

Supplementary Information for

**Anthracene-Based Mechanophores for Compression-Activated
Fluorescence in Polymeric Networks**

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Supplementary Information:

Materials

Instrumentation and Experimental Procedures

Supplementary Figures S1-S69

Supplementary Scheme S1

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Materials

Furan, maleic anhydride, toluene, methanol, ethanolamine, triethylamine, isopropanol, 9-anthracenemethanol, acryloyl chloride, 4-dimethylaminopyridine (DMAP), *N,N*-dimethylacrylamide (DMA), Irgacure 2959, *p*-benzoquinone, isoprene, potassium hydroxide, dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), sulfonyl chloride, azobisisobutyronitrile (AIBN), zinc powder, ammonium hydroxide, *N*-methylmaleimide, *N,N*-diisopropylethylamine (DIPEA), and di(ethylene glycol) diacrylate (DEGDA) were purchased from Sigma-Aldrich and used as received unless noted otherwise. Diethyl ether, dichloromethane, ethanol, ethyl acetate, and hexanes were purchased from Fisher Scientific and were used as received. Monomers and crosslinkers were passed through basic alumina prior to use to remove inhibitor and acidic impurities.

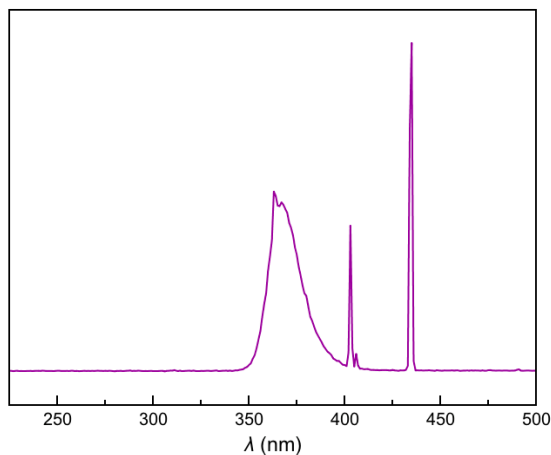
Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 or $\text{DMSO}-d_6$ using an Inova 500 MHz spectrometer at 25 °C. gHSQC, gHMBC, and NOESY spectra were recorded in CDCl_3 using an Inova 500 MHz spectrometer at 25 °C.

Electrospray Ionization-High Resolution Mass Spectrometry (ESI-HRMS). HRMS was carried out using an Agilent 6220 TOF-MS mass spectrometer in the electrospray ionization (ESI) mode.

UV-Vis and Fluorescence Spectroscopy. All solution measurements were taken using a Molecular Devices SpectraMax M2 Multimode Microplate Reader at 25 °C. Absorbance measurements were conducted with 200 μL of sample on clear 96-well polypropylene microplates (Greiner Bio-One) and fluorescence measurements were conducted with 200 μL of sample on black 96-well polypropylene microplates (Greiner Bio-One).

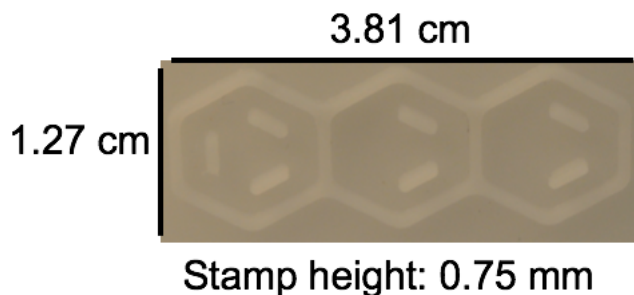
UV Irradiation. Long-wave UV irradiation was performed with a commercial UV nail-curer lamp (4 bulbs with a λ_{max} of 365 nm) operating at 5 mW/cm^2 . The emission spectrum of the lamp is shown below.



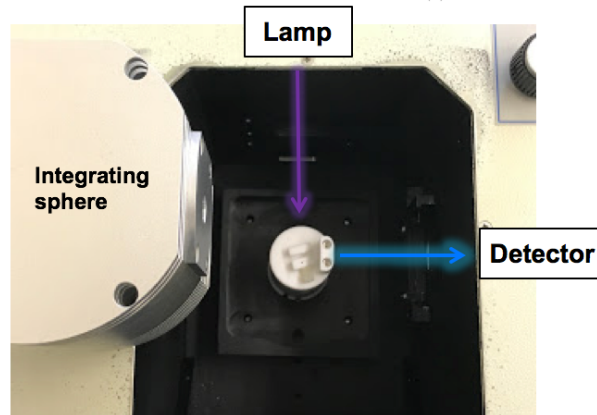
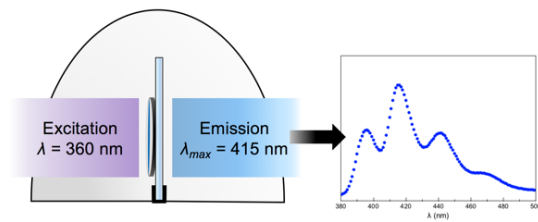
Indentation Measurements. Mechanical indentation experiments were performed using a custom micro-indenter consisting of a 1.6 mm radius of curvature hemispherical glass tip fastened to a double-leaf cantilever ($k = 49.94$ N/m). The cantilever was mounted to a piezoelectric stage (Physik Instrumente) to allow vertical displacement of the indentation tip. Normal forces were calculated by measuring the deflection of the cantilever using a linear displacement capacitance probe (Lion Precision). Prior to indentation, the indentation probe was plasma cleaned and coated with 0.1 wt% F-127 pluronic solution to mitigate the effects of adhesion.

Compression Experiments. Circular discs with a thickness of 1 mm and a diameter of ~ 7 mm (each sample was measured with a caliper prior to compression; caliper contained a digital readout with resolution of 0.01 mm and accuracy of ± 0.02 mm) were compressed using a Carver hydraulic press with an attached manometer. The samples were compressed at a predetermined load for 10 s, then removed for analysis by solid-state fluorescence spectroscopy.

Stamp Preparation. A $12'' \times 2'' \times 0.5''$ block of Delrin stock (McMaster Carr, part no. 8739K21) was cut to $2'' \times 2'' \times 0.5''$ on a band saw to fit the dimensions of the press. After drawing the structure in SolidWorks and creating the cutting trajectory with HSMWorks, the footprint of the stamp was set as $1.5'' \times 0.5'' \times 0.03''$ (3.81 cm \times 1.27 cm \times 0.075 cm). The Delrin block was cut on a Tormach PCN440 with a $5/64''$ 2 flute, carbide end mill at 4500 rpm and a feed rate of 125 mm/min. An image of the stamp with dimensions is included below.

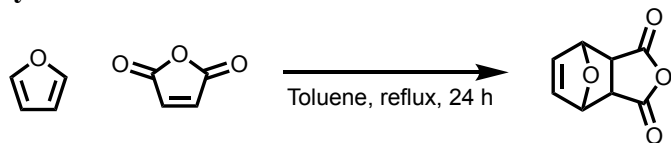


Solid-State Fluorescence Spectroscopy. Fluorescence spectroscopy of compressed networks was conducted on a Horiba Fluorolog-3 spectrophotometer with an Ushio Xenon arc lamp and Horiba photomultiplier tube (detector range: 290-850 nm). The excitation wavelength was 360 nm and emission was scanned from 380 to 500 nm. The instrument was equipped with a petite integrating sphere. Three individual measurements were taken and averaged for a single sample to account for any heterogeneity present. Each compression test measurement was run in triplicate.



Experimental Procedures

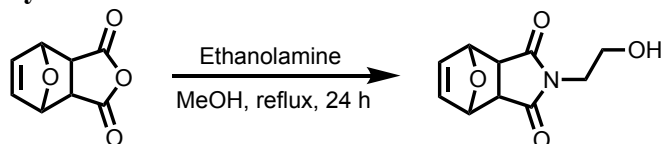
Synthesis of Fur-MAn



Fur-MAn was synthesized according to a previous report.^{1,2} Maleic anhydride (30.0 g, 0.306 mol) and furan (32.8 g, 0.481 mol, 35.0 mL) were dissolved in toluene (350 mL). The solution was refluxed for 24 h, then cooled to room temperature, at which time a white precipitate formed. The mixture was placed in a freezer overnight and the product was collected using vacuum filtration and washed on the filter with cold diethyl ether. The product was dried *in vacuo* and the resultant white powder was used directly in the next step.

¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.58 (s, 2H), 5.46 (s, 2H), 3.17 (s, 2H).

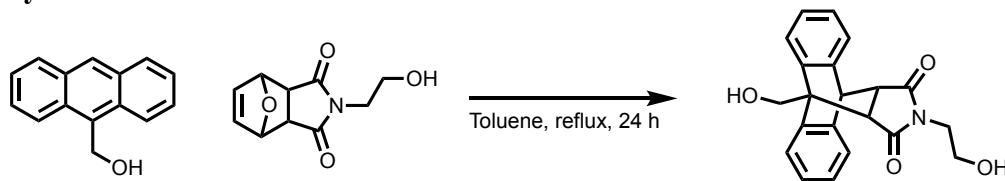
Synthesis of Fur-MalOH



Fur-MalOH was synthesized according to a previous report.^{1,2} Fur-MAn (6.00 g, 36.1 mmol) was dissolved in methanol (125 mL) and cooled to 0 °C. Ethanolamine (2.43 g, 39.7 mmol, 2.40 mL) and triethylamine (4.02 g, 39.7 mmol, 5.53 mL) in methanol (25 mL) were added dropwise to the solution. The reaction mixture was warmed to room temperature, then refluxed for 12 h. At this time, ethanolamine (0.505 g, 8.27 mmol, 0.500 mL) was added and the mixture was refluxed an additional 2 h. The reaction mixture was cooled to room temperature, then placed in a freezer overnight. The resulting solid was collected using vacuum filtration and washed on the filter with cold isopropanol. The product was dried *in vacuo* and the resultant white powder was used directly in the next step.

¹H NMR (500 MHz, CDCl₃): δ (ppm) 6.52 (s, 2H), 5.28 (s, 2H), 3.77 (t, 2H), 3.70 (t, 2H), 2.89 (s, 2H).

Synthesis of AnthOH-MalOH Adduct

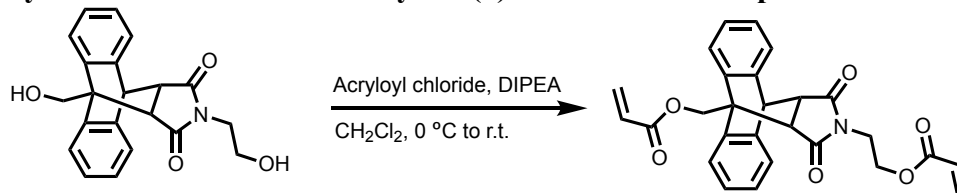


AnthOH-MalOH was synthesized according to a previous report.^{1,2} Fur-MalOH (6.30 g, 30.1 mmol) and 9-anthracenemethanol (6.27 g, 30.1 mmol) were dissolved in toluene (300 mL). The solution was heated at reflux (oil bath set to 140 °C) for 24 h. The solution was cooled to room temperature, then placed in a freezer overnight. The resulting solid was collected using vacuum filtration and dried *in vacuo*. This white solid was used directly in the next step.

¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) 7.68 (d, 1H); 7.44 (d, 1H); 7.17 (m, 6H); 5.33 (t, 1H); 4.85 (m, 2H); 4.70 (s, 1H); 4.60 (t, 1H); 3.26 (s, 2H); 3.01 (t, 2H); 2.57 (m, 2H);

^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): δ (ppm) 176.44, 175.73, 142.55, 142.50, 139.93, 139.45, 126.25, 126.09, 125.84, 125.80, 124.72, 124.40, 123.64, 122.41, 58.18, 56.40, 49.24, 47.47, 45.39, 44.97, 39.33.

Synthesis of Anth-Mal Diacrylate (1): Classic Mechanophore



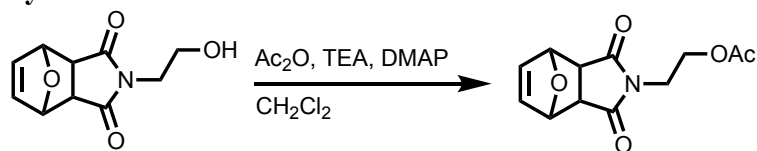
AnthOH-MalOH (7.31 g, 20.9 mmol) and triethylamine (8.47 g, 83.7 mmol, 11.7 mL) were dissolved in anhydrous dichloromethane (205 mL). The solution was cooled to 0 °C, and acryloyl chloride (7.58 g, 83.7 mmol, 6.76 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. At this time, the solvent was evaporated using a rotary evaporator. The crude solid was triturated with cold methanol to remove residual acid halide and base, and the resulting off-white powder was collected using vacuum filtration. The crude product was purified by column chromatography on silica gel with 3:7 EtOAc:hexanes as the mobile phase to yield a fine, white powder.

^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.40 (m, 1H), 7.33 (m, 1H), 7.29 (1H, m), 7.21-7.12 (m, 5H), 6.50-5.86 (m, 6H), 5.58 (dd, 2H), 4.79 (s, 1H), 3.56 (m, 2H), 3.42 (t, 2H), 3.32 (t, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 176.22, 175.12, 165.98, 165.62, 141.95, 141.22, 138.64, 138.17, 131.78, 131.42, 128.19, 128.12, 127.33, 127.29, 126.95, 126.84, 125.39, 124.24, 123.17, 122.22, 61.93, 61.23, 47.90, 47.82, 46.42, 45.81, 37.14.

ESI-HRMS: Calcd. for $[\text{M}+\text{H}]^+$: 458.1598; Found: 458.1609. Calcd. for $[\text{M}+\text{NH}_4]^+$: 475.1864; Found: 475.1879. Calcd. for $[\text{M}+\text{Na}]^+$: 480.1418; Found: 480.1441.

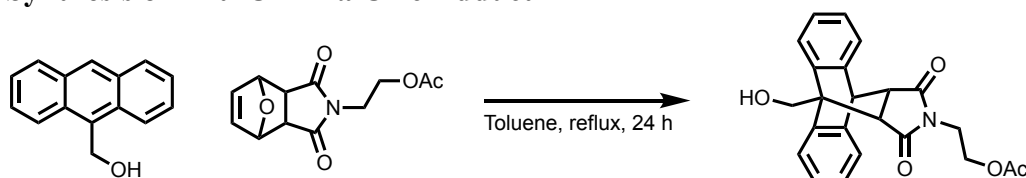
Synthesis of Fur-MalOAc



Fur-MalOH (5.00 g, 23.9 mmol), triethylamine (7.26 g, 71.7 mmol, 9.99 mL), and DMAP (0.292 g, 2.39 mmol) were dissolved in anhydrous dichloromethane (95 mL). Acetic anhydride (2.93 g, 28.7 mmol, 2.71 mL) was added and the reaction was allowed to stir at room temperature for 24 h. At this time, the reaction mixture was diluted with dichloromethane and washed with NaHCO_3 (2×100 mL), 0.1 M HCl (2×100 mL), deionized water (1×100 mL), and brine (1×100 mL). The solution was dried over magnesium sulfate, filtered, and concentrated *in vacuo* to yield the product was a white solid. The crude product was used in the next step without further purification.

^1H NMR (500 MHz, CDCl_3): δ (ppm) 6.52 (s, 2H), 5.26 (s, 2H), 4.22 (t, 2H), 3.75 (t, 2H), 2.87 (s, 2H), 2.01 (s, 3H).

Synthesis of AnthOH-MalOAc Adduct

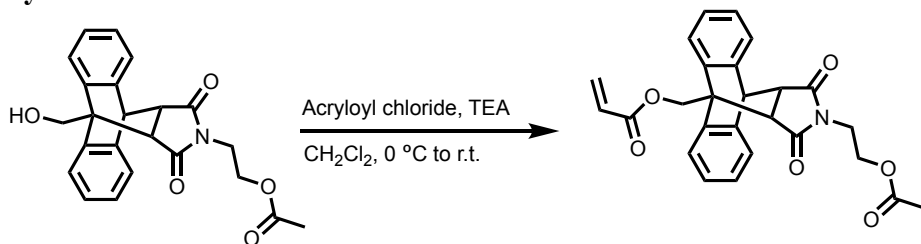


Fur-MalOAc (2.00 g, 7.96 mmol) and 9-anthracenemethanol (1.66 g, 7.96 mmol) were dissolved in toluene (50 mL). The solution was heated at reflux (oil bath set to 140 °C) for 24 h. The solution was cooled to room temperature, then placed in a freezer overnight. The white solid was collected using vacuum filtration and dried *in vacuo*. The crude product was used in the next step without further purification.

$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ (ppm) 7.67 (d, 1H), 7.44 (d, 1H), 7.24-7.07 (m, 6H), 5.33 (t, 1H), 4.85 (m, 2H), 4.71 (s, 1H), 3.34 (m, 2H), 3.28 (s, 2H), 3.21 (t, 2H), 1.89 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$): δ (ppm) 176.37, 175.64, 169.94, 142.63, 142.57, 139.81, 139.36, 126.27, 126.09, 125.83, 125.78, 124.63, 124.36, 123.63, 122.34, 60.25, 58.20, 49.16, 47.47, 45.46, 44.87, 36.21, 20.67.

Synthesis of Control Monomer 2



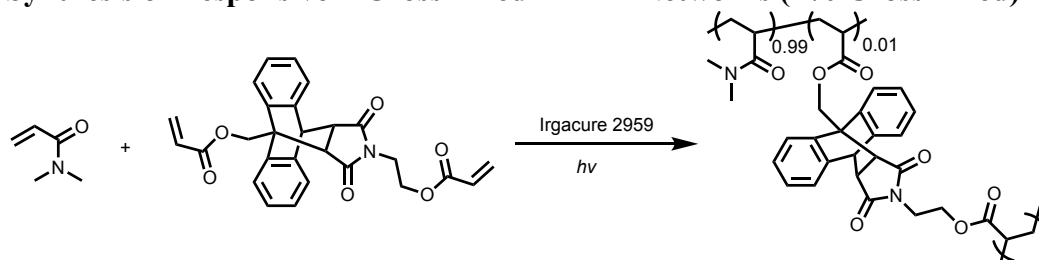
AnthOH-MalOAc (2.53 g, 6.46 mmol) and triethylamine (0.981 g, 9.70 mmol, 1.35 mL) were dissolved in anhydrous dichloromethane (65 mL) and cooled to 0 °C. Acryloyl chloride (0.878 g, 9.70 mmol, 0.784 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 24 h. At this time, the solvent was evaporated using a rotary evaporator. The crude solid was triturated with cold methanol to remove residual acid halide and base, and the resulting white powder was collected using vacuum filtration. The crude product was purified by column chromatography on silica gel with 1:1 EtOAc:hexanes as the mobile phase to yield a fine, white powder.

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm) 7.41 (m, 1H), 7.32 (m, 2H), 7.22-7.15 (m, 5H), 6.49 (d, 1H), 6.22 (dd, 1H), 5.90 (d, 1H), 4.79 (s, 1H), 3.57-3.47 (m, 2H), 3.37-3.30 (m, 4H), 1.96 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ (ppm) 176.33, 175.24, 170.64, 166.02, 142.01, 141.28, 138.74, 138.27, 131.80, 128.15, 127.31, 127.27, 126.98, 126.87, 125.43, 124.27, 123.20, 122.26, 61.97, 60.83, 47.86, 46.40, 45.84, 37.27, 21.00.

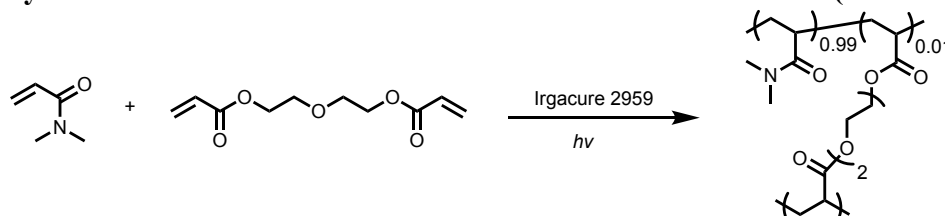
ESI-HRMS: Calcd. for $[\text{M}+\text{H}]^+$: 446.1598; Found: 446.1605. Calcd. for $[\text{M}+\text{NH}_4]^+$: 463.1864; Found: 463.1869. Calcd. for $[\text{M}+\text{Na}]^+$: 468.1418; Found: 468.1434.

Synthesis of Responsive 1-Crosslinked PDMA Networks (1% Crosslinked)



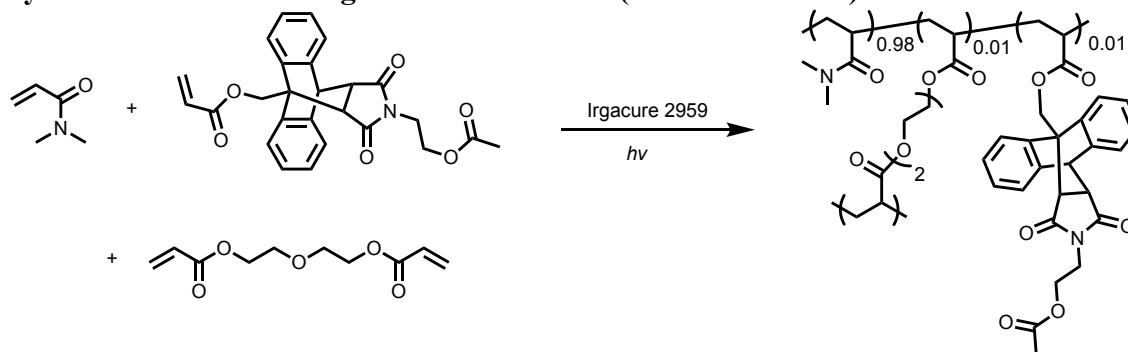
DMA (1.00 g, 10.1 mmol), **1** (46.0 mg, 0.101 mmol, [1] = 0.097 M), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of DEGDA-Crosslinked PDMA Control Networks (1% Crosslinked)



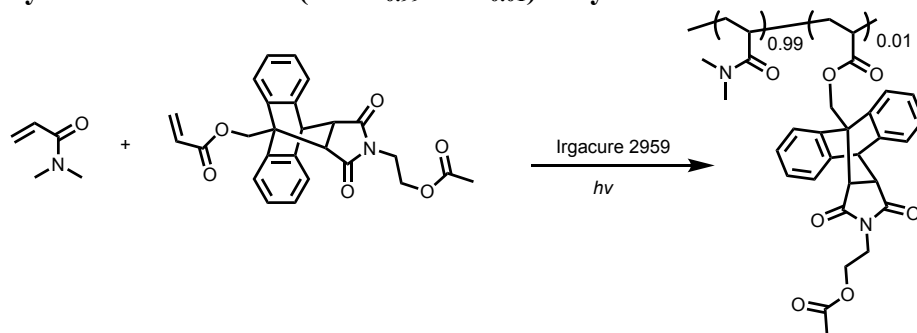
DMA (1.00 g, 10.1 mmol), DEGDA (21.8 mg, 0.102 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of 2-Containing Control Networks (1% Crosslinked)



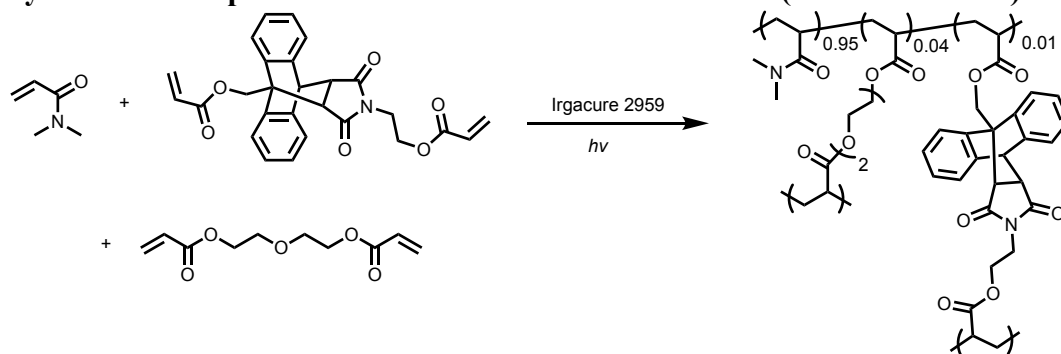
DMA (1.00 g, 10.1 mmol), **2** (45.9 mg, 0.103 mmol), DEGDA (22.1 mg, 0.103 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of Linear P(DMA_{0.99-co-2}_{0.01}) Polymer



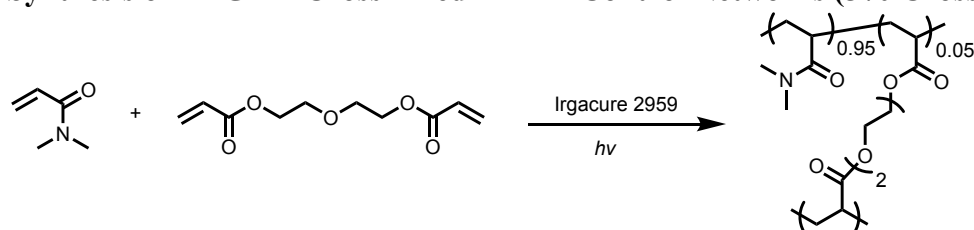
DMA (1.00 g, 10.1 mmol), **2** (45.4 mg, 0.102 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was irradiated with a 365 nm light for 10 min. The polymer was diluted with dichloromethane and precipitated into an excess of cold diethyl ether.

