Electronic Supplementary Information

for

A Dinoflagellates-Inspired Mechanochromic Film for Fast and Reversible Information Encryption and Display

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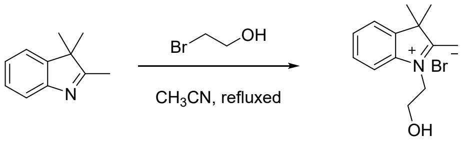
MATERIALS AND METHODS

Materials

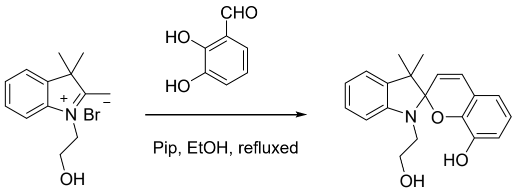
2,3,3-trimethyl-3H-indole, 2-bromoethanol, 2,3-dihydroxybenzaldehyde, triethylamine, sodium bicarbonate, ammonium chloride, sodium chloride, sodium sulfate anhydrous, 4-Dimethylaminopyridine (DMAP), methacrylic anhydride, Ethyl acrylate (EA), di(ethylene glycol) methyl ether acrylate (DEGMEA), acrylamide (AAm), phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (PBPO) and Tween 80 were purchase from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). All acrylate monomers were passed through basic aluminium oxide to remove inhibitor before use. Dimethacrylate spiropyran (SPMA) was synthesized according to the previous literatures.[1-3] Milli-Q water was used in all experiments.

Synthesis of 1-(2-hydroxyethyl)-2,3,3-trimethyl-3H-indol-1-bromide



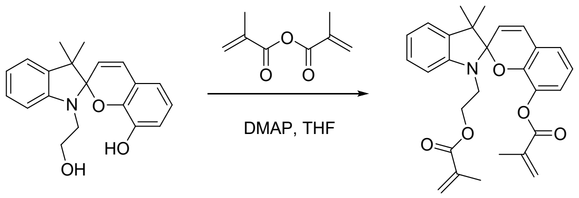
2,3,3-trimethyl-3H-indole (5 g, 30.8 mmol) and 2-bromoethanol (2.94 mL, 5.88 g, 40.0 mmol) in 20 mL of acetonitrile. The reaction mixture was refluxed at 85°C for 24 h and cooled to room temperature. The solvent was eliminated under reduced pressure on a rotary evaporator. The remaining solid was washed twice with diethyl ether to obtain red-brown crystals as the product. (8.5g, 92% yield). ^{1}H NMR (400 MHz, DMSO-*d6*): 7.94-7.99 (m, 1H), 7.83-7.88 (m, 1H), 7.60-7.65 (m, 2H), 4.60 (t, 2H), 3.88 (t, 2H), 2.82 (s, 3H), 1.55 (s, 6H). The above ^{1}H NMR spectral data were consistent with the reported literature.[1]

Synthesis of 1'-(2-hydroxyethyl)-3',3'-dimethylspiro[chromene-2,2'-indolin]-8-ol



1-(2-hydroxyethyl)-2,3,3-trimethyl-3H-indol-1-bromide (6 g, 18 mmol), 2,3-dihydroxybenzaldehyde (2.5 g, 18 mmol) and triethylamine (2.2 g, 21.8 mmol) were dissolved in 70 ml of anhydrous ethanol. The solution was purged with bubbled with nitrogen for 15 mins and refluxed at 100°C for 8 hours. The solution was concentrated in vacuo and redissolved in 100 mL of chloroform. Combined organics were with DI water (3 x 50 mL), saturated $NaHCO_3$ (3 x 50 mL), saturated aqueous NH_4Cl (3 x 50 mL), brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to obtain the title compound as a pinkish-white powder (3.2 g, 55% yield). ^{1}H NMR (400 MHz,$CDCl_3$): 7.16 (td, 1H), 7.08 (dd, 1H), 6.82-6.89 (m, 2H), 6.81-6.72 (m, 2H), 6.64 (dd, 2H), 5.71 (d, 1H), 5.35 (s, 1H), 3.83-3.74 (m, 1H), 3.69 (dt, 1H), 3.49 (td, 1H), 3.31 (dt, 1H), 1.66 (s, 1H), 1.30 (s, 3H), 1.18 (s, 3H). The above ^{1}H NMR spectral data were consistent with the reported literature.[2]

Synthesis of dimethacrylate spiropyran (SPMA)



