

An autonomic self-healing organogel with a photo-mediated modulus

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Experimental section

Materials

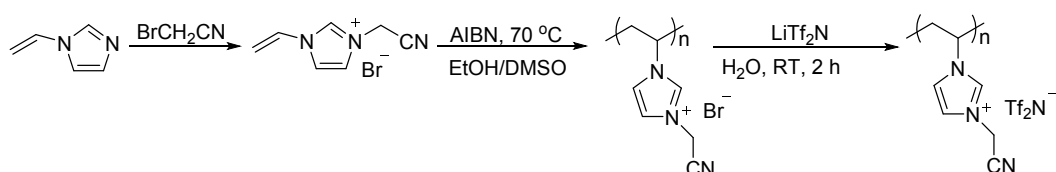
4-Phenylazophenol (Aldrich, **95%**), 1-vinylimidazole (Aldrich, 99%), bromoacetonitrile (Aldrich, 97%) and bistrifluoromethanesulfonimide lithium salt (Aldrich, 99%) were used as received without further treatment. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%) was recrystallized from methanol before use. Poly(acrylic acid) (PAA, $M_w = 250 \text{ kg mol}^{-1}$) and guanidine hydrochloride were purchased from Sigma Aldrich. 4-(Dimethylamino)pyridine (DMAP) and N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC) were purchased from Carl Roth. All the solvents (HPLC grade) and other chemicals were purchased from Sigma Aldrich, and were used without further purification. Milli-Q water (resistivity: $18.2 \text{ M}\Omega\cdot\text{cm}$) provided by a Sartorius Arium 611 VF Purification System was used throughout the research.

Methods

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 250 MHz spectrometer. Mass spectra (MS) were obtained using a VG instrument ZAB 2-SE-FPD. UV-Vis absorption spectra were measured on a Lambda 900 spectrometer (Perkin Elmer). Photoisomerization was induced by the LEDs with the wavelengths of 365 nm and 530 nm (device types LCS-0365-03-22 and LCS-0530-03-22, Mightex Systems). The output intensities of the LEDs were controlled by an LED controller (device type SLC-MA04-MU, Mightex Systems) and were calibrated by an optical powermeter (Model 407A, Spectra-Physics Corporation). Dynamic rheology measurement was conducted on ARES Rheometer (Rheometric Scientific) equipped with parallel plates (diameters of 8 mm). Frequency dependencies of the storage G' and the loss G'' parts of the shear modulus were determined from frequency sweeps measured within the frequency range 10^{-1} – 10^2 rad/s at 25°C . Isothermal titration calorimetry (ITC) measurement was carried out on a VP-ITC microcalorimeter (Microcal, Inc., Northampton, MA) at 25°C . The titration was conducted by stepwise injections of 5 mM PIL solution in DMF from a 278 μL injection syringe into the sample cell filled with 1.0 mM PAA-Azo solution in DMF.

Synthesis

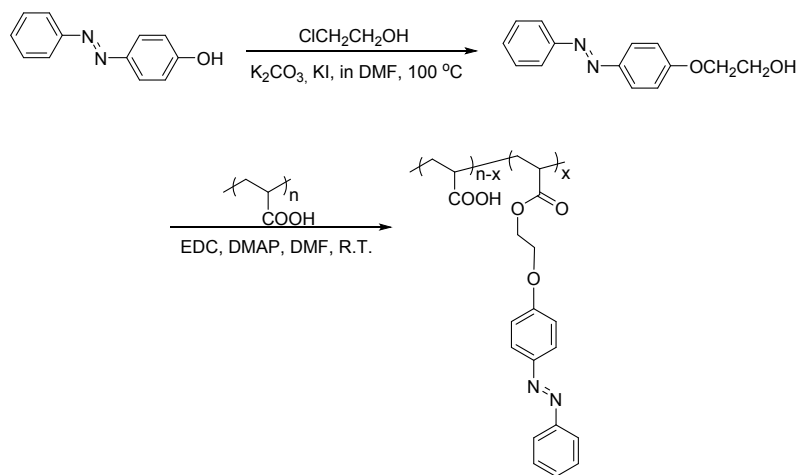
Synthesis of poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (PCMVImTf₂N)