Synthesis of Responsive 1-Crosslinked PDMA Networks (5% Crosslinked)



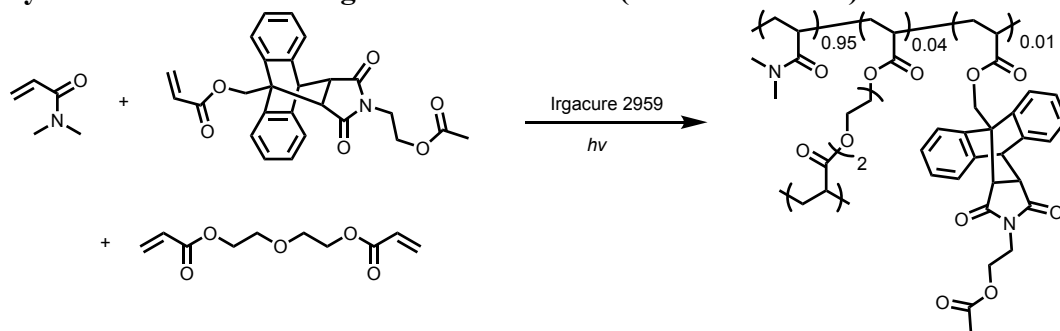
DMA (1.00 g, 10.1 mmol), **1** (48.6 mg, 0.106 mmol, [1] = 0.094 M), DEGDA (0.091 g, 0.425 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of DEGDA-Crosslinked PDMA Control Networks (5% Crosslinked)



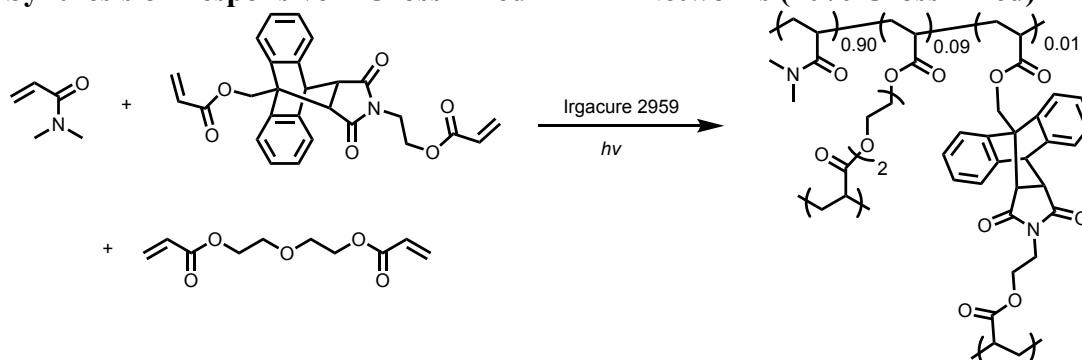
DMA (1.00 g, 10.1 mmol), DEGDA (114 mg, 0.531 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of 2-Containing Control Networks (5% Crosslinked)



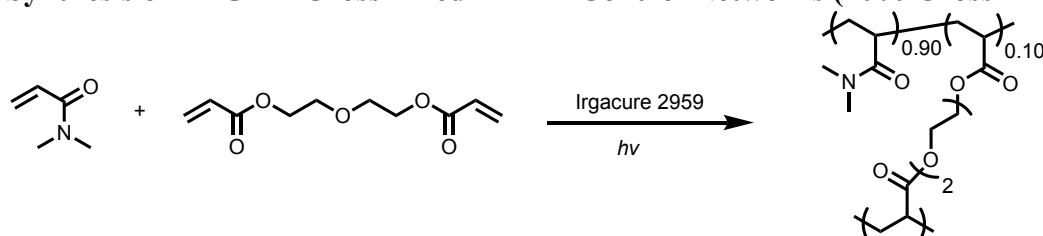
DMA (1.00 g, 10.1 mmol), **2** (47.8 mg, 0.107 mmol), DEGDA (115 mg, 0.537 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of Responsive 1-Crosslinked PDMA Networks (10% Crosslinked)



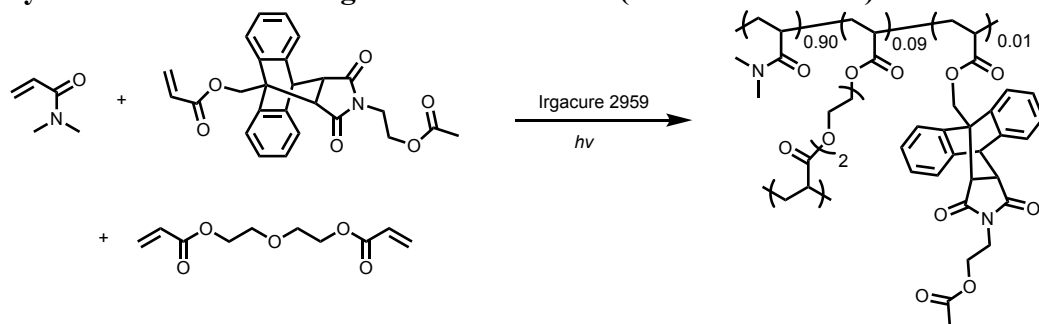
DMA (1.00 g, 10.1 mmol), **1** (51.3 mg, 0.112 mmol, [1] = 0.091 M), DEGDA (216 mg, 1.01 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of DEGDA-Crosslinked PDMA Control Networks (10% Crosslinked)



DMA (1.00 g, 10.1 mmol), DEGDA (240 mg, 0.112 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of \sim 7 mm) within a silicone sheet (thickness of \sim 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of 2-Containing Control Networks (10% Crosslinked)

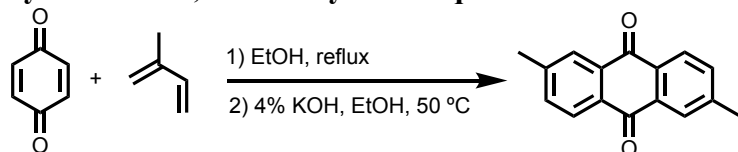


DMA (1.00 g, 10.1 mmol), **2** (49.9 mg, 0.112 mmol), DEGDA (216 mg, 1.01 mmol), and Irgacure 2959 (2.00 mg, 8.92 μ mol) were mixed in a scintillation vial. The solution was cast in circular punches (diameter of ~ 7 mm) within a silicone sheet (thickness of ~ 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of 9-Anthracenemethanol-Containing Networks for Calibration Curve

A stock solution (4.5 mg/mL) of 9-anthracenemethanol in DMA was prepared. An appropriate amount (10 μ L for 0.2 mM, 50 μ L for 1 mM, or 100 μ L for 2 mM) of the solution was added to a scintillation vial and the mass was brought to 1 g with DMA. DEGDA (20 mg) and Irgacure 2959 (1 mg) were added. The solution was cast in circular punches (diameter of ~ 7 mm) within a silicone sheet (thickness of ~ 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Synthesis of 2,6-Dimethylantraquinone

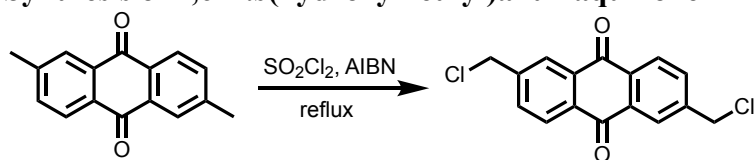


2,6-Dimethylantraquinone was synthesized according to a previous report.³ *p*-Benzoquinone (21.0 g, 194 mmol) and isoprene (53.8 g, 790 mmol, 79 mL) were dissolved in ethanol (300 mL). The mixture was refluxed for 48 h (oil bath set at 120 $^{\circ}$ C and condenser equipped with chiller maintaining coolant temperature at 10 $^{\circ}$ C) then cooled to room temperature. The resultant crystals were filtered and washed with ethanol. The intermediate was dissolved in 4 % KOH solution in ethanol (500 mL) and heated at 50 $^{\circ}$ C while air was bubbled through the solution for 5 h. During this time, the solution became a dark green color, followed by precipitation of a solid and further color change to orange. At this time, the solvent was removed with a rotary evaporator, and the solid was washed with water and ethanol. The pale-yellow powder was dried *in vacuo* and used in the next step. Melting point: 235-237 $^{\circ}$ C; lit. melting point: 239-243 $^{\circ}$ C.⁴

¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.18 (d, 2H), 8.08 (s, 1H), 7.57 (d, 2H), 2.52 (s, 6H).

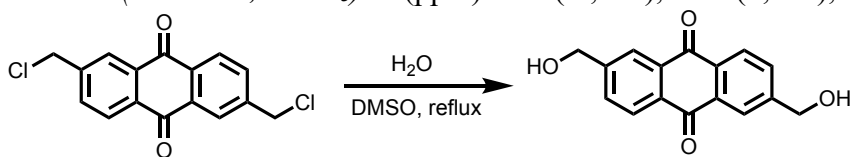
¹³C NMR (125 MHz, CDCl₃): δ (ppm) 183.41, 145.31, 134.86, 133.63, 131.48, 127.56, 127.52, 22.05.

Synthesis of 2,6-Bis(hydroxymethyl)anthraquinone



2,6-Bis(chloromethyl)anthraquinone was synthesized according to a previous report.⁵ 2,6-Dimethylantraquinone (5.70 g, 23.7 mmol) and azobisisobutyronitrile (0.240 g, 1.46 mmol) were dissolved in sulfuryl chloride (75 mL, 125 g, 928 mmol). The reaction mixture was refluxed for 24 h. At this time, the solution was cooled to room temperature and excess sulfuryl chloride was removed *in vacuo*. The resultant solid was filtered and washed on the filter with petroleum ether. The crude product was purified further by recrystallization in DMF to yield a light brown solid and then used in the next step.

¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.32 (m, 4H), 7.85 (d, 2H), 4.72 (s, 4H).

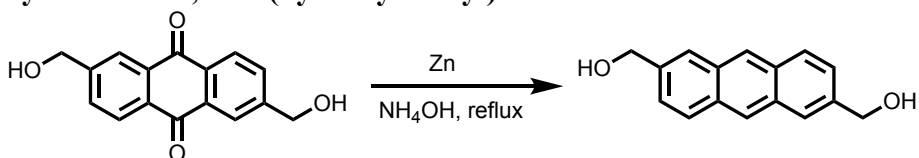


2,6-Bis(hydroxymethyl)anthraquinone was synthesized according to a previous report.⁵ 2,6-Bis(chloromethyl)anthraquinone (3.90 g, 12.8 mmol) was suspended in a mixture of water (300 mL) and DMSO (400 mL) and refluxed for 48 h. At this time, the reaction mixture was cooled to room temperature and the product precipitated from solution. The crude product was collected by vacuum filtration and recrystallized from DMF.

¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) 8.16 (m, 4H), 7.82 (d, 2H), 5.58 (t, 2H), 4.69 (d, 4H).

¹³C NMR (125 MHz, DMSO-*d*₆): δ (ppm) 182.43, 149.90, 132.98, 131.80, 131.71, 126.87, 123.93, 62.24.

Synthesis of 2,6-Bis(hydroxymethyl)anthracene

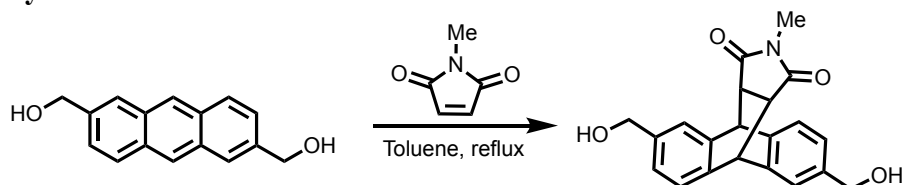


2,6-Bis(hydroxymethyl)anthracene was synthesized according to a previous report.⁵ 2,6-Bis(hydroxymethyl)anthraquinone (0.875 g, 3.26 mmol) was dissolved in concentrated ammonium hydroxide (22 mL). Zinc powder (1.88 g, 28.7 mmol) was added to the solution and the mixture was refluxed overnight. The insoluble material was filtered and washed with hot DMSO. The solution was precipitated in 25 mL of 1 M HCl. The resultant solid was collected by vacuum filtration and dried *in vacuo*.

¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) 8.49 (s, 2H), 8.03 (d, 2H), 7.95 (s, 2H), 7.45 (d, 2H), 5.36 (t, 2H), 4.70 (d, 4H).

¹³C NMR (125 MHz, DMSO-*d*₆): δ (ppm) 139.45, 130.95, 130.78, 127.84, 125.49, 125.40, 123.91, 63.15.

Synthesis of AnthDiol-NMeMal Adduct

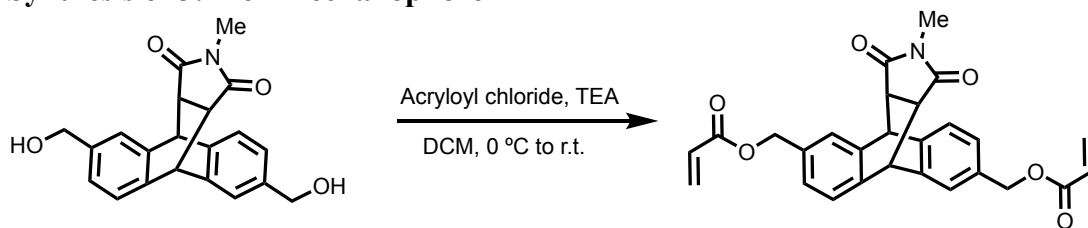


2,6-Bis(hydroxymethyl)anthracene (0.170 g, 0.731 mmol) and *N*-methyl maleimide (0.081 g, 0.731 mmol) were dissolved in toluene (5 mL). The reaction mixture was heated at reflux (oil bath set to 140 °C) for 24 h. At this time, the solution was cooled to room temperature and placed in a freezer overnight. The product was collected by vacuum filtration and dried *in vacuo*. The white solid was used directly in the next step.

¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) 7.39 (d, 2H), 7.16 (d, 2H), 7.05 (dd, 2H), 5.11 (t, 2H), 4.72 (d, 2H), 4.43 (d, 2H), 4.40 (d, 2H), 3.23 (t, 2H), 2.37 (s, 3H).

¹³C NMR (125 MHz, DMSO-*d*₆): δ (ppm) 176.73, 176.72, 141.87, 140.79, 140.64, 140.46, 139.10, 137.60, 124.32, 124.23, 124.16, 123.77, 122.60, 122.59, 62.86, 62.58, 46.58, 46.56, 44.42, 44.35, 23.93.

Synthesis of 3: Flex Mechanophore



AnthDiol-NMeMal (0.225 g, 0.644 mmol) and DIPEA (0.250 g, 1.93 mmol, 0.337 mL) were dissolved in anhydrous dichloromethane (5.60 mL) and cooled to 0 °C. Acryloyl chloride (0.146 g, 1.61 mmol, 0.130 mL) was added dropwise in anhydrous dichloromethane (1.40 mL). The reaction mixture was warmed to room temperature and stirred for 24 h. At this time, the solvent was evaporated using a rotary evaporator. The crude solid was triturated with cold methanol to remove residual acid halide and base, and the resulting white powder was collected using vacuum filtration. The crude product was purified by column chromatography on silica gel with 3:7 EtOAc:hexanes as the mobile phase.

¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.45-7.12 (m, 6H), 6.44 (m, 2H), 6.15 (m, 2H), 5.86 (m, 2H), 5.20-5.10 (m, 4H), 4.82 (s, 2H), 3.23 (t, 2H), 2.53 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ (ppm) 176.76, 176.71, 166.08, 165.95, 141.80, 141.53, 138.89, 138.60, 135.03, 134.79, 131.44, 131.28, 128.31, 128.29, 127.18, 127.00, 125.23, 124.88, 124.59, 124.47, 66.13, 66.02, 46.94, 46.92, 45.42, 45.42, 24.48.

ESI-HRMS: Calcd. for [M+NH₄]⁺: 475.1864; Found: 475.1882. Calcd. for [M+Na]⁺: 480.1418; Found: 480.1438.

Synthesis of 2,6-Bis(hydroxymethyl)anthracene-Containing Networks for Calibration Curve

A stock solution (4.8 mg/mL) of 2,6-bis(hydroxymethyl)anthracene in DMA was prepared. An appropriate amount (10 μL for 0.2 mM, 50 μL for 1 mM, or 100 μL for 2 mM) of the solution was added to a scintillation vial and the mass was brought to 1 g with DMA. DEGDA (20 mg) and Irgacure 2959 (1 mg) were added. The solution was cast in circular punches (diameter of ~7 mm)

within a silicone sheet (thickness of ~ 1 mm) placed between two glass slides. The solution was irradiated with a 365 nm light for 10 min to polymerize the networks.

Supplemental Figures

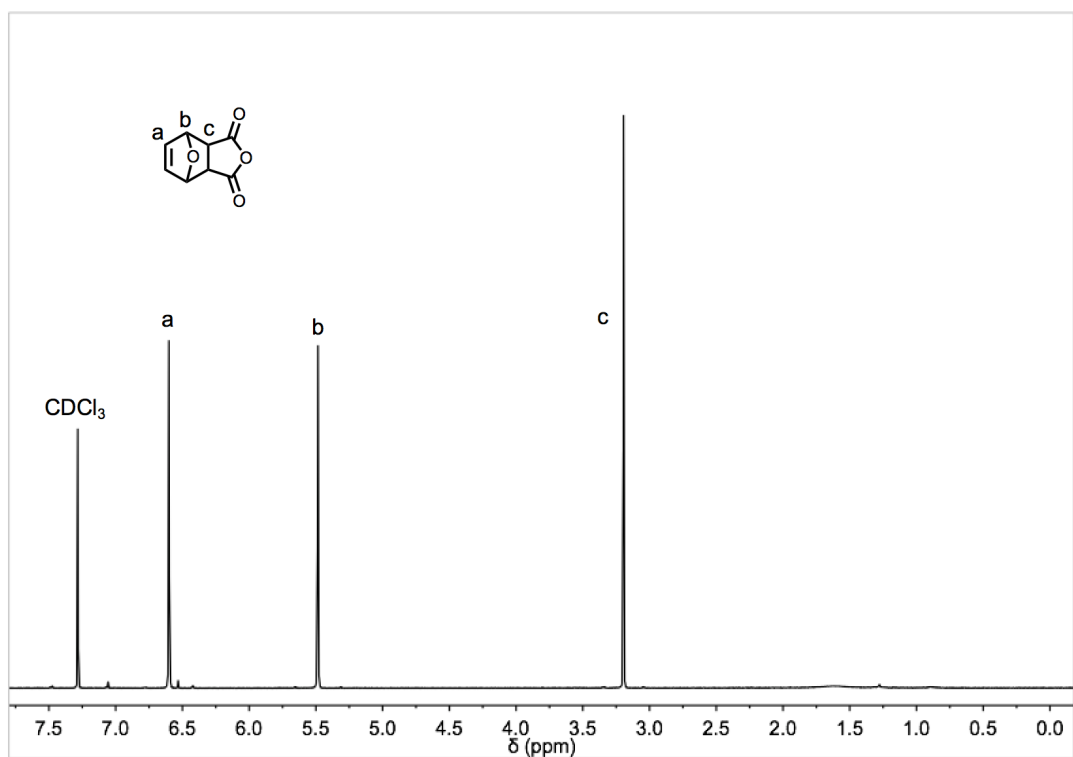


Figure S1. ^1H NMR spectrum of Fur-MAn (500 MHz, CDCl_3)

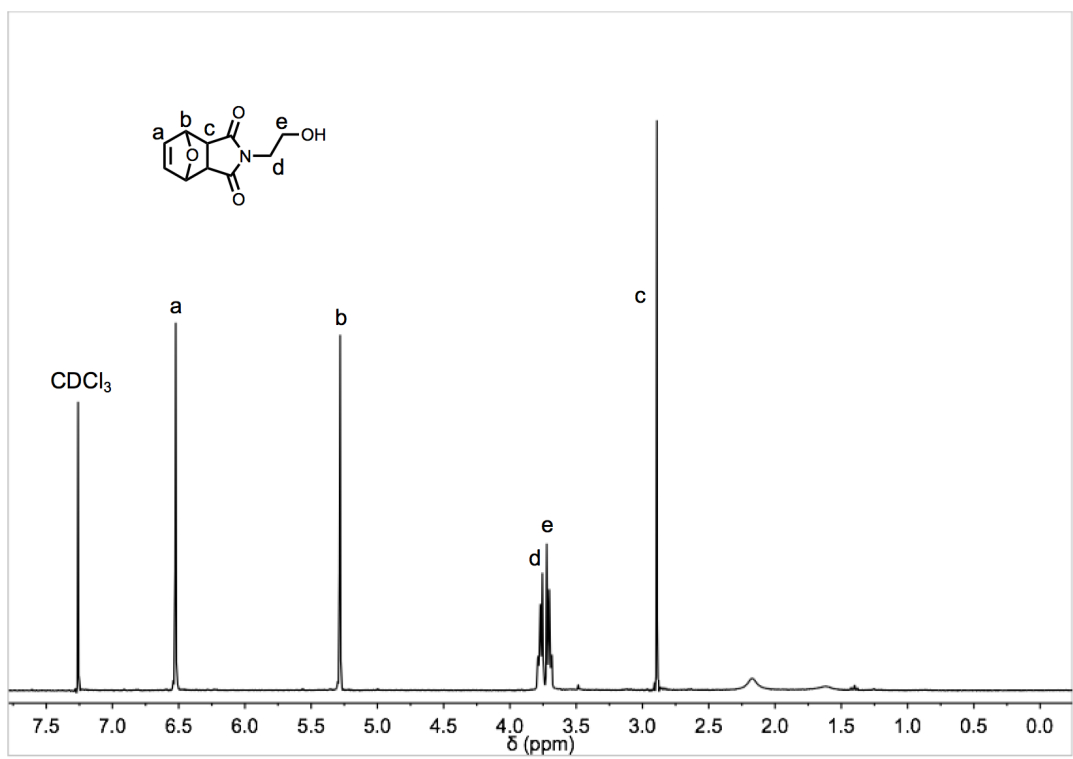


Figure S2. ^1H NMR spectrum of Fur-MalOH (500 MHz, CDCl_3)

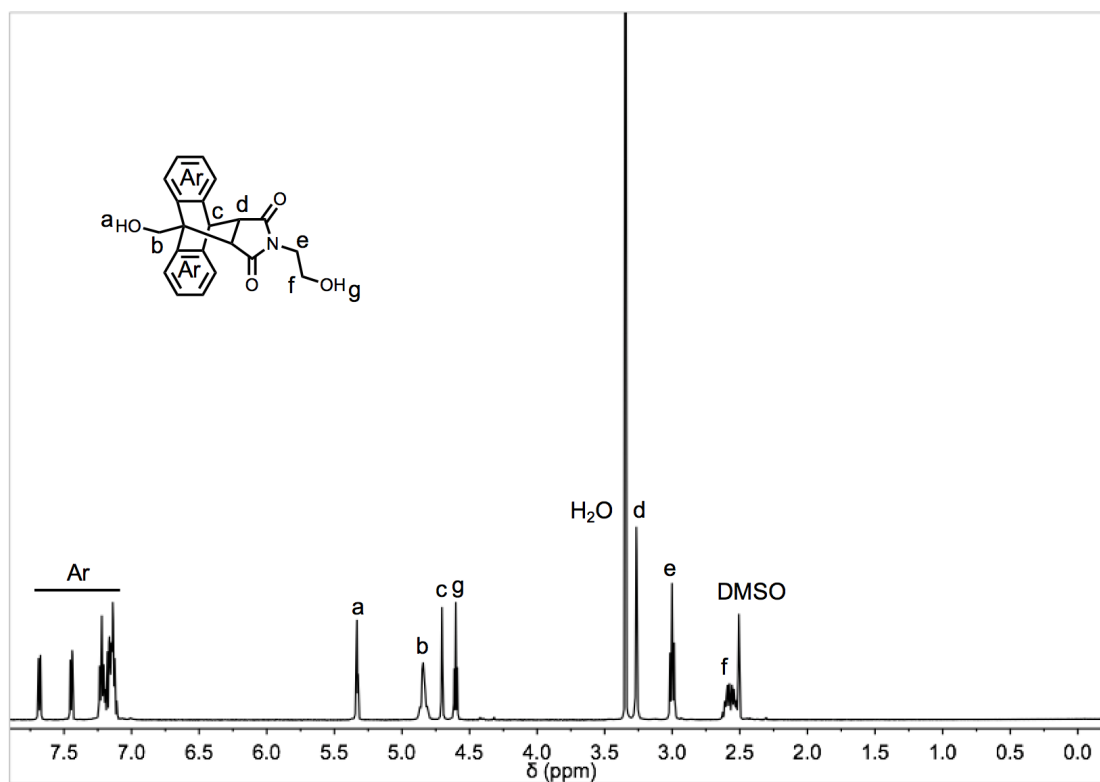


Figure S3. ^1H NMR spectrum of AnthOH-MalOH (500 MHz, $\text{DMSO}-d_6$)