1'-(2-hydroxyethyl)-3',3'-dimethylspiro[chromene-2,2'-indolin]-8-ol (0.20 g, 0.62 mmol, 1.0 equiv) and DMAP (0.18 g, 1.49 mmol, 2.4 equiv) dissolved in tetrahydrofuran (10 mL) was added to methacrylic anhydride (0.33 mL, 2.23 mmol, 3.6 equiv). After stirring for 24 h under nitrogen at room temperature, the solvent was removed. The crude product was dissolved in dichloromethane, and then passed through basic alumina with dichloromethane as eluent to obtain the product (0.18 g, 64% yield). ^{1}H NMR (400 MHz,$CDCl_3$): 7.09 (td, 1H), 6.99 (dd, 1H), 6.92-6.94 (m, 2H), 6.88 (d, 1H), 6.76-6.84 (m, 2H), 6.59 (d, 1H), 6.08 (dt, 1H), 5.84 (t, 1H), 5.76 (d, 1H), 5.54 (p, 1H), 5.31 (p, 1H), 4.25 (t, 2H), 3.29-3.45 (m, 2H), 1.92 (t, 3H), 1.62 (t, 3H), 1.25 (s, 3H), 1.15 (s, 3H). The above ^{1}H NMR spectral data were consistent with the reported literature.[3]

Preparation of SPMA-linked films

The preparation of SPMA-linked films is similar with the previous literature.[4] In brief, DEGMEA (3 g), EA (0.8 g), SPMA (44 mg, 0.4 mol% to total acrylate monomer) and photoinitiator PBPO (20 mg, 0.2 mol% to total acrylate monomer) were added into a 20 mL glass bottle. After dissolution, followed by the addition of 1 wt% Tween 80 aqueous solution (8 mL), and vortexed for 2 min. Then, AM (1.13 g) was added to the emulsion and vortexed for another 1 min. A glass mold assembled by sandwiching a 0.5 mm-thick silicone spacer between two glass sheets was used to shape and cure the materials under exposure to white light (6 W, 400 lm) for 2 h. The as-prepared hydrogels were soaked in a solution of water/ethanol with 1:1 volume ratio for 24 h, and then dried in a vacuum oven to afford polymer film.

Preparation of SPMA-linked films contained with different metal ions

The as-prepared films were immersed into the 0.01 M ethanol solution of different metal salts for 1 h.

After that, all samples were dried in a vacuum oven to obtain the SP-linked films contained with different metal ions. Then each film was cut out 10 × 5 mm sized samples by laser cutting machine, respectively.

Absorption and transmission spectra testing of films

The absorption and transmission spectra of poly(EA-DEGMEA-SP/AAm) and poly(EA-DEGMEA-SP/AAm)@$Zn(OTf)_2$ films were recorded in a UV-visible spectrophotometer (Lambda 950, Perkin-Elmer). Prior to the tests, the poly(EA-DEGMEA-SP/AAm) film was immersed in ethanol for 1 h and then completely dried in a 60^{o}C oven.

Mechanical tests[5]

Mechanical tests of films were performed at room temperature on a mechanical testing instrument (Z1.0, ZwickRoell). The poly(EA-DEGMEA-SP/AAm) and poly(EA-DEGMEA-SP/AAm)@$Zn(OTf)_2$ films were firstly cut into 20 × 5 mm sized samples by laser cutting machine. For uniaxial tensile tests, samples were stretched until failure at a 60 mm/min deformation rate. For loading–unloading tests, samples were loaded for 20 cycles without stopping at a 60 mm/min deformation rate. For stress relaxation tests, samples were loaded to extension ratio $\lambda = 1, 2, 3$ in sequence. Between each step, the samples were held for 10 min.

Fluorescence spectra testing of films

Fluorescence spectra data of each film was obtained by using a Fluorescence spectrometer (FL3-111, HORIBA). The excitation wavelength is 365 nm. All 10 × 5 mm size films were tested for fluorescence spectra before and after stretching. To measure the fluorescence spectra changes of stretched poly(EA-DEGMEA-SP/AAm)@$Zn(OTf)_2$ film under visible light, the film was irradiated under a daylight tube (0.4W/m^2) for a specific time and tested immediately.

Fluorescence quantum efficiency testing of films

Fluorescence quantum efficiency of poly(EA-DEGMEA-SP/AAm)@$Zn(OTf)_2$ films before and after strected were obtained by using a quantum efficiency testing system (QE-2100, OTSUKA). The single excitation wavelength was set at 365 nm. $BaSO_4$ power was used as a reference.

