

Electronic Supplementary Information (ESI)

Light- and Heat-Triggered Reversible

Luminescent Materials Based on Polysiloxanes and Anthracene Groups

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Synthesis

The prepolymer of PAPMS-1 was successfully prepared from 9-anthracenylmethyl acrylate and PAPMS through aza-Michael reaction. As shown in Scheme 2, 9-anthracenylmethyl acrylate (0.399 g 1.53×10^{-3} mol) and PAPMS (2.57 g 1.53×10^{-3} mol) were added to a flask. The mixture was dissolved in mixed solvents of methanol (1 mL) and toluene (10 mL), then the resulting mixture was refluxed and stirred at 45 °C. FT-IR spectra of the mixture are presented in the Supporting Information (Figure S1). As shown in Figure S1, in the unreaction mixture, peak at 1642 cm^{-1} was observed, which was caused by C=Cst in 9-anthracenylmethyl acrylate. But, the double bond (C=C) disappeared after 8 h, which meant the aza-Michael reaction was completed.

PAPMS-2 was prepared via "salt-forming vulcanization" by neutralizing PAPMS with anthracene-9-carboxylic acid to yield an ion-association complex. Typically, anthracene-9-carboxylic acid (0.32 g 1.48×10^{-3} mol) and PAPMS (2.50 g 1.48×10^{-3} mol) were added to a flask. The mixture was dissolved in mixed solvents of methanol (1 mL) and toluene (10 mL). Figure S2 depicts the IR spectrum of anthracene-9-carboxylic acid, PAPMS and elastomers PAPMS-2. The results confirmed the formation of an ion-association complexes. In anthracene-9-carboxylic acid solution the absorption band observed at 1680 cm^{-1} was caused by C=Ost of -COOH groups in anthracene-9-

carboxylic acid. In PAPMS-2, $-\text{COOH}$ and $-\text{NH}_2$ groups were responded completely. Therefore, the $\text{C}=\text{O}$ disappeared in PAPMS-2 solution. Meanwhile, new absorption band observed at 1570 cm^{-1} , was caused by asymmetric deformation of $-\text{COO}^-$. This result shows that the complex formation of $-\text{COO}^-$ with $-\text{NH}_3^+$.

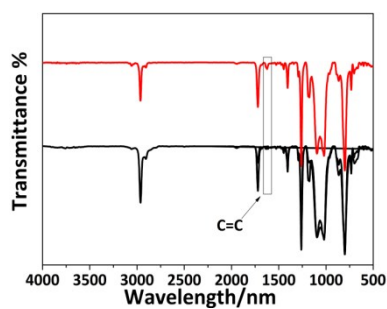


Figure S1 FT-IR spectra of PAPMS -1 solution before (top) and after(bottom) aza-Michael reaction

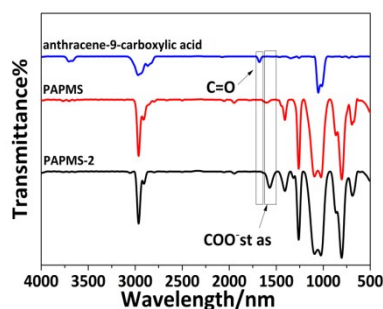


Figure S2 FTIR spectra of anthracene-9-carboxylic, PAPMS solution and PAPMS-2 solution

In order to confirm the effectiveness of dimerization upon UV light, control experiments were performed using 9-anthracenylmethyl acrylate or anthracene-9-carboxylic acid under the same conditions. For example, (0.1150g) 9-anthracenylmethyl acrylate was dissolved in mixed solvents of methanol (1 mL) and toluene (10 mL), and the solution was stirred for 1h in an ice bath upon UV-irradiation. The treatment of anthracene-9-carboxylic acid is similar to that of acrylic acid-9-anthracene methyl ester. Mass spectra of 9-anthracenylmethyl acrylate was shown in Figure S3, mass spectra showed a dimer peak (Figure 3b $m/z + \text{Na}^+$)=547, and a monomer peak (Figure 3a, $m/z=262$), which indicates that the dimerization reaction was incomplete. Mass spectra of anthracene-9-carboxylic acid was shown in Figure S4, mass spectra showed a dimer peak (Figure 4 $m/z + \text{Na}^+$ =467), and a monomer peak (Figure 4, $m/z=223$), which indicates that the dimerization reaction was incomplete.

