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Supporting information

Anthracene Dimer-Crosslinked Polyurethanes as Mechanoluminescent Polymeric Materials

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1. Basic characterization of PUA_n2 materials

The similar characterization was carried out of PUA_n2. Gel permeation chromatography, UV absorption spectra and static mechanical tests were carried out. Figure S1a showed the gel permeation chromatography tests of original monomer PUA_n2 and dimerized PUA_n2. The difference between retention time demonstrated that after exposure to UV light for 12 h the molecular weight increased dramatically, indicating that the anthracene dimer linked the monomer into a long polymer chain.

Figure S1b demonstrated the static mechanical test of the dimerized film. The monomer of PUA_n2 was a gum like yellow solid when the solvent was evaporated and after the irradiation, a rubber like polymer film solid was obtained and it had a relative good mechanical property which could be used in practical applications. The UV absorbance spectra was shown in Figure S1c and 1d. The solution in chloroform (about 1 mg/mL) and the film on the silica glass was exposure under 365 nm for different intervals and the UV absorbance of monomer anthracene decreased gradually with the exposure time prolonged, indicating that the monomers gradually convert to the dimer.

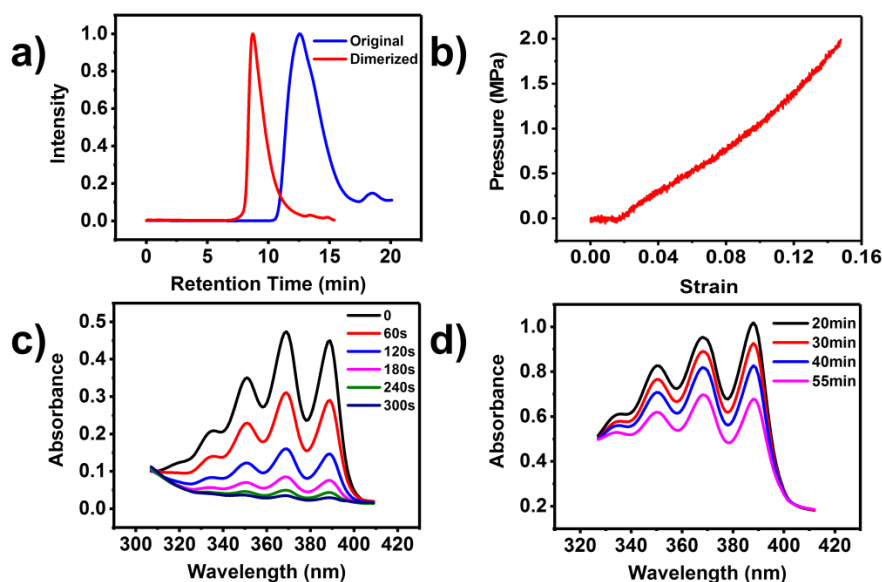


Figure S1 Characterization of PUA_n2. a) Gel permeation chromatography spectra, b) The mechanical tests of PUA_n2, c) UV-spectra of solvent in chloroform and d) UV-spectra of film of PUA_n2. Be like PUA_n1, the PUA_n2 showed photo-dimerization properties both in solution and solid film.

2. Mechanoluminescence studies on PUA_n1 and PUA_n2

In order to investigate the reversibility of the anthracene dimerization, the UV spectra of the film after the cyclic application of the pressure were recorded. (Figure S2, ESI). The PUA_n1 film sample was prepared by casting onto a quartz plate and irradiate with the UV light for 6 h. Then the film was squashed and cracked at about 2.5 MPa to ensure that most the anthracene dimers in the film were destroyed to monomers. Though a slight decrease of UV absorbance of anthracene was found with the crack-UV irradiation cycles, it is quite closed to the original value. Considering that there may be a little amount of the polymer lost during the squashing and cracking, the efficiency of the force-induced cleavage of the anthracene dimers was relatively high. These results indicated the good reversibility of this anthracene dimer crosslinked PU material upon mechanical destroy and UV-induced recovery.

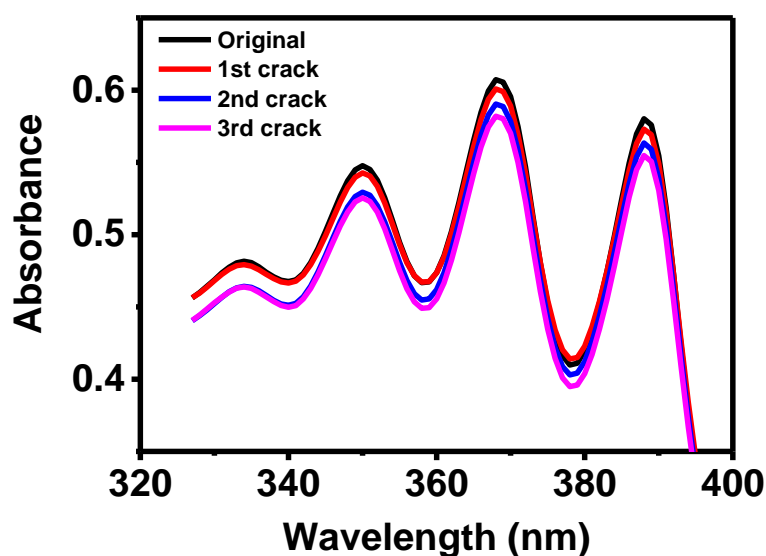


Figure S2 The UV spectra of the PUA_n1 film with 3 crack-UV irradiation cycles under about 2.5 MPa pressure.

