# Supporting information

## Chemodynamic covalent adaptable network-induced robust, self-healing, and degradable fluorescent elastomers for multicolor information encryption

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**Materials**

Polycaprolactone polyol (Mn=2000 g $mol^{-1}$), dibutyltin dilaurate (DBTDL, 95%), tetrahydrofuran (THF), anhydrous ethanol, methanol, lipase (10,000 U $g^{-1}$), sodium hydroxide (NaOH), hydrochloric acid (HCl) were purchased from Shanghai Macklin Biochemical Co., Ltd. Isophorone diisocyanate (IPDI, 99%), curcumin (Cur, 98%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 1,4-benzenediboronic acid (BDA, 98%) was purchased from Bide Pharmatech Ltd. N, N-dimethylformamide (DMF, 99.5%) was purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Phosphate-buffered saline (PBS, 0.01 mol $L^{-1}$) was purchased from Shanghai yuanye Bio-Technology Co., Ltd. All reagents were used without further purification.

**Fabrication of Elastomers**

PCL diol (5 mmol) was added to a three-necked round-bottomed flask, which was subsequently heated and stirred under vacuum at 120 °C for 1 h to remove water, and then the flask was cooled to 70 °C. Then, DMF (10 mL), IPDI (10 mmol), and DBTDL (3 drops) were added followed by continued stirring for 1.5 h. Subsequently, a solution of curcumin (5 mmol) dissolved into 5 mL of DMF was added and the temperature was raised to 90 °C to continue the reaction for 18h. Then, the temperature was cooled to 70 °C and a solution of BDA dissolved into 5 mL of DMF was added (the feeding ratios are listed in Table S1) to keep stirring for 1 h. The whole process was carried out under nitrogen protection. Finally, the resulting viscous reactants were poured into PTFE molds and dried at 60 °C for 48 h, followed by drying under vacuum at 80 °C for 48 h to obtain the final elastomers. The fabricated elastomers were named PICPU, $PICB_{0.25}PU$, $PICB_{0.5}PU$, $PICB_{1.0}PU$, $PICB_{1.5}PU$ according to the BDA contents. In addition, OH-PCL-OH, IPDI, and BDA (10, 10, and 2.5 mmol), as well as OH-PCL-OH and IPDI (10 and 10 mmol), were used as comparisons to explore the hydrogen-bonding effect of BDA with urethane groups. Furthermore, we regulated the pH of the system by introducing different levels of acids (10 μL, 20 μL, 50 μL, pH=1 HCl) and alkali (50 μL, pH=14 NaOH) at the stage of BDA addition to study the effect of acid and alkaline on the structures of curcuminoids and the mechanical properties of the elastomers.

**Characterization of the Elastomers**

The elemental composition of the elastomer surface was analyzed by using energy-dispersive X-ray spectroscopy (EDS, Xplore). The content of element B in elastomers was performed by

inductively coupled plasma optical emission spectrometer (ICP-OES) on an Agilent 5110 (OES) instrument in the USA, pump rate: 60 r/min, plasma gas: 12.0 L/min, nebulizer flow: 0.70 L/min, stable time: 20 s, auxiliary gas: 1.0 L/min, reading access time: 5 s, sample flush time: 20 s, RF power: 1250 W. Fourier transform infrared spectroscopy (FT-IR) was performed on a Thermo Scientific Nicolet iS20 spectrometer (USA) under 4000 to 500 $cm^{-1}$ with 16 scans at 4 $cm^{-1}$ resolution. For temperature-controlled measurements, the sealed samples were heated in transmission mode from 20 °C to 90 °C at 5 °C intervals on a Bruker VERTEX 80v (Germany) FTIR spectrometer. 2D correlation analysis was performed using the temperature-dependent FTIR spectra of $PICB_{1.0}PU$ elastomers from 20 to 90 °C. 2D correlation analysis was performed using the software 2D Shige ver. 1.3 (©Shigeaki Morita, Kwansei Gakuin University, Japan, 2004-2005). In the contour plots, the red color is defined as positive intensity while the blue color is defined as negative intensity. The molecular weight of the samples was determined by gel permeation chromatography (Agilent GPC 50, USA). The calibration curve used PS as a standard, and the mobile phase was room temperature DMF (salt-free), using an RI detector, eluting at a flow rate of 1 mL/min in a WAT044223 7.8*300 mm Column. Differential scanning calorimetry (DSC) measurements were taken on a Netzsch DSC 200 F3 analyzer (Germany) with a heating rate of 10 °C $min^{-1}$ under the $N_2$ atmosphere. Thermogravimetric analysis (TGA) tests were carried out on a TGA/DSC 3+ instrument with a temperature range of 30 to 750 °C and a heating rate of 20°C $min^{-1}$ under an argon atmosphere. Dynamic Thermomechanical Analyzer (DMA) was conducted in tensile mode on a DMA Q800 (TA Instruments, USA) in the temperature range from -80 to 80 °C with a ramp rate of 3 °C $min^{-1}$ at 10 Hz. The contact angle of 5 μL of liquid was measured using a contact angle meter (SDC-350H, China), and the results were determined by measuring the contact angle at at least five different locations on the surface. Two-dimensional small-angle X-ray scattering (2D-SAXS) patterns of materials were measured on a Xeuss system (Xeuss 3.0 SAXS, France) equipped with a semiconductor detector (Eiger2R 1M) and connected to a multilayer focused Cu Kα X-ray source. The wavelength of the X-ray radiation was 1.5418 Å. The sample-to-detector distance was 1500 mm. $^1H$ nuclear magnetic resonance ($^1H$ NMR) measurements were recorded on a Bruker Avance III HD 500 MHz instrument with DMSO-d6 as the solvent.

