

## Supporting Information

# A Recyclable Silicone Elastic Light-Triggered Actuator with Reconfigurable Janus Structure and Self-Healable Performance

*Xiaowei Xu<sup>1</sup>, Xinyue Hao<sup>1</sup>, Jing Hu<sup>1</sup>, Weisheng Gao<sup>1,4</sup>, Nanying Ning<sup>1,2,3</sup>, Bing Yu<sup>1,2,3\*</sup>, Liqun Zhang<sup>1,2,3</sup>, Ming Tian<sup>1,2,3\*</sup>*

1. State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China;

2. Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China;

3. Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China;

4. China National Petroleum & Chemical Planning Institute, Beijing 100013, China;

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<sup>1</sup> Corresponding authors. E-mail addresses: [tianm@mail.buct.edu.cn](mailto:tianm@mail.buct.edu.cn) (M. Tian); [yubing@mail.buct.edu.cn](mailto:yubing@mail.buct.edu.cn) (B. Yu).

# 1 Synthesis of 3-aminopropyl-terminated polydimethylvinylsiloxane (APT-PDMVS)

## 1.1 Synthesis of polydimethylsiloxane (PDMS) prepolymer.

Octamethylcyclotetrasiloxane ( $D_4$ , 40 g, 0.135 mol), potassium hydroxide (KOH, 0.8 g, 0.014 mol), DI water (1.89g, dissolving KOH), and dimethyl sulfoxide (DMSO, 1g, dispersing KOH aqueous solution) were added into a three-neck flask with a stir bar and vacuum apparatus, stir at 200 rpm. After removal of the water (in  $D_4$  and previously added) at 60°C for 2 h in vacuum condition, the system was heated to 120°C and held for 4 h under a nitrogen atmosphere. Then, transfer the synthesized PDMS prepolymer to a glass vessel and seal it in the refrigerator (2-8°C).

## 1.2 Synthesis of APT-PDMVS.

$D_4$  (156.96 g, 0.529 mol), 2,4,6,8-tetravinyl-2,4,6,8-tetramethylcyclotetrasiloxane ( $V_4$ , 45.61 g, 0.132 mol) were added into a three-neck flask with a stir bar and vacuum apparatus, stir at 200 rpm. After removal of the water in  $D_4$  and  $V_4$  at 60°C for 2 h in vacuum condition, 1,3-bis(3-aminopropyl)tetramethyldisiloxane (BAPTMDs, 10.6 g, 0.043 mol) and PDMS prepolymer (5.88 g) were added to a flask and heated to 153°C and held for 8 h under nitrogen atmosphere. The system was then cooled to 60°C, adding excess acetic acid (HAc, 0.173 g, 2.88 mmol) to neutralize KOH in the PDMS prepolymer. Low-molecular products were eliminated at a vacuum at 110°C for 2 h. The transparent sticky liquid was collected in a glass vessel for characterization. Yield: 81%. The number of molecular weight of APT-PDMVS is 5464 g/mol, PDI 1.52 (characterized by GPC). FTIR (KBr,  $cm^{-1}$ ): 3055, 2963 (C-H), 1598 (C=C), 1409, 1262 (Si-C), 1096, 1022 (Si-O-Si), 801 (Si-C).  $^1H$  NMR (600 MHz, Chloroform- $d$ ,  $\delta_H$ , ppm): 6.05 – 5.88 (m, -CH=CH $_2$ ), 5.80 (dd, -CH=CH $_2$ ), 2.67 (td, -CH $_2$ -CH $_2$ -CH $_2$ -NH $_2$ ), 1.50 – 1.41 (m, -CH $_2$ -CH $_2$ -CH $_2$ -), 1.17 (s, -CH $_2$ -NH $_2$ ), 0.57 – 0.49 (m, -SiO-CH $_2$ -CH $_2$ -CH $_2$ -), 0.20 – 0.02 (m, -SiCH $_3$ ). The molar percentage of vinyl groups (determined as the percentage of -SiO(CH $_3$ )(CH = CH $_2$ ) -

in the sum of  $-SiO(CH_3)_2-$  and  $-SiO(CH_3)(CH=CH_2)-$ ) and the molecular weight of APT-PDMVS were calculated from corresponding integration values ( $S$ ) in  $^1H$  NMR spectrum of APT-PDMVS as follows (**Figure S2A a**), the molecular weight of APT-PDMVS is 4275 g/mol, the molar percentage of vinyl groups is 21.2%. The peak that represented the TMS was overlapped with the methyl groups and can't be separated, but the content was too few to affect the calculating results.

*the molar percentage of vinyl groups*

$$= \frac{S_{-SiO(CH_3)(CH=CH_2)-}}{S_{-SiO(CH_3)(CH=CH_2)-} + S_{-SiO(CH_3)_2-}}$$

$$= \frac{\frac{S_1}{3}}{\frac{S_1}{3} + \frac{S_6 + S_7 - S_1 - 3S_4}{6}} * 100\%$$

*the molecular weight of APT - PDMVS*

$$= M_{-SiO(CH_3)_2-} * n_{-SiO(CH_3)_2-} + M_{-SiO(CH_3)(CH=CH_2)-} * n_{-SiO(CH_3)(CH=CH_2)-} + M_{BAPTMDs} * n_{BAPTMDs}$$

Where  $M$  and  $n$  correspond to the molecular weight ( $M$ ) and the amount of substance ( $n$ ) in different segments of an APT-PDMVS molecular chain. The ratio of the amount of substances can be obtained by the following methods:

$$n_{-SiO(CH_3)_2-} : n_{-SiO(CH_3)(CH=CH_2)-} : n_{BAPTMDs} = \frac{S_6 + S_7 - S_1 - 3S_4}{6} : \frac{S_1}{3} : \frac{S_4}{4}$$

Theoretically, there is only one BAPTMDs molecule in an APT-PDMVS molecular chain, that is,  $n_{BAPTMDs} = 1$ , so the  $n_{-SiO(CH_3)_2}$  and  $n_{-SiO(CH_3)(CH=CH_2)}$  can be easily obtained.

