Supporting Information for

Sunlight Helps Self-Healing of Liquid-Crystalline Gels of Lignin-graft PMMA Doped with GO and Azobenzene

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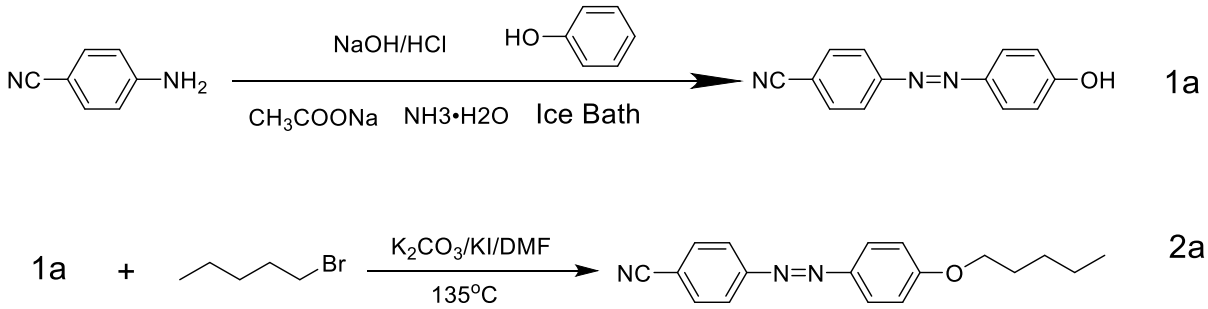
Synthesis and characterization of the azobenzene compound (5CAZ).

The azobenzene compound (5CAZ) was synthesized through two steps of chemical reactions, as shown in **Scheme S1**.



Scheme S1. Synthesis of the azobenzene compound 5CAZ.

Synthesis of 4-cyano-4'-pentyloxyazobenzene

4-cyano-4'-hydroxyl azobenzene(1a): 4-aminobenzonitrile (2.1g, 17.5mmol) was dissolved in a mixture of 5mL concentrated hydrochloric acid and 30ml water, and after cooling to about 5 °C diazotized by dropping a mixture of 2.1g sodium nitrite (18.5mmol) in 3ml water at 0～5°C to the acid mixture. After stirring for 30min, the coupling was carried out by slowly adding the diazotization solution to a solution of 1.4g NaAc (17.5mmol) and 1.65g phenol (17.5mmol) in 5.4ml $NH_3 \cdot H_2O$ (35mmol) aqueous solution at 0～5 °C , and then keep stirring for 1h. The yellow precipitate was collected by filtering off, washing with water and drying over a vacuum for 24 h. Yield: 80%.

4-cyano-4'-pentyloxyazobenzene (2a): To a mixture of 1.6g 4-cyano-4'-hydroxyl azobenzene (7.2mmol), 1.63g potassium hydroxide and a trace of potassium iodide in 25 mL DMF, 1.63g 1-Brompentane (10.8mmol) was added dropwise and refluxed for 10 h at 135 °C. After cooling to room temperature, the resulting mixture was poured into water and extracted with ethyl acetate. The solvent was removed by the rotary evaporator. Subsequently, the crude products was purified by silica gel column chromatography with ethyl acetate as eluent. Finally, 1.38g of the pure product was obtained as a yellow powder. Yield: 65%. The ^{1}HNMR spectrum of compound 2a was recorded in $CDCl_3$ solution, as shown in **Figure S1**. ^{1}H NMR (500MHz, $CDCl_3$-*d*, 25°C, TMS): δ 7.94 (d,4H, ArH), δ 7.78 (d,2H, ArH), δ 7.01 (d,2H, ArH), δ 4.05 (t,2H, CH_2), δ 1.8 (m,2H, CH_2), δ 1.37-1.53 (m,4H, CH_2), δ 0.95 (t,3H, CH_3).

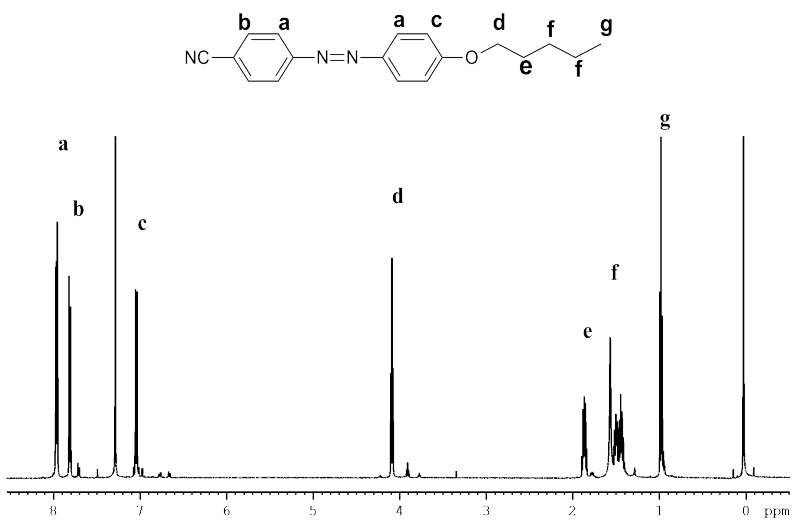


Figure S1. ^{1}H NMR spectra of 5CAZ in $CDCl_3$.