**Mechanical and Self-Healing Performance Testing**

The tensile test was carried out by a universal tensile machine (WDW-5) with a tensile rate of 50

mm min-1, and the specimen was a dumbbell-shaped specimen (L × W=50 mm × 4 mm). The average of the results of at least three individual tensile tests for each sample was recorded.

To assess the self-healing ability of the fabricated elastomer samples, the dumbbell-shaped specimens were completely cut in half in the air, followed by close contact of the cuts, and no external stress was applied to the interface during the self-healing process. The healing conditions were set as no treatment at room temperature, 50 vol.% ethanol treatment of cross sections for 5 min at room temperature, and no treatment at 70°C for different times of healing, respectively. The healed specimens were again subjected to tensile tests. The tensile test conditions were the same as described above. The healing efficiency was expressed by the following equation:

$$\text{Healing efficiency } (\%) = \frac{\text{Healed } \textit{tensile strength}}{\text{Original } \textit{tensile strength}} \times 100\%$$

**Fluorescence Performance Testing**

Preparation of ethanol solutions with different pH: 100 mL of anhydrous ethanol was taken to adjust its pH with 0.1M HCl and 0.1M NaOH to prepare ethanol solutions with pH values of 1, 3, 5, 7, 9, 11, and 13, respectively.

Then, based on the different pH ethanol solutions, an ethanol solution of curcumin with a content of $4 \times 10^{-5}$ mol $L^{-1}$ was prepared, labeled as solution A; and a ligand-composite ethanol solution of curcumin with $4 \times 10^{-5}$ mol $L^{-1}$ curcumin and $2 \times 10^{-5}$ mol $L^{-1}$ BDA was prepared, labeled as solution B.

Absorption measurements were performed using a UV-visible spectrophotometer (Shimadzu UV-3600, Japan) with a measurement range of 300 to 600 nm. $PICB_{1.0}PU$ elastomers were subjected to fluorescence experiments including excitation spectra, emission spectra, and quantum yields at a steady-state/transient fluorescence spectrometer (Edinburgh FLS1000, UK). The samples were excited at 468 nm and quantum yields were calculated from the comparison of the integral signals of the excitation and emission signals. Cold light photographs were taken by a mobile phone at room temperature under the irradiation of a UV lamp (395 nm, 300 W).

**Degradation Performance Testing**

In vitro enzyme degradation test: Dry samples (1 cm × 1 cm, ~40 mg) were placed in 10 mL PBS buffer solution without and with 0.1 g of lipase (100,000 U/g) and incubated at 37°C for different times. The degradation solution was changed every 24 h to maintain enzyme activity.

Alkaline degradation test: Dry samples (1 cm × 1 cm, ~150 mg) were immersed in 15 mL of 0.1M NaOH solution (organic solvent and water volume ratio of 1/1) at 25°C for different times. The organic solvents included methanol, ethanol, and THF.

Hot water degradation test: Dry samples (1 cm × 1 cm, ~150 mg) were placed in 15 mL of deionized water and degraded at 90 °C at different times. Samples were removed at intervals, washed with distilled water, and dried. The degree of degradation was determined by the change in dry weight and the test was repeated three times. The degradation rate can be calculated according to the formula by $(m_0\text{-}m_1)/t$, where $m_0$ represents the initial mass of the specimen, $m_1$ represents the weight of the specimen after drying, and $t$ is the degradation time.

