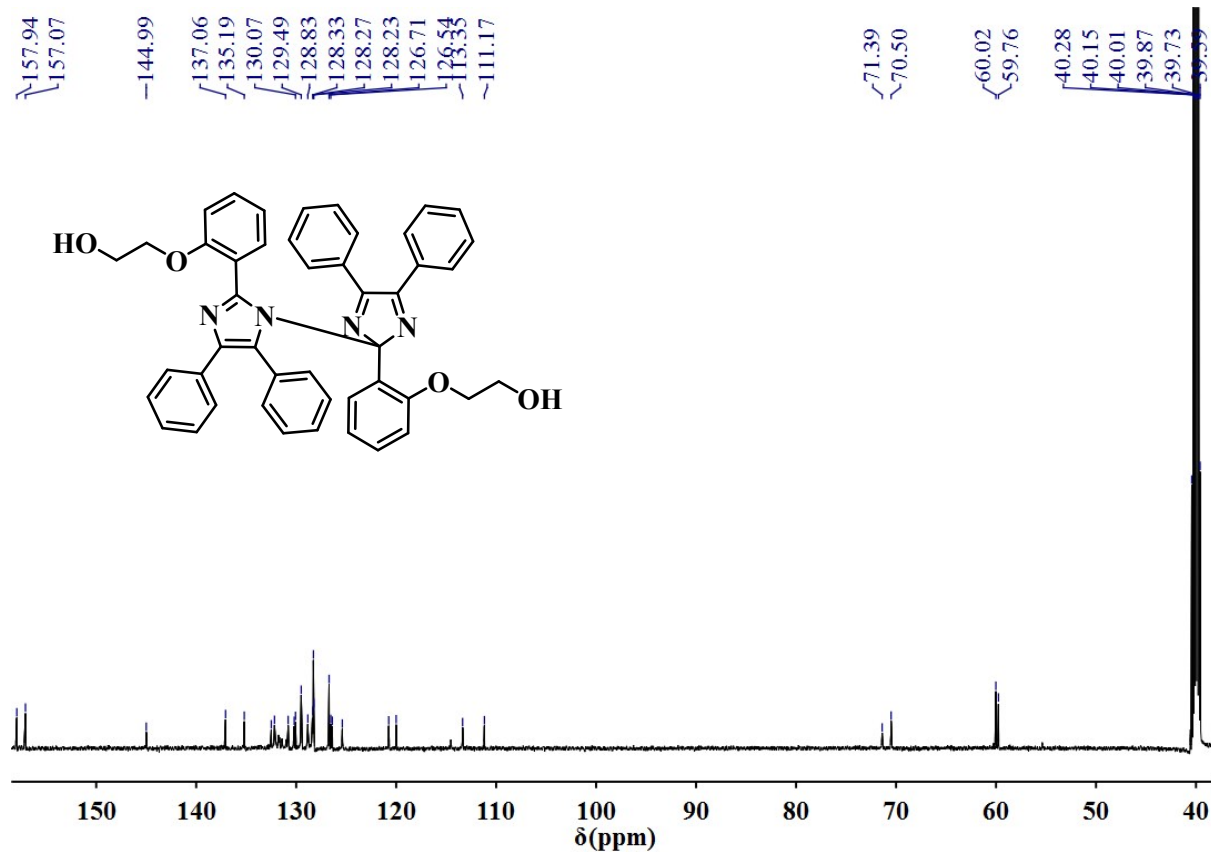


Fig. S12 ¹H NMR spectra of all the compounds.