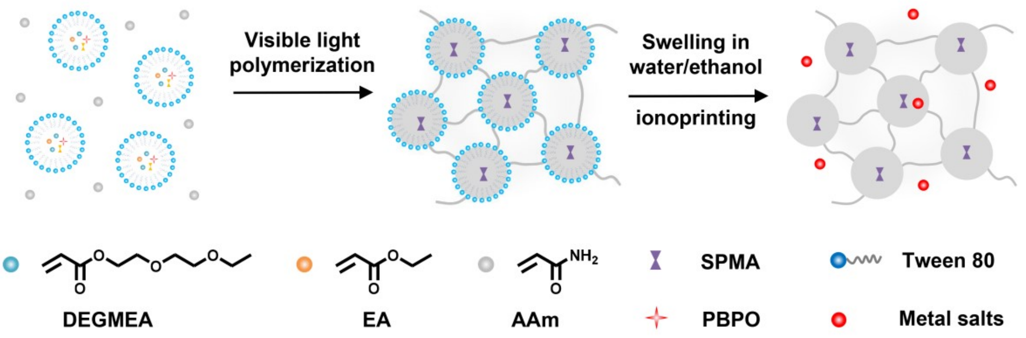


Fig. S1 Schematic preparation process of poly(EA-DEGMEA-SP/AAm)@metal salts elastic films by using visible light-initiated emulsion polymerization and ionic dyeing method.

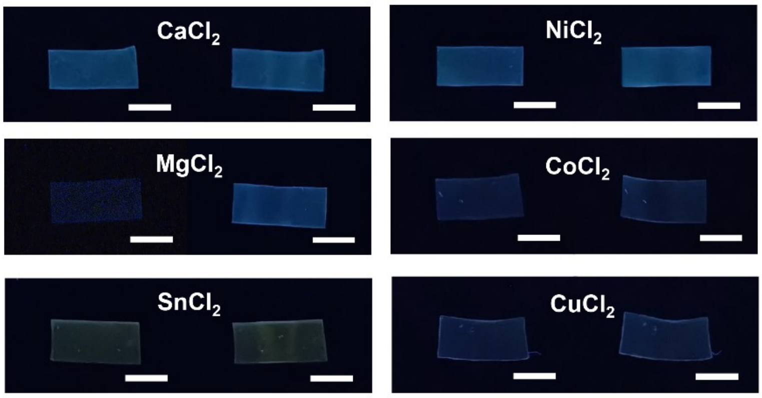


Fig. S2 Photographs of poly(EA-DEGMEA-SP/AAm) films treated with ethanol solutions of a variety of different metal salts. Left: initial state; Right: after stretching. Scale bar: 5 mm.

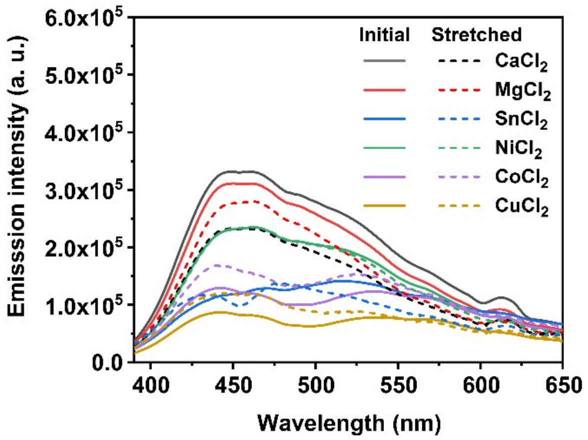


Fig. S3 The fluorescence spectra of poly(EA-DEGMEA-SP/AAm) films treated with different metal salts before and after stretching.

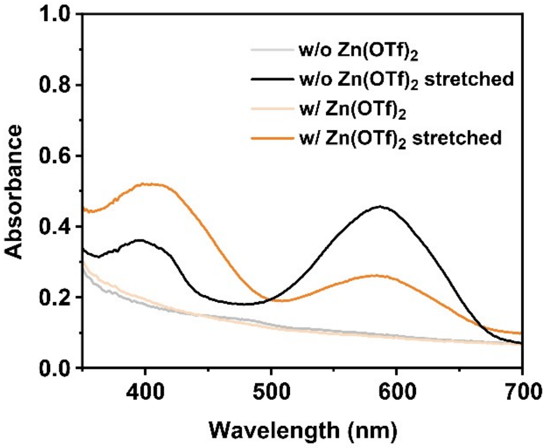


Fig. S4 The UV-Vis absorption spectra of poly(EA-DEGMEA-SP/AAm) and poly(EA-DEGMEA-SP/AAm)@Zn$(OTf)_2$ films before and after stretching.