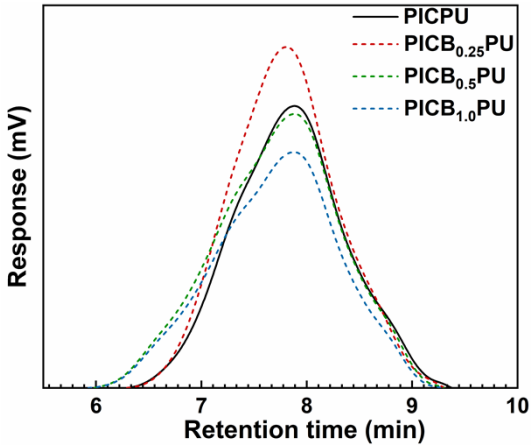


**Figure S1.** GPC curves for different elastomers.

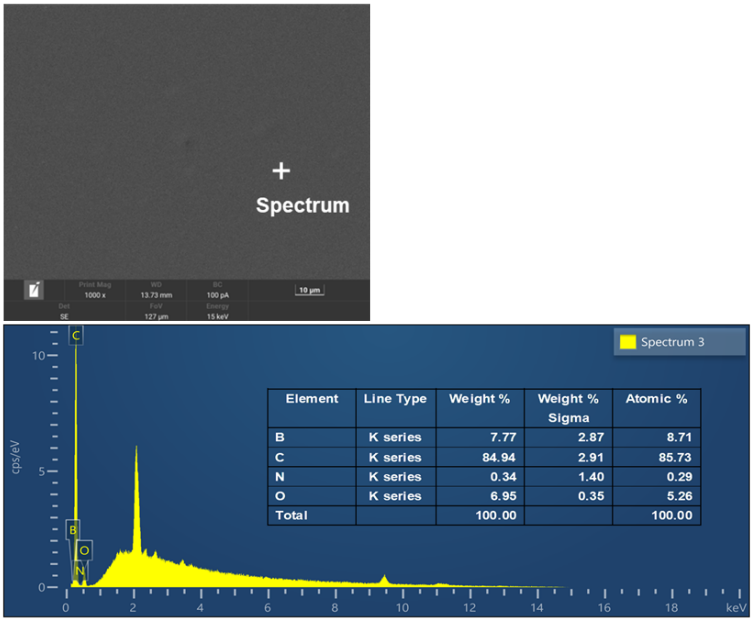


**Figure S2.** Elemental composition of $PICB_{1.0}PU$ elastomer surfaces.

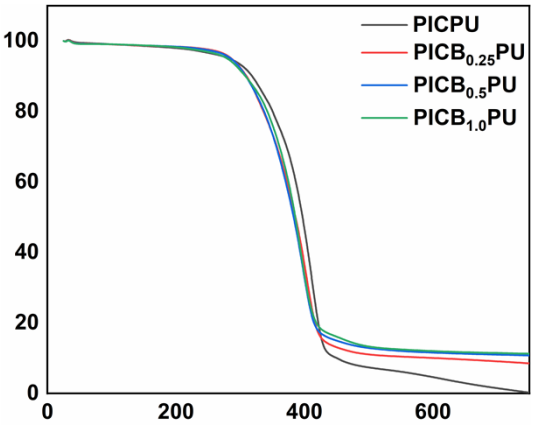


**Figure S3.** TGA curves for different elastomers.

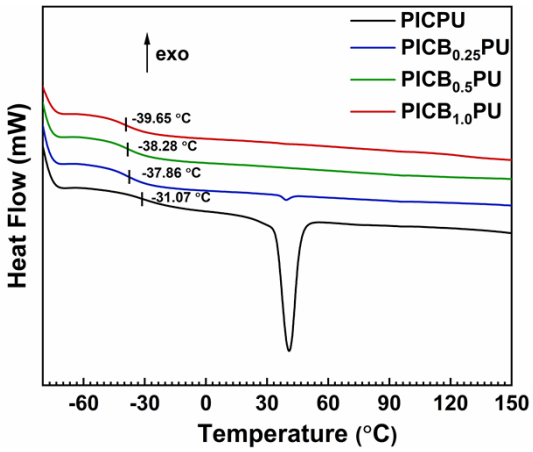


**Figure S4.** DSC curves for different elastomers.

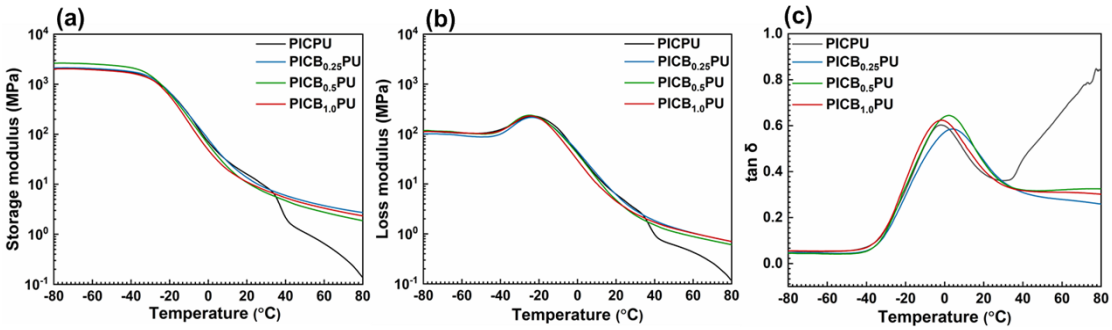


**Figure S5.** DMA curves for different elastomers with (a) energy storage modulus (*E*'), (b) loss modulus (*E*''), and (c) tan*δ*.

