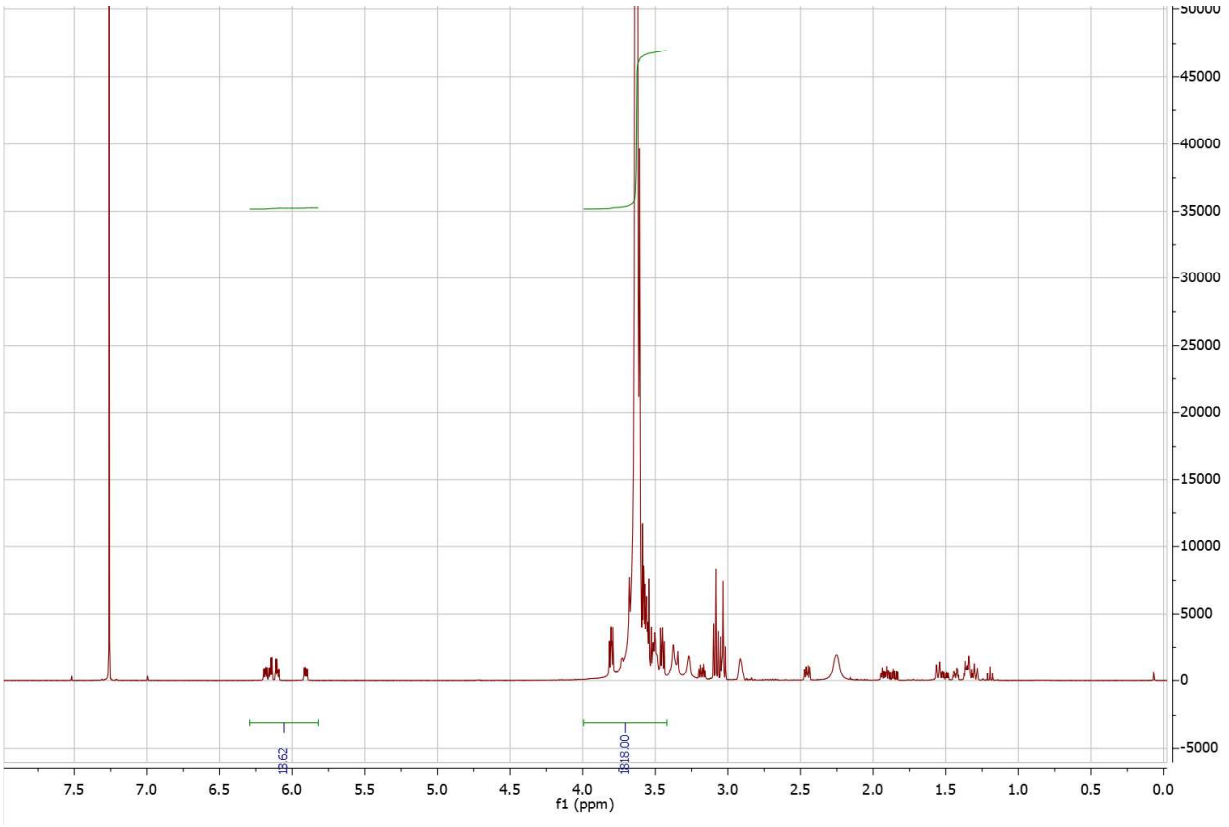


Figure S1 Nuclear magnetic resonance spectrum of 8-arm 20kDa Poly(ethylene glycol) Thioester Norbornene (TENB) in $CDCl_3$. (400 Hz) δ 6.29–5.82 (m, 2H), 3.99–3.42 (m, 1818H).