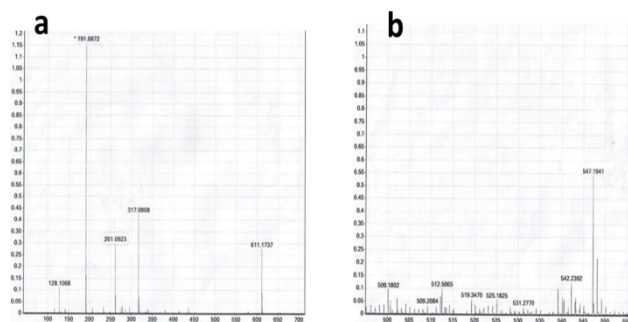


Figure S3 Mass spectra of 9-anthracenylmethyl acrylate after UV irradiation in different mass ranges (b is . B is a local amplification of a at 500-550)

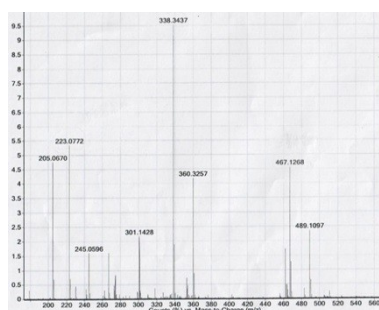


Figure S4 Mass spectra of anthracene-9-carboxylic acid after UV irradiation in different mass ranges

The PAPMS-1 solution and PAPMS-2 solution were stirred for 1h in the ice bath under UV light (365nm). And the photo-dimerization reaction ([4 + 4] photo-cycloaddition) in polymer solution also can be determined by UV-vis spectroscopy. Figure S5 showed the UV-vis spectra of the PAPMS-1 (Figure S5a) and PAPMS-2(Figure S5b) solution before and after UV-irradiation. The absorption intensity of anthracene modified polysiloxane before irradiation was higher than after irradiation. Although the absorption intensity of the two polymer solutions decreased after UV- irradiation, however, the PAPMS-2 solution decreased more than the PAPMS-1 solution, which is mainly attributed to the substituents of the anthracene rings.

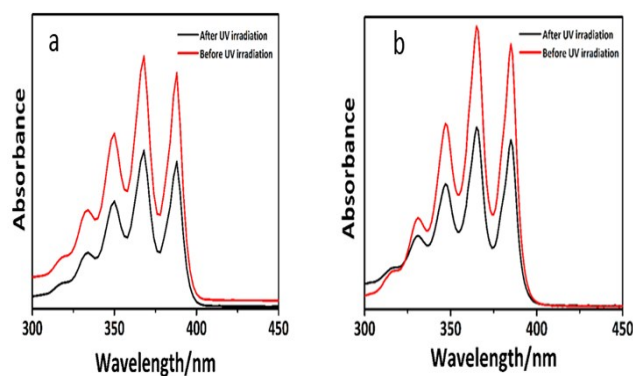


Figure S5 UV-vis spectra of the PAPMS-1 solution (a) and PAPMS-2 solution (b) before and after UV-irradiation (365nm)

In order to detect the reversible property of films, the PAPMS-1 film was heated at 150 °C for 2 h under vacuum as shown in Figure S6. After that we found that the sample was still an elastomer due to the π - π interaction of anthracene groups. The shape of UV-vis absorption peak was little changed because of the reorganization of self-assembled anthracene groups under high temperature. In the meantime, the absorption intensity of the anthracene groups can increase again after heating at 150 °C for 2 h under vacuum. The results also reveal the dimerization under UV-irradiation at 365nm and bond cleavage of the anthracene dimers by heat treatment.