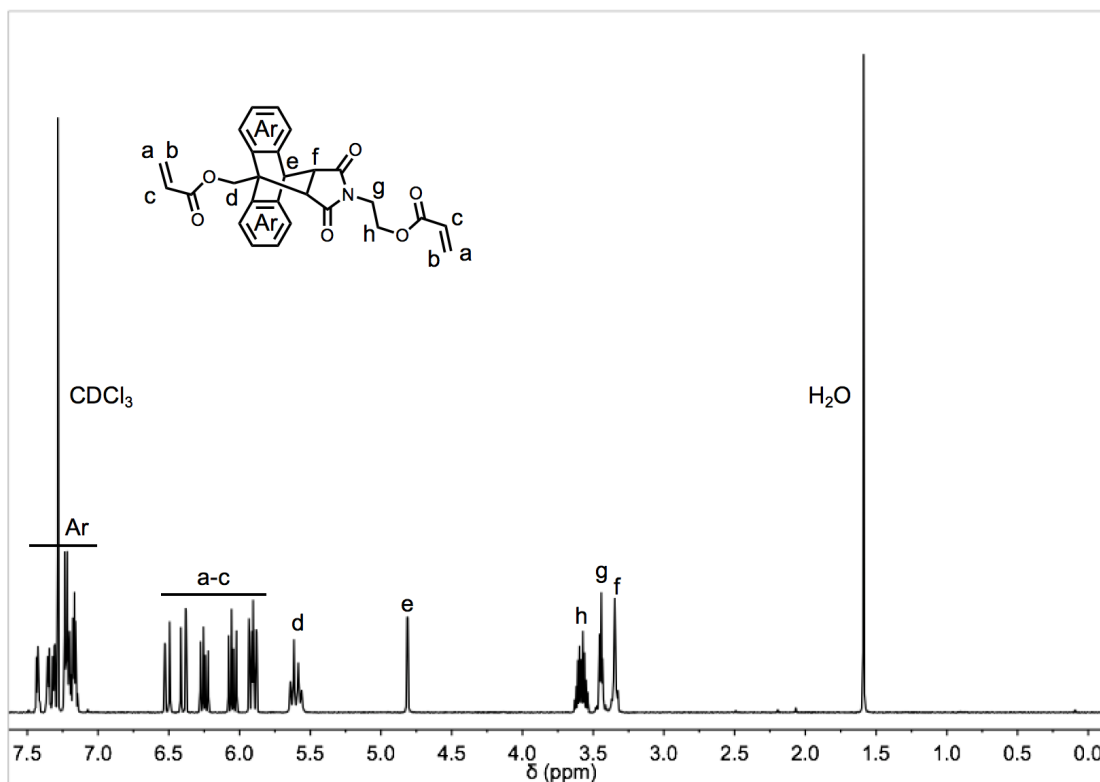


Figure S4. ^1H NMR spectrum of **1** (500 MHz, CDCl_3)

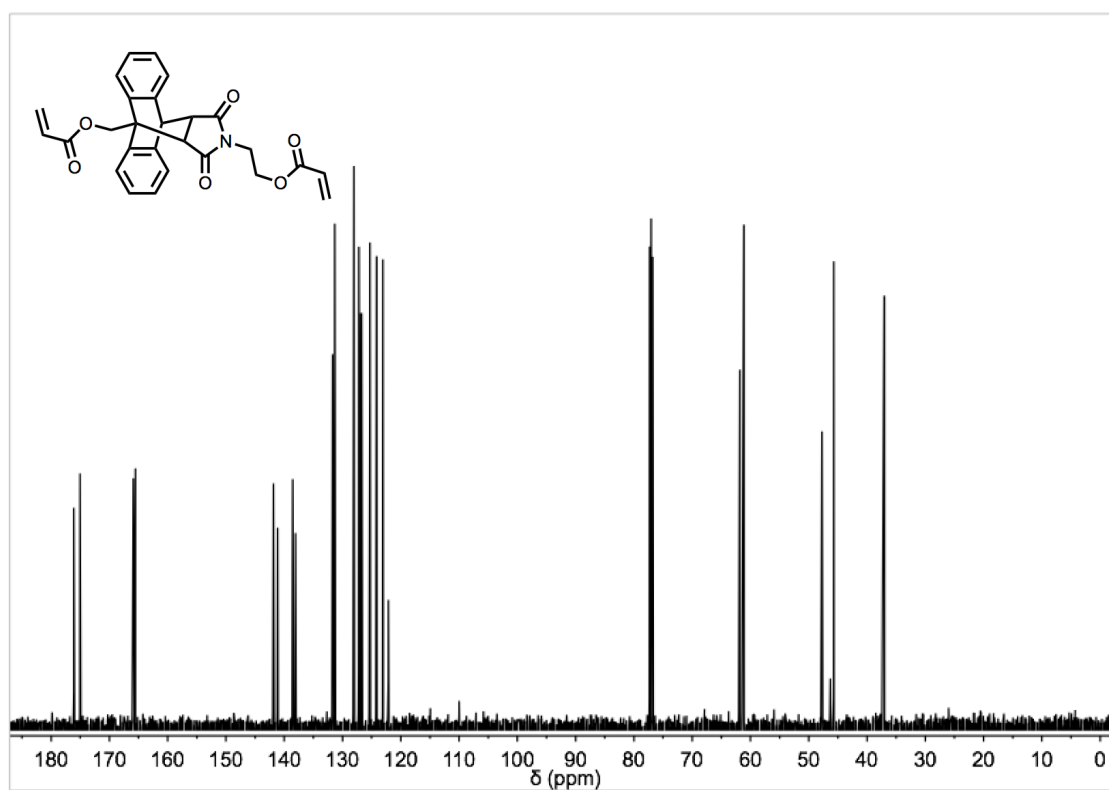


Figure S5. ^{13}C NMR spectrum of 1 (125 MHz, CDCl_3)

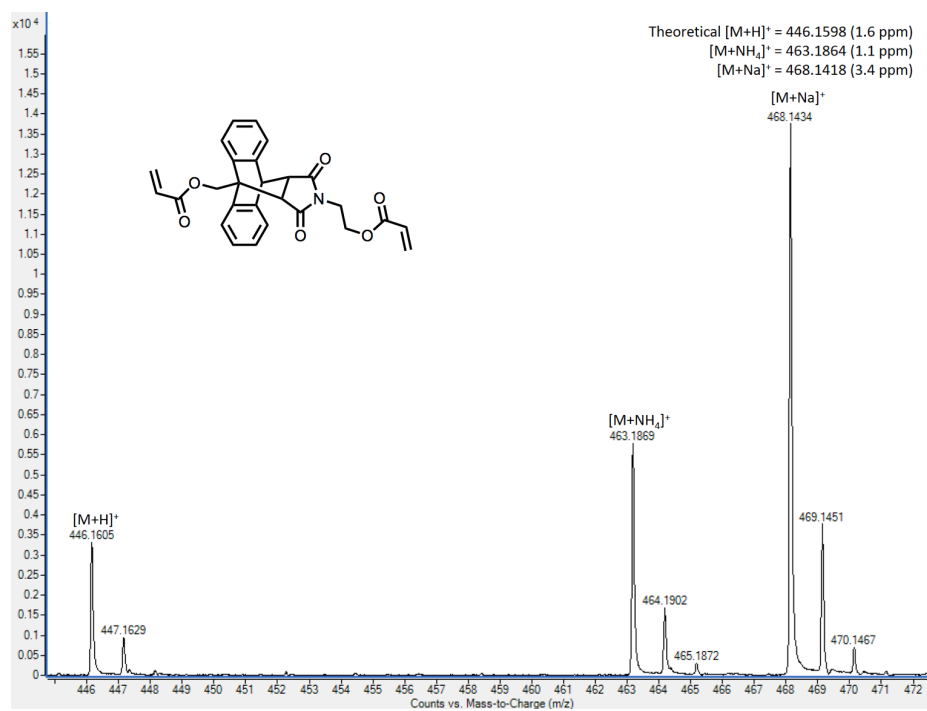


Figure S6. ESI-HRMS spectrum of 1

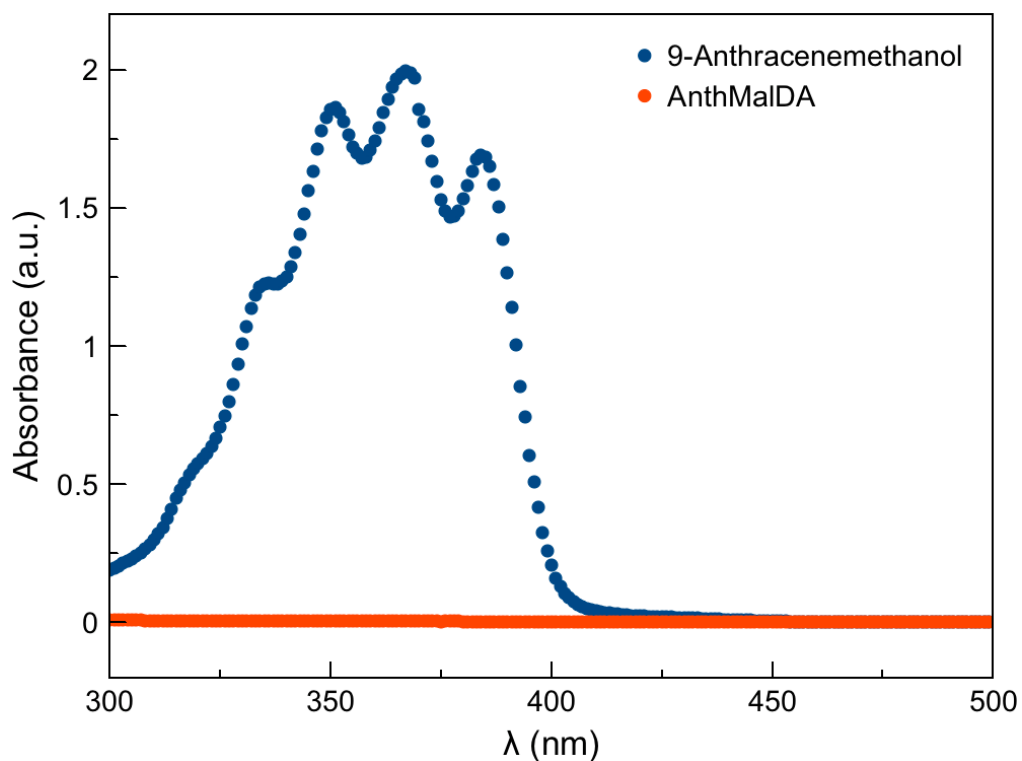


Figure S7. UV-vis absorption spectra (0.2 mM in DMSO) of 9-anthracenemethanol (blue) and 1 (orange)

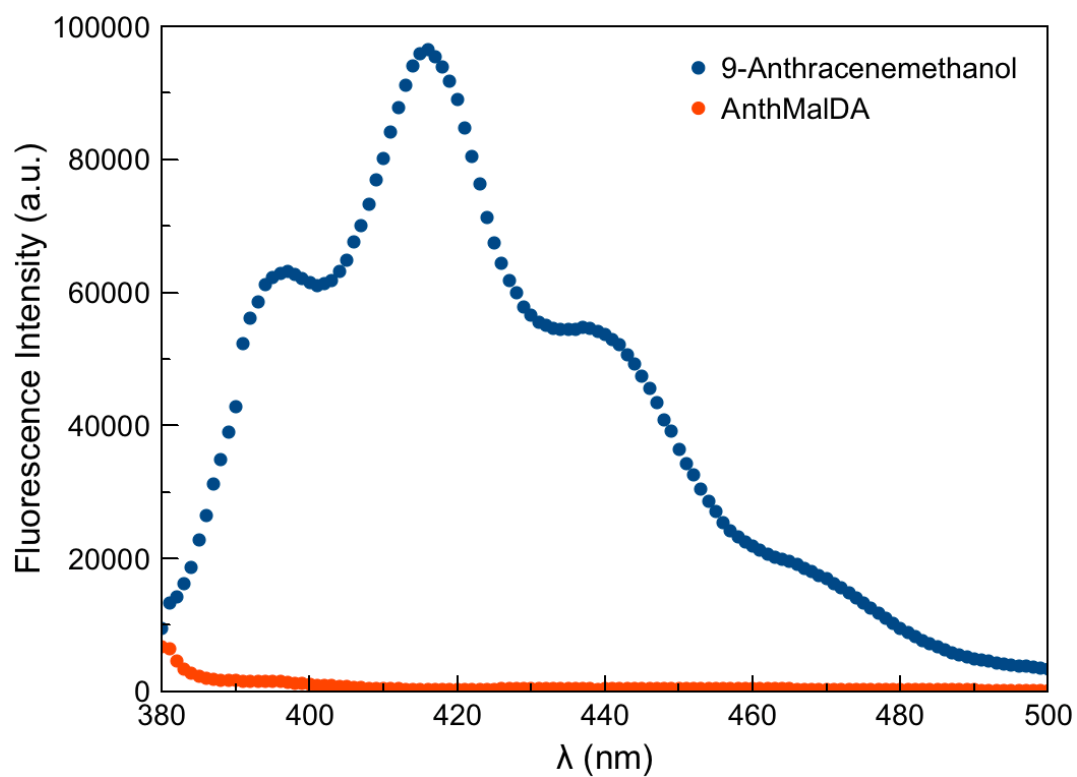


Figure S8. Fluorescence spectra (0.2 mM in DMSO) of 9-anthracenemethanol (blue) and 1 (orange)

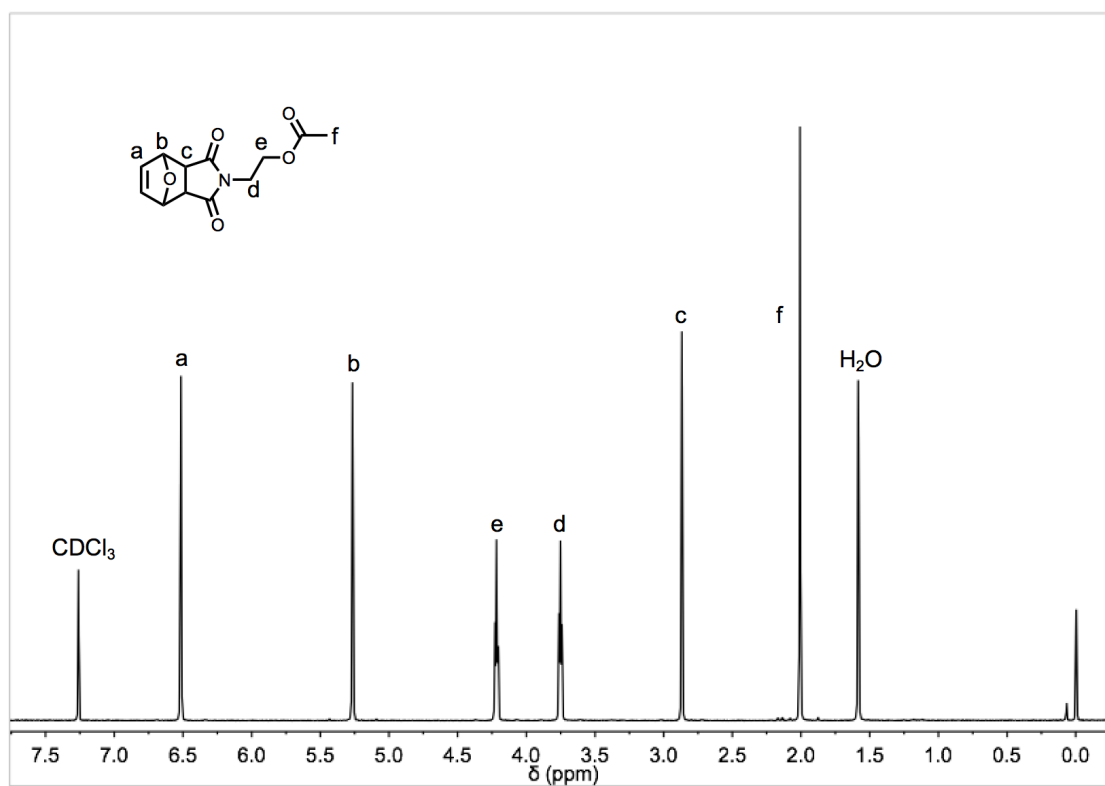


Figure S9. ^1H NMR spectrum of Fur-MalOAc (500 MHz, CDCl_3)

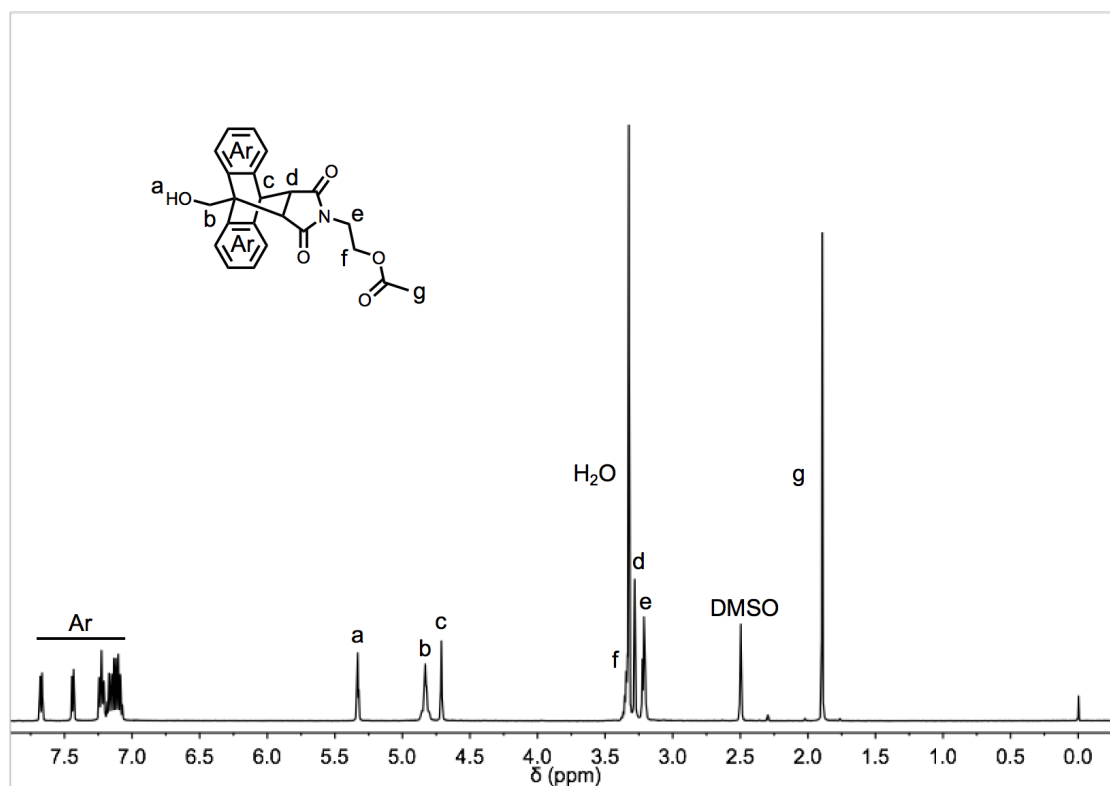


Figure S10. ^1H NMR spectrum of AnthOH-MalOAc (500 MHz, $\text{DMSO}-d_6$)

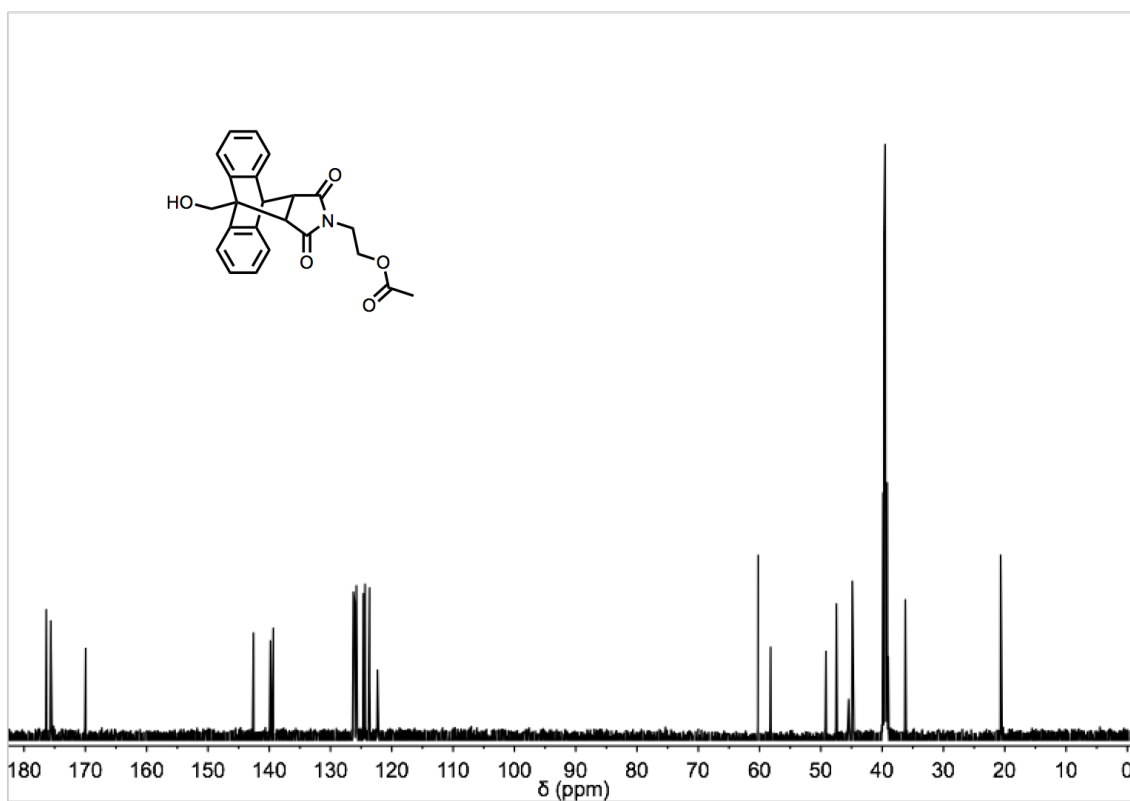


Figure S11. ^{13}C NMR spectrum of AnthOH-MalOAc (125 MHz, $\text{DMSO}-d_6$)

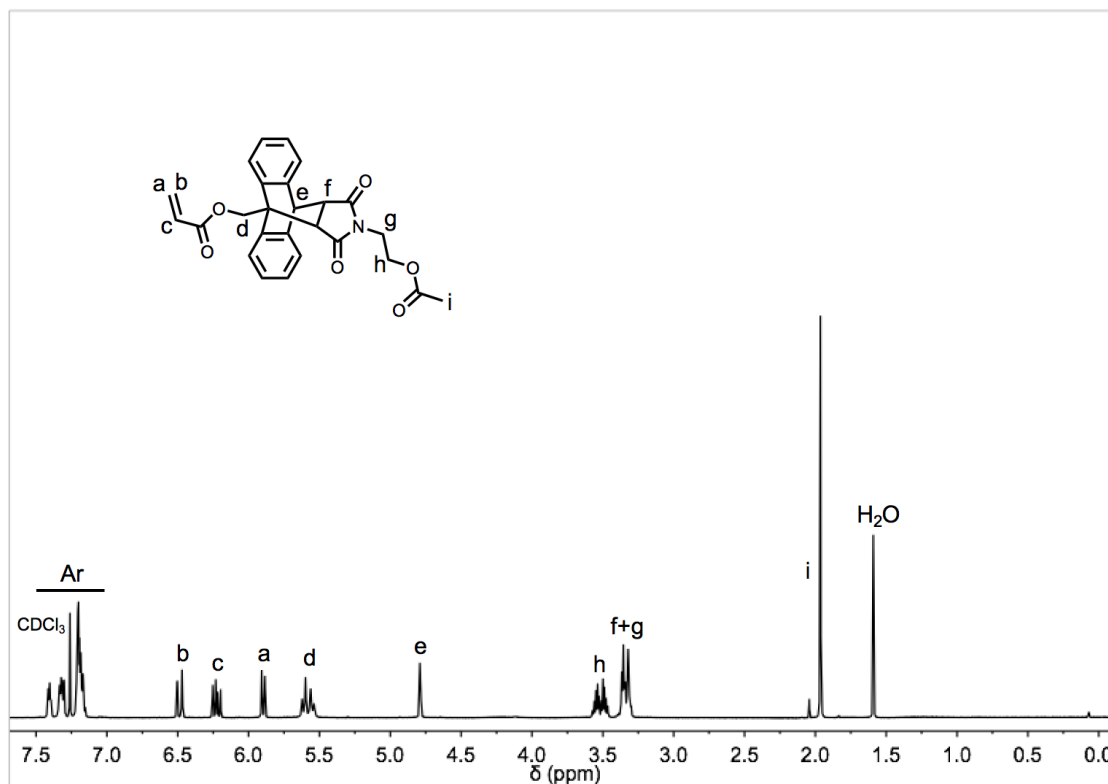


Figure S12. ^1H NMR spectrum of 2 Monomer (500 MHz, CDCl_3)

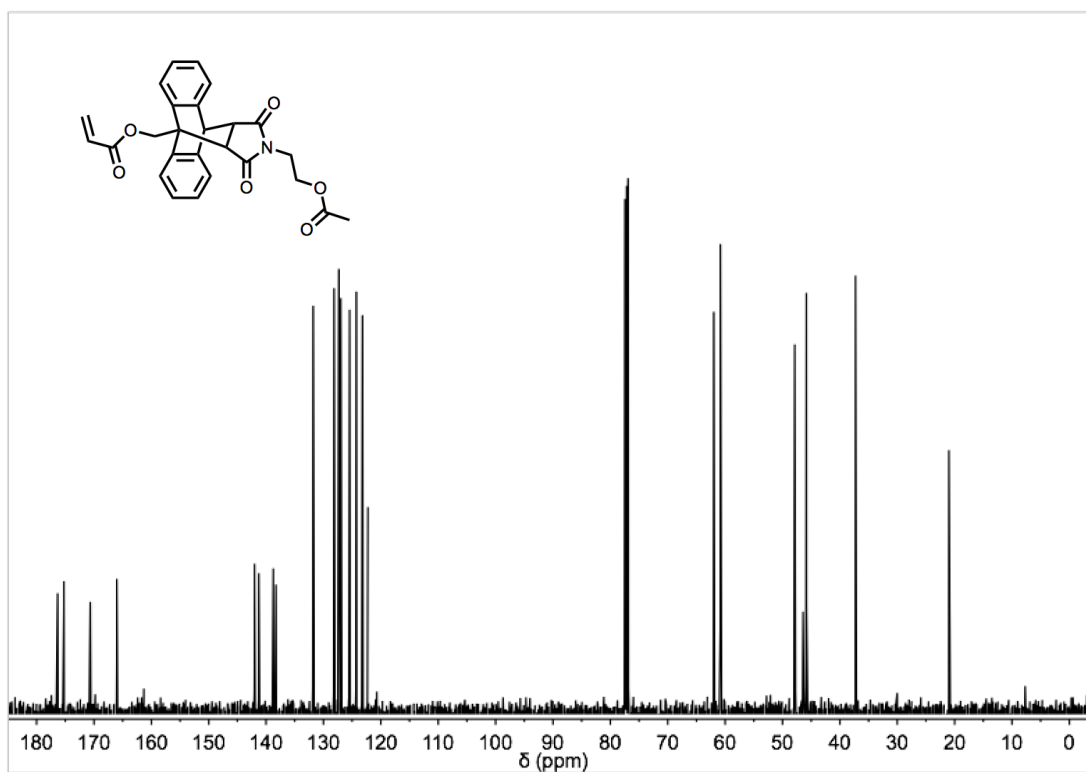


Figure S13. ^{13}C NMR spectrum of 2 Monomer (125 MHz, CDCl_3)