## 2. Synthesis of anthracen-9-ylmethyl-3-mercaptopropanoate (ANMEPA)

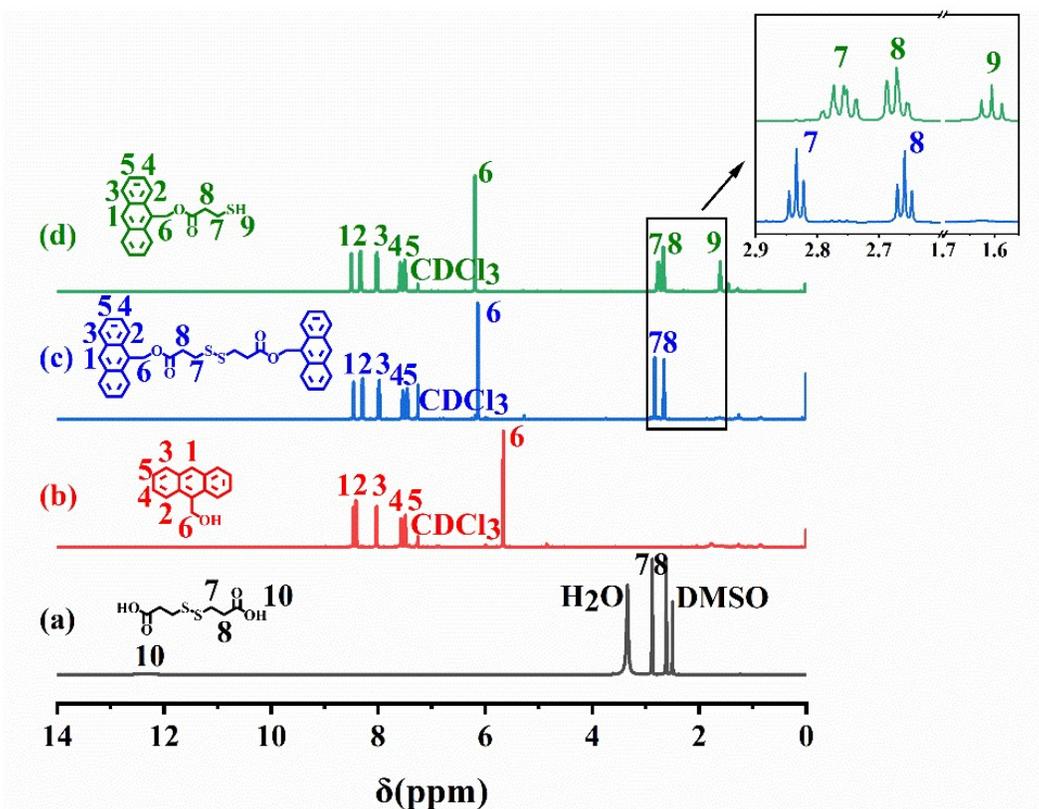
### 2.1 Synthesis of bis(anthracen-9-ylmethyl) 3,3'-disulfanedioldipropionate (BIAN-DSDPA).

First, 3,3'-dithiodipropionic acid (DTDP, 5.47 g, 26 mmol) was dissolved in 50 mL anhydrous tetrahydrofuran (THF) with magnetic stirring in a three-neck round-bottom flask under a nitrogen atmosphere and placed in an ice-water bath. Then, N,N'-dicyclohexylcarbodiimide (DCC, 12.37 g, 60 mmol) and 4-dimethylaminopyridine (DMAP, 0.49 g, 4 mmol), dissolved in 50 mL anhydrous THF, were added dropwise using a constant pressure funnel and the mixture gradually became turbid. Finally, 9-anthracenemethanol solution (8.3 g, 40 mmol in anhydrous THF) was added into the above mixture solution drop by drop. The reactions were allowed to naturally warm up to room temperature and continued to react for 24 h. The mixture was kept in the freezer overnight and then filtered twice to discard 1,3-dicyclohexylurea (DCU), the solvent was eliminated through rotary evaporation, and the solid obtained was washed with ethanol/toluene (1:1), filtered and collected for drying. Yield 85%, light yellow amorphous powder.  $^1\text{H}$  NMR (600 MHz, Chloroform-d,  $\delta_{\text{H}}$ , ppm): s 8.46, dd 8.29, dd 7.99, ddd 7.54, ddd 7.46 (aromatic, 18H), 6.14 (s, An-CH<sub>2</sub>-, 4H), 2.83 (t, -CH<sub>2</sub>-CH<sub>2</sub>-S-, 4H), 2.66 (t, -CH<sub>2</sub>-CH<sub>2</sub>-S-, 4H). FTIR (KBr, cm<sup>-1</sup>): 3054, 2925 (C-H), 1731 (C=O in -COO-), 1623, 1447 (C=C in anthracene), 731 (substituents with five adjacent H atoms in the aromatic ring).