Differential Scanning Calorimetry (DSC) of 5CAZ

As shown in **Figure S2**, we investigated the thermal property of 5CAZ by using DSC. We can see that the peak at 107 °C resulted from the crystallization of 5CAZ and the nematic LC-to-isotropic phase transition temperature is 116.5 °C from the DSC curve of 5CAZ.

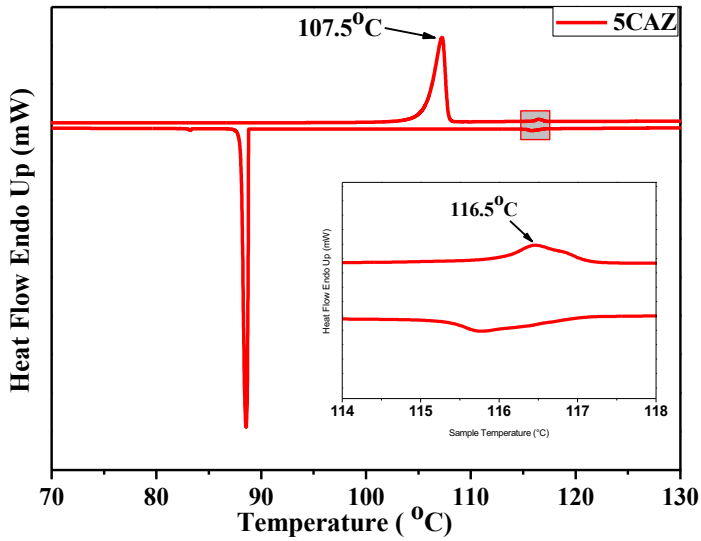


Figure S2. DSC curve of 4-cyano-4'-pentyloxyazobenzene (5CAZ).

Figure S3 shows the FT-IR spectra of lignin, lignin-Br and lignin-g-PMMA copolymer. Lignin-Br shows the incorporation of the bromoisobutyryl ester moiety as evident from the –C=O and –C-O stretching vibrations at 1750 and 1260 cm^{-1}, respectively. Furthermore, the spectra of lignin-g-PMMA copolymers showed characteristic bands of PMMA, such as the bands appearing at 2997cm^{-1} assigned to the –C-H group, 1726 cm^{-1} assigned to the –C=O group and 978cm^{-1} assigned to the –C-O group, indicating the successfully graft of PMMA.

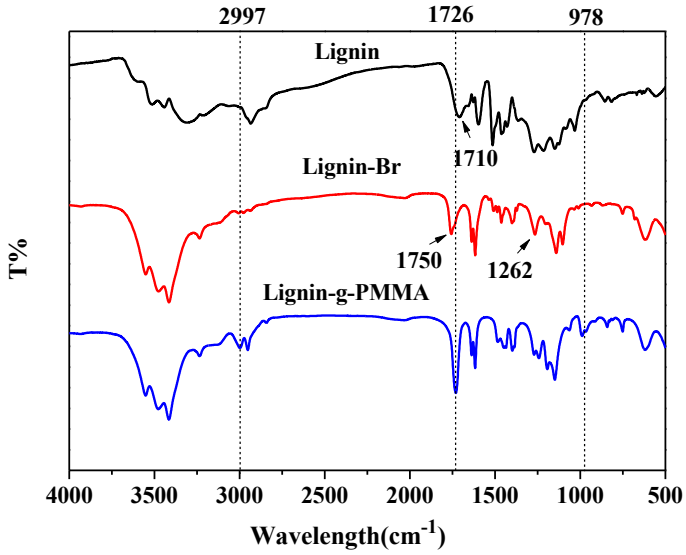


Figure S3. FT-IR spectra of lignin, lignin-Br and lignin-g-PMMA.

Figure S4 shows the thermal properties of lignin and lignin-g-PMMA copolymer (TGA and DSC). The thermal stability was investigated by TGA and DSC under N_2 atmosphere. As shown in the Figure S4, the structure of lignin was slowly decomposed and 5% of the weight loss (thermal decomposition temperature) was 240 °C, while that of lignin-g-PMMA was 310 °C. After decomposition, the residual of lignin was about 36%, while the residual of lignin-g-PMMA was about 0.3%. However, the melting point of both lignin and lignin-g-PMMA weren't obtained from DSC.