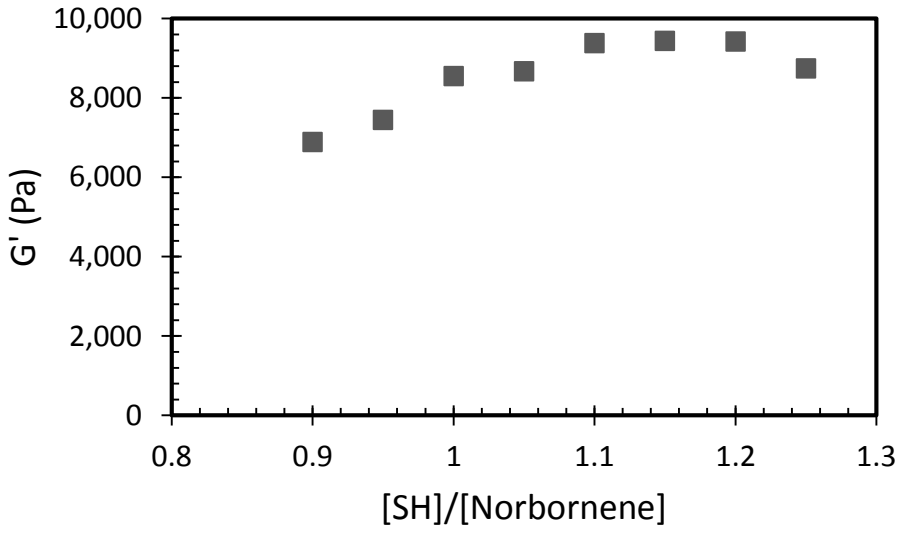


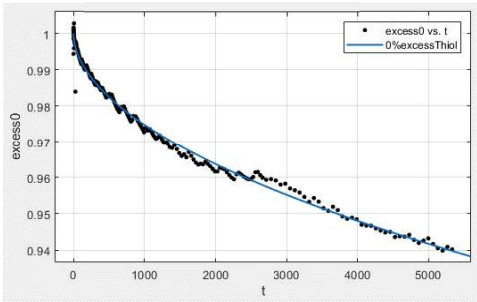
Figure S2 8-arm PEG thiol (Mw = 20 kDa) and 8-arm PEG thioester norbornene (Mw = 21 kDa) were combined in a pre-gel mixture at various stoichiometric ratios assuming 85% functionalization of the thioester macromer determed by NMR and a total polymer content of 4 wt% by mass. LAP was

incorporated at a final concentration of 1 mM. Hydrogels were fully formed *in-situ* after exposure to 10 $[mW][cm]^{-2}$ of 365 nm UV light for 60 s. Using this method, the true stoichiometric formulation corresponds to the hydrogel with the largest number of formed crosslinks, and therefore the highest modulus. The results of this experiment displayed here show a modulus maximum at a formulation with a 15% excess of thiol. Assuming equal molar quantities of thiol and norbornene function groups at this point, the true PEG TENB functionality was calculated to be 97%.

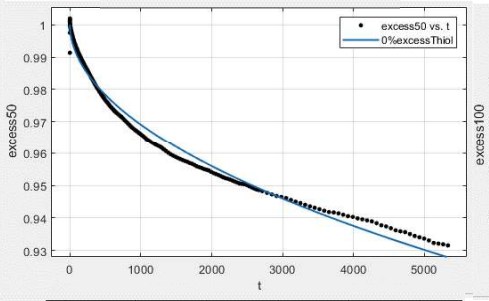
Table S1: Fitting Parameters for Stress Relaxation

Excess Thiol (%)	τ_k [s]	β	$<\tau>$ [s]	R^2 Value
0	1.00E+06	0.53	1.80E+06	0.994
50	7.93E+05	0.52	1.49E+06	0.989
100	3.99E+05	0.52	7.40E+05	0.993
150	2.82E+05	0.48	6.02E+05	0.996
200	9.77E+04	0.49	2.01E+05	0.994