### 2.2 Synthesis of ANMEPA.

BIAN-DSDPA (11.82 g, 20 mmol), DL-1,4-dithiothreitol (DTT, 4.63 g, 30 mmol) and triethylamine (Et<sub>3</sub>N, 1.01 g, 10 mmol) were total dissolved in THF with magnetic stirring in a three-neck round-bottom flask under a nitrogen atmosphere and placed in a

30°C water bath, DI water (~1:5 v/v water:THF) was then added to the reaction system. After 24 h, the reaction stopped and the solvent was eliminated through rotary evaporation, the solid obtained was dissolved in dichloromethane (DCM, 30 mL) and moved into a separating funnel, and washed with DI water (30 mL) for three times. Then the resulting product was washed with saturated NaCl solution (30 mL, three times) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Finally, the solvent was evaporated and yellowish-brown viscous oil-like liquid was obtained with the yield 89%. <sup>1</sup>H NMR (600 MHz, Chloroform-d, δH, ppm): s 8.50, dd 8.34, dd 8.03, dd 7.59, dd 7.50 (aromatic, 9H), 6.19 (s, An-CH<sub>2</sub>-, 2H), 2.82 – 2.71 (m, -CH<sub>2</sub>-CH<sub>2</sub>-SH, 2H), 2.67 (td, -CH<sub>2</sub>-CH<sub>2</sub>-SH, 2H), 1.61 (t, -SH, 1H). FTIR (KBr, cm<sup>-1</sup>): 3054, 2925 (C-H), 2569 (S-H), 1731 (C=O in -COO-), 1623, 1447 (C=C in anthracene), 731 (substituents with five adjacent H atoms in the aromatic ring).



**Figure S1.** <sup>1</sup>H NMR spectra of DTDP, 9-anthracenemethanol, BIAN-DSDPA and ANMEPA.

The structures of BIAN-DSDPA and ANMEPA are shown in **Figure S1-2**. <sup>1</sup>H NMR spectrum is firstly applied here to characterize the structure. As shown in **Figure S1 c**, two

new peaks (2.66 ppm and 2.83 ppm) were observed toward BIAN-DSDPA after the Steglich esterification, and the signal from H-6 was shifted toward a lower field value (from  $\delta=5.66$  ppm to  $\delta=6.14$  ppm) because of the weakening of diamagnetic effect due to the presence of the electron-withdrawing carbonyl group, which proved the successful synthesis of BIAN-DSDPA. A new peak located at 1.61 ppm were detected after the disconnection of disulfide bonds (**Figure S1d**), and moreover, the signal from H-7 was shifted toward a higher field value (from  $\delta=2.83$  ppm to  $\delta=2.77$  ppm) and the peak was transformed from triple peak to quadruple peak due to the changes in chemical environment surrounding, which indicated that ANMEPA was successfully synthesized.

FTIR spectrum was also applied here to prove the structure of BIAN-DSDPA and ANMEPA. As shown in **Figure S2**, the presence of absorbance at  $1731\text{ cm}^{-1}$  corresponding to C=O stretching vibration of ester groups and the disappearance of absorbance at  $3414\text{ cm}^{-1}$  corresponding to -OH stretching vibration of 9-anthracenemethanol indicated the successful synthesis of BIAN-DSDPA. Compared with BIAN-DSDPA, new peaks at  $2569\text{ cm}^{-1}$  assigned to sulfhydryl groups appear in the FTIR spectrum of ANMEPA, and it was declared that the disulfide bonds were successfully disconnected.

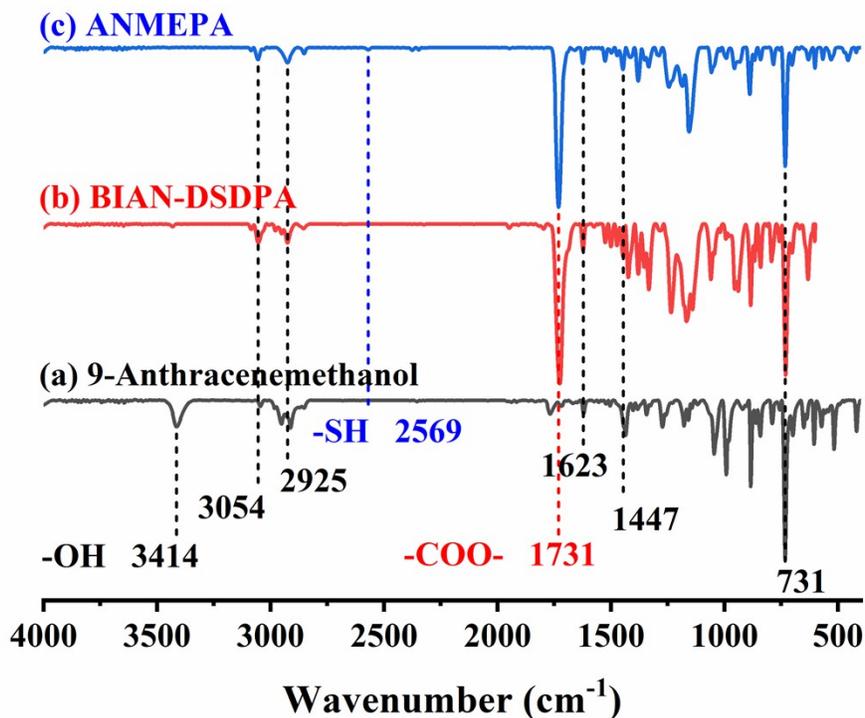
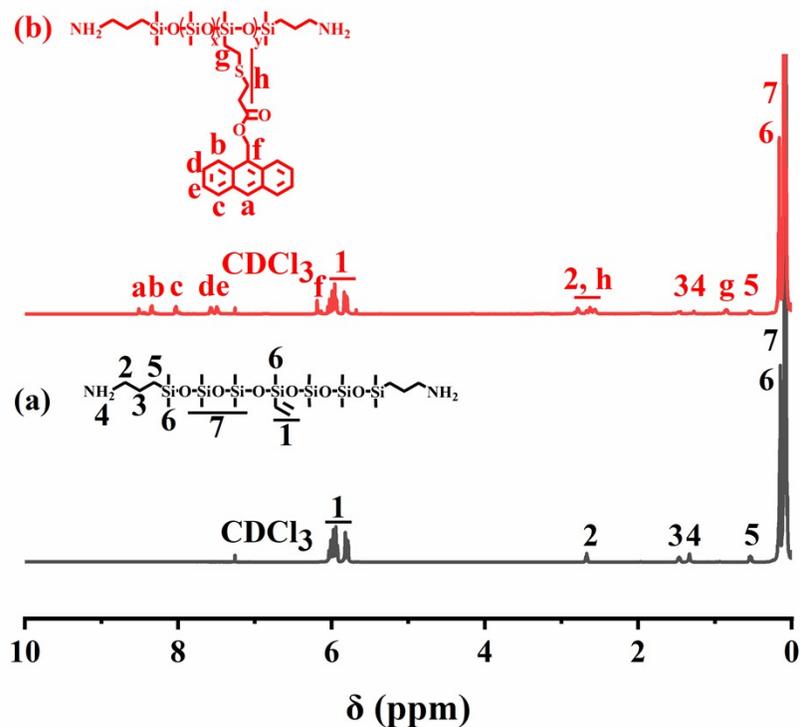