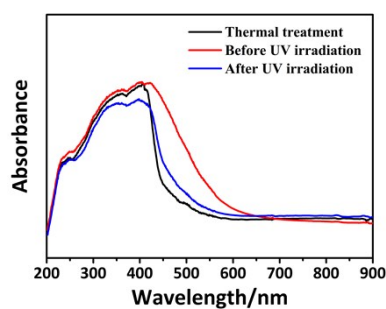


Figure S6 UV-vis spectra of PAPMS-1 films in different processes

In order to further prove the reversible process of PAPMS-1, the model experiment was performed. As shown in Figure 7, the prepolymer PAPMS-1 is viscous liquid at room temperature, however, that solidified with exposure to 365 nm light. It is surprising that, the viscous liquid reappeared when heated to the PAPMS-1, in the same way, the solid sample will be recovered and irradiated again at 365nm.

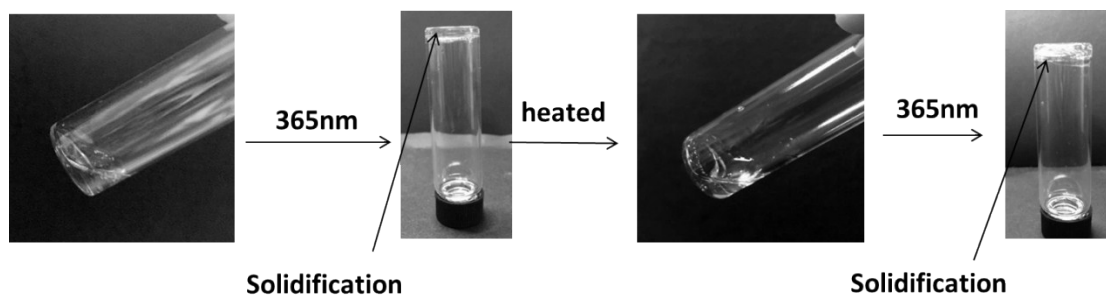


Figure S7 Illustration of PAPMS-1 at 365 nm upon repeating irradiation and heating cycles.

Thermodynamic Analysis

The thermal stability of the PAPMS-1 films was investigated by thermal gravimetric analysis (TGA) under N_2 , as illustrated in Figure S8. Material occurred decomposition when temperature increased from 270 °C to 600 °C, and we detected two distinct weight-loss regions. For the reason of organic decomposition, films initially lost weight when the temperature was from 270°C to 390 °C. The mass loss rate in the second weight-loss region when the temperature ascended from 390 °C to 600 °C, which is due to the decomposition of the heat resistant Si-C and Si-O backbones. All in all, we can conclude that the film has excellent thermal stability.

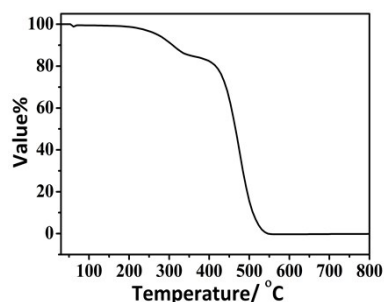


Figure S8 thermal gravimetric analysis (TGA) under N_2 of cured film

Morphology of Cross-Linked Silicone Films

The microphase separation in PAPMS-1 film was not observed because of the networks obtained were highly transparent. The scanning electronic microscopy (SEM) was used to investigate the cured film, shown in the Figure S9. Figure S9 exhibits that there is no macroscopic phase separation or aggregation of small molecules which indicated the phases is strictly interconnected.

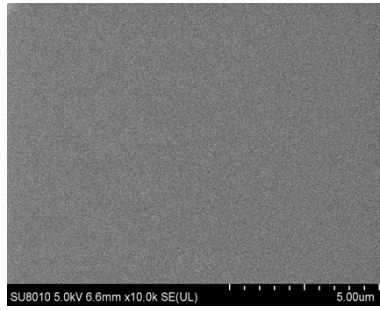


Figure S9 SEM images of PAPMS-1 film