Scheme S1 Synthesis of PCMVImTf₂N

Poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoro methanesulfonyl)imide) (PCMVImTf₂N) was prepared according to the reference.^[1,2] As illustrated in Scheme S1, 3-cyanomethyl-1-vinylimidazolium bromide ([CMVIm]Br) was firstly prepared by combining of 1-vinylimidazole and bromoacetonitrile in methanol at room temperature for 24 h. [CMVIm]Br was obtained as a gray powder (Yield 95 %). Then, [CMVIm]Br (10.38 g, 50.8 mmol), AIBN (30 mg, 0.183 mmol), and DMF (100 mL) were added into a 250 mL flask. The solution was deoxygenated three times by a freeze-pump-thaw procedure. The flask was then refilled with nitrogen and placed in an oil bath at 70 °C for 24 h. After the reaction was quenched by immersing into liquid nitrogen, the mixture was then exhaustively dialyzed against water for 1 week and freeze-dried from water. Poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoro methanesulfonyl)imide) (PCMVImTf₂N) was prepared by anion exchange of PCMVImBr with bis(trifluoromethanesulfonyl)imide lithium salts (LiTf₂N) in H₂O at room temperature for 2 h. ¹H NMR spectra and gel permeation chromatography (GPC) curves of PCMVImBr are illustrated in Figure S3, and Figure S4, respectively. The apparent molecular weight and PDI value of PCMVImBr was 5.80×10^5 g mol⁻¹ and 3.85, respectively (measured by GPC, eluent: water with a mixture of 80% acetate buffer and 20% methanol). PCMVImTf₂N was obtained by anion exchange of PCMVImBr with LiTf₂N salt. Therefore, the apparent molecular weight of the PCMVImTf₂N is calculated to be 1.12×10^6 g mol⁻¹.

Synthesis of azobenzene-grafted poly(acrylic acid) (PAA-Azo)



Scheme S2 Synthesis of azobenzene grafted PAA (PAA-Azo).

Azobenzene-grafted poly(acrylic acid) (PAA-Azo) was prepared according to the reported method.^[3,4] Firstly, 4-hydroxyethyl azobenzene (HE-AZO) was synthesized and a typical procedure is as follows: 4-phenylazophenol (3.96 g, 20 mmol), 2-chloroethanol (1.61 g, 20 mmol) and K₂CO₃ (3.76 g, 20 mmol) were dissolved in 100 mL DMF, a pinch of KI was added. The mixed solution was refluxed at 100 °C under a nitrogen atmosphere overnight. After cooling to room temperature, the precipitated potassium chloride was filtered off and the filtrate was evaporated on vacuum. The crude product was purified by column chromatography (methanol : dichloromethane = 1:3, v/v). Yield 3.79 g (78%). ¹H

NMR (250 MHz, CDCl_3): δ = 7.88–8.0 (d, 4H), 7.42–7.58 (d, 3 H), 7.02–7.12 (m, 2H), 4.21 (t, 2H), 4.04(t, 2H), 1.95(s, 1H). ^{13}C NMR (100 MHz, CDCl_3): 160.99, 152.58, 147.16, 130.48, 129.00, 124.80, 122.57, 114.75, 69.45, 61.40.

Azobenzene-grafted PAA was prepared from PAA and 4-hydroxyethyl azobenzene in the presence of EDC according to a reported procedure.^[4] The following protocol is representative of all PAA-Azo syntheses. PAA (0.36 g, 5 mmol accounted by CH_2CHCOOH units, MW 250 kg mol⁻¹) were dissolved in DMF (150 mL) at 60 °C for 24 h. HE-AZO (0.72 g, 1.5 mmol) and DMAP (0.035 g, 20% accounted by EDC) were added into PAA DMF solution. After a solution was obtained, EDC (0.43 g, 2.25 mmol) was added, and the mixture was stirred at R.T. for 48 h. The product was purified by dialysis using a dialysis tube (cut-off molecular weight: 7000) against methanol/water (3:1, v/v) for 48 h. Then, the solution after dialysis was evaporated on vacuum. The grafting degree of azobenzene was determined by ^1H -NMR spectroscopy. Yield 0.68 g (63.0%). ^1H -NMR (250 MHz, d^6 -DMSO): δ = 7.73–7.91 (b, Ar-H), 7.43–7.60 (b, Ar-H), 7.01–7.21 (m, Ar-H), 4.29 (t, 2H), 3.52(t), 2.21(s, 1H), 1.73(t, 2H), 1.49(t, 2H). ^{13}C NMR (100 MHz, d^6 -DMSO): 162.36, 151.84, 146.05, 130.72, 129.14, 124.49, 122.08, 114.94, 68.92, 62.48.