Figure S2. FTIR spectra of 9-anthracenemethanol, BIAN-DSDPA and ANMEPA.

### 3. Synthesis of APT-PDMVS-g-An

ANMEPA (10.53 g, 35.53 mmol) and APT-PDMVS (10.52 g, 2.46 mmol, ~27.33 mmol vinyl group) were dissolved in THF with magnetic stirring in a three-neck round-bottom flask with a condensation and reflux device, then cooled to 0°C with an ice-water bath. After 30 min, 2,2'-azobis(2-methylpropionitrile) (AIBN, 0.057 g, 0.35 mmol) was added, and the reaction mixture was slowly heated to 70°C for 10 h under nitrogen flow protection. At the end of the reaction, the solution was concentrated under reduced pressure. The concentrate was collected and then poured into a dialysis bag, and the dialysis bag was placed in a container filled with a mixture solution of ethanol and THF ( $V_{\text{ethanol}}/V_{\text{THF}}=7:1$ ) and dialyzed for 24 h. Finally, the product was oven-dried at 60°C to a constant weight.  $^1\text{H}$  NMR (600 MHz, Chloroform-d,  $\delta\text{H}$ , ppm): s 8.51, d 8.35, d 8.03, t 7.57, t 7.48 (aromatic), 6.19 (s, An- $\text{CH}_2$ -), 6.07 – 5.92 (m, - $\text{CH}=\text{CH}_2$ ), 5.82 (dd, -

$\text{CH}=\text{CH}_2$ ), 2.86 – 2.52 (m,  $-\text{CH}_2-$ ), 1.28 (d,  $-\text{CH}_2-\text{NH}_2$ ), 0.93 – 0.81 (m,  $-\text{Si}-\text{CH}_2-\text{CH}_2-\text{S}-$ ), 0.61 – 0.47 (m,  $-\text{SiO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ), 0.23 – 0.02 (m,  $-\text{SiCH}_3$ ). FTIR (KBr,  $\text{cm}^{-1}$ ): 3055, 2963 (C-H), 1731 (C=O in  $-\text{COO}-$ ), 1623, 1447 (C=C in anthracene), 1598 (C=C), 1409, 1262 (Si-C), 1096, 1022 (Si-O-Si), 801 (Si-C), 731 (substituents with five adjacent H atoms in the aromatic ring).