The patterned motif was built on the dimerized PUA_n2 film which was shown in Figure S3a top. For the contrary, the pure polyurethane without anthracene was displayed below. The patterned motif showed clearly and defined fluorescence under 365 nm UV light while the pure polyurethane didn't have any fluorescence. Figure S3b was the photograph under fluorescent lamp. The fluorescence intensity before and after crack of the film was tested which was showed in

Figure S3c. The origin film with dimer of anthracene showed little intensity of the fluorescence while after cracked, the fluorescence increased dramatically, indicating that a large quantity of dimer turned to the monomer when the force was applied on the film and cracked. Here, the ^1H NMR spectra was used to detect the mechanism of the changes of molecular structures. As shown in Figure S3d, the top red spectra were the origin PUA_n2 monomer, the hydrogen atom distribute to each peak between 8.6 ppm to 7.6 ppm. After irradiated under 365 nm light for 3 h, the character hydrogen peak of the monomer disappeared meantime the typical hydrogen resonance peak of dimer arose, indicating that most of the monomer in the origin PUA_n2 transformed into the dimer. (Figure S3d blue spectra) After then, the film was squashed and cracked and the ^1H NMR spectra was collected again. Figure S3d, the black spectra showed the character hydrogen resonance peaks of anthracene appear again meaning that a large quantity of dimers transformed into monomer.

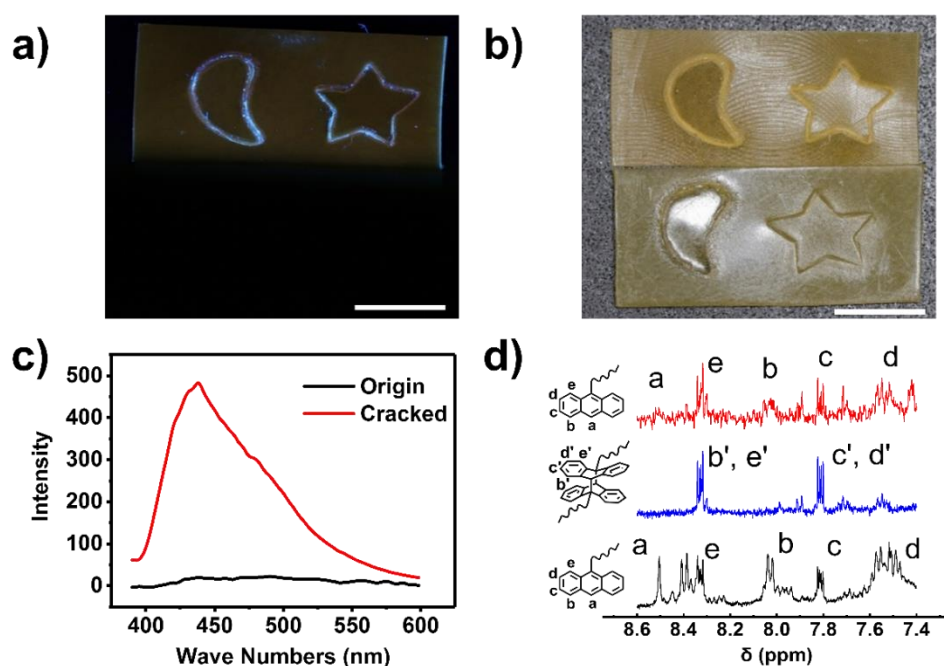


Figure S3 a) The photograph of the patterned dimerized PUA_n2 film under 365 nm UV light. For the contrary, the pure PU film without anthracene was displayed together, which showed no fluorescence. b) The photograph under fluorescent lamp. Scale bar 1 cm. c) The emission fluorescence spectra of the dimerized film of PUA_n2 (black line) and the cracked film (red line) with the 365 nm excite light. The fluorescence excited at about 438 nm was observed. d) The ^1H NMR spectra of the PUA_n2 before and after UV irradiation and after scratched (from top to bottom).

For characterizing the performance of PUAn2 on variable pressures, the film was compressed with the Torx screwdriver to different forces. As shown in Figure S4, the pressure increased to more than 80 MPa while there was little fluorescence change of the indentation which could not even be detected via the instrument. Figure S4c showed the brightfield image of the indentation of b and there was relative slight crack compared to PUAn1 film, hence the sensitive to pressure and pressure changes of PUAn2 was far less than PUAn1.

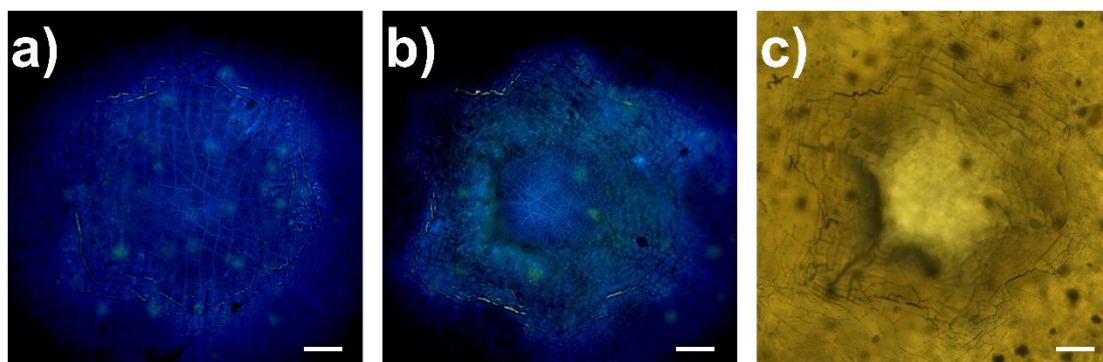


Figure S4 The compression-induced fluorescence test of PUAn2 film with different pressure. a) 36.2, b) 82.7 MPa, c) Brightfield image of b. Scale bar, 100 μm . The fluorescence change was too slight to be monitored and calculated. Because of the tough mechanical properties of PUAn2, the film was not so sensitive to the compression stimulus.