## Supporting Information

# Ionogel surface patterns fabricated by photodimerization-induced self-organized spatial reconstruction

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#### **1. Experimental Section**

#### **1.1 Materials**

PVA (Mn = 74000; 99% hydrolyzed) was purchased from Sigma-Aldrich chemical Co. (Shanghai, China). 9-Anthraldehyde and 4-Methylbenzenesulfonic acid monohydrate (TSOH) were provided by Adamas-Beta Co. Ltd. (Shanghai, China). 1-Ethyl-3-methylimidazolium Dicyanamide (EMIMDCA) was purchased from Meryer Chemical Technology Co. Ltd. (Shanghai, China). All other chemicals were provided by Adamas-Beta Co. Ltd. (Shanghai, China).

#### 1.2 Characterizations

<sup>1</sup>H NMR spectra were acquired using a 500 MHz ADVANCE NMR spectrometer (Bruker, Germany) with tetramethylsilane (TMS) as the internal standard, and Dimethyl Sulfoxide (DMSO) –  $d_6$  as the solvent at room temperature. FT-IR spectra were obtained using a PerkinElmer Spectrum 100 FT-IR spectrometer (U.K.) with a diamond ATR probe and In-situ infrared spectrometer (Nicolet iS50, Thermo Fisher, USA). Data collection parameters included: spectral range 4000-500 cm<sup>-1</sup>, resolution of 0.5 cm<sup>-1</sup> (PerkinElmer) and 0.005 cm<sup>-1</sup> (Nicolet), and 32 co-added scans per measurement. Background spectra (ambient air) were recorded before each sample scan and automatically subtracted. All spectra were baseline-corrected and normalized. The storage modulus and loss modulus curves were recorded using a dynamic thermomechanical analyzer (DMA 850, TA, USA) in tension mode under 1 Hz frequency, 0.5% strain amplitude, and temperature ramp from -30 °C to 120 °C at 5 °C ·min<sup>-1</sup>. The mechanical properties were measured using an electronic material testing machine (Instron 3365, Instron, USA) with a 5 KN load cell. Samples were stretched at 50 mm·min<sup>-1</sup> crosshead speed. Ultraviolet-visible (UV-vis) absorbance spectra were obtained using a UV-vis spectrophotometer (TU-1901, Perkin-Elmer, China). The patterned surfaces with microstructures were captured using laser scanning confocal microscopy (LSCM, LEXT VK-X1000, Keyence, Japan). Fluorescence images of the AnPVA ionogel were visualized using a Super-Resolution Multiphoton Confocal Microscope (TCS SP8 STEDM 3X, Leica, Germany). Fluorescence intensity changes were measured using an advanced fluorescence steady-state transient measurement system (QM/TM/IM, PTI, USA) with a xenon arc lamp source. The excitation wavelength was set to 365 nm, with emission collected from 380 to 600 nm at 1 nm intervals. The surface modulus of the microstructure was observed by atomic force microscopy (FastScan Bio, Bruker, Germany). An LCR meter (TH2830) was utilized to record the resistive signals at a 10 kHz sweep frequency and 1 V AC voltage, Pressure provided by the electronic material testing machine. The UV light source is an LED and the intensity is about 60 mW ⋅ cm<sup>-2</sup>.

#### 1.3 Synthesis of AnPVA

The AnPVA was synthesized using the one-step method outlined in Figure S1. The synthesis involved dissolving 5 g PVA and 2.34 g 9-anthraldehyde in 100 mL DMSO solvent. Subsequently, 0.5 g TSOH was added, and the reaction was carried out under a nitrogen atmosphere at 80 °C for 8 hours. After the reaction was complete, the product was precipitated using anhydrous ethanol to obtain a light-yellow material. The product was washed several times and vacuum-dried at 60 °C for 10 hours. As shown in Figure S2, the structure of AnPVA was confirmed by <sup>1</sup>H NMR and FTIR spectroscopy.

#### **1.4 Preparation of AnPVA-IL Ionogel**

Under vigorous stirring at 80 °C, EMIMDCA was gradually added to a 10 wt.% AnPVA/DMSO solution to obtain a homogeneous AnPVA-IL solution. The solution was then slowly poured onto a glass plate and dried at 80 °C for 24 hours. Subsequently, the material was further dried in a vacuum oven at 70 °C for 4 hours to yield the AnPVA-IL ionogel. The ionogel was then carefully peeled from the glass plate.

#### **1.5 Preparation of AnPVA-IL surface microstructures**

The glass plate with AnPVA-IL was placed on a heating stage at 80°C, with a mask positioned approximately 3 mm above the AnPVA-IL surface. The AnPVA-IL was

irradiated with UV light at a height of 10 cm to induce microstructure growth. After irradiation, the AnPVA-IL with the microstructure was manually peeled off from the glass plate.

### 2. Results and discussion



Figure S1. The synthesis route to AnPVA.



**Figure S2.** Molecular Structure Analysis of AnPVA. (a) <sup>1</sup>H NMR spectrum of An-Am in DMSO- $d_6$ . (b) FTIR spectrum of PVA and AnPVA.



Figure S3. Comparison of microstructure growth under different conditions. Scale bars:  $500 \ \mu m$ .



Figure S4. The process of producing ionogel and the photo.



**Figure S5.** Mechanical properties of the ionogel. (a) The stress-strain curve of AnPVA. (b) Stress-strain curves and (c) tensile resilience curves of AnPVA-IL at different ionic liquid contents. (d) DMA curve of AnPVA-IL 2.



**Figure S6.** Degree of anthracene dimerization. (a) Evolution of UV-vis spectra during the photodimerization process of AnPVA-IL upon 365 nm UV exposure. (b) Quantification of reactant anthracene content through variations in 368 nm absorption intensity.



Figure S7. Height evolution of the surface structure at different exposure times.



**Figure S8.** The modulus distribution maps of the AnPVA-IL surface structure under different exposure times.



**Figure S9.** Optical photographs of ionogel surface morphology obtained by controlling the range of exposure area.



**Figure S10.** Fluorescence changes of AnPVA-IL under UV irradiation. (a) Evolution of fluorescence intensity under full exposure. (b) Changes in fluorescence distribution before and after localized exposure.



**Figure S11.** Pattern control of AnPVA-IL surfaces. (a) Optical images of the surface morphology obtained through stripe masks with different spacings. (b) Optical images of the pattern growth evolution under the same photomask. All scale bars:  $500 \mu m$ .



Figure S12. Optical photographs of disordered complex patterns. All scale bars: 1 mm.



Figure S13. Change in the height of the pattern before and after the second full UV exposure.