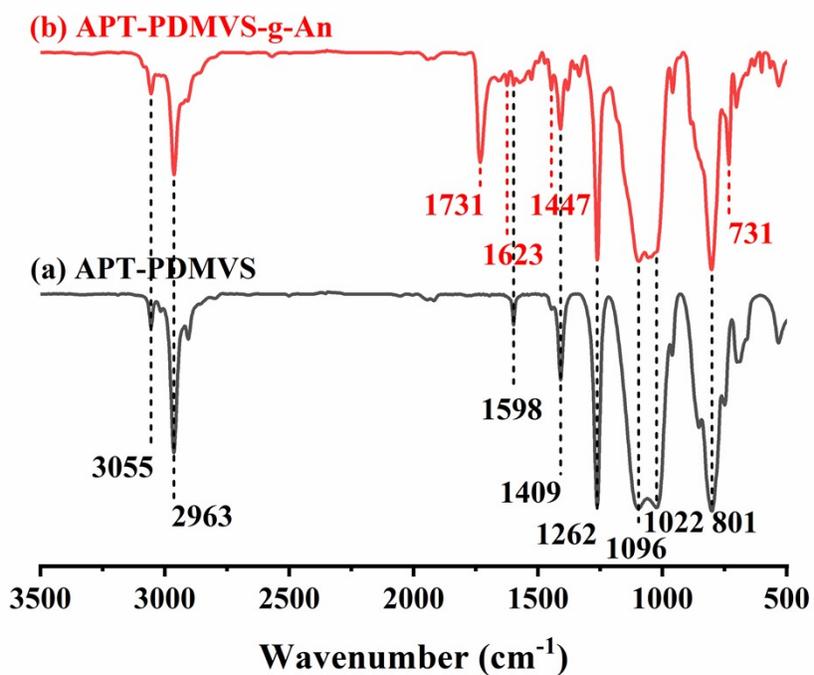


**Figure S3.**  $^1\text{H}$  NMR spectra of APT-PDMVS and APT-PDMVS-g-An.

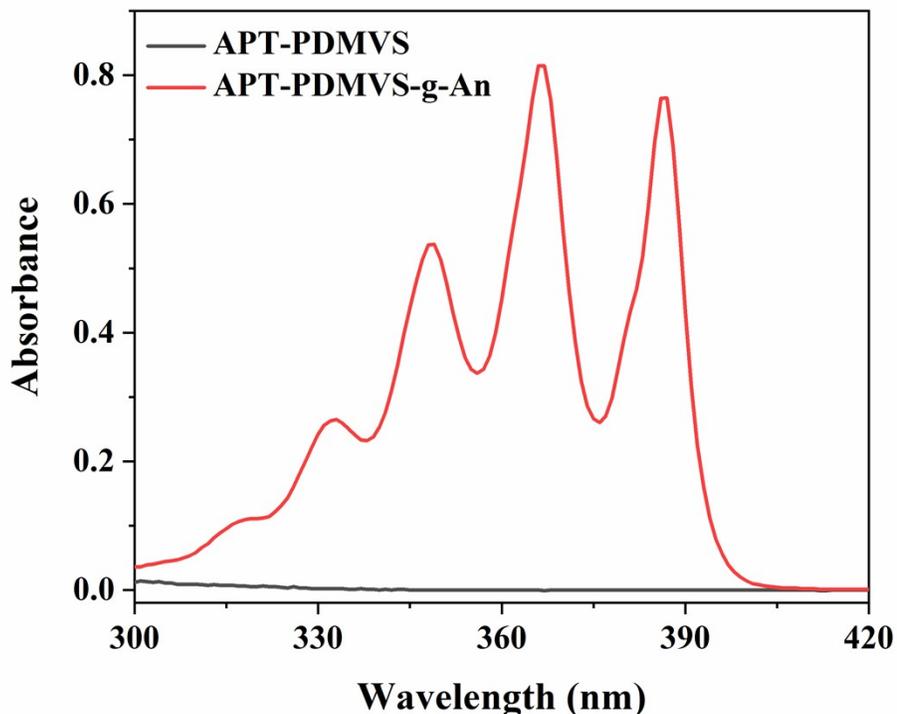
The structure of APT-PDMVS and APT-PDMVS-g-An are shown in **Figure S3-5**.  $^1\text{H}$  NMR spectrum is firstly applied here to characterize the structure evolution. As shown in **Figure S3 b**, several new peaks located at 8.51, 8.35, 8.03, 7.57, 7.48, 6.19, 2.86, 2.52 and 0.86 ppm were detected after the further thiol-ene click reaction of APT-PDMVS with ANMEPA, which indicated that anthracene was successfully linked into the chains of APT-PDMVS through the heat-triggered thiol-ene click reaction to prepare APT-PDMVS-g-An. According to the  $^1\text{H}$  NMR result, it is obtained that 27.3% of vinyl groups on APT-PDMVS chains have reacted with the sulfhydryl group on ANMEPA during the synthesis process

of APT-PDMVS-g-An.

FTIR spectrum was also applied here to prove the structure of the modified APT-PDMVS. As shown in **Figure S4**, the presence of absorbance at  $1731\text{ cm}^{-1}$  corresponding to C=O stretching vibration of ester groups and  $1623$ ,  $1447$ ,  $731\text{ cm}^{-1}$  assigned to anthracene groups indicated the successful incorporation of ANMEPA onto the APT-PDMVS chains.



**Figure S4.** FTIR spectra of APT-PDMVS and APT-PDMVS-g-An.



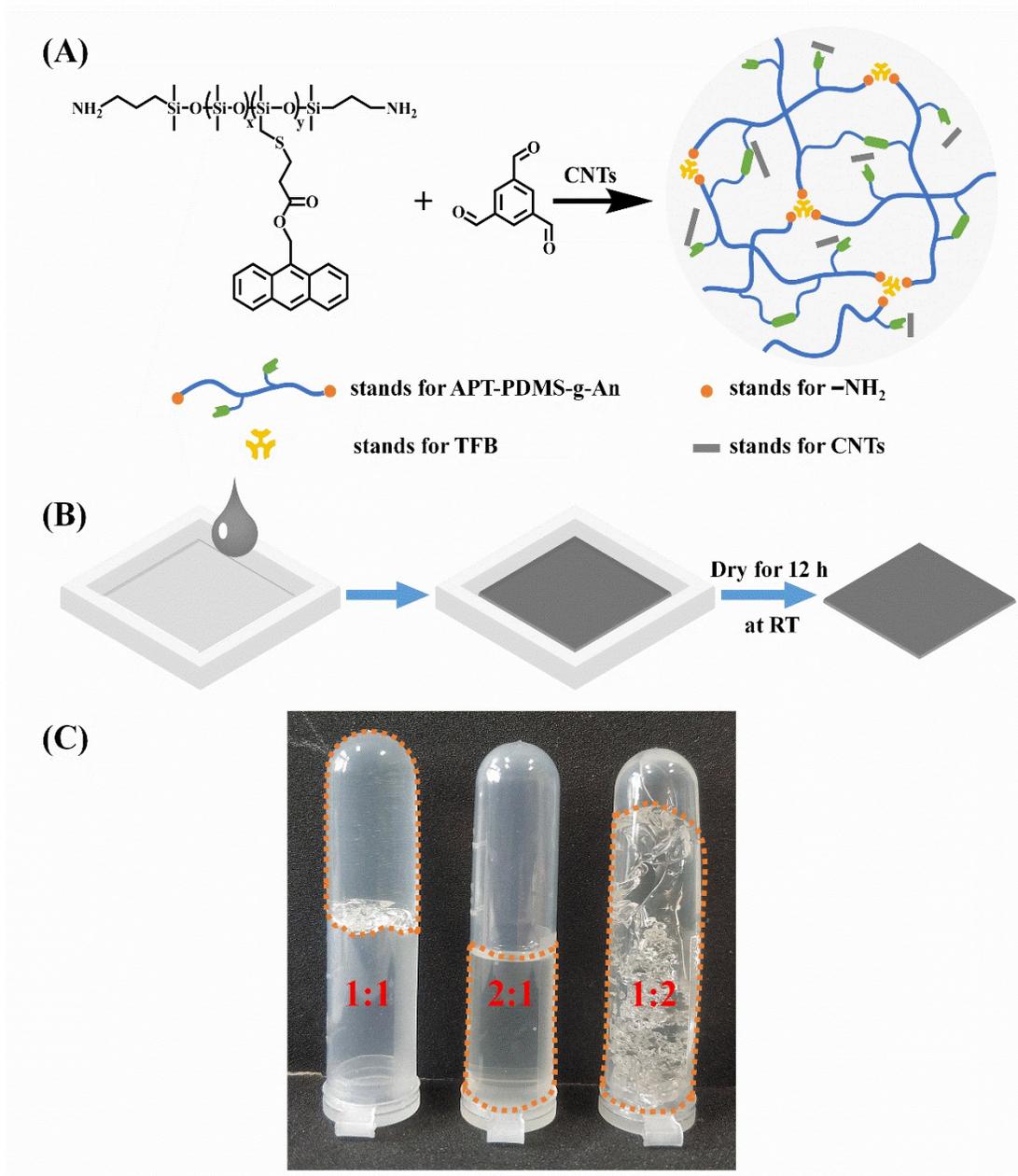
**Figure S5.** UV-vis spectra of APT-PDMVS and APT-PDMVS-g-An. The concentration of polymers was  $0.15 \text{ mg mL}^{-1}$  when they were tested.