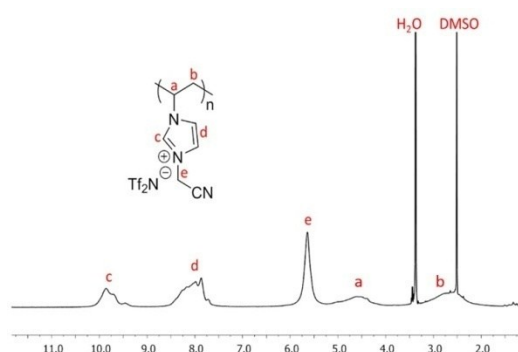


Figure S1 ^1H -NMR spectra of PCMVImTf₂N in DMSO- d^6

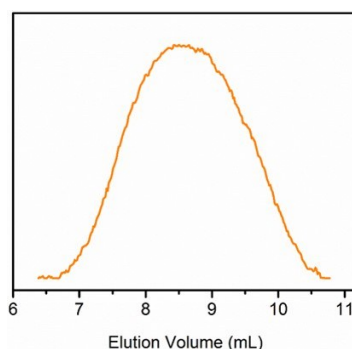


Figure S2 GPC trace for PCMVImBr (eluent: water with a mixture of 80% acetate buffer and 20% methanol).



Figure S3 Photographs of PIL and PAA-Azo in DMF before and after shaking.

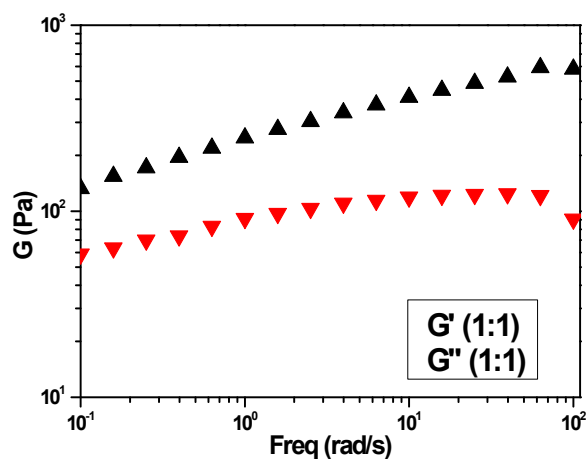


Figure S4 Rheological properties of 10 wt% PIL@PAA-Azo organogel with PIL to PAA-Azo of 1:1 (w/w) at 25 °C (storage modulus G' and loss modulus G'' as a function of frequency).