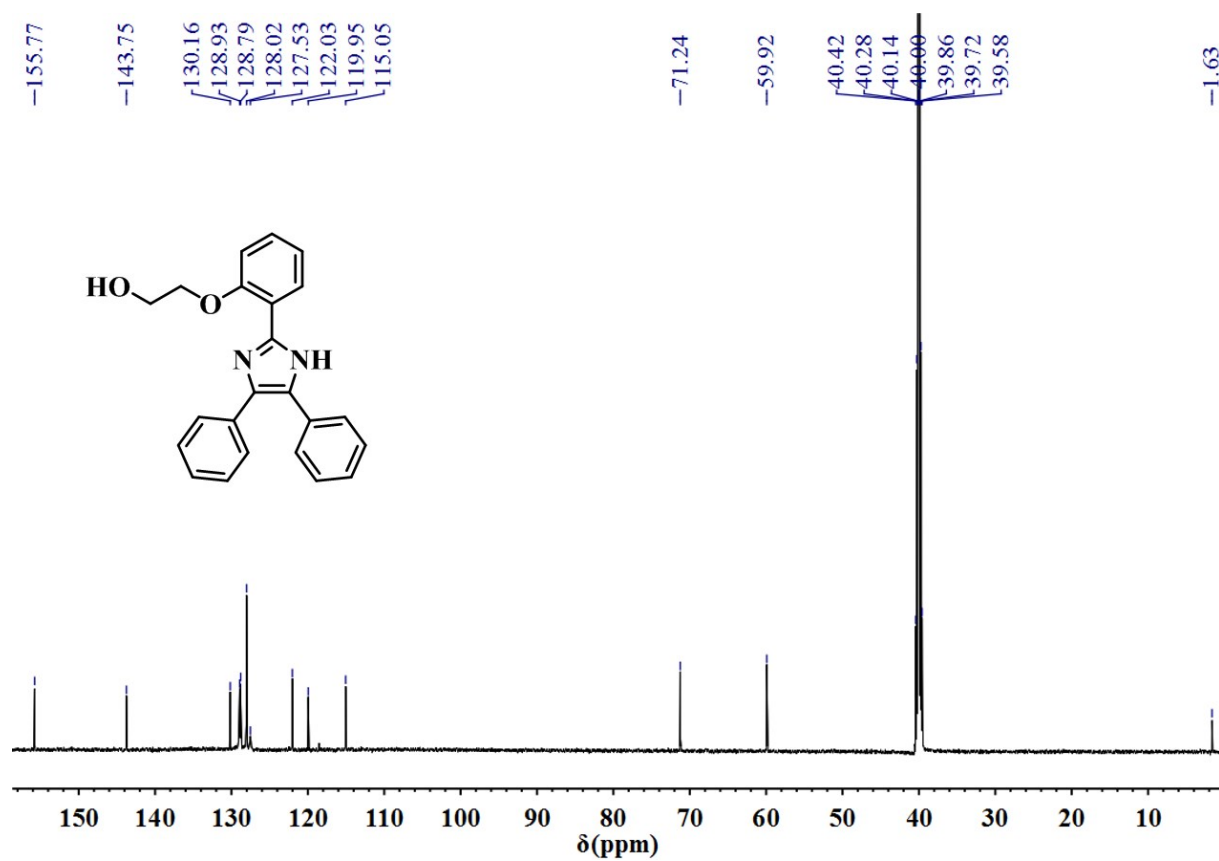
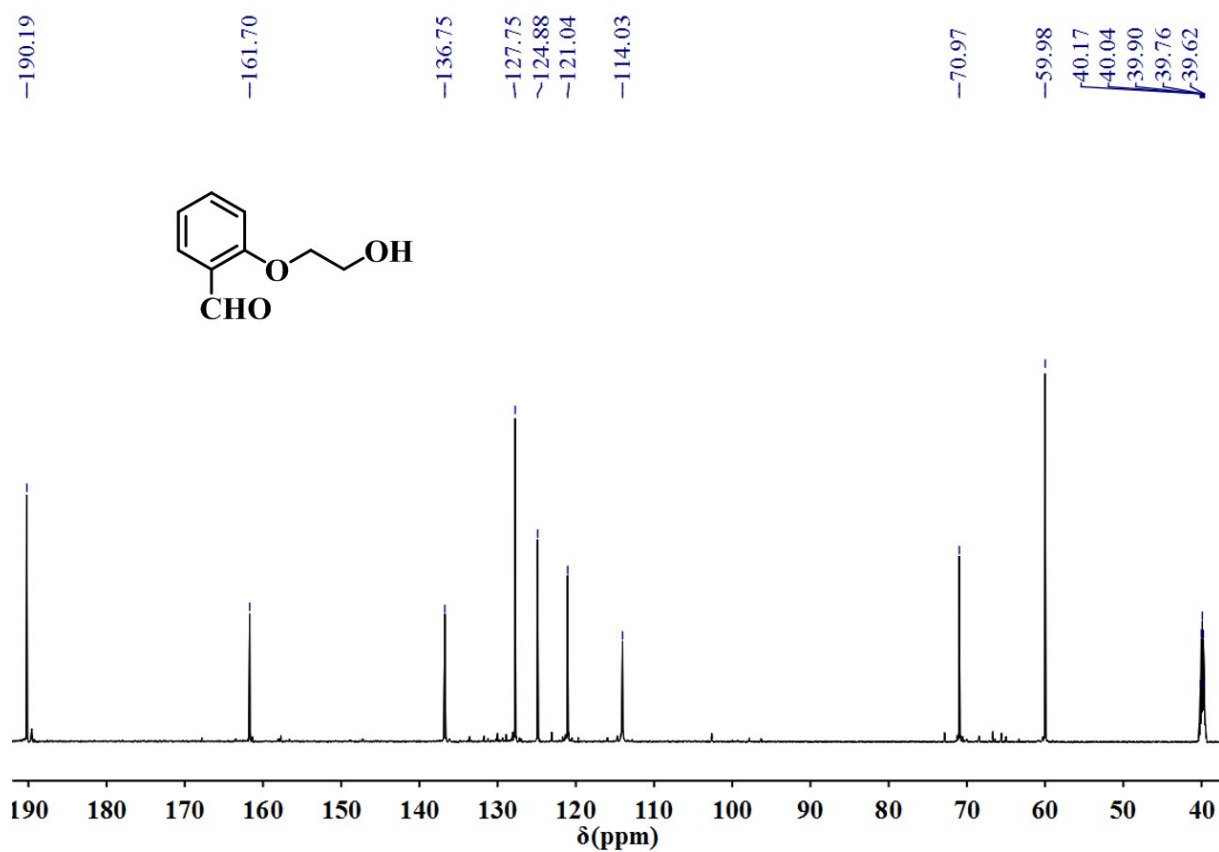