As shown in **Figure S5**, the typical absorption for anthracene appears on the UV-vis spectrum of APT-PDMS-g-An at 319, 333, 348, 366, and 386 nm, which declared the successful grafting of anthracene groups to the APT-PDMVS chains.

#### **4. Preparation of PDMS-An/TFB@CNTs composite membranes**

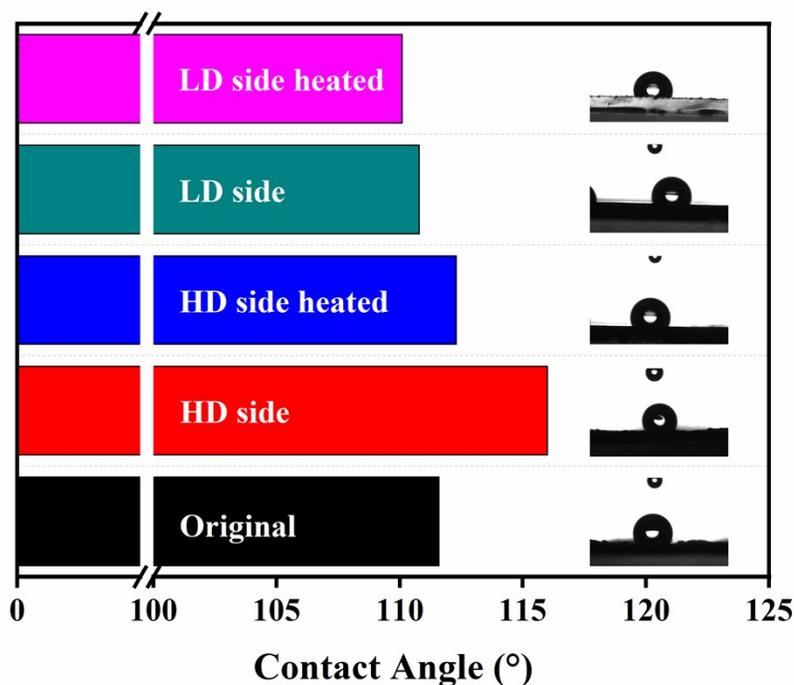
To determine the appropriate amount of crosslinker, a series of pre-experiments were carried out and the results showed that the molar ratio of TFB to APT-PDMVS-g-An had a significant effect on the formation of PDMS-An/TFB@CNTs composite elastomer. As shown in **Figure S6C**, when the molar ratio was 2:1, the mixture always remains liquid and there was no sol-gel transition, which indicates that there were not enough crosslinking points to construct the elastic networks. However, when the ratio was reduced to 1:1, the PDMS oligomers rapidly transformed into a uniform elastomer within several minutes. As the ratio was further reduced to 1:2, only PDMS fragments but not elastomers can be formed, which is the result of the locally high concentration of amino groups during the

mixing process, leading to the rapid crosslinking reaction and nonuniform dispersion of TFB in the mixture. Based on these results, all samples were prepared by mixing TFB and APT-PDMVS-g-An at a ratio of 1:1, that is, the molar ratio of aldehyde groups to amino groups is 3:2.



**Figure S6.** (A) Synthesis routes and (B) typical procedures of preparation of PDMS-An/TFB@CNTs composite membranes. (C) The mixtures with different molar ratios of TFB to APT-PDMVS-g-An.