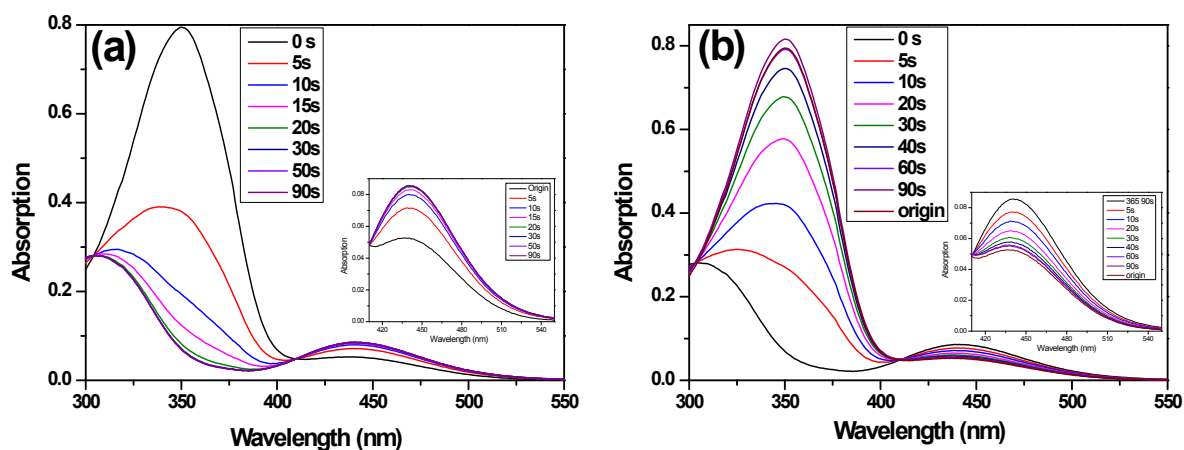


Figure S5 UV-Vis absorption spectra of PAA-Azo (0.03 mg mL^{-1} in DMSO). (a) Irradiated by 365 nm UV light (365 nm) and (b) irradiated by green light (530 nm).

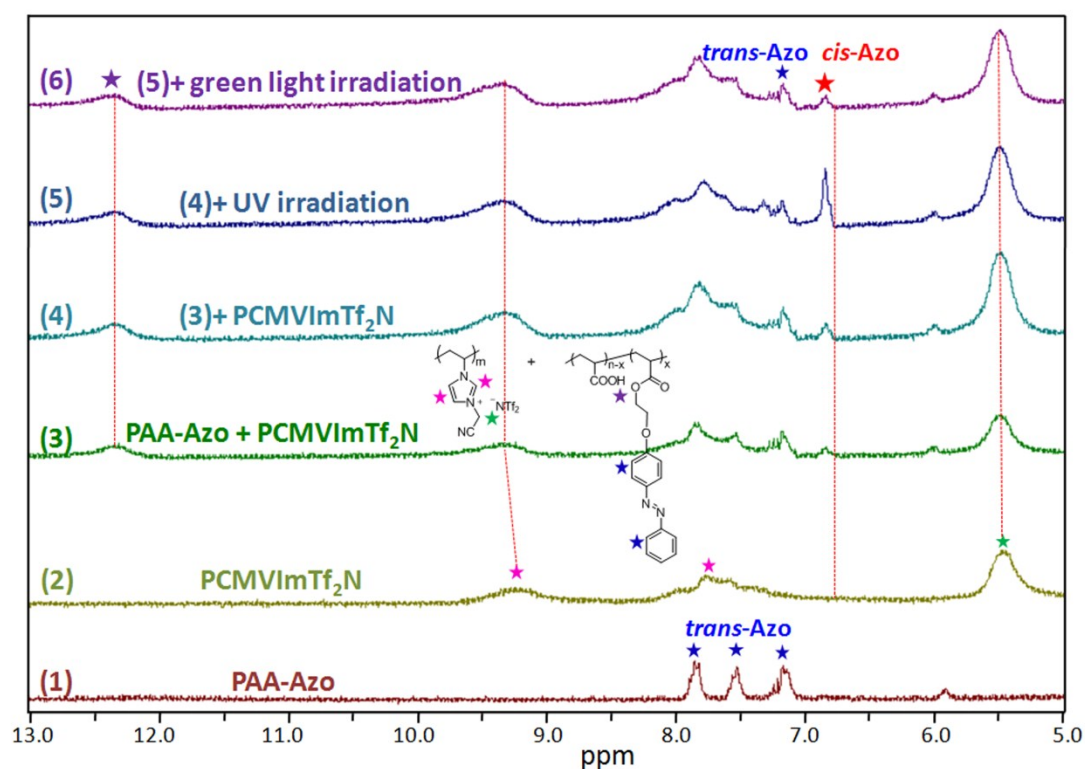


Figure S6 Partial ^1H NMR spectra (250 MHz, 0.5 mL d^6 -DMSO, 25 $^\circ\text{C}$) of PAA-Azo and PIL.

Legends to the Supplementary Movies

Video 1. Self-healing behavior of PIL@PAA-Azo organogel after damage under stretching.

Video 2. Stretchable behavior of PIL@PAA-Azo organogel.

Video 3. PIL@PAA-Azo organogel after Gdn-HCl treatment.

Reference

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3. Y. L. Zhao, J. F. Stoddart, *Langmuir*, **2009**, *25*, 8442.
4. I. Iliopoulos, R. Audebert, *Polym. Bull.*, **1988**, *20*, 577.