Fig. S13 ^{13}C NMR spectra of all the compounds.

4. LC-MS Spectra

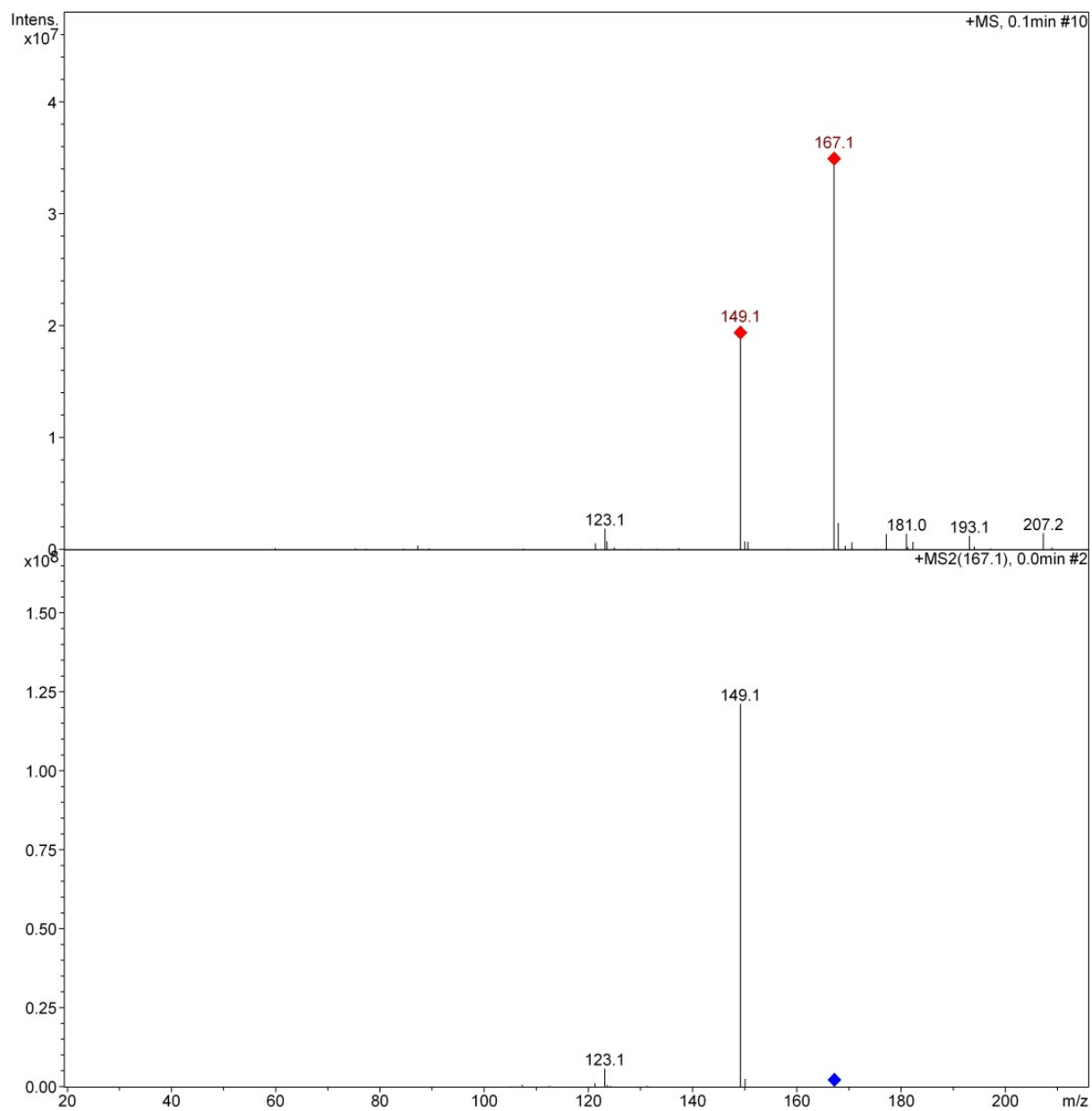