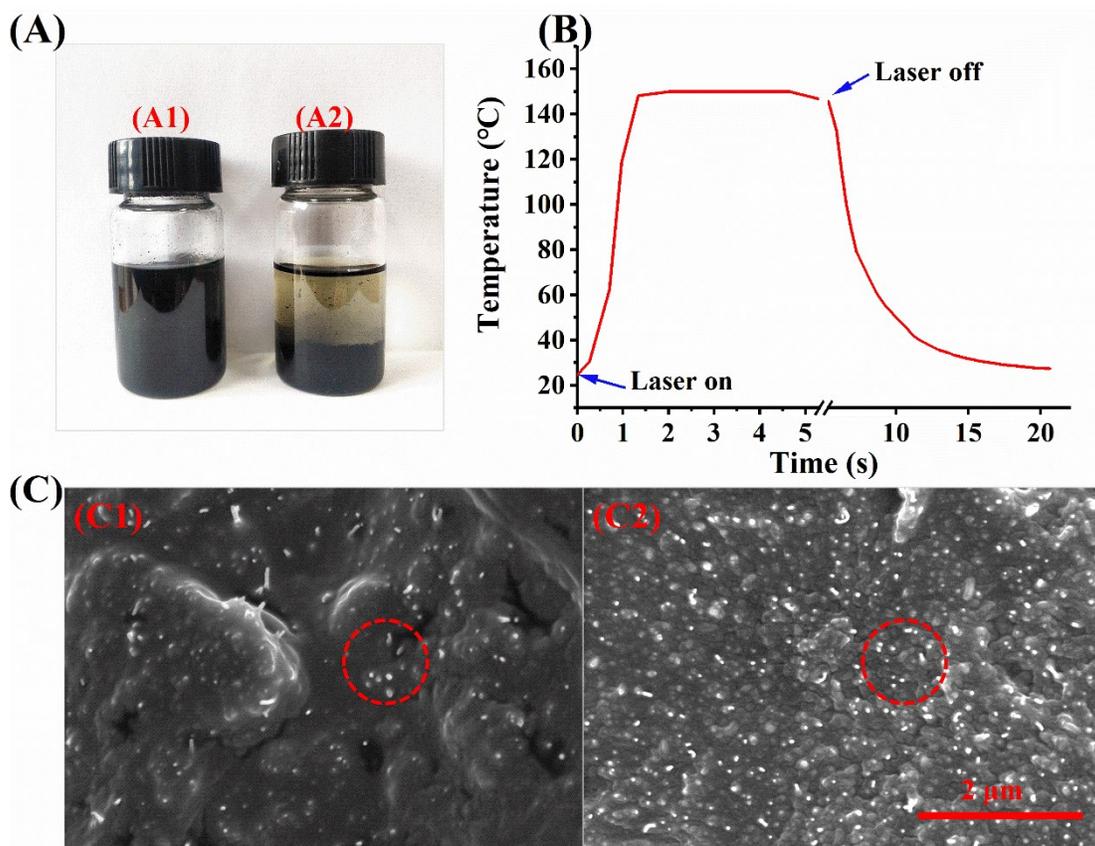
The typical procedures of preparation of PDMS-An/TFB@CNTs composite membranes is shown in **Figure S6A-B**. APT-PDMVS-g-An (10 g, 1.93 mmol), TFB (0.33 g, 1.93 mmol), and 0.2 g CNTs were dissolved in THF and stirred for 2 h at 60°C, after that, the mixed solution was concentrated to about 15 mL and then poured the concentrated solution into the PTFE mold and dried at room temperature for 12 h.



**Figure S7.** Water contact angles of the composite membrane PDMS-An/TFB@CNTs surface. All samples were tested ten times. “Original” represents the composite membrane before UV light irradiation. “HD side” and “LD side” represent the irradiated and unirradiated surfaces of the sample after UV light irradiation. “HD side heated” and “LD side heated” represent the irradiated and unirradiated surfaces of the sample after thermal treatment at 150°C for 10 min.

The uniform dispersion of CNTs in the polymer matrix is the prerequisite for CNTs to function in the system. As reported, the DA bonds<sup>1</sup> and strong  $\pi$ - $\pi$  interaction between the anthracene groups<sup>2,3</sup> help to reduce the aggregation of CNTs and make them disperse homogeneously.<sup>4,5</sup> As shown in **Figure S8A**, CNTs could be uniformly dispersed in the

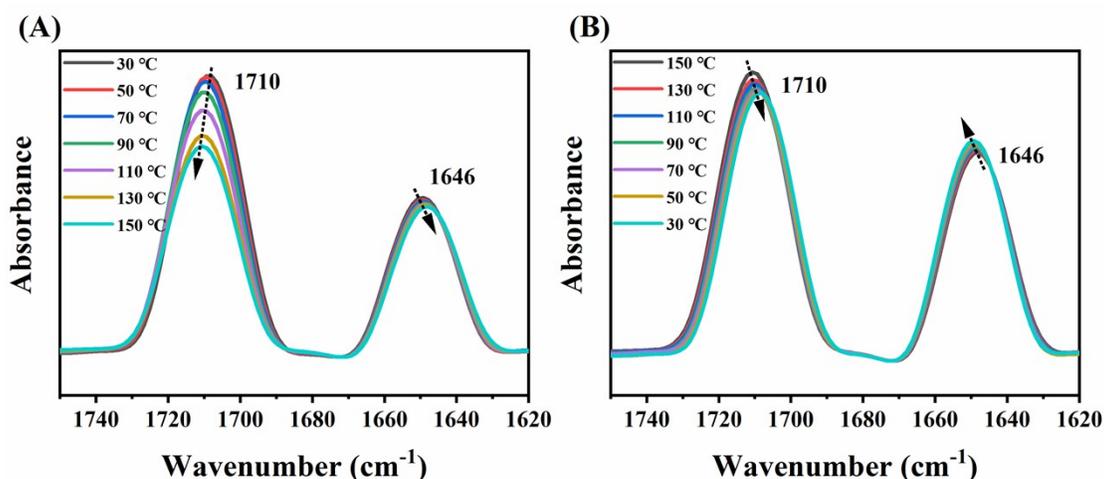
APT-PDMS-An solution without noticeable aggregation even putting it aside for at least 48 h (*Figure S8A1*). While for the control example, CNTs could soon fall onto the bottom of the pristine APT-PDMS solution (*Figure S8A2*). The dispersion of CNTs in the crosslinked composite membranes can be seen in the SEM image as shown in *Figure S8C*, the CNTs in the PDMS-An/TFB@CNTs membrane (*Figure S8C2*) are more uniform than those in the PDMS/TFB@CNTs membrane (*Figure S8C1*).