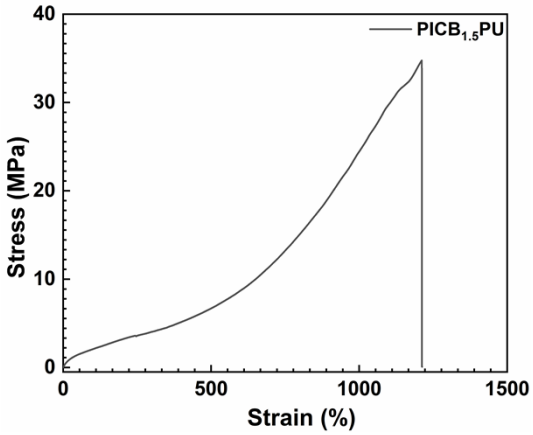


**Figure S6.** Stress-strain curves of $PICB_{1.5}PU$ elastomers.

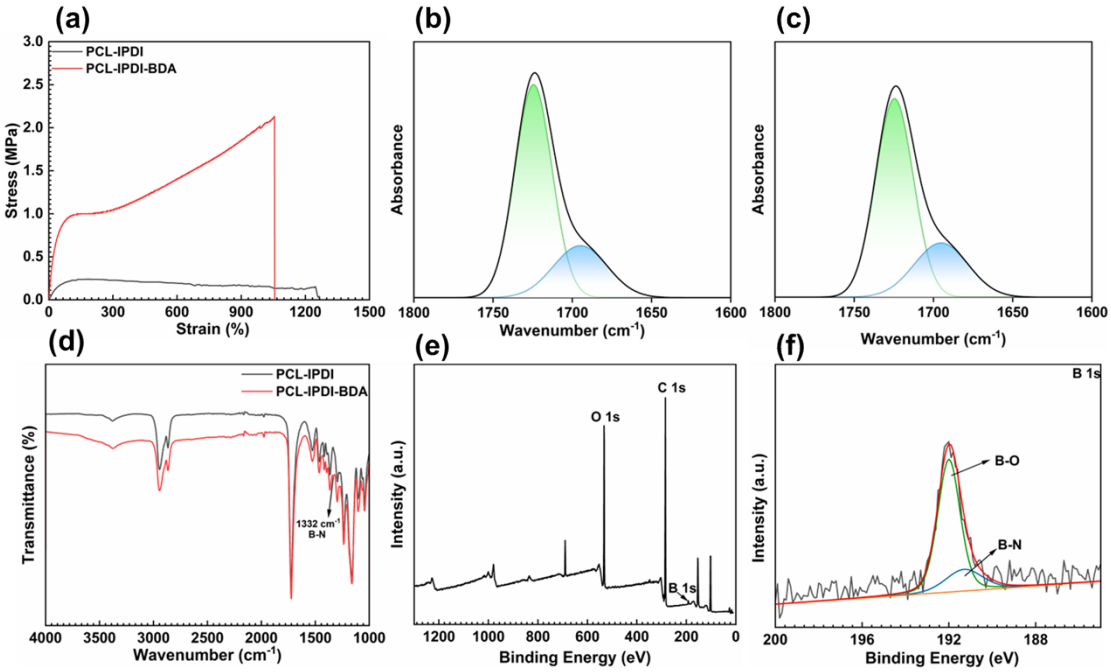


**Figure S7.** (a) Stress-strain curves. FTIR spectra and fitting of the C=O stretching vibration peaks of (b) PCL-IPDI and (c) PCL-IPDI-BDA elastomers. (d) FTIR spectra of PCL-IPDI and PCL-IPDI-BDA elastomers. XPS characterization: (e) XPS survey and (f) B 1s spectra of PCL-IPDI-BDA.