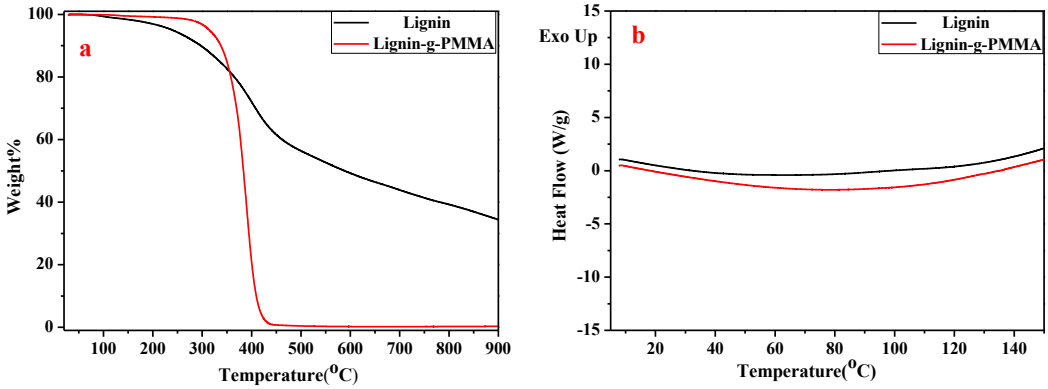


Figure S4. thermal properties of lignin and lignin-g-PMMA. a) TGA; b) DSC.

Figure S5 gives the polarized optical photomicrograph of composite gel containing 5CAZ and GO. The liquid crystalline gel was observed on the rubbed polyimide films. Based on the liquid crystalline behavior of composite gel, the gel films can orient along the rubbing direction. The orientation is parallel to one of polarization direction, there was lowest transmittance (**Figure S5b S5d**). Nevertheless, the highest transmittance (**Figure S5a S5c**) occurred when the angle between the rubbing direction and the polarization direction of either polarizer was 45°.

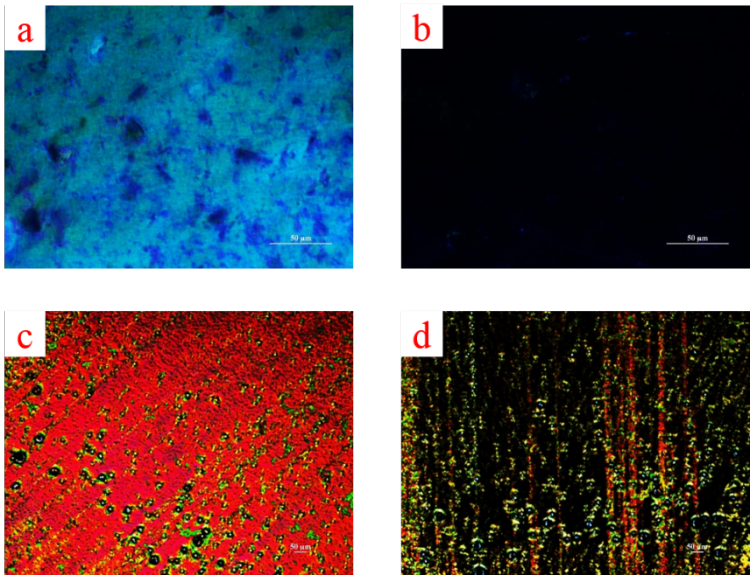


Figure S5. Polarized optical photomicrograph of the anisotropically oriented gel. a,b) composite gel containing GO. c,d) composite gel containing 5CAZ.

Supporting Videos

Video S1 shows the whole self-healing process of lignin-g-PMMA/5CB/5CAZ composite gel. Firstly, we made cracks on the surface of composite gel. And then irradiate the composite gel with UV-light for 10 min, inducing the trans-cis isomerization, subsequently, we irradiated the composites with VIS-light for 10 min, inducing cis-trans isomerization. After the composites transferred into gel, the cracks was healed spontaneously.

Video S2 shows the nemetic-isotropic-nemetic phase transition with and without UV-light irradiation. Upon irradiation, trans-cis photoisomerization of 5CAZ would occurred, resulting in liquid crystalline phase transition based on molecular cooperative motion between 5CAZ and 5CB. When removal of UV-light, cis-trans photoisomerization of 5CAZ happened, isotropic-nemetic phase transition also transformed in seconds.

Video S3 shows the whole self-healing process of composite gel containing GO. Firstly, we made cracks with tool to demonstrate the self-healing properties. Secondly, irradiating the surface of composite gel, the temperature of composites would increase to induce gel-sol transition. After irradiation for 10 min, remove the NIR-light, and let it for about 5 min. Finally, the cracks on the surface of composite gel were healed accompanied with sol-gel transition.

Video S4 shows the self-healing process of composite gels with and without GO upon irradiation with VIS-light. Firstly, we made cracks on both composite gels. And then, the composite gels were irradiated by VIS-light, which induced the gel-sol transition of both composite gels. Because GO acts as photo-thermal conversion material, the temperature of gel with GO increased fast, while that of gel without GO increased

slowly. Based on this mechanism, the gel with GO could heal cracks spontaneously, while the gel without GO couldn't.

Video S5 shows the whole healing process of composite gel dopes with GO and 5CAZ upon solar irradiation. Firstly, the gel containing with GO and 5CAZ and composite gel by contrast were cracked. Then put them expose to sunlight for 30min, the crack on the gel doping with GO and 5CAZ was healed, while cracks on the gel without GO and 5CAZ weren't healed by contrast.