Fig. S14 LC-MS Spectra of 2-(2-hydroxyethoxy)benzaldehyde.

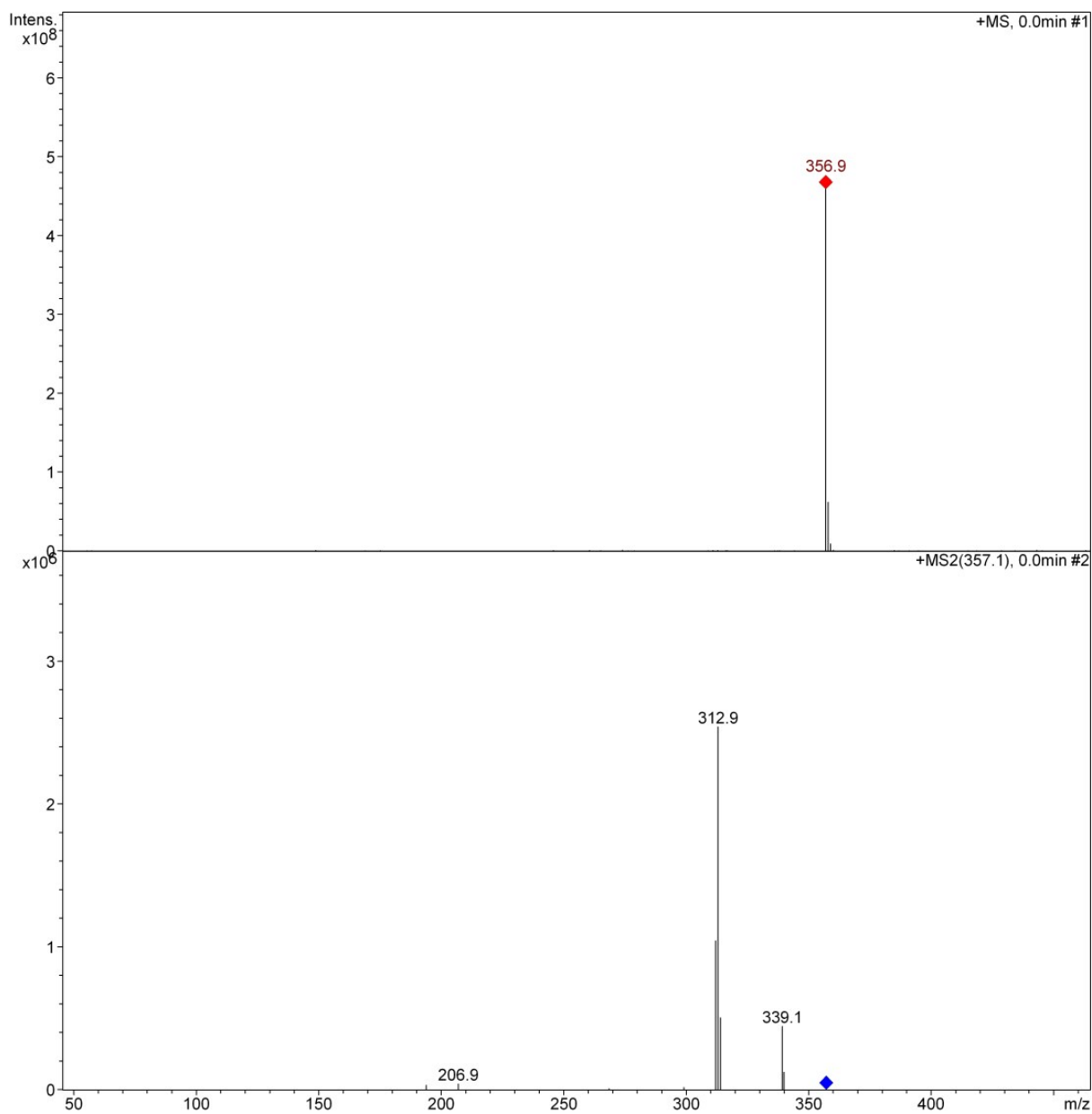


Fig. S15 LC-MS Spectra of 2-glycol-TPI.