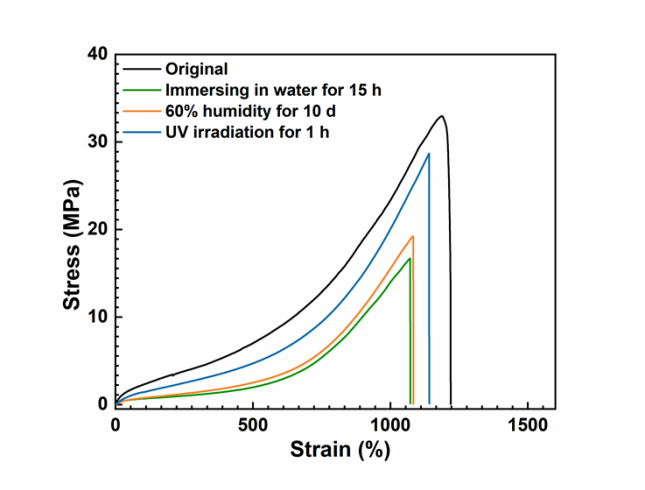


**Figure S8.** Stress-strain curves of $PICB_{1.0}PU$ elastomers under different conditions.

In addition, curcumin is a photosensitive biomaterial that decomposes under prolonged light exposure. In addition, the B−O bond is a dynamic chemical bond that is water sensitive and tends to dissociate in humid environments. These can adversely affect the prepared elastomers. For this

reason, long-term exposure experiments of elastomers under sunlight and UV irradiation and in high humidity and water environments were investigated, and the results are shown in Figure S8. It can be found that the prepared elastomers showed a large decrease in mechanical properties and poor moisture resistance after 10 days at 60% humidity and 15 h of complete immersion in water. It can also be found that the tensile strength of the elastomers can be maintained above 25 MPa after 1 h of UV irradiation (395 nm, 300 W), with a slight decrease in their mechanical properties and a certain degree of photostability.

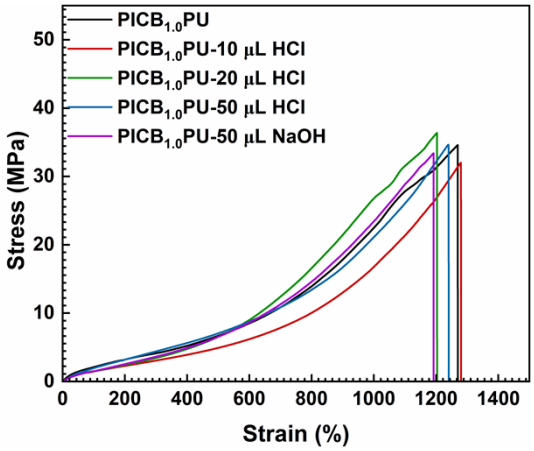


**Figure S9.** Stress-strain curves of $PICB_{1.0}PU$ elastomers with different contents of acid (pH=1 HCl) and alkaline (pH=14) added.

Since curcumin is an acid/alkali-sensitive material, to further understand the effect of this structural change on the mechanical properties of the elastomers, the pH of the system is adjusted by adding different levels of acid and base solutions during the incorporation of BDA. The results of the mechanical properties are displayed in Figure S9, in which we can find that either a small amount of acid or a small amount of alkali has a small effect on the mechanical properties of the elastomer. It is worth noting that the keto and enol structures in curcumin in solution undergo conversion between them under pH adjustment, which in turn affects the way BDA binds to it, including keto coordination and enol B–O bonding. However, in the later stages of solvent removal and curing of the elastomer, most of the added HCl will evaporate, and some of the added NaOH will react with $CO_2$ to form $Na_2CO_3$, which will lose its original function, and then it is difficult to affect its mechanical properties.

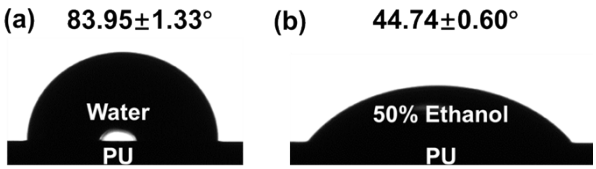


**Figure S10.** Hydrophobicity of $PICB_{1.0}PU$ elastomer surfaces.

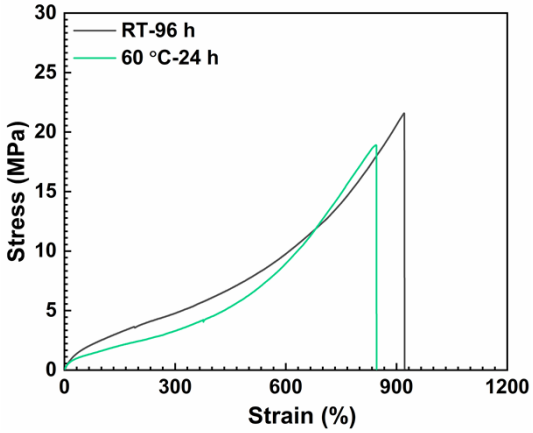


**Figure S11.** Stress-strain curves of $PICB_{1.0}PU$ elastomers after healing for 96 h assisted by aqueous ethanol solution at room temperature and 24 h at 60 °C.