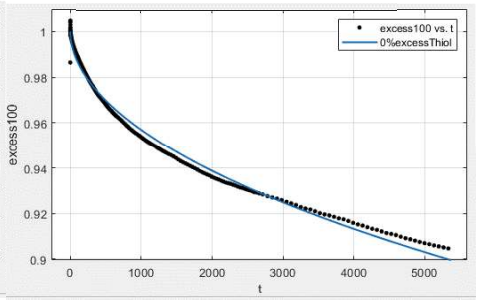
0% Excess Thiol

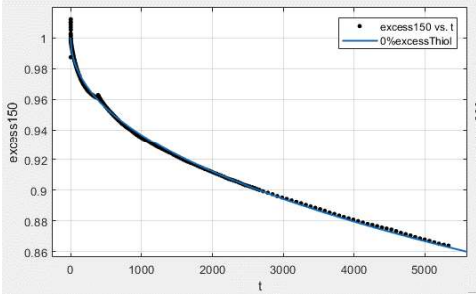


50% Excess Thiol

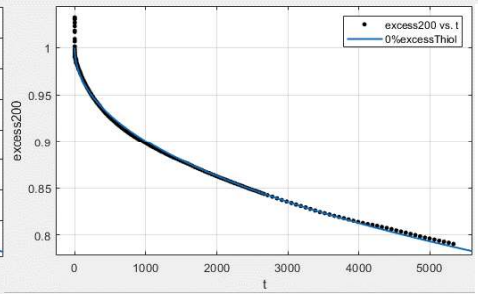


100% Excess Thiol





150% Excess Thiol



200% Excess Thiol

The initial stress was taken to be the average stress observed the first five seconds directly following the application of a 10% strain. The normalized stress data was then imported into MATLAB and fitted to

equation (1) using the curve fitting toolbox. During the fitting process, beta was bound between 0 and 1 and τ_k was left unbounded.

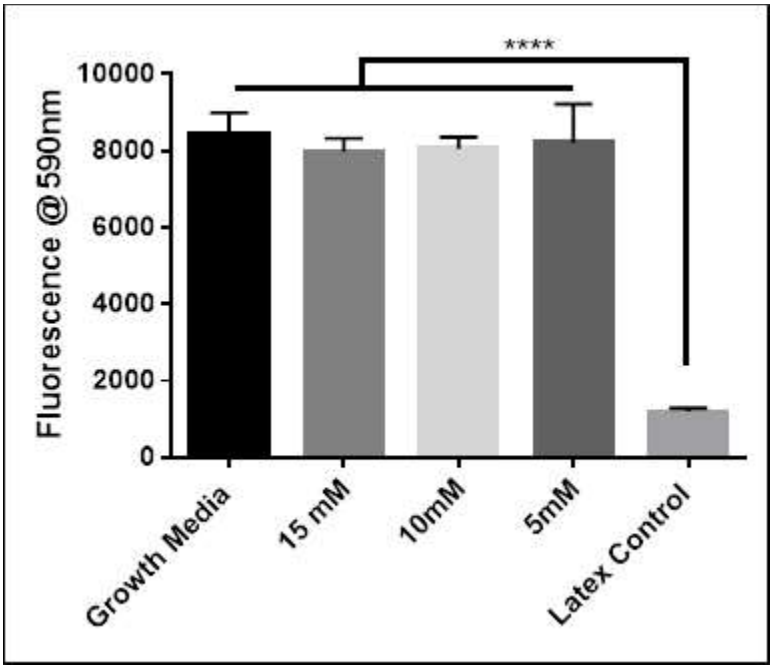


Figure S3 NIH 3T3 fibroblasts were seeded at 25000 [cells][cm]$^{-2}$ into a 24 well plate and cultured for 24 hours in experimental media. Media was then replaced by each solution indicated above for 30 min, namely: fluorobrite media solutions containing 15, 10, 5, and 0 mM concentrations of 5-norbornene-2-carboxylic acid, experimental media as a positive control, and experimental media steeped with latex as a negative control. The cells were cultured for an additional 24 hours in experimental media, before media was replaced with 500 microliters of media containing Alamar Blue (1:10, Invitrogen) for a 5 hour pulse. (n=3 wells, **** indicates p<0.0001)

	Growth Media		No Cell Control	
	570nm	600nm	570nm	600nm
Sample 1	0.335	0.223	0.305	0.303
Sample 2	0.35	0.232	0.312	0.305
Sample 3	0.347	0.233	0.313	0.307

Table S2 Alamar Blue reagent was calculated to be 51% reduced using protocols described in the technical datasheet for alamar blue provided by the manufacturer (Bio-Rad).