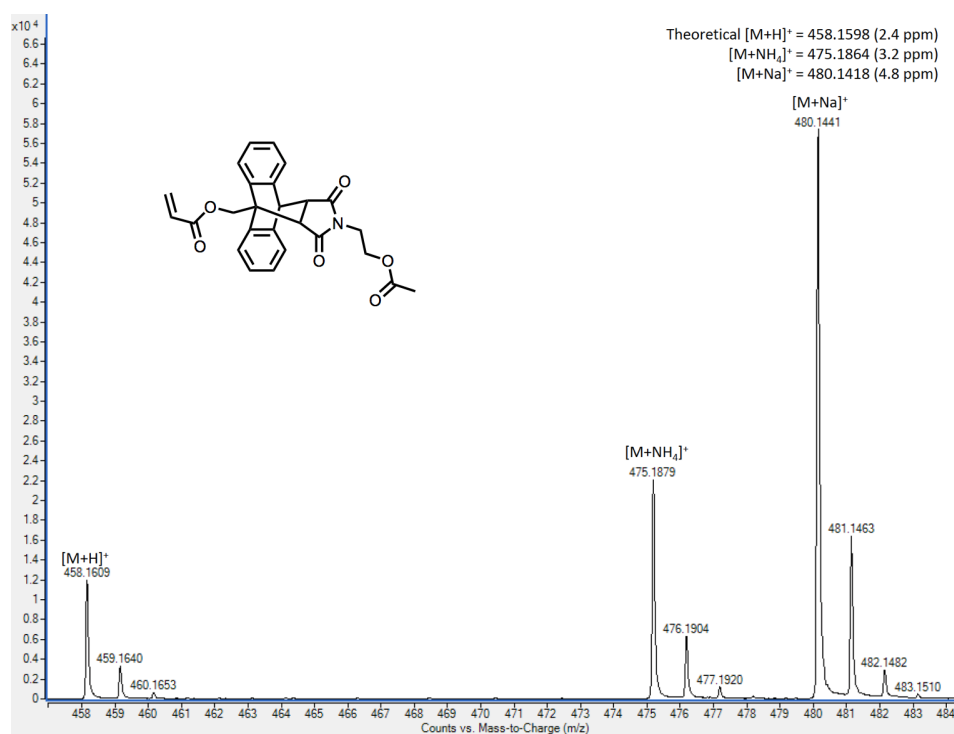


Figure S14. ESI-HRMS spectrum of 2 Monomer

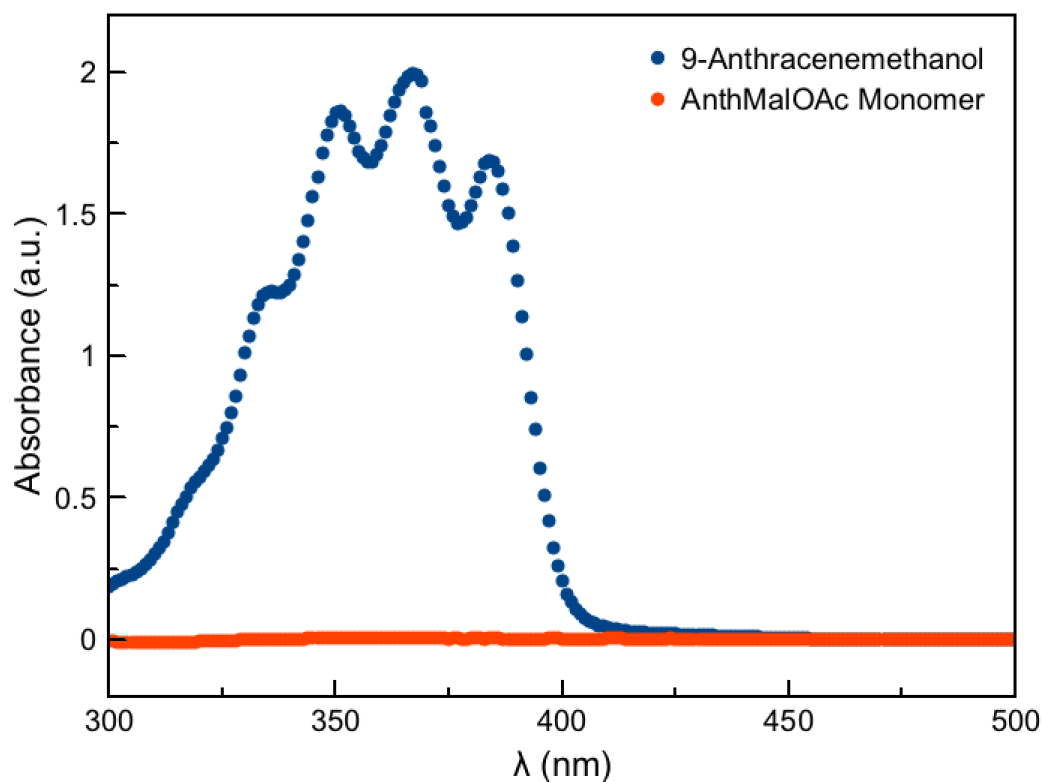


Figure S15. UV-vis absorption spectra (0.2 mM in DMSO) of 9-anthracenemethanol (blue) and 2 monomer (orange)

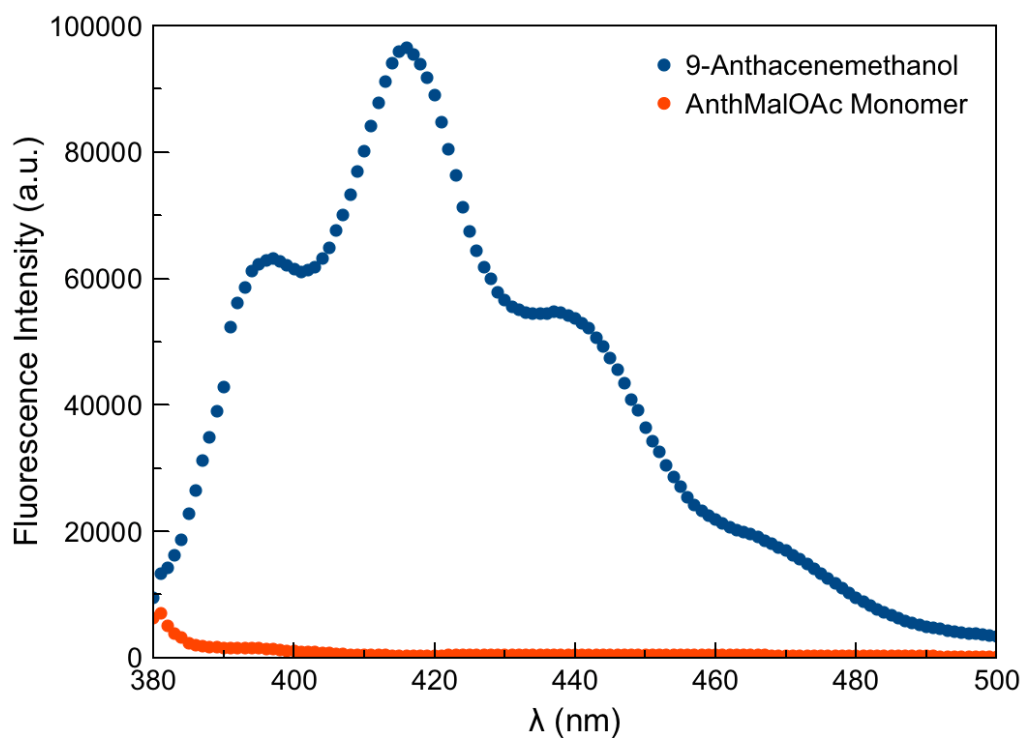


Figure S16. Fluorescence spectra (0.2 mM in DMSO) of 9-anthracenemethanol (blue) and 2 monomer (orange)

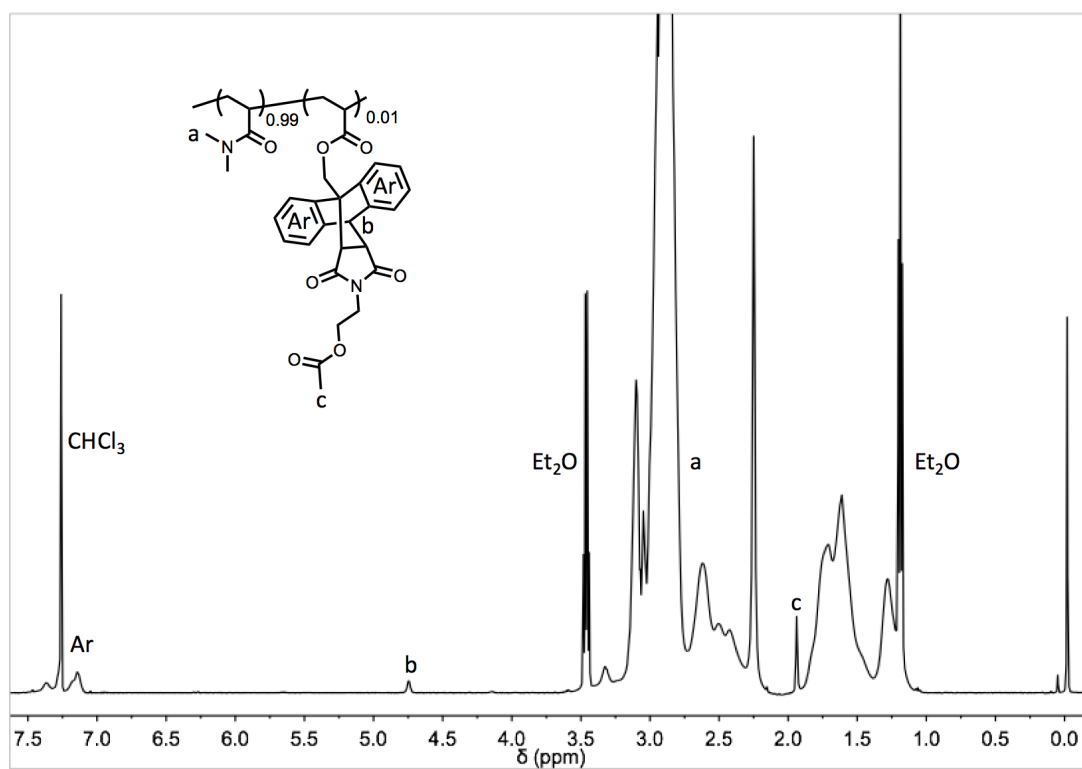


Figure S17. ^1H NMR spectrum of $\text{P}(\text{DMA}_{0.99}\text{-co-}2_{0.01})$ (500 MHz, CDCl_3)

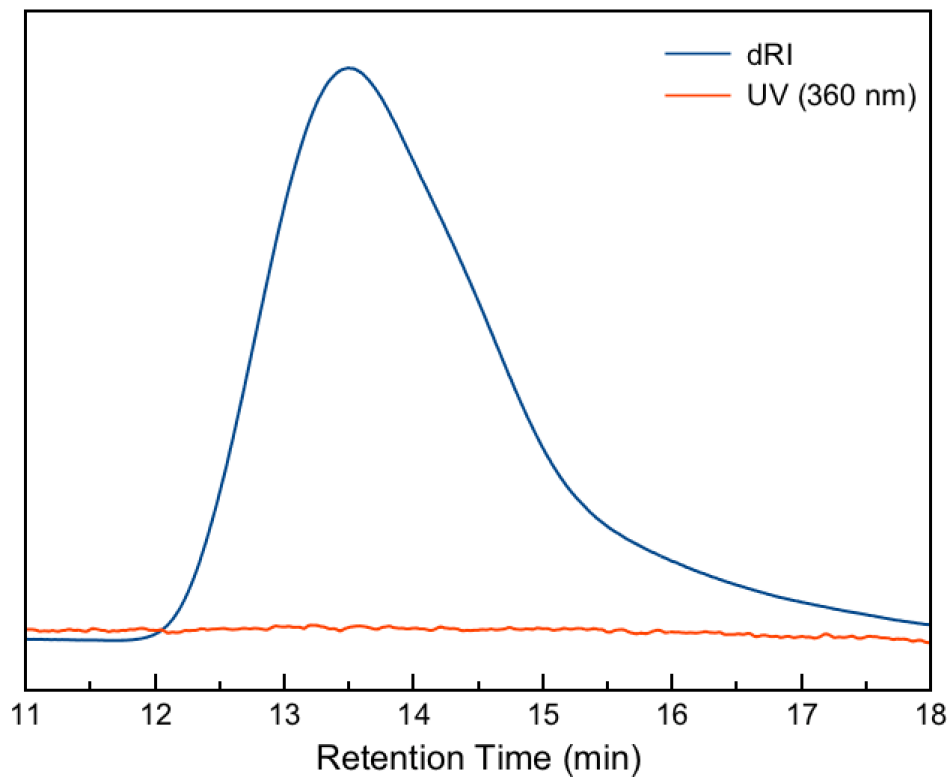


Figure S18. GPC spectra of $\text{P}(\text{DMA}_{0.99}\text{-co-}2_{0.01})$ with differential refractive index (blue) and UV (360 nm, orange) detection

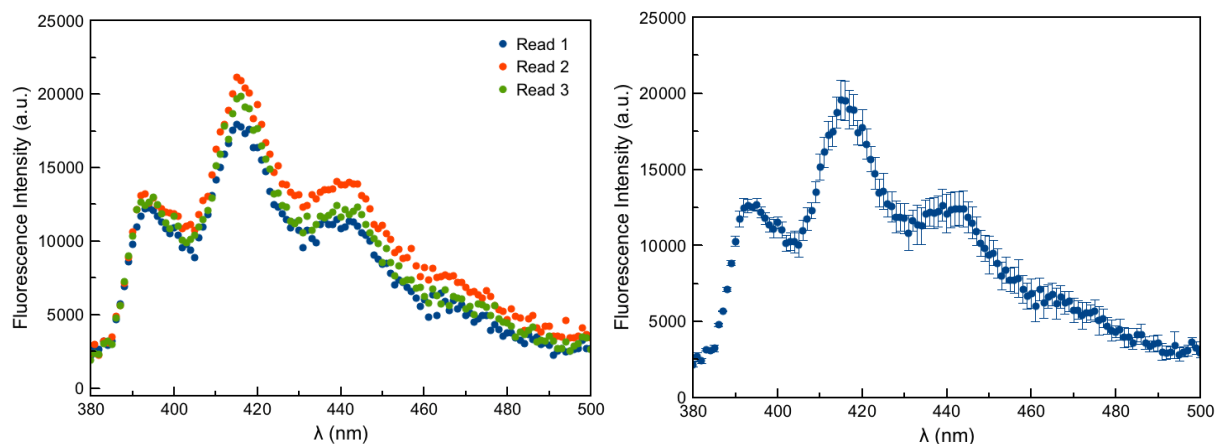


Figure S19. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 50 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 50 MPa for 10 s.

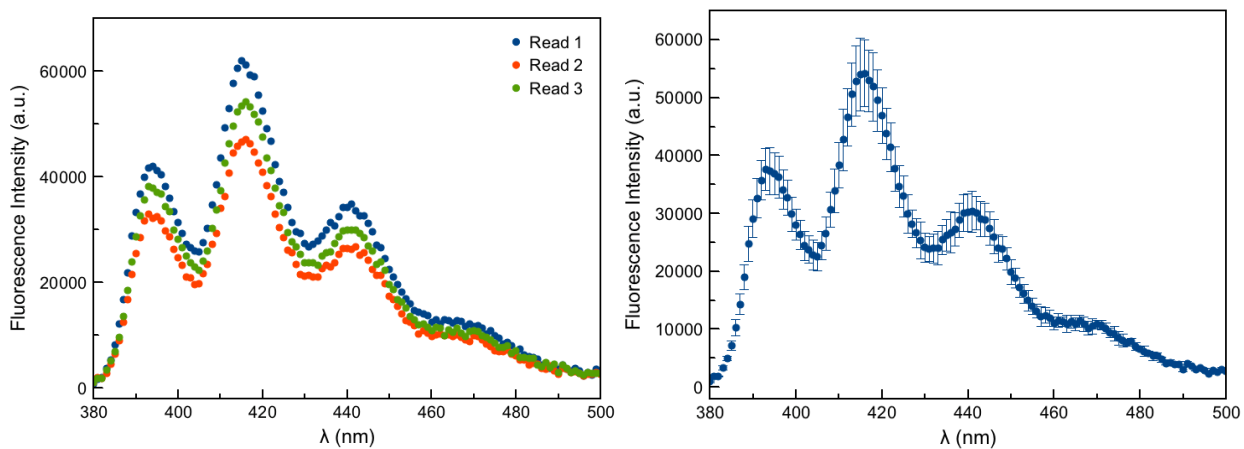


Figure S20. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 150 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 150 MPa for 10 s.

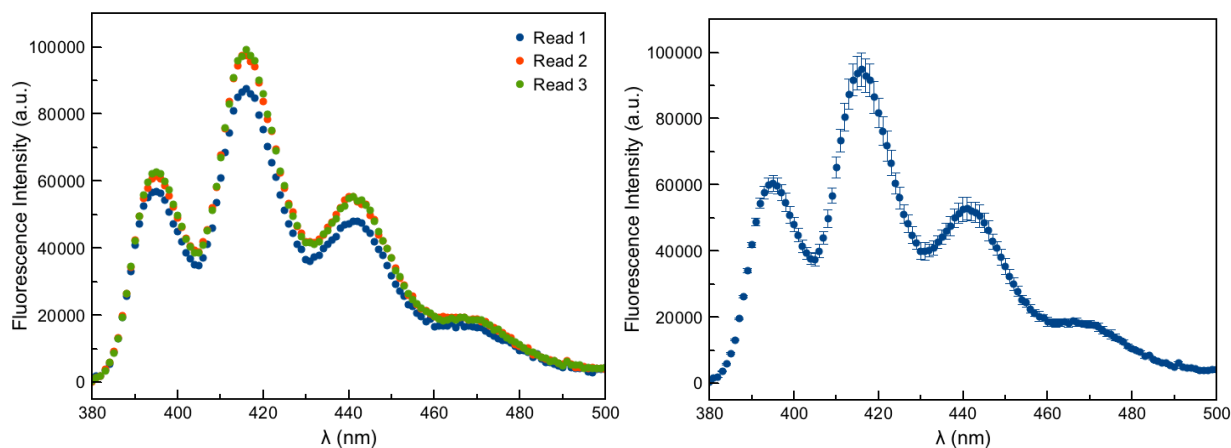


Figure S21. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 275 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 275 MPa for 10 s.

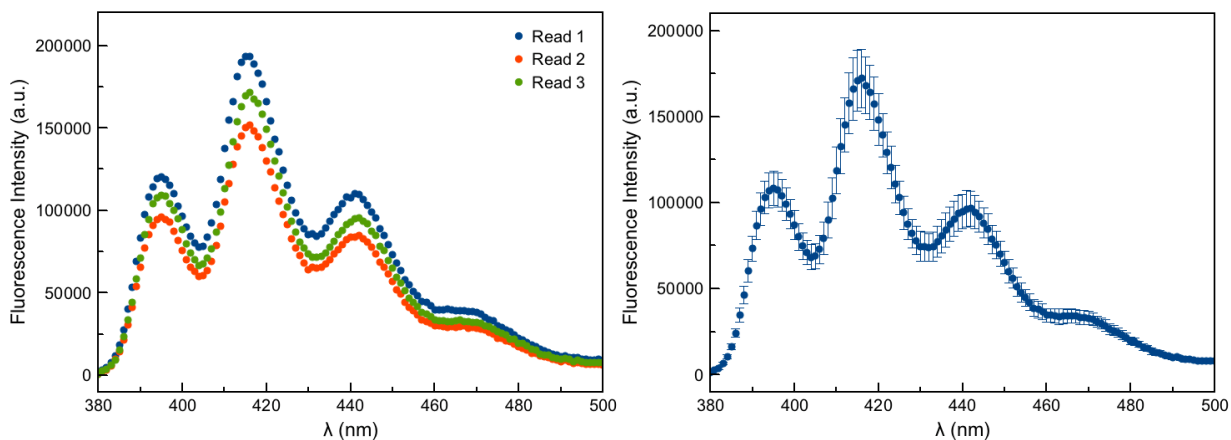


Figure S22. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 400 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 400 MPa for 10 s.

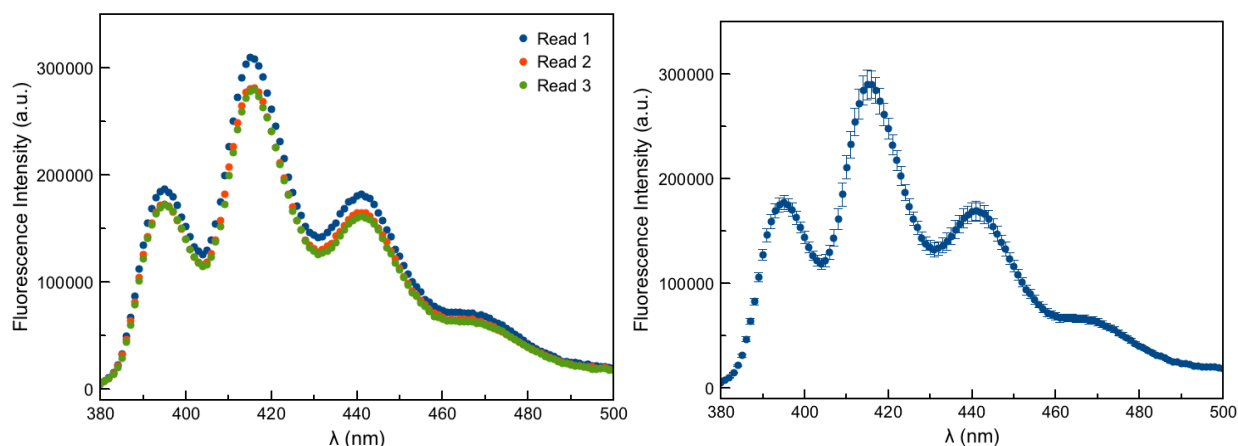


Figure S23. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 500 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 500 MPa for 10 s.

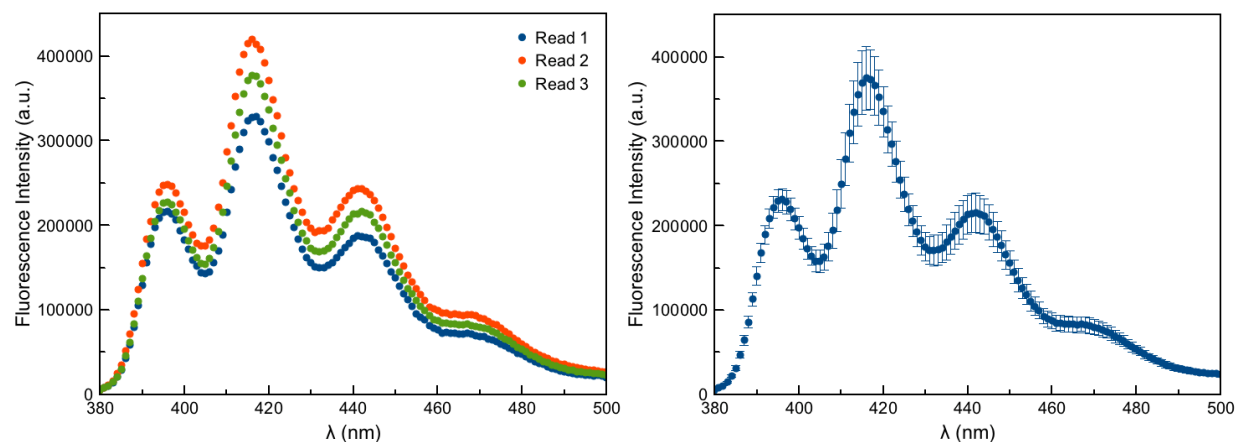


Figure S24. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 560 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 560 MPa for 10 s.

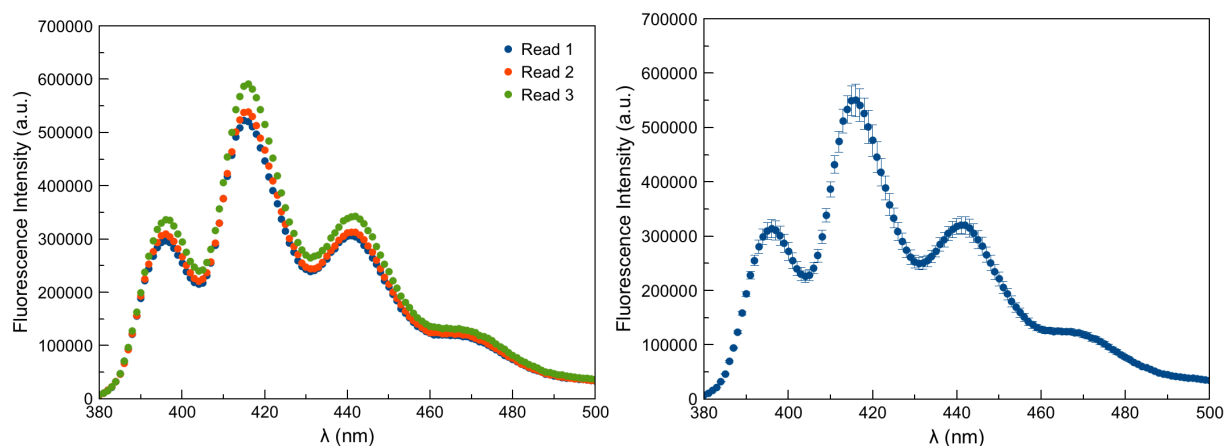


Figure S25. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 700 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 700 MPa for 10 s.