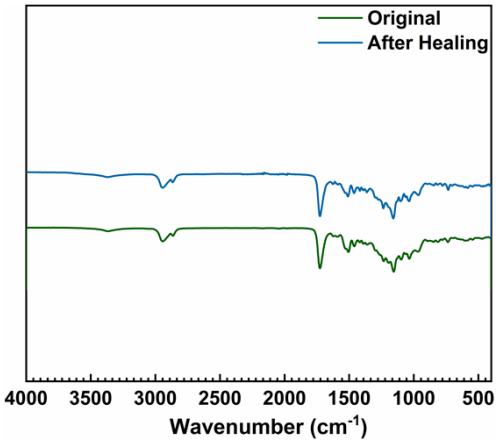


**Figure S12.** FT-IR spectrum of $PICB_{1.0}PU$ elastomer after and before self-healing.

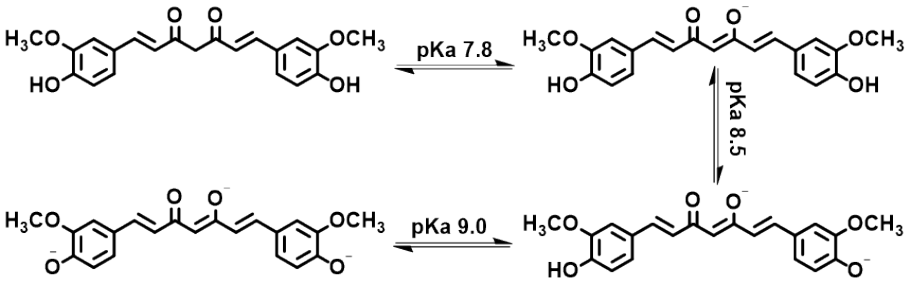


**Figure S13.** Schematic illustration of the structural isomerization of curcumin at different pH.

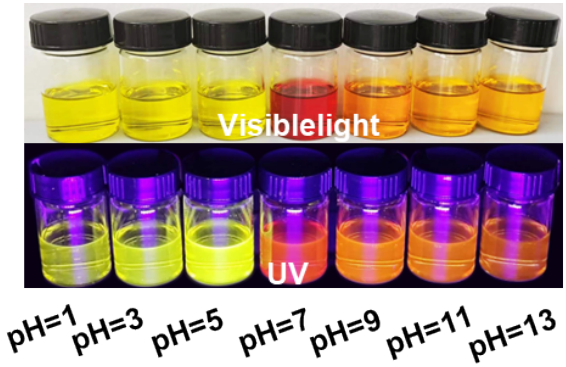


**Figure S14.** Color development photographs of ethanol solutions of curcumin at different pH under visible and UV irradiation.

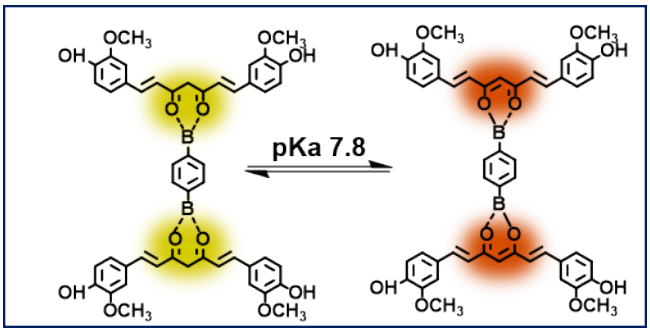


**Figure S15.** Schematic illustration of the structural isomerization of curcumin coordinated with BDA under acid/alkaline conditions.

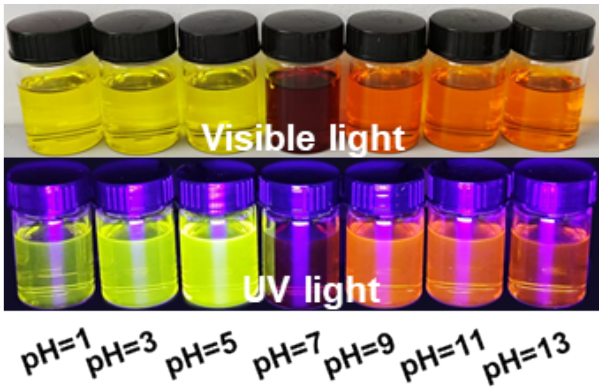


**Figure S16.** Photographs of curcumin coordinated with BDA in ethanol solutions of different pH under visible and UV light.