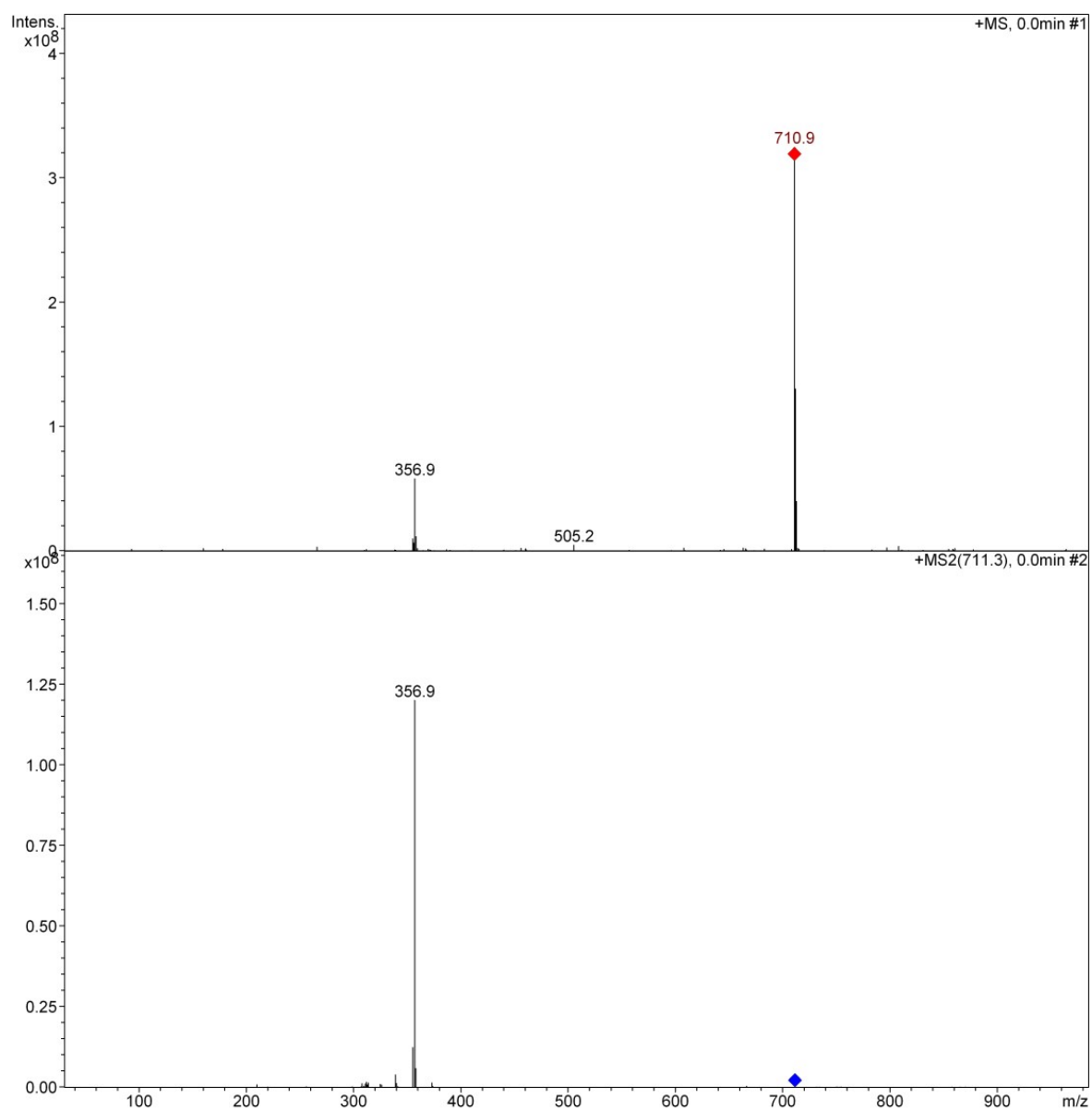


Fig. S16 LC-MS Spectra of 2-glycol-HABI.

5. References

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