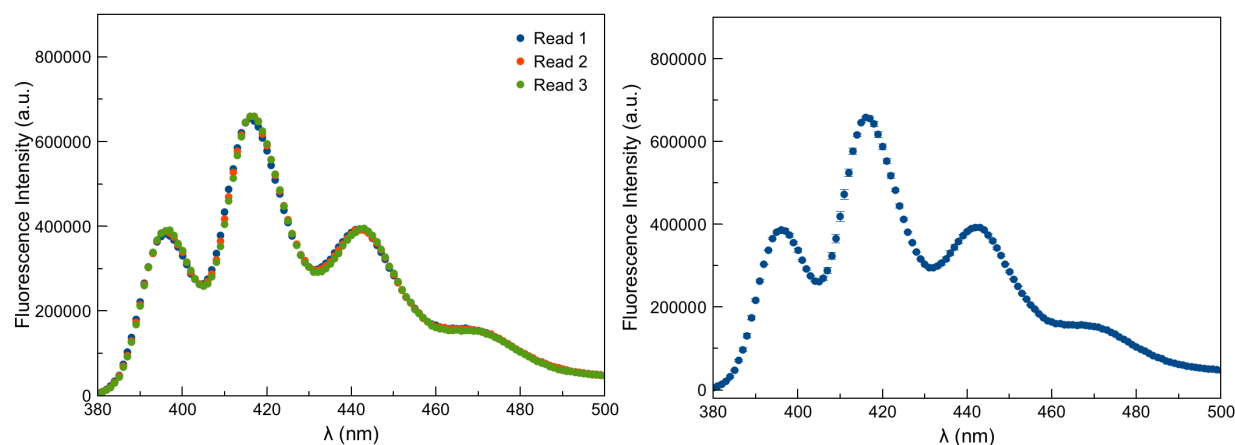


Figure S26. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 800 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 800 MPa for 10 s.

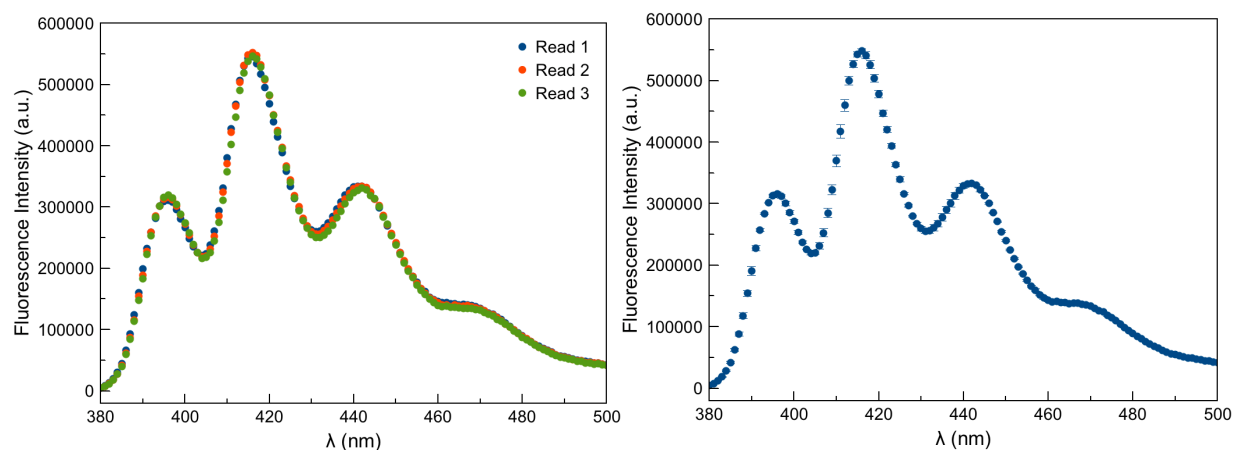


Figure S27. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 900 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 900 MPa for 10 s.

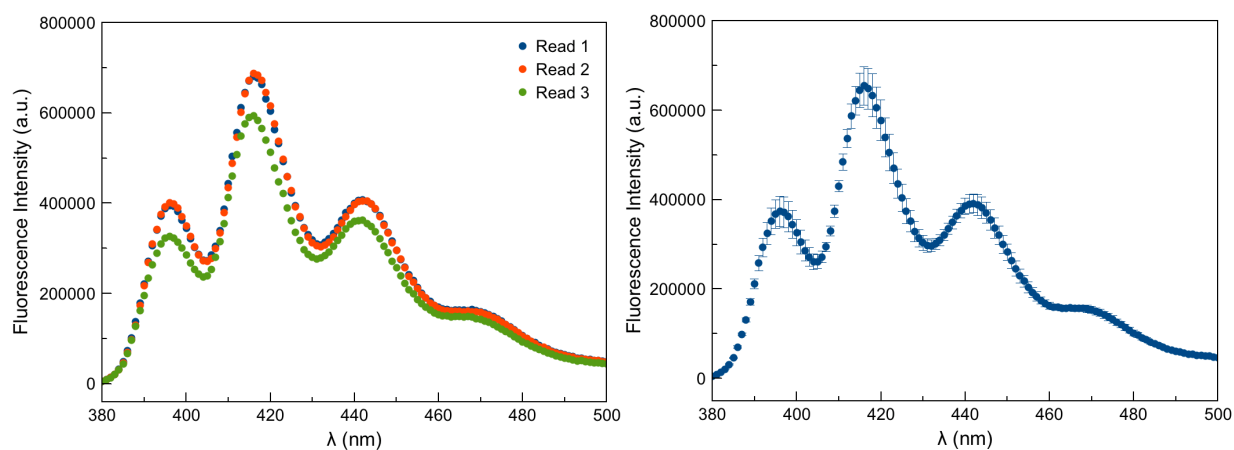


Figure S28. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 1065 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1 = 99:1) that was compressed with a pressure of 1065 MPa for 10 s.

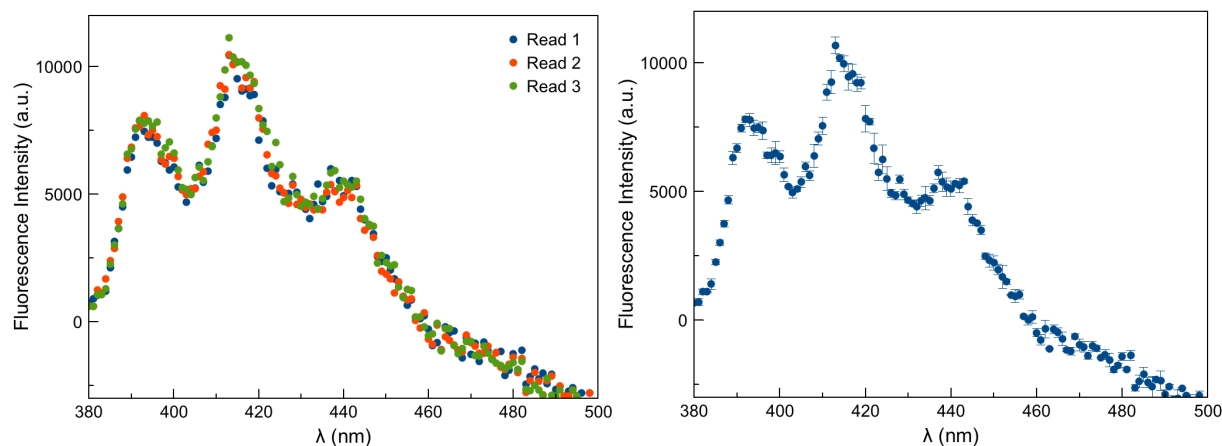


Figure S29. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 50 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 50 MPa for 10 s.

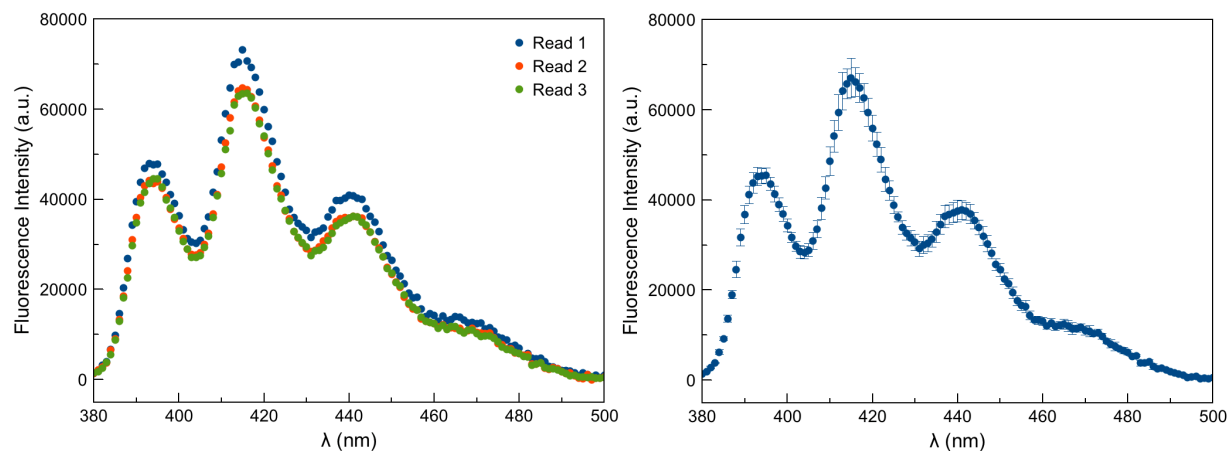


Figure S30. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 150 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 150 MPa for 10 s.

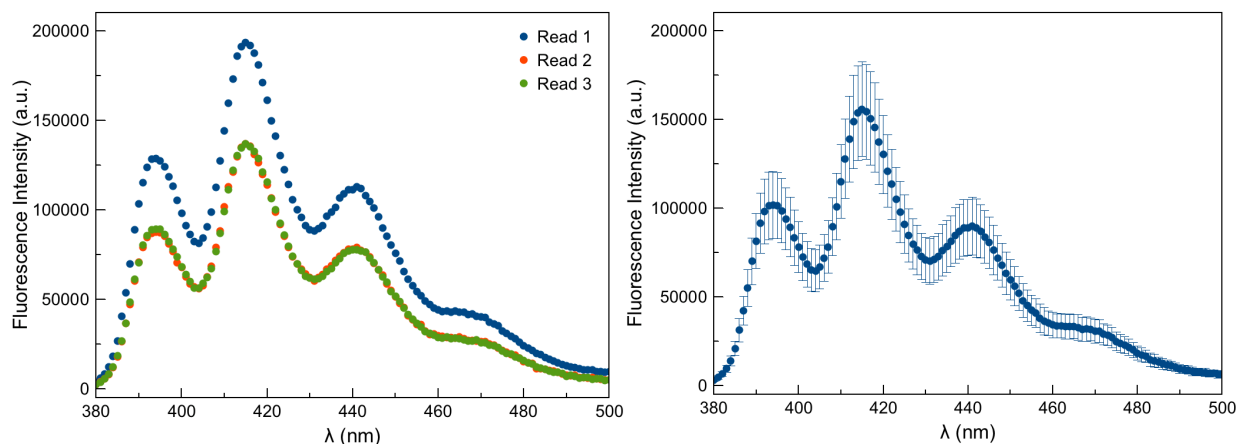


Figure S31. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 275 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 275 MPa for 10 s.

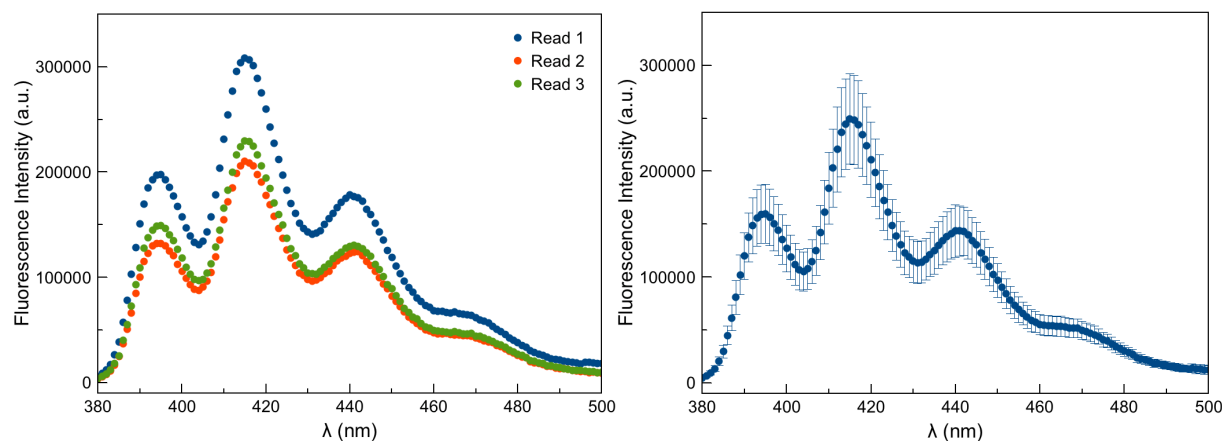


Figure S32. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 400 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 400 MPa for 10 s.

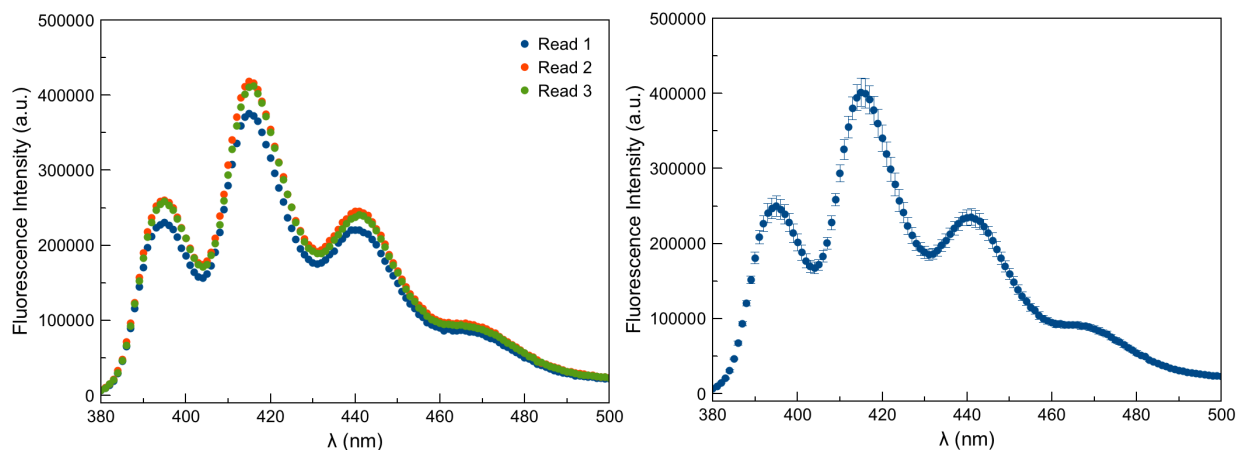


Figure S33. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 500 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 500 MPa for 10 s.

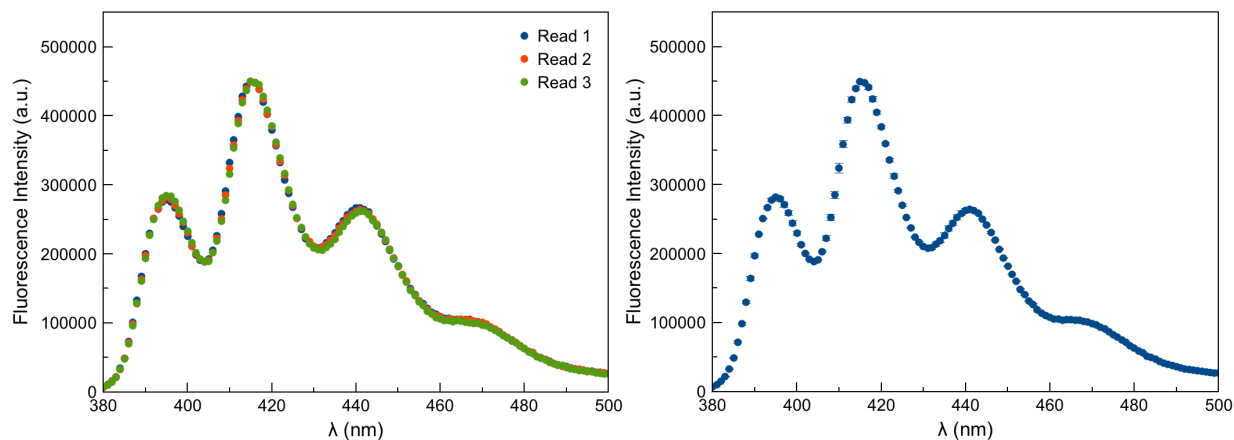


Figure S34. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 560 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 560 MPa for 10 s.

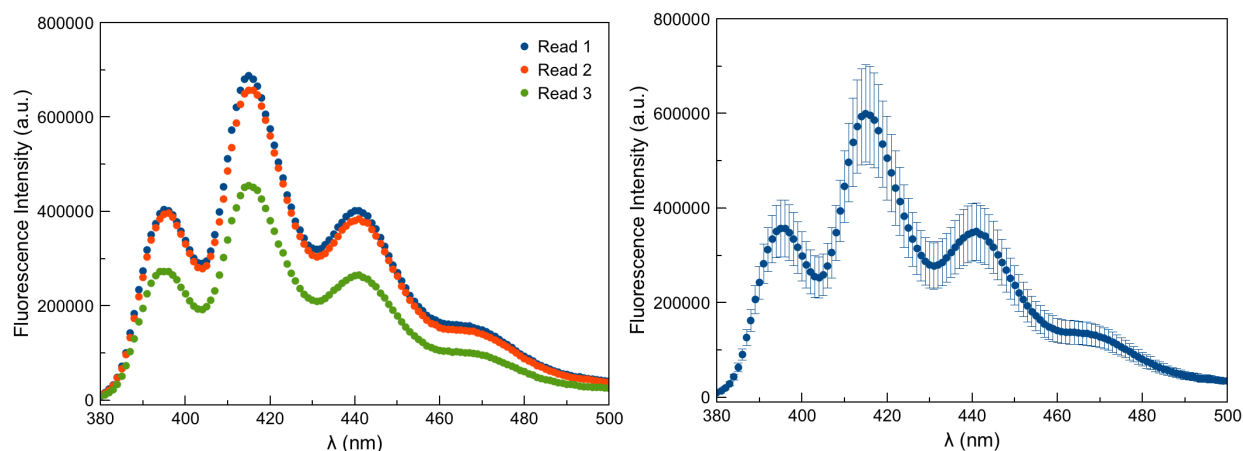


Figure S35. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 700 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 700 MPa for 10 s.

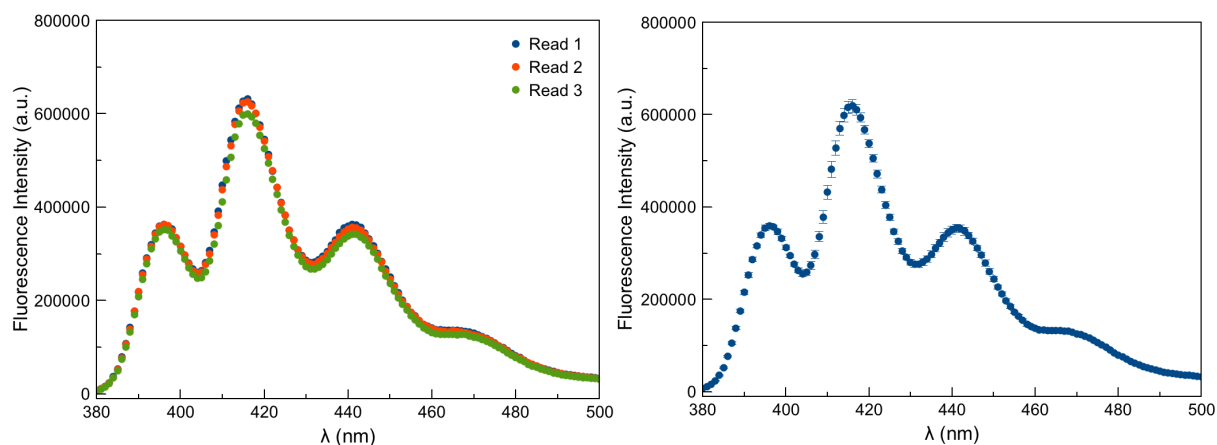


Figure S36. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 800 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 800 MPa for 10 s.

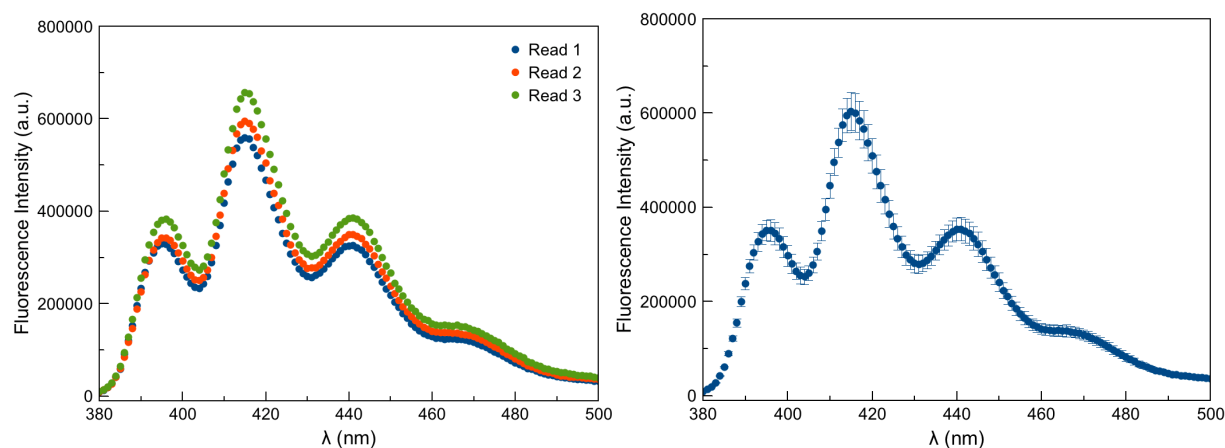


Figure S37. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 900 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 900 MPa for 10 s.

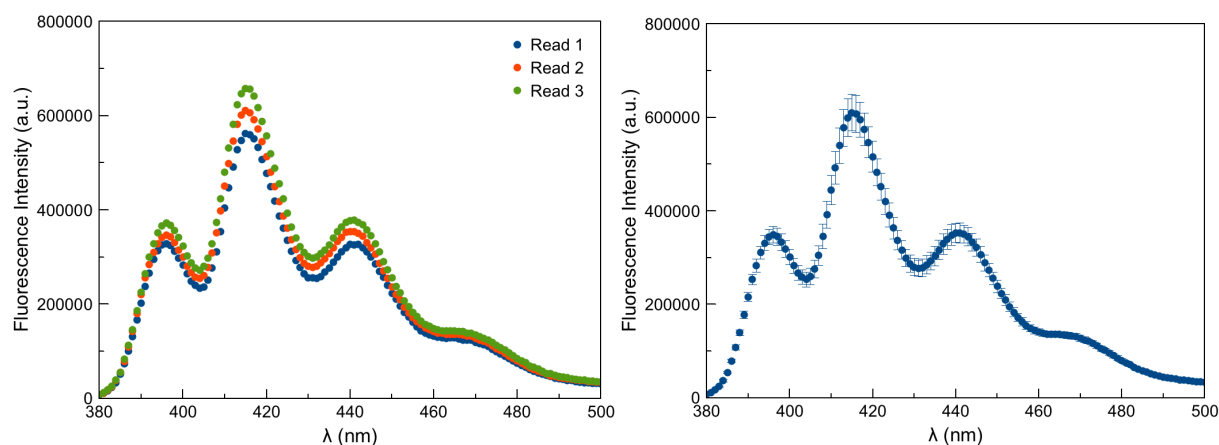


Figure S38. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 1065 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:4) that was compressed with a pressure of 1065 MPa for 10 s.

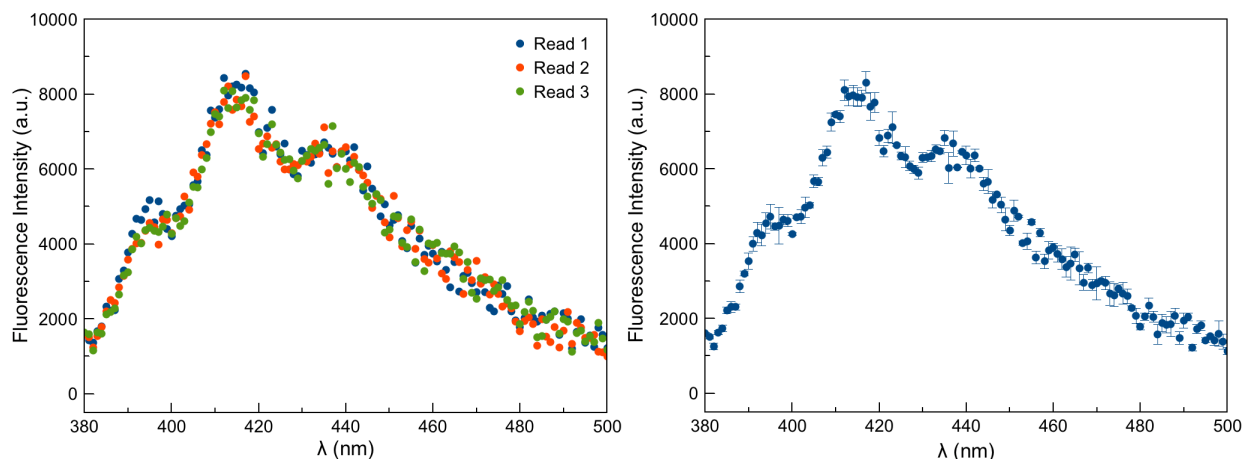


Figure S39. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 50 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 50 MPa for 10 s.