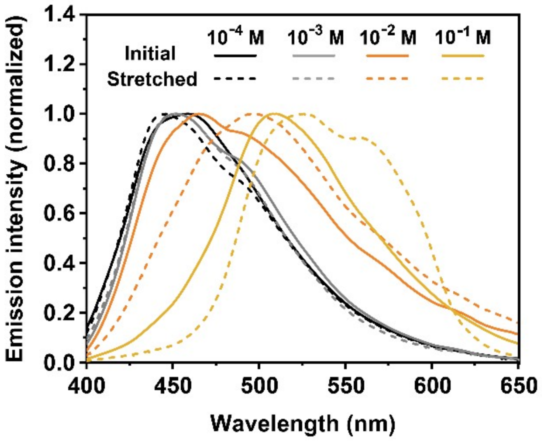


Fig. S5 The fluorescence spectra of poly(EA-DEGMEA-SP/AAm) films treated with different concentration of Zn$(OTf)_2$ ethanol solution.

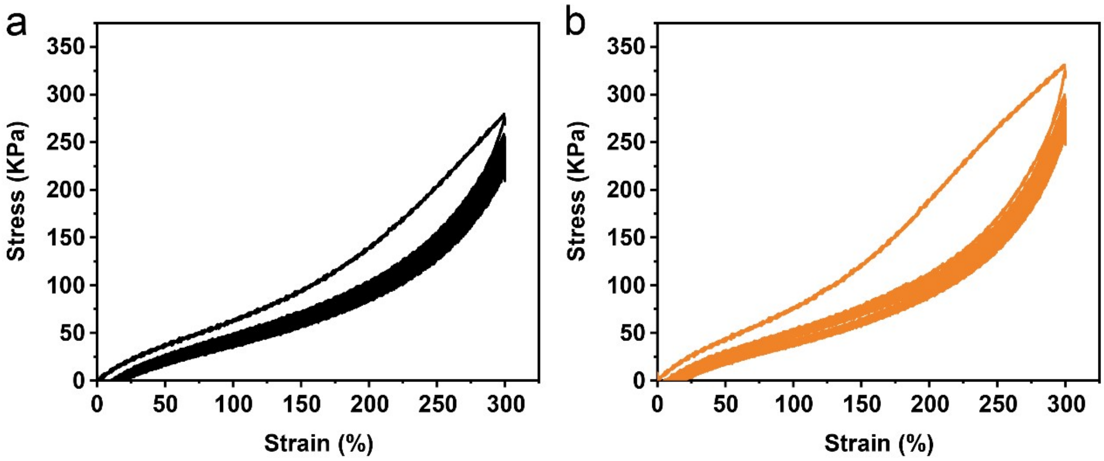


Fig. S6 Stress-strain curves under 20 cycles of stretching. a) poly(EA-DEGMEA-SP/AAm) film. b) poly(EA-DEGMEA-SP/AAm)@Zn$(OTf)_2$ film.

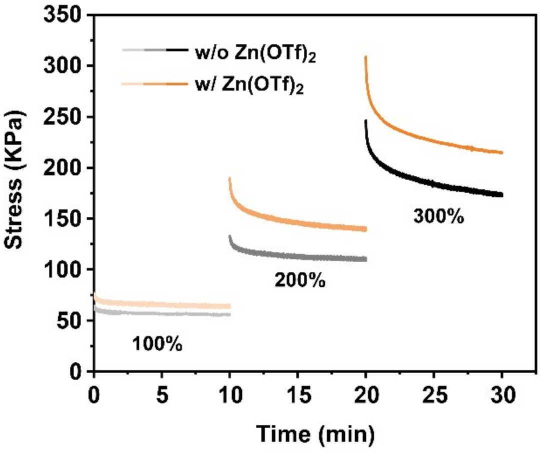


Fig. S7 Relaxation test of poly(EA-DEGMEA-SP/AAm) and poly(EA-DEGMEA-SP/AAm)@Zn(OTf)$_2$ films with extension ratio λ = 1, 2, and 3.

References

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