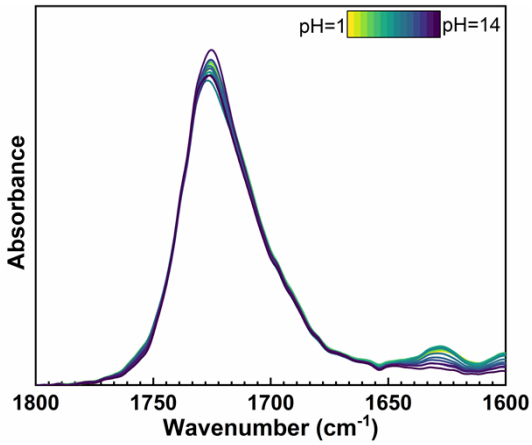


**Figure S17.** FT-IR spectra of the pH response of the $PICB_{1.0}PU$ elastomer surface after 10 s of continuous treatment by acid/alkali solutions from pH=1 to pH=14.

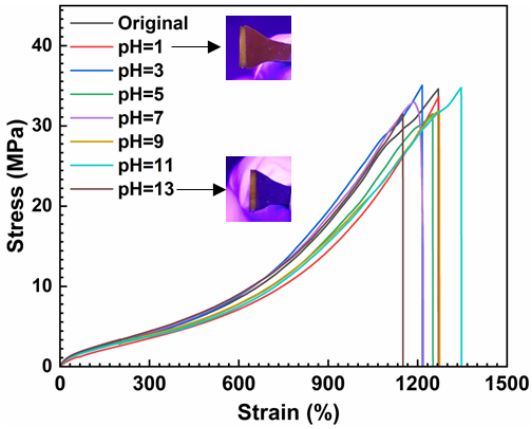


**Figure S18.** Stress-strain curves of $PICB_{1.0}PU$ elastomers after treatment with different pH ethanol solutions for 20 min. The inset shows the fluorescence images of the specimen cross-

section and surface under UV after 20 min of acid/alkali treatment.