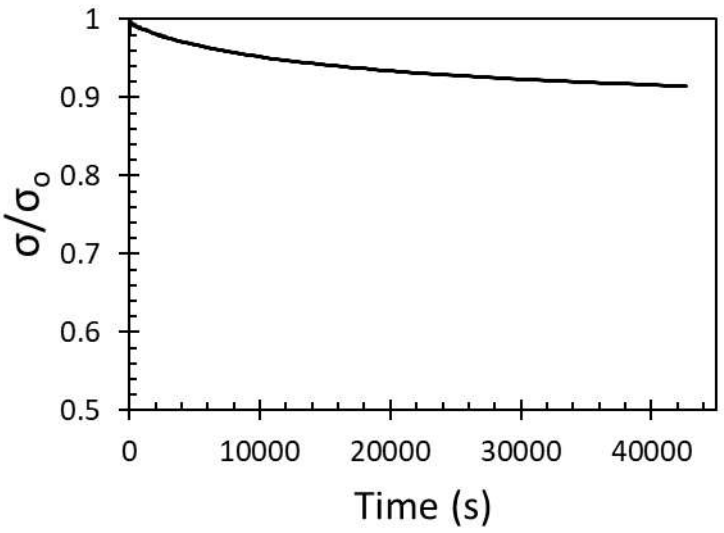


Figure S4 A purely elastic hydrogel with a modulus (G') of 2.9 kPa was subjected to a stress relaxation for 12 hours. After 5400s 3.5% of stress had relaxed in a similar manner to the control reported previously, however, in this experiment it is clear that the material continued to relax 10% of stress by the end of the 12 hour experiment. Since this thiol-ene hydrogel has no capacity to rearrange crosslinks, we believe this effect is poroelasticity as a result of continued compression under a constant normal force. The use of a normal force to maintain good contact between the tool and a swollen sample is common in literature[6], and given the small magnitude of this effect we do not feel it meaningfully impacts the analysis.

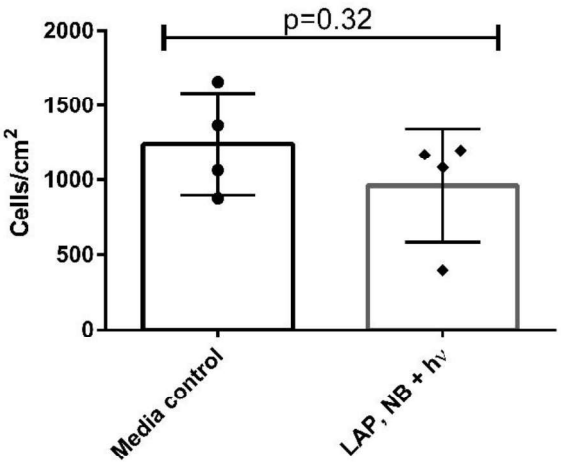


Figure S5 We conducted an experiment that most accurately assess whether cell viability of the switch condition was affected by the photochemical reaction used to turn of viscoelastic properties of the thioester hydrogels. A study was conducted in which viscoelastic thioester hydrogels were seeded with NIH 3T3 fibroblasts, treated with light, LAP and norbornene at 24 hr, and fixed at 48 hr. Specifically, treatment either included 30 minutes if incubation in a solution of fluorobrite media, 1 mM LAP, 10 mM norbornene, and subsequent irradiation with 10 mW/cm^2 of 365nm light for 100s, or 30 minutes of incubation in fluorobrite media and no irradiation. Samples were stained for the DAPI (1:500) and rhodamine phalloidin (1:300, Invitrogen), then nuclei were counted on each sample. Data suggest no significant difference in cell viability between the switch condition and control. From this we conclude that no toxic effects were observed as a result of treatment with LAP, NB and UV light.