**Figure S8.** (A) Pictures of the CNTs in the (A1) APT-PDMVS-g-An solution and (A2) APT-PDMVS solution. (B) The temperature variation on the surface of the PDMS-An/TFB@CNTs membrane with the irradiation of the 808 nm NIR laser. (C) SEM image of a (C1) PDMS/TFB@CNTs membrane cross-section, and (C2) PDMS-An/TFB@CNTs membrane cross-section.

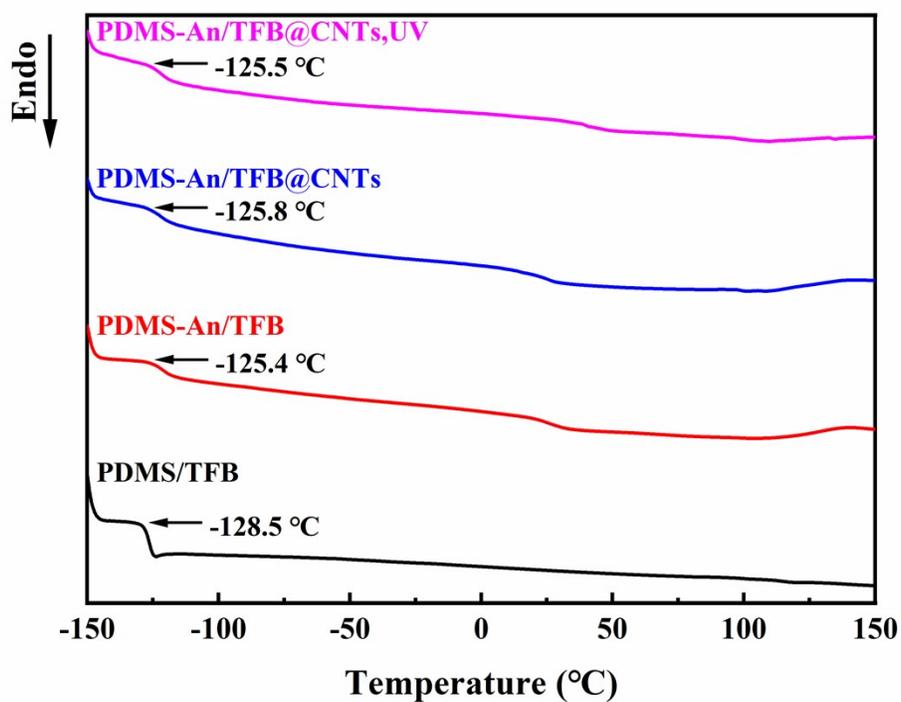
An important role of CNTs in PDMS-An/TFB@CNTs membrane is to act as a photothermal agent for converting the energy of the NIR laser into thermal stimulation. In *Figure S8B*, the temperature variation on the surface of PDMS-An/TFB@CNTs

membrane was recorded with the irradiation of the 808 nm NIR laser. It can be found that the temperature rises rapidly to 120°C in approximately 1 second, above 150°C in 2 seconds (beyond the range of the IR camera). After turning off the light source, the sample temperature gradually went down to room temperature in about 15 seconds. Therefore, CNTs can be used as effective photothermal agents to realize the remote heating of the PDMS-An/TFB@CNTs membrane by laser irradiation, thus triggering the shape deformation behavior.

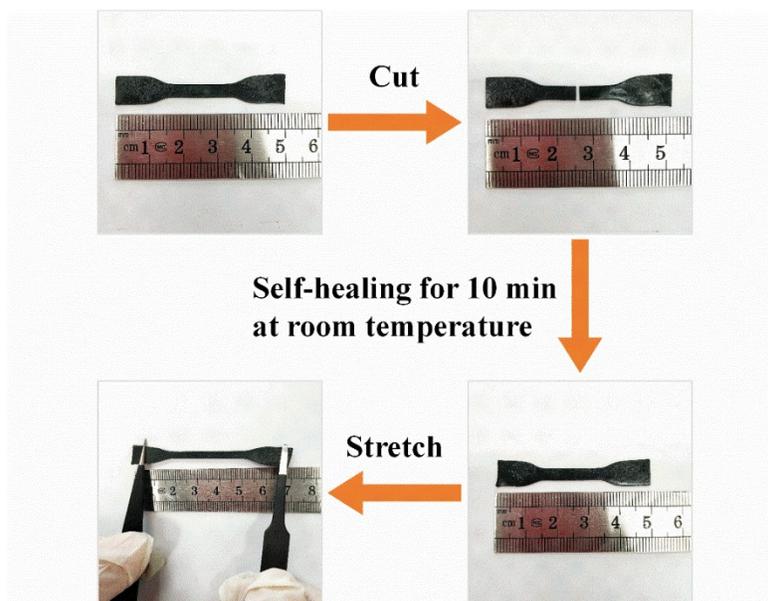


**Figure S9.** In-suit FTIR spectra of APT-PDMVS@TFB during (A) heating process and (B) cooling process.

As shown in **Figure S10**, the glass transition temperatures ( $T_g$ ) of all samples were determined using *DSC*. It could be found that the  $T_g$  of PDMS/TFB is the lowest (-128.5 °C), while the  $T_g$  of other samples increases slightly with the introduction of anthracene and CNTs, which may be caused by the hindrance of the movement of PDMS chains. But overall, all samples have a very low  $T_g$ , which contributes to the movement of molecular chains at lower temperatures and promotes self-healing behavior.



**Figure S10.** DSC curves of PDMS/TFB, PDMS-An/TFB, PDMS-An/TFB@CNTs, PDMS-An/TFB@CNTs irradiated by UV light for 20 min.



**Figure S11.** Photographs of the cracked PDMS-An/TFB@CNTs spline healing at room temperature for 10 min.

## References

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