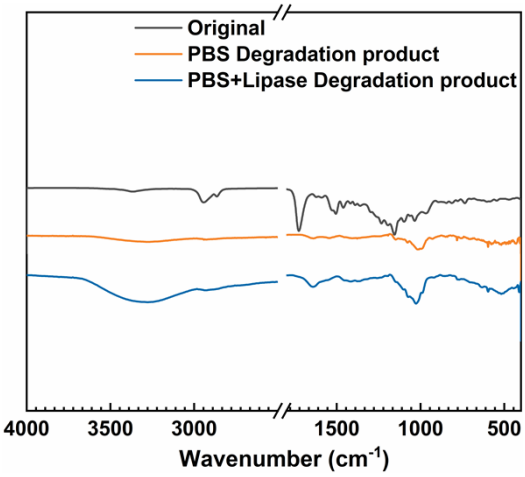


**Figure S19.** FT-IR spectrum of $PICB_{1.0}PU$ elastomer after degradation in the presence of lipase and PBS.

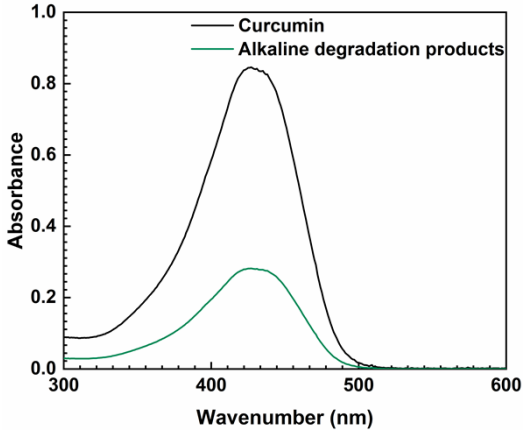


**Figure S20.** UV absorption spectrum of curcumin before and after degradation in 0.1M NaOH solution.

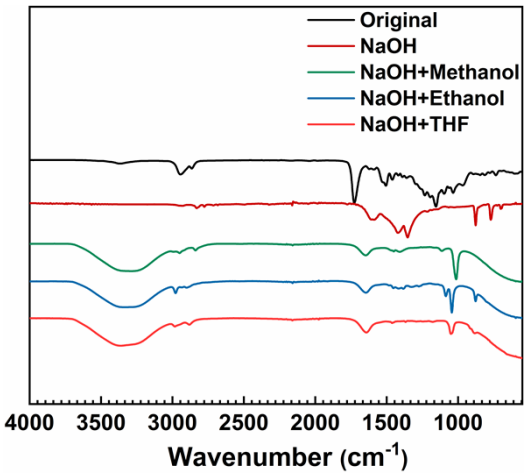


**Figure S21.** FT-IR spectrum of $PICB_{1.0}PU$ elastomer after degradation in the presence of alkaline.

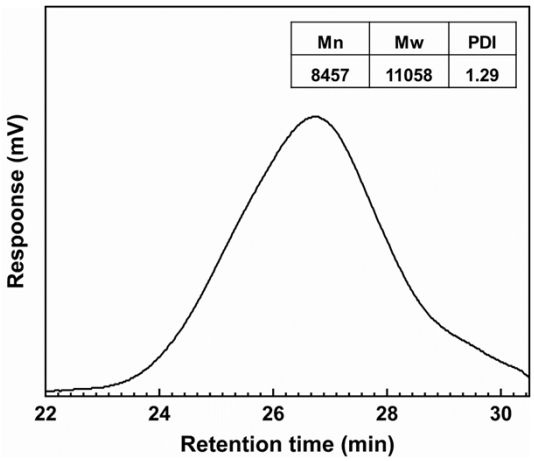


**Figure S22.** GPC curves of $PICB_{1.0}PU$ elastomer after degradation in the presence of 90 ℃ water.

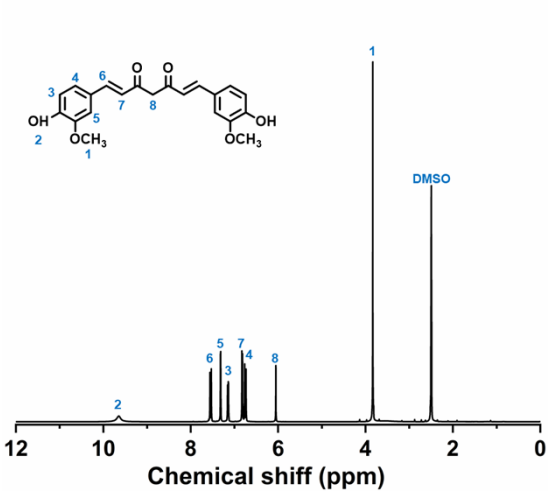


**Figure S23.** $^1$H NMR spectra of the Degradation products in hot water.

$^1$H NMR (500 MHz, DMSO-$d_6$) δ 9.65 (s, 1H), 7.54 (d, $J$ = 15.8 Hz, 1H), 7.32 (d, $J$ = 1.9 Hz, 1H), 7.14 (dd, $J$ = 8.2, 1.9 Hz, 1H), 6.82 (d, $J$ = 8.1 Hz, 1H), 6.75 (d, $J$ = 15.8 Hz, 1H), 6.05 (s, 1H), 3.83 (s, 3H).

**Table S1.** Component contents of different elastomers.

| Samples | HO-PCL-OH (mmoL) | IPDI (mmoL) | Curcumin (mmoL) | BDA (mmoL) | (C=O+C-OH): B-OH |
|---|---|---|---|---|---|
| PICPU | 5 | 10 | 5 | 0 | 0 |
| $PICB_{0.25}PU$ | 5 | 10 | 5 | 0.625 | 1:0.25 |
| $PICB_{0.5}PU$ | 5 | 10 | 5 | 1.25 | 1:0.5 |
| $PICB_{1.0}PU$ | 5 | 10 | 5 | 2.5 | 1:1 |
| $PICB_{1.5}PU$ | 5 | 10 | 5 | 3.75 | 1:1.5 |

**Table S2.** GPC results for different elastomers.

| Samples | Mn | Mw | PDI |
|---|---|---|---|
| PICPU | 54480 | 117130 | 2.2 |
| $PICB_{0.25}PU$ | 60351 | 122159 | 2.0 |
| $PICB_{0.5}PU$ | 61706 | 158987 | 2.6 |
| $PICB_{1.0}PU$ | 64006 | 163368 | 2.6 |

**Table S3** Mechanical properties of different elastomers.

| Samples | Tensile strength (MPa) | Breaking elongation (%) |
|---|---|---|
| PICPU | 0.10 | 2161.42 ± 3.76 |
| $PICB_{0.25}PU$ | 9.35 ± 0.96 | 1983.62 ± 95.69 |
| $PICB_{0.5}PU$ | 16.07 ± 0.95 | 1795.29 ± 142.21 |
| $PICB_{1.0}PU$ | 33.44 ± 1.49 | 1265.34 ± 43.75 |

**Table S4** Final results of the multiplication of the signs of each cross-peak in 2DCOS synchronous and asynchronous spectra of $PICB_{1.0}PU$ elastomer (Figure 2d).

| | | | | | |
|---|---|---|---|---|---|
| 1314 | - | + | + | + | |
| 1340 | - | - | - | | |
| 1361 | - | - | | | |
| 1612 | - | | | | |
| 1635 | | | | | |
| | 1635 | 1612 | 1361 | 1340 | 1314 |