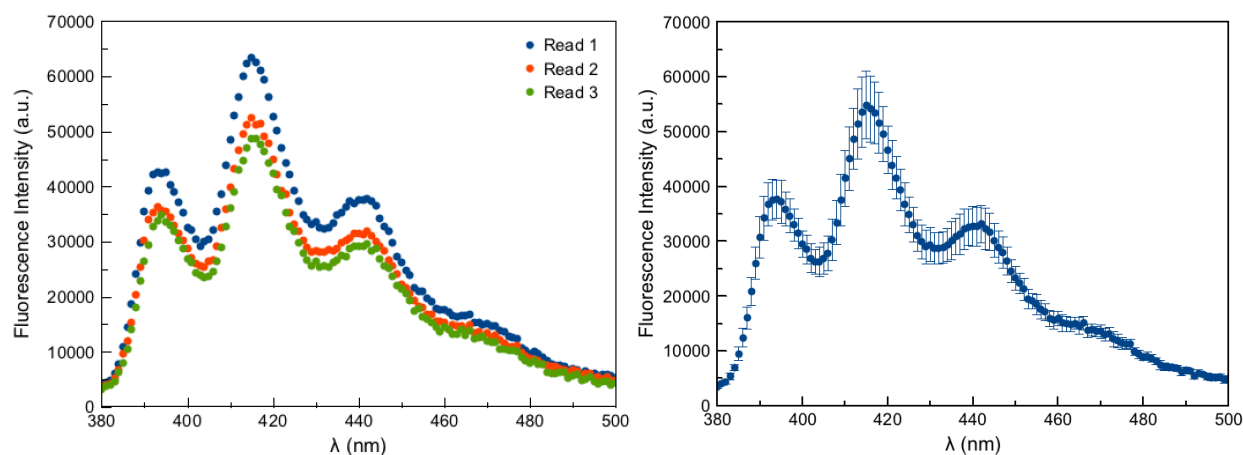


Figure S40. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 150 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 150 MPa for 10 s.

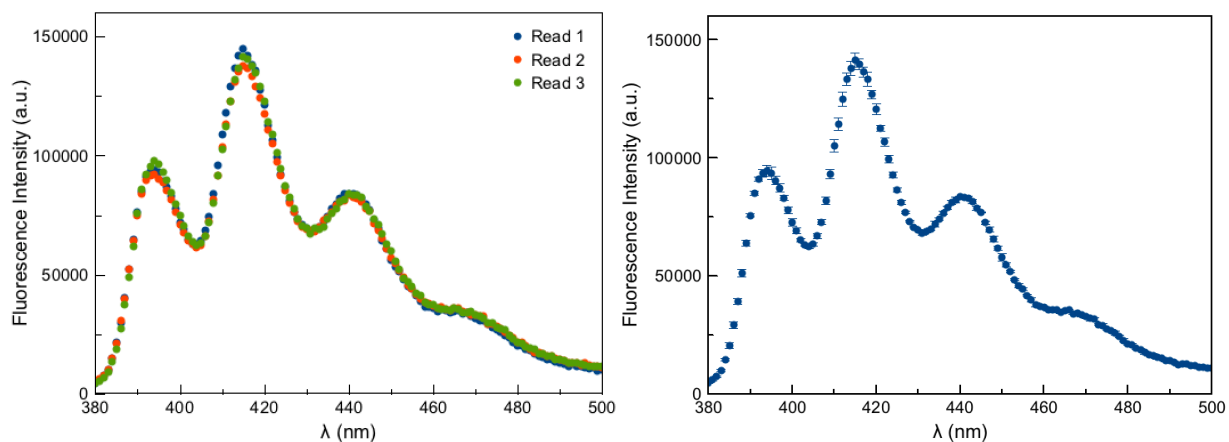


Figure S41. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 275 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 275 MPa for 10 s.

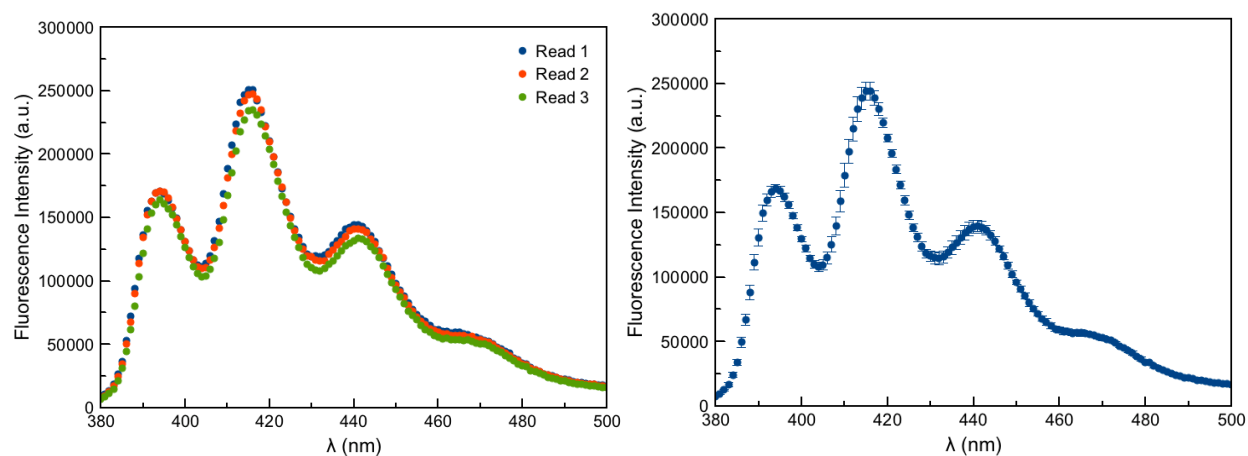


Figure S42. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 400 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 400 MPa for 10 s.

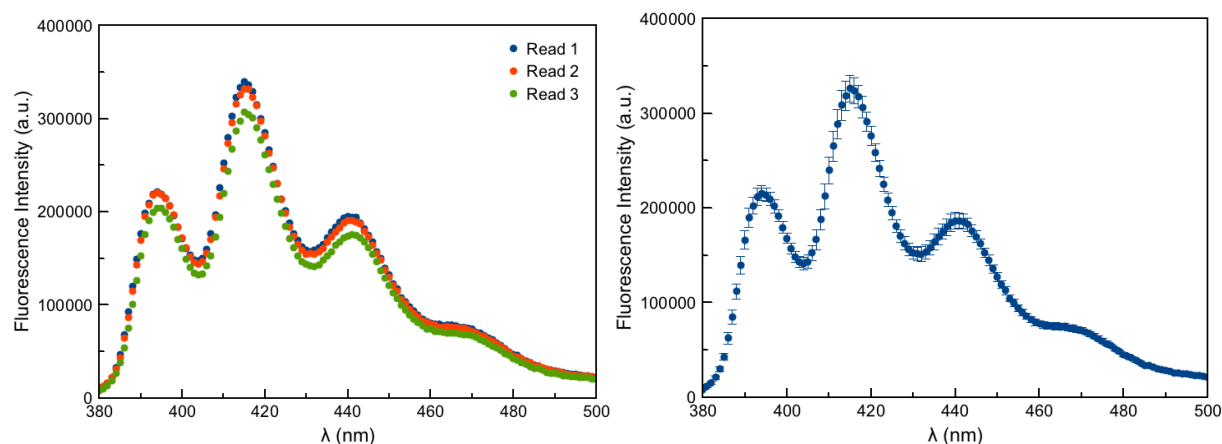


Figure S43. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 500 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 500 MPa for 10 s.

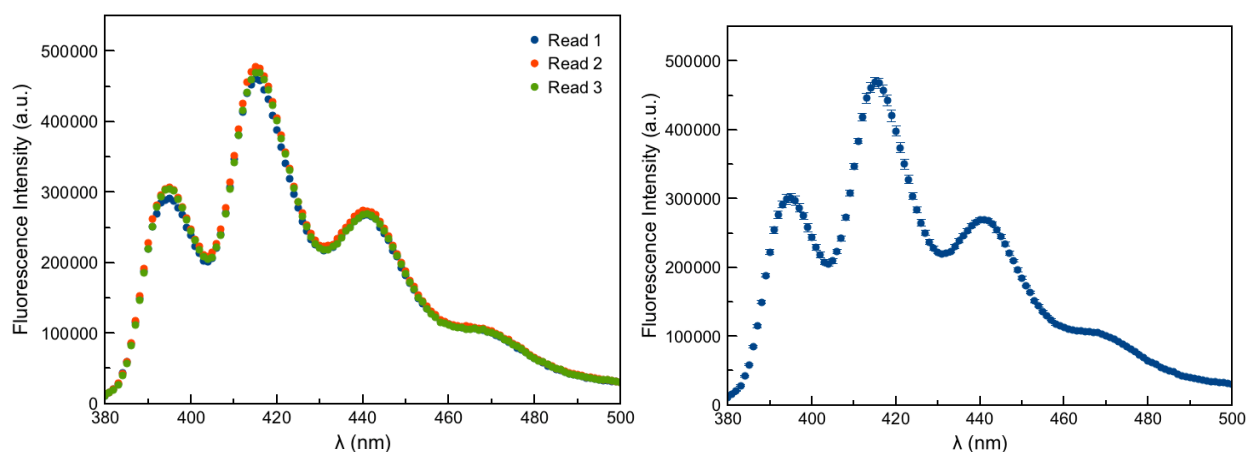


Figure S44. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 560 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 560 MPa for 10 s.

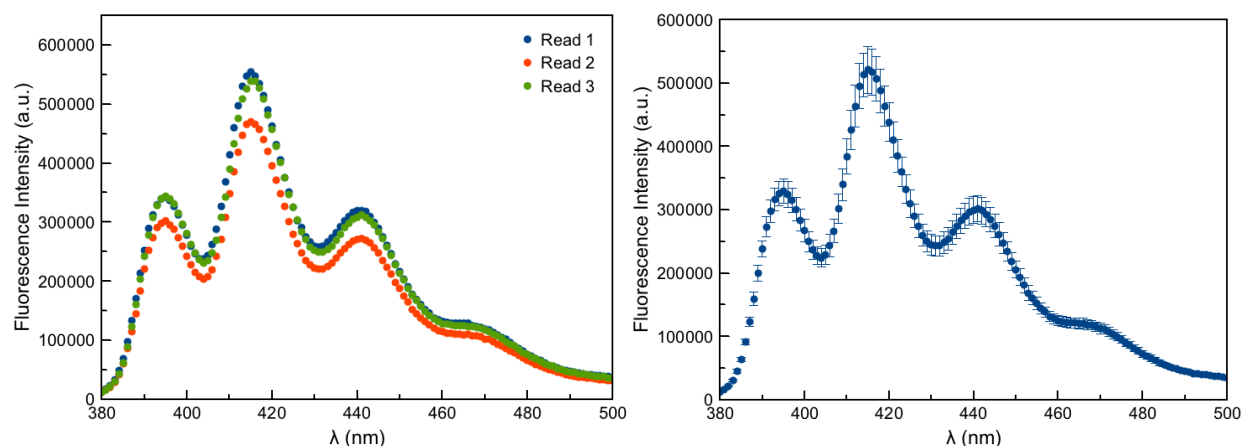


Figure S45. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 700 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 700 MPa for 10 s.

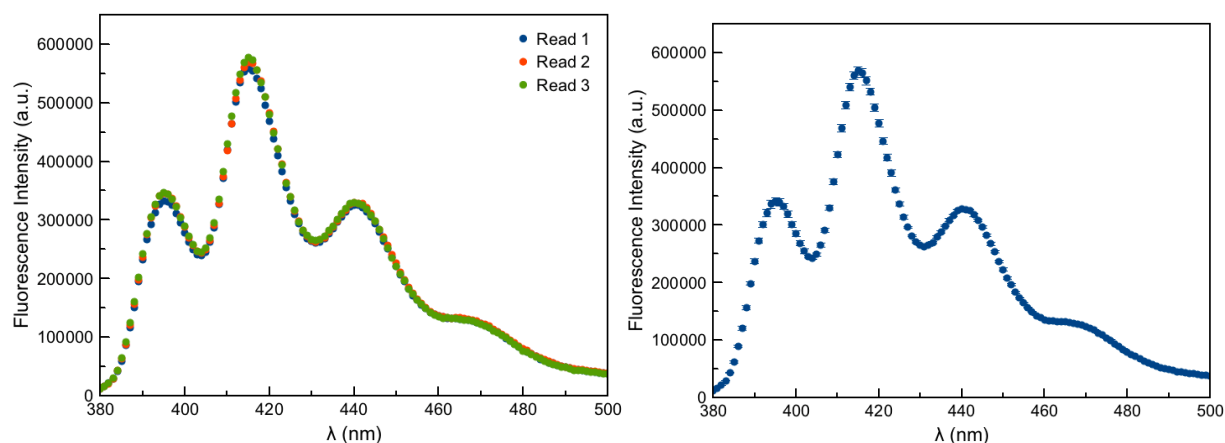


Figure S46. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 800 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 800 MPa for 10 s.

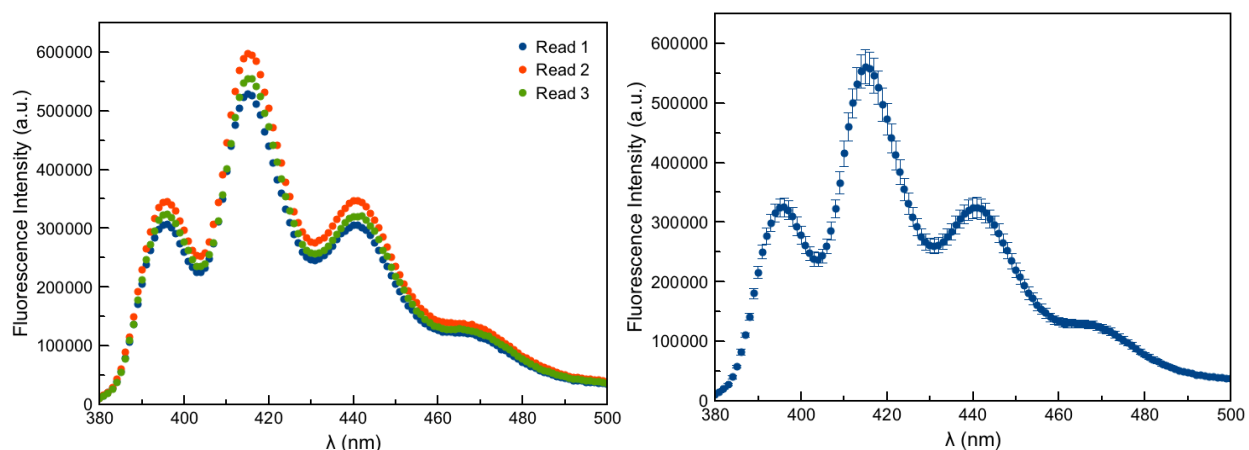


Figure S47. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 900 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 900 MPa for 10 s.

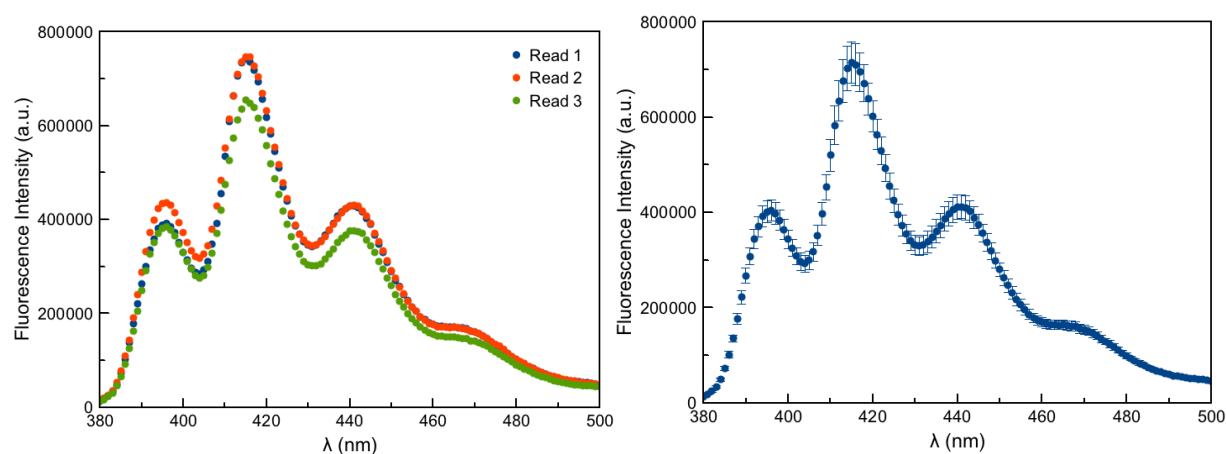


Figure S48. (Left) Representative solid-state fluorescence spectra for multiple reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 1065 MPa for 10 s. **(Right)** Representative fluorescence spectrum of the average of three reads on a sample (DMA:1:DEGDA = 90:1:9) that was compressed with a pressure of 1065 MPa for 10 s.

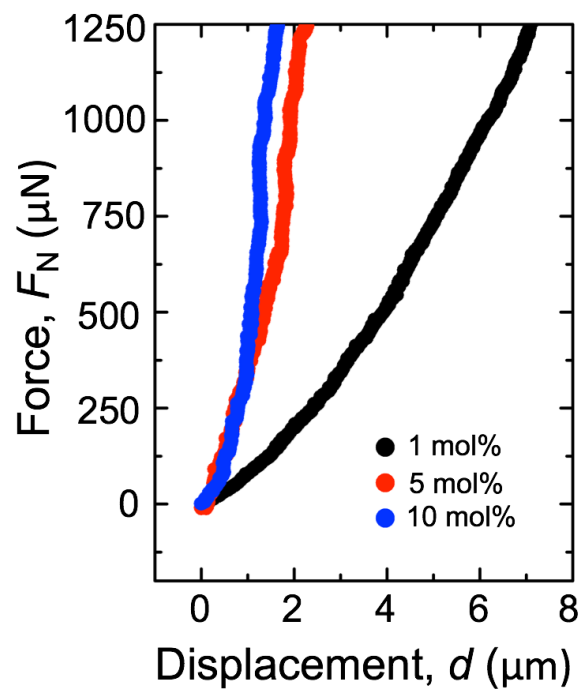


Figure S49. Force vs. displacement as measured by indentation for networks with 1 mol%, 5 mol%, and 10 mol% crosslinker.

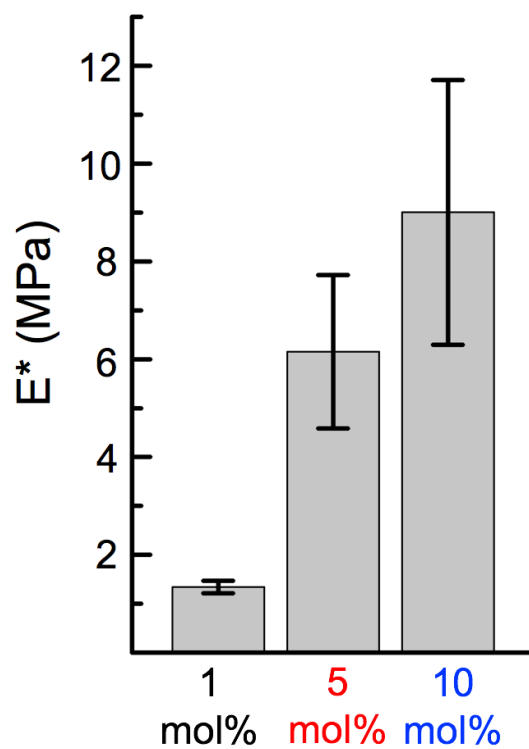


Figure S50. Young's moduli from indentation for networks with 1 mol%, 5 mol%, and 10 mol% crosslinker.

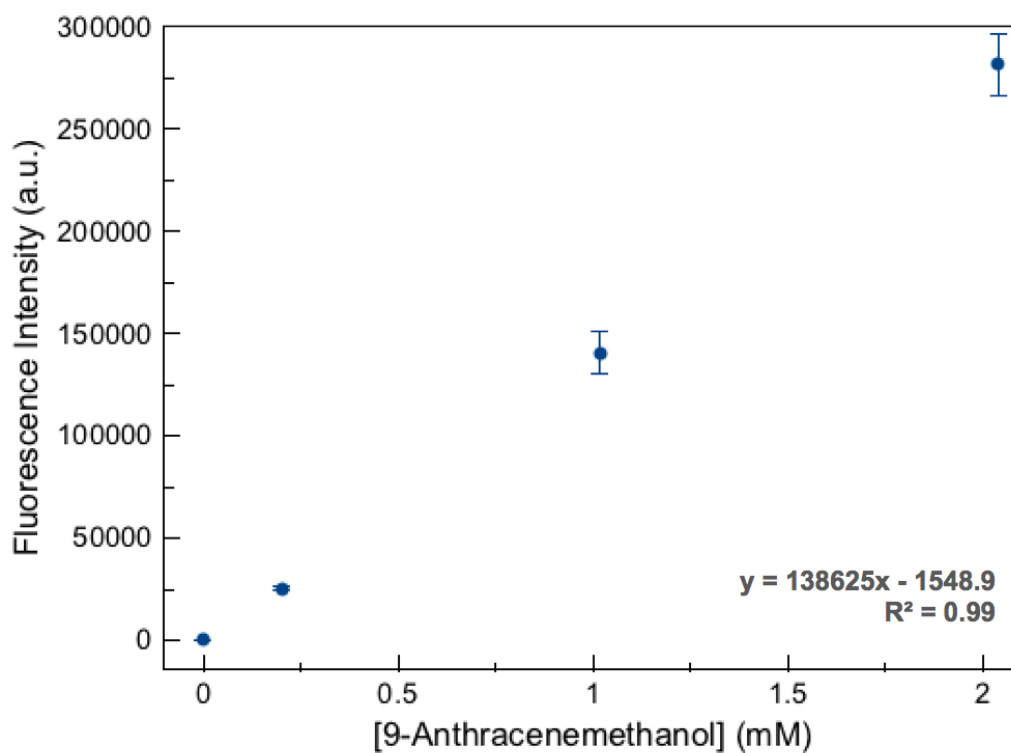


Figure S51. Calibration curve of fluorescence intensity vs. 9-anthracenemethanol embedded in PDMA networks.

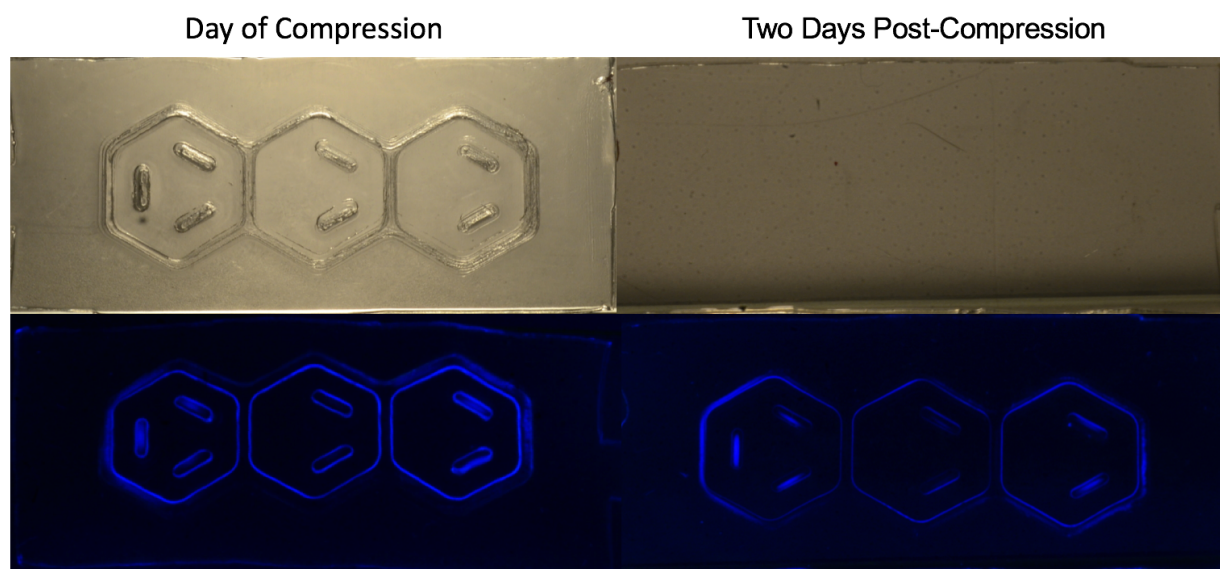


Figure S52. Images of stamped P(DMA_{0.99-co-10.01}) network under white light and long-wave UV irradiation. (Left) Imaged directly after compressing sample; (Right) Imaged two days after compressing sample.

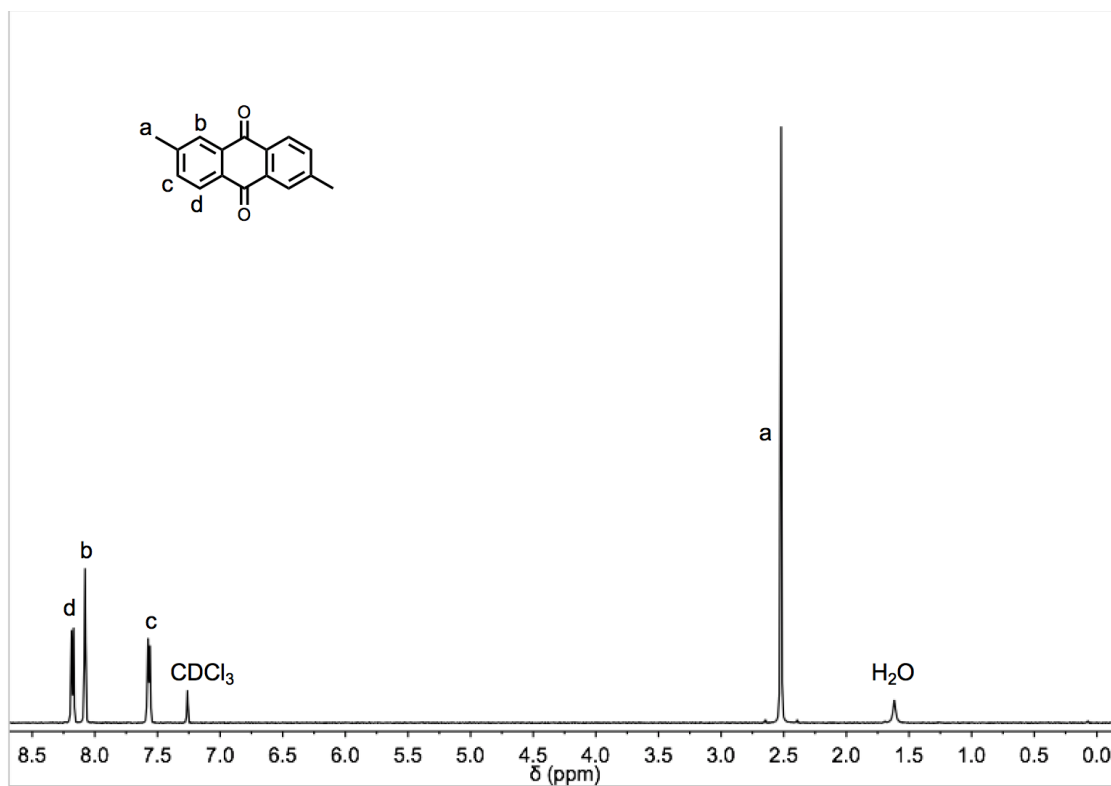


Figure S53. ^1H NMR spectrum of 2,6-dimethylantraquinone (500 MHz, CDCl_3)

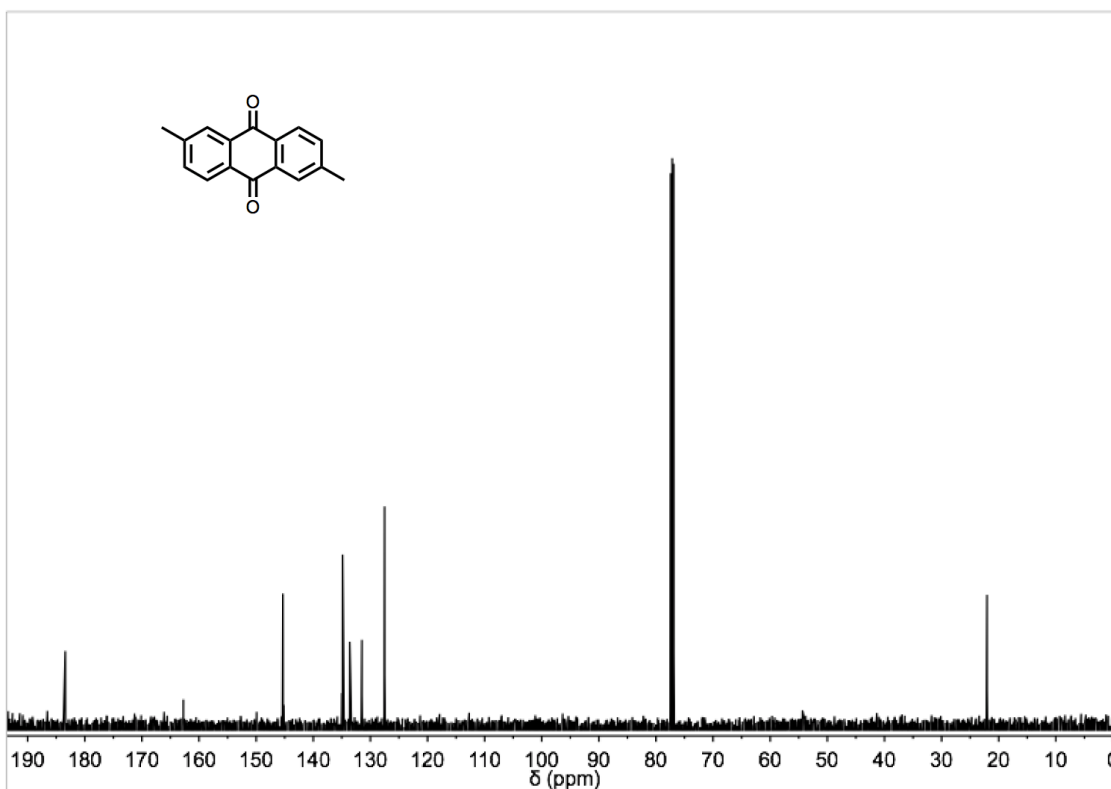


Figure S54. ^{13}C NMR spectrum of 2,6-dimethylantraquinone (125 MHz, CDCl_3)

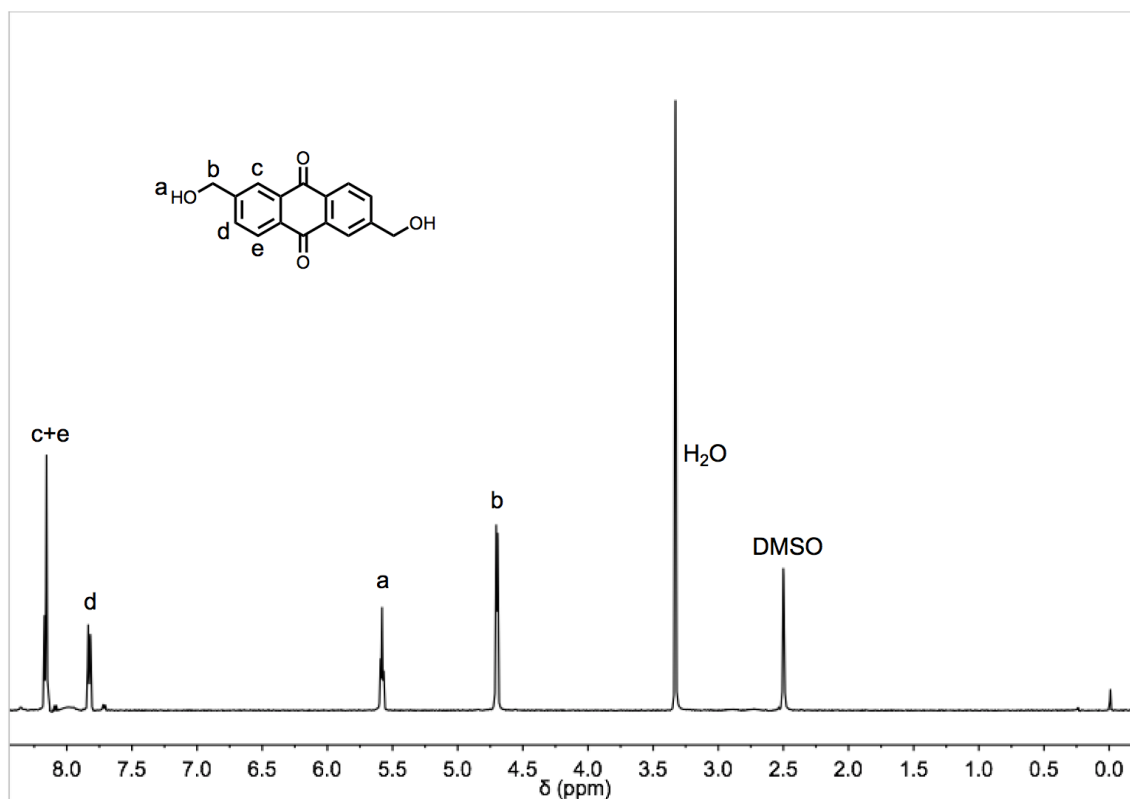


Figure S55. ¹H NMR spectrum of 2,6-*bis*(hydroxymethyl)anthraquinone (500 MHz, DMSO-*d*₆)

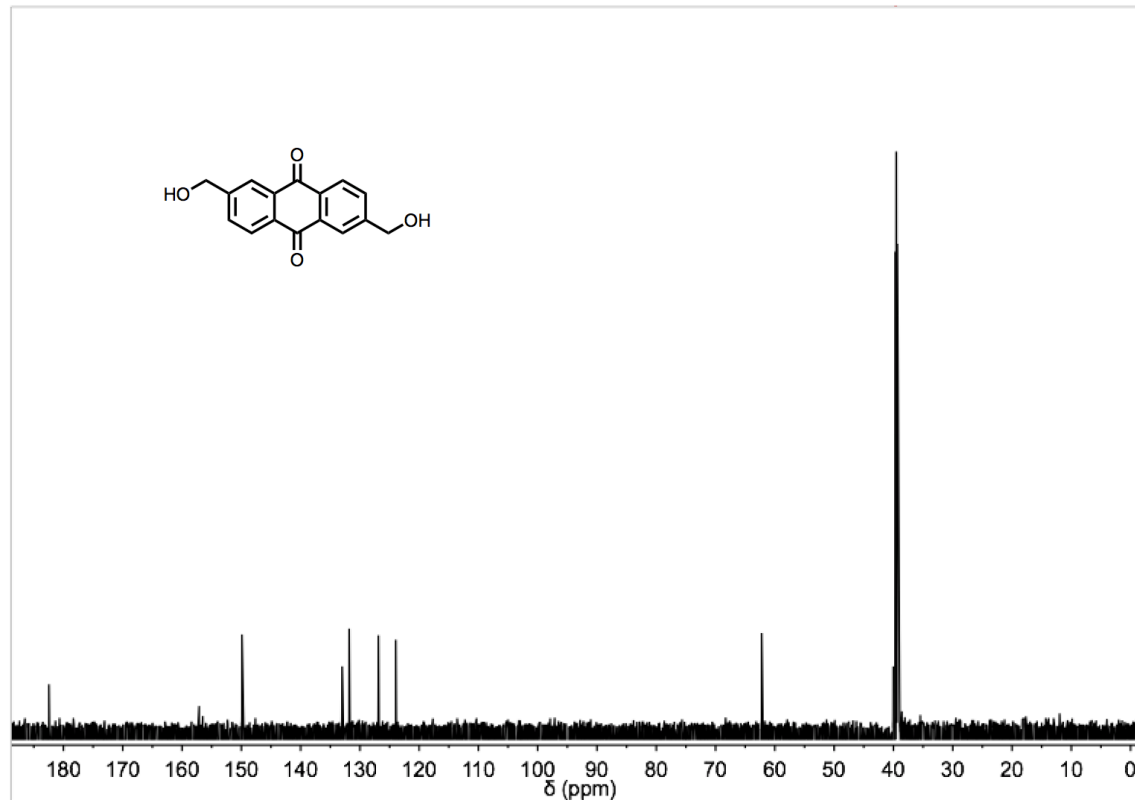


Figure S56. ¹³C NMR spectrum of 2,6-*bis*(hydroxymethyl)anthraquinone (125 MHz, DMSO-*d*₆)

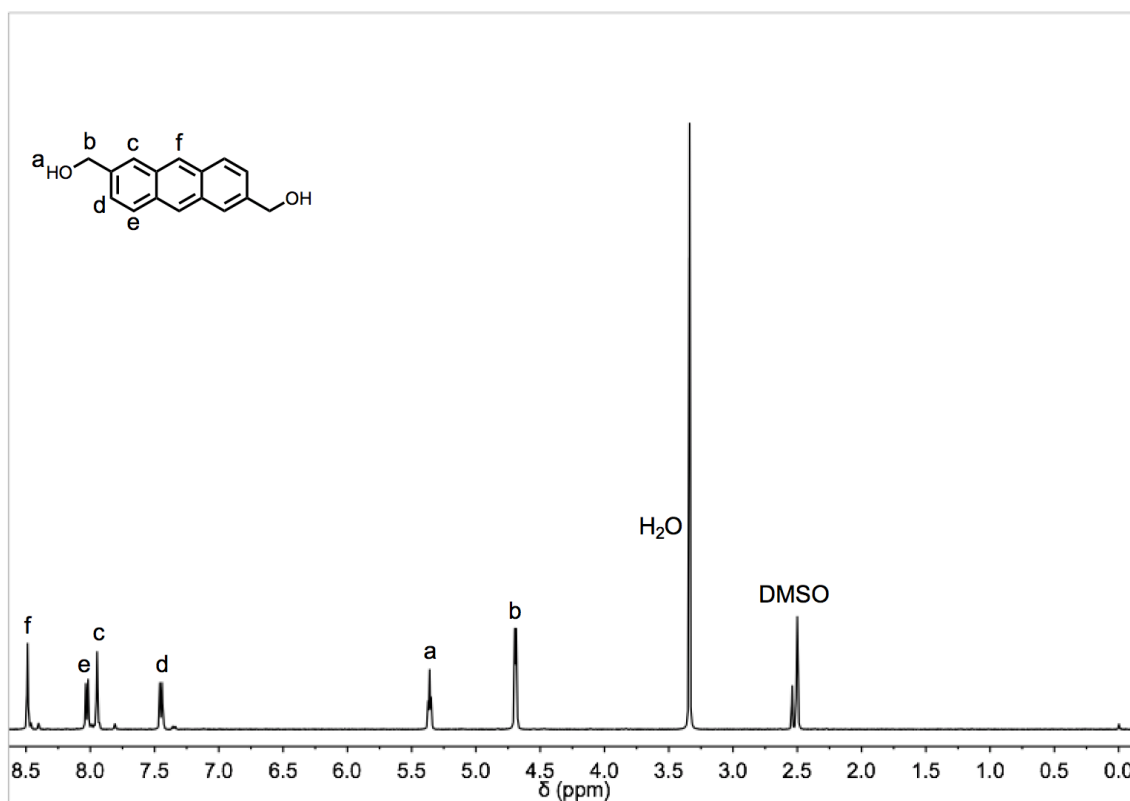


Figure S57. ¹H NMR spectrum of 2,6-*bis*(hydroxymethyl)anthracene (500 MHz, DMSO-*d*₆)

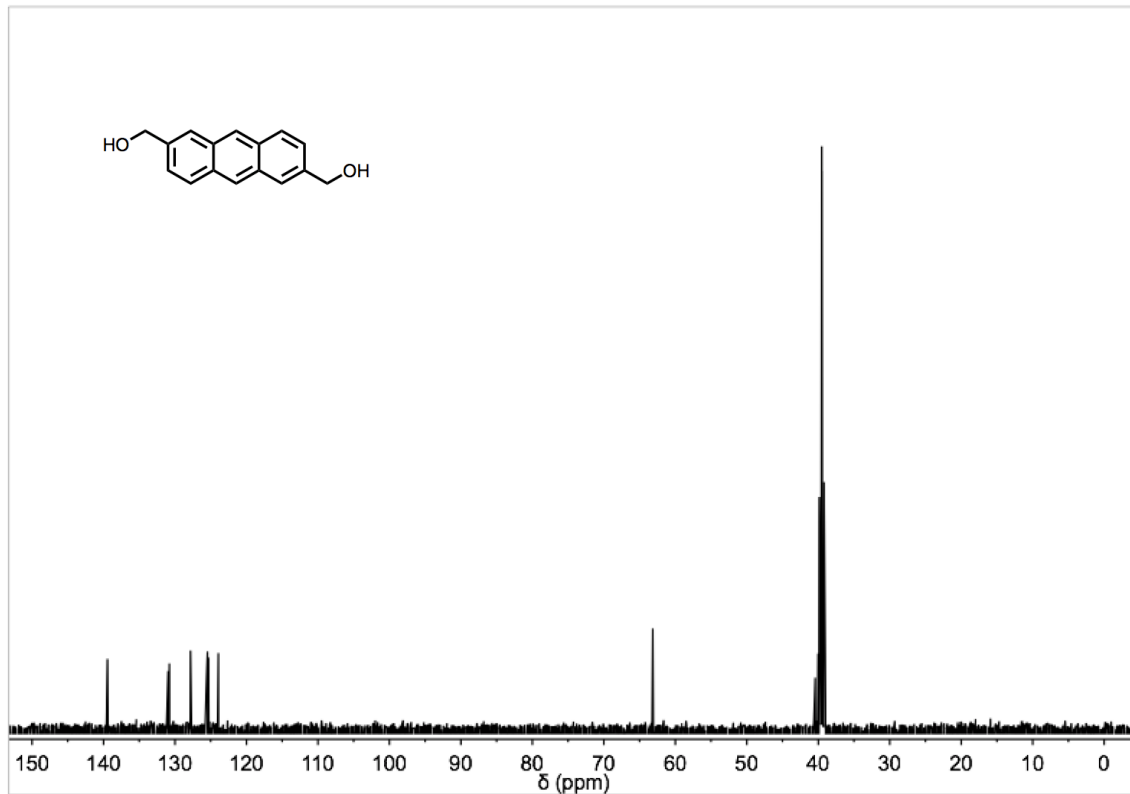


Figure S58. ¹³C NMR spectrum of 2,6-*bis*(hydroxymethyl)anthracene (125 MHz, DMSO-*d*₆)

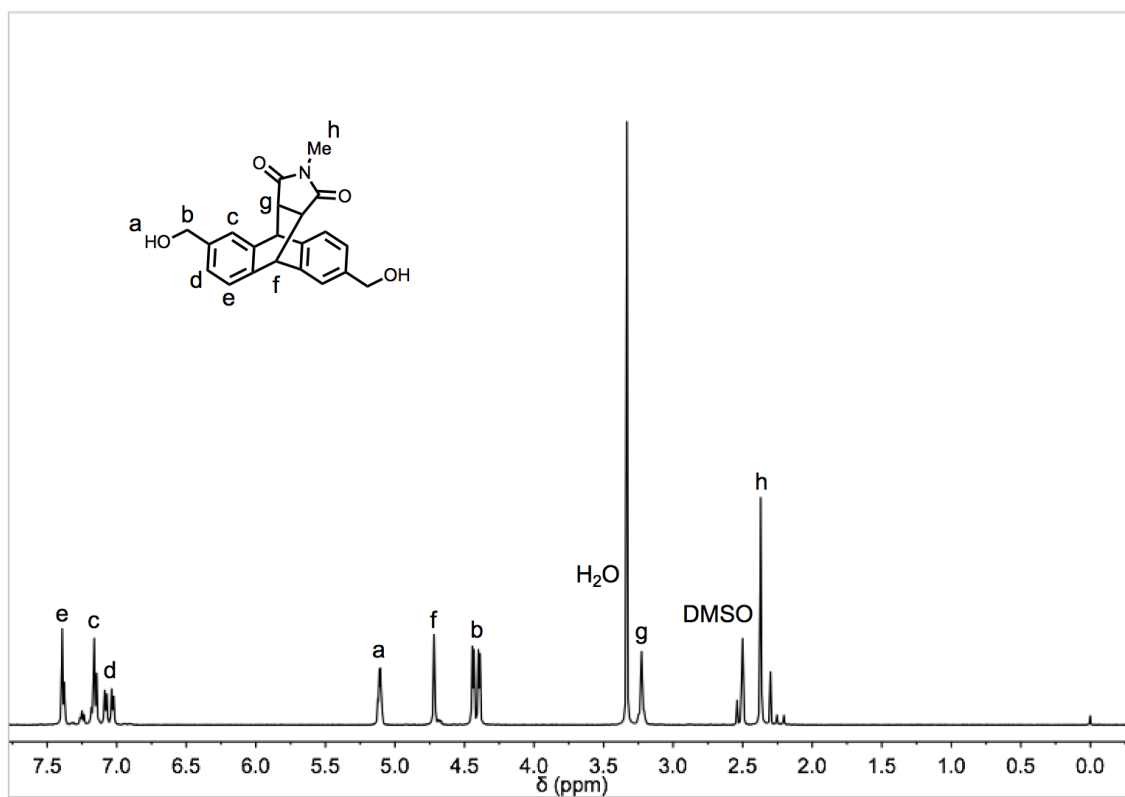


Figure S59. ¹H NMR spectrum of AnthDiol-NMeMal Adduct (500 MHz, DMSO-*d*₆)

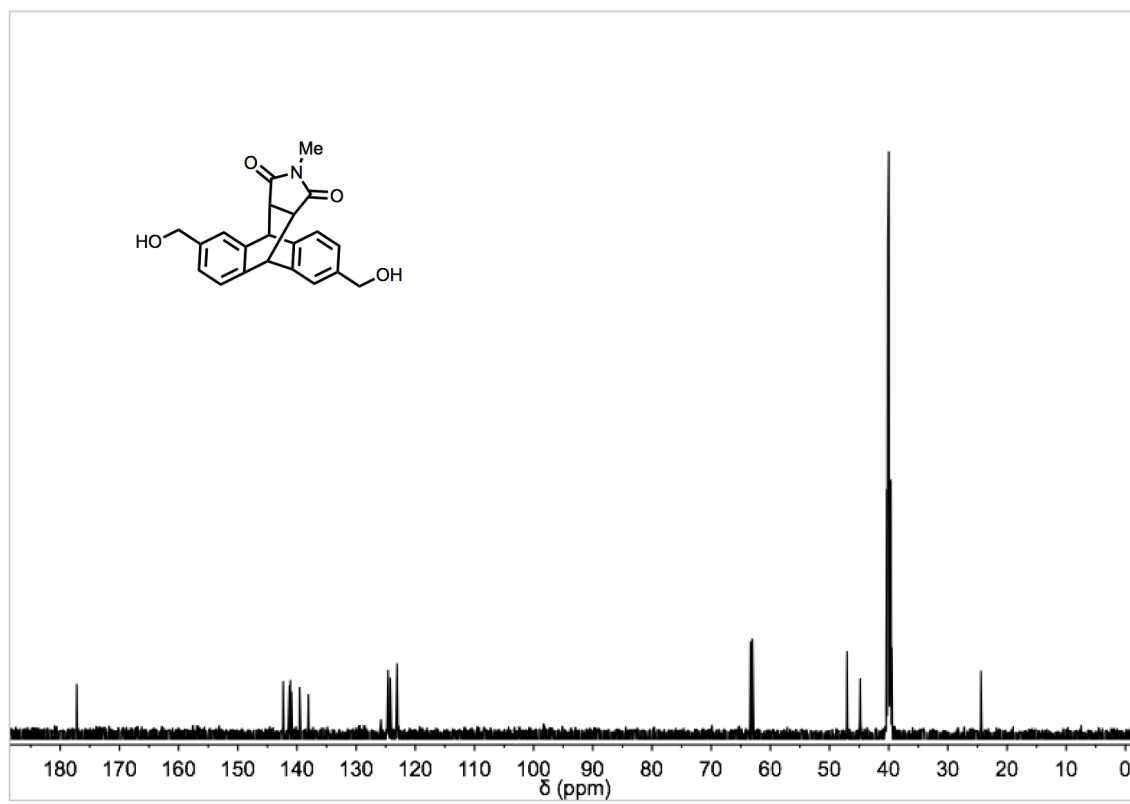


Figure S60. ¹³C NMR spectrum of AnthDiol-NMeMal Adduct (125 MHz, DMSO-*d*₆)

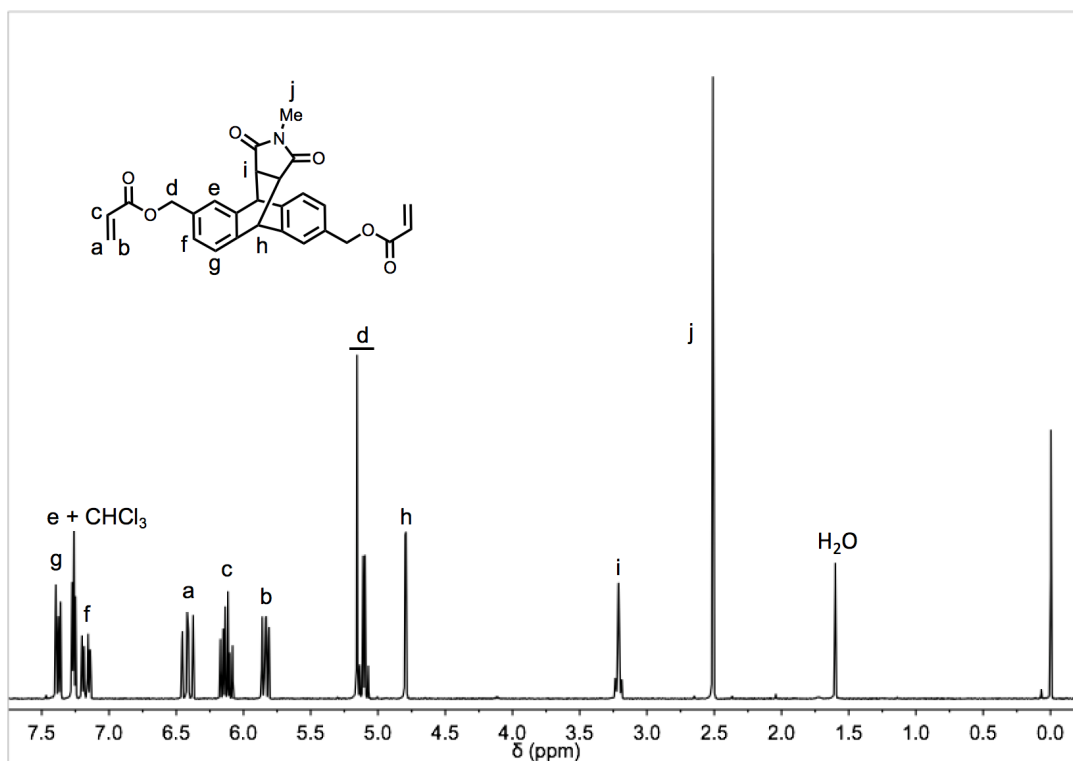


Figure S61. ^1H NMR spectrum of 3: Flex Mechanophore (500 MHz, CDCl_3)

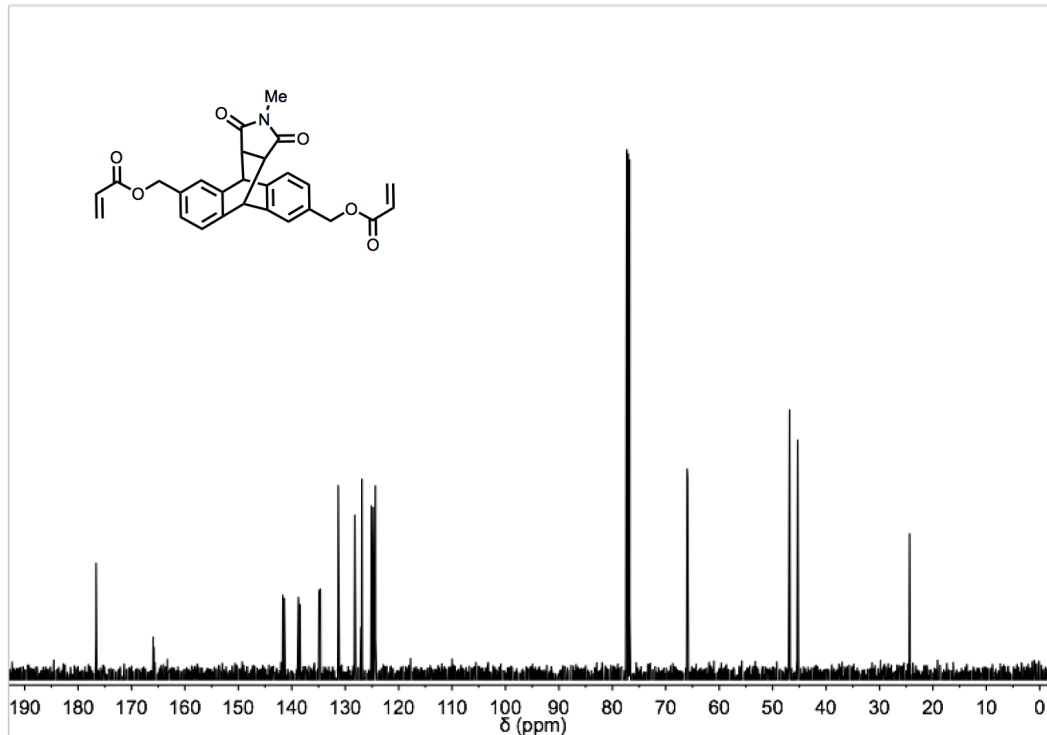


Figure S62. ^{13}C NMR spectrum of 3: Flex Mechanophore (125 MHz, CDCl_3)

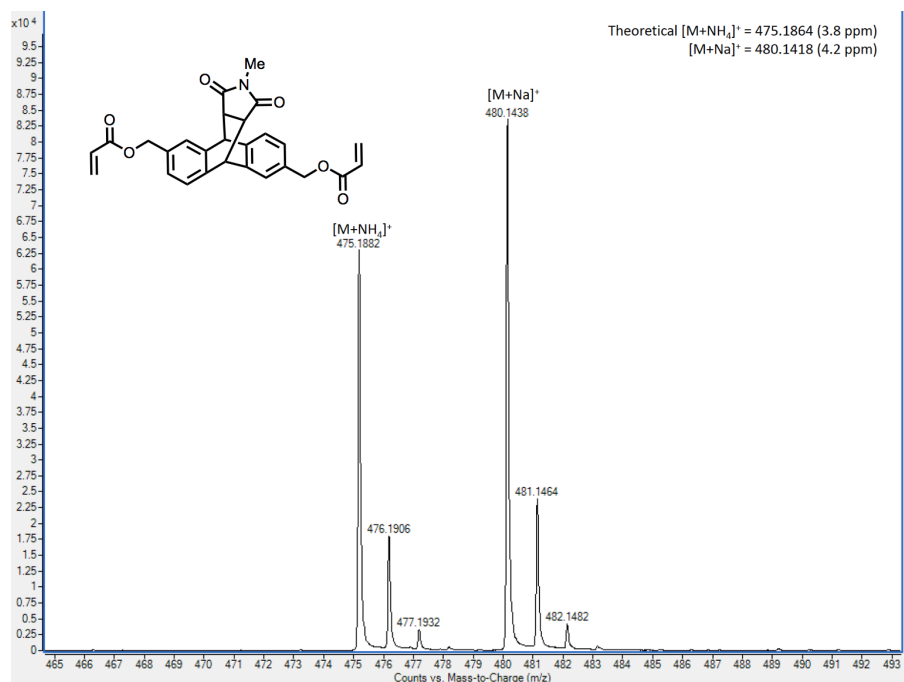


Figure S63. ESI-HRMS spectrum of 3: Flex Mechanophore

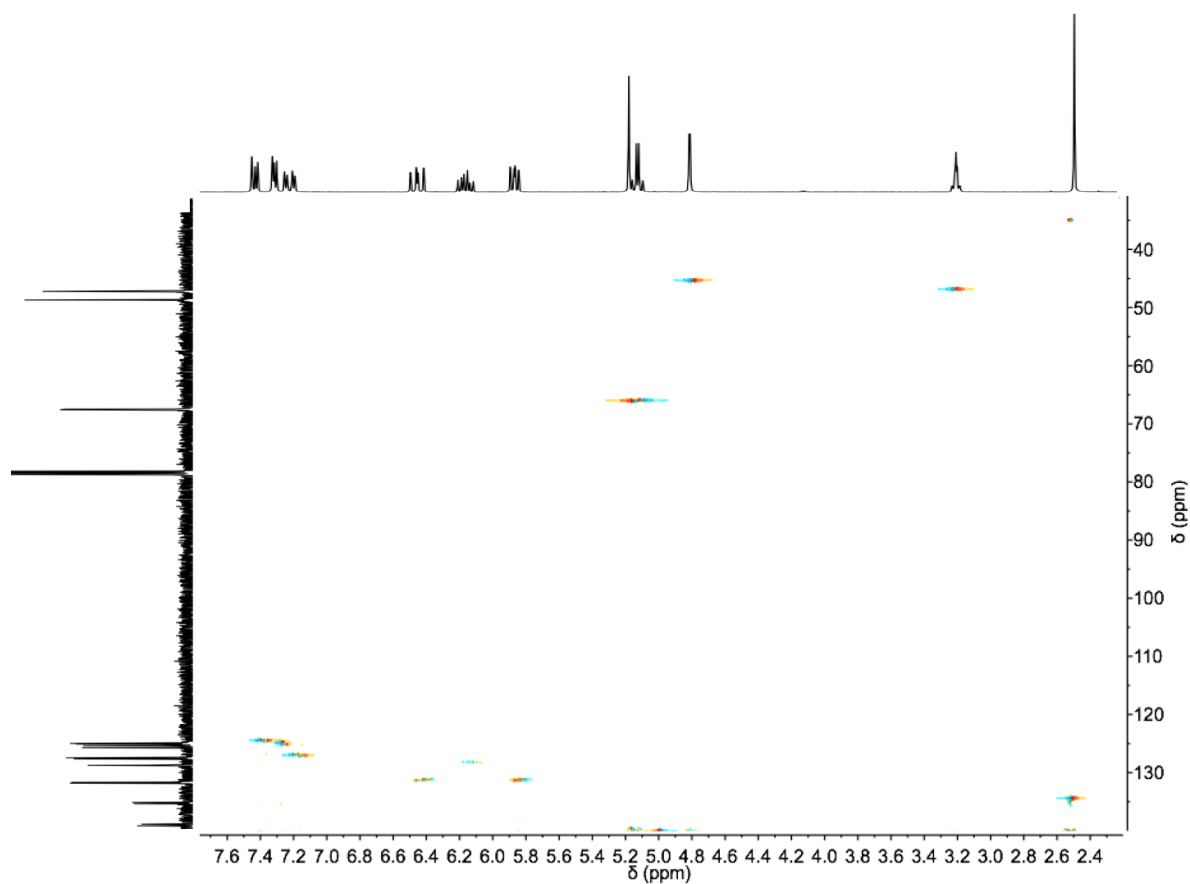


Figure S64. gHSQCAD spectrum of 3: Flex Mechanophore ($CDCl_3$)

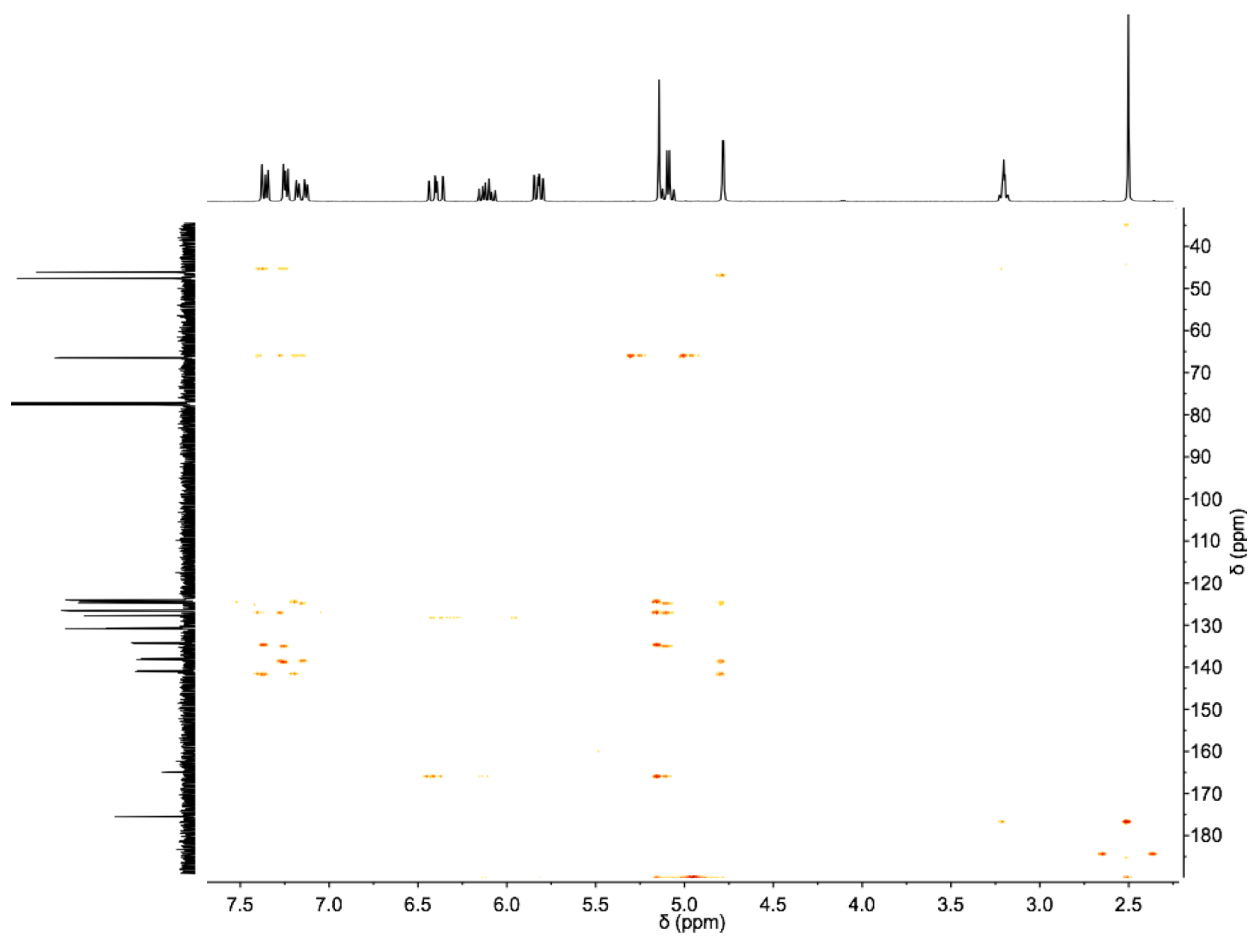


Figure S65. gHMBCAD spectrum of 3: Flex Mechanophore (CDCl_3)

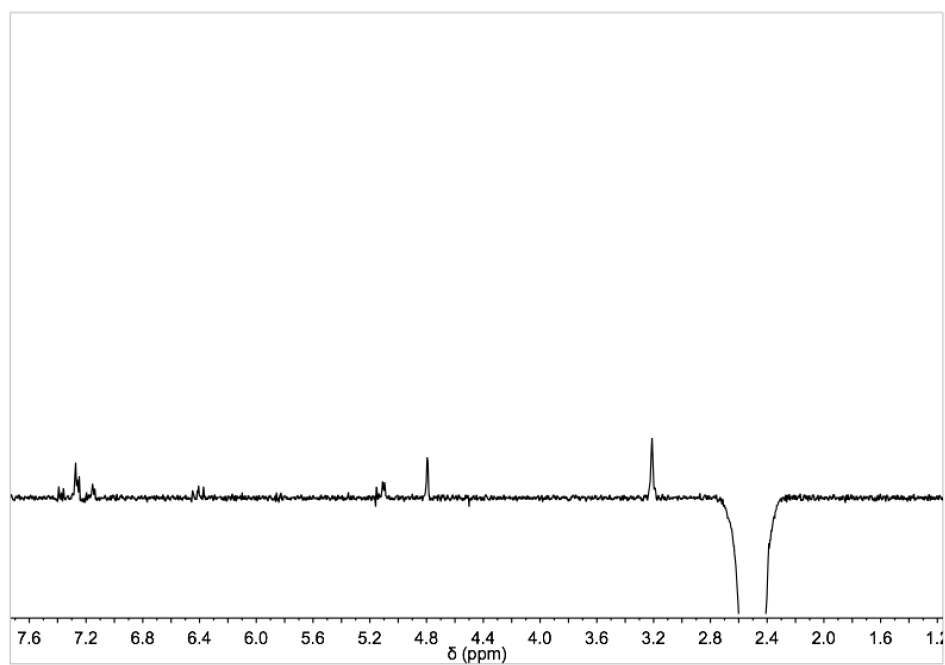


Figure S66. NOESY spectrum of 3: Flex Mechanophore (CDCl_3)

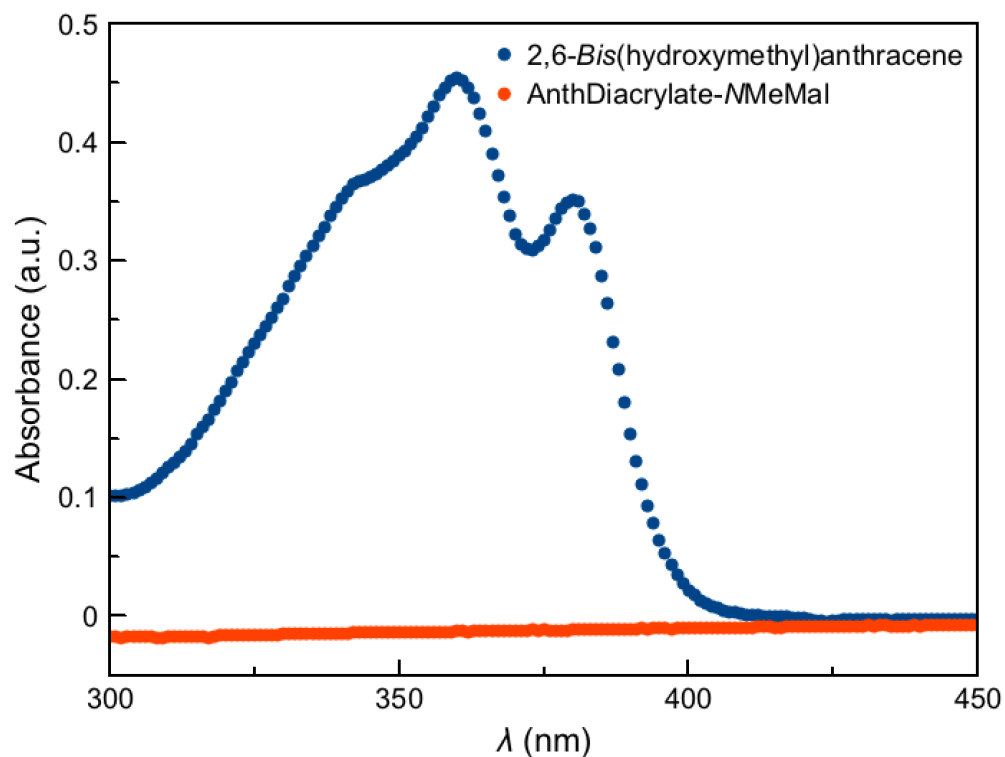


Figure S67. UV-vis absorbance spectra (0.2 mM in DMSO) of 2,6-*bis*(hydroxymethyl)anthracene (blue) and 3 (orange)

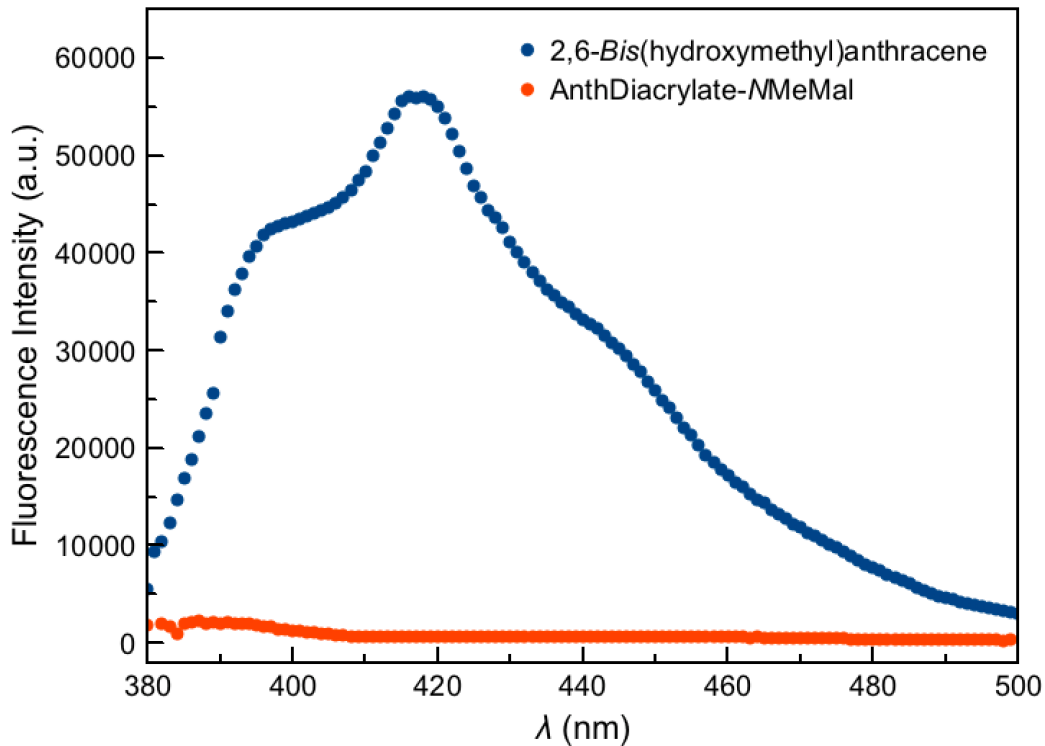


Figure S68. Fluorescence spectra (0.2 mM in DMSO) of 2,6-*bis*(hydroxymethyl)anthracene (blue) and 3 (orange)

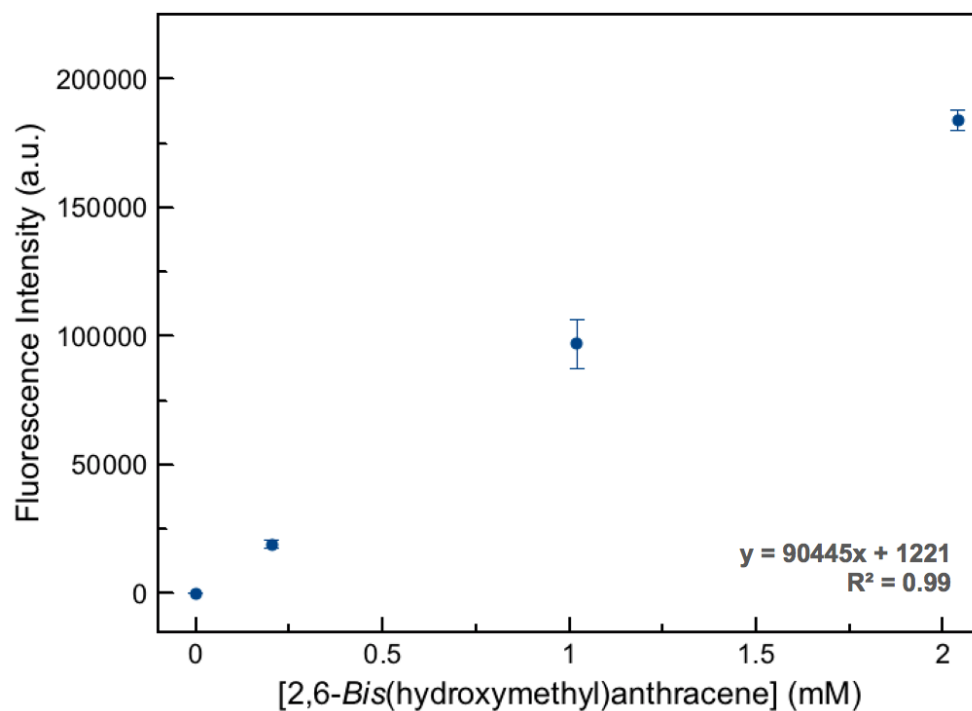


Figure S69. Calibration curve of fluorescence intensity vs. 2,6-*bis*(hydroxymethyl)anthracene embedded in PDMA networks

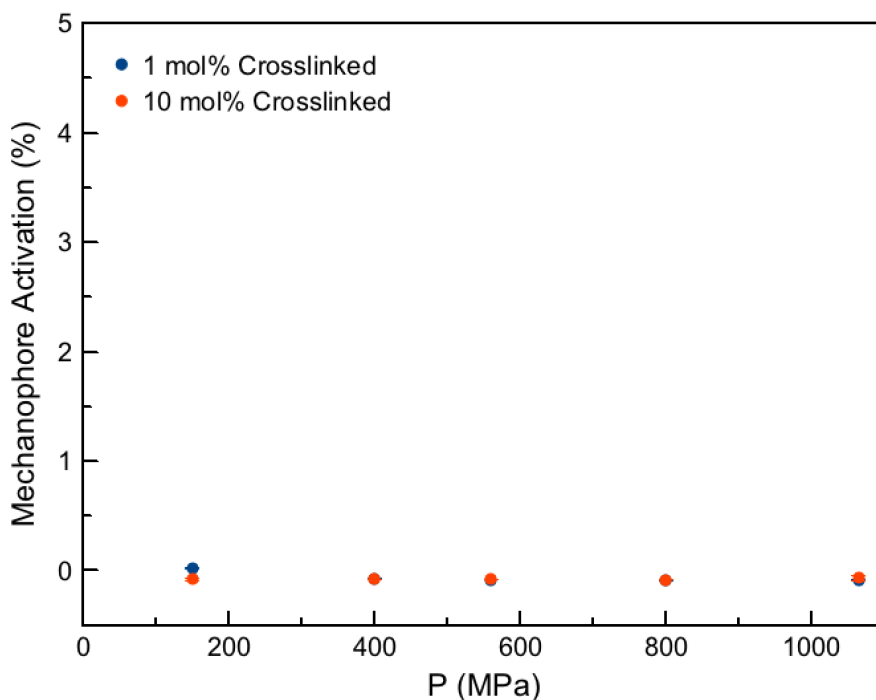


Figure S70. Percent mechanophore activation as a function of applied pressure for PDMA networks crosslinked with the flex mechanophore (1 mol% flex crosslinker with 0 mol% and 9 mol% DEGDMA, respectively)

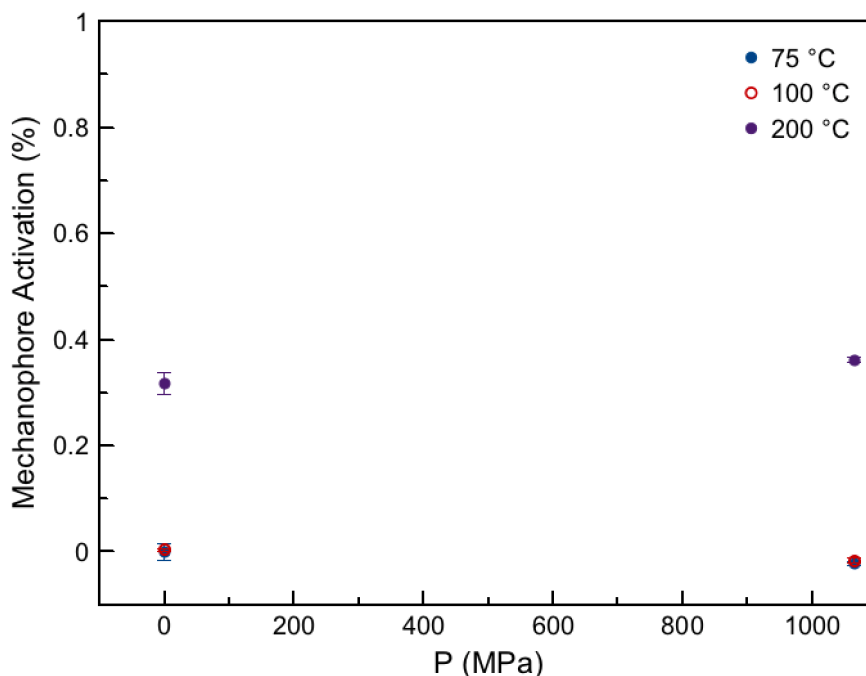


Figure S71. Percent flex mechanophore activation in PDMA networks at 75 °C (blue), 100 °C (red), and 200 °C (purple) in the absence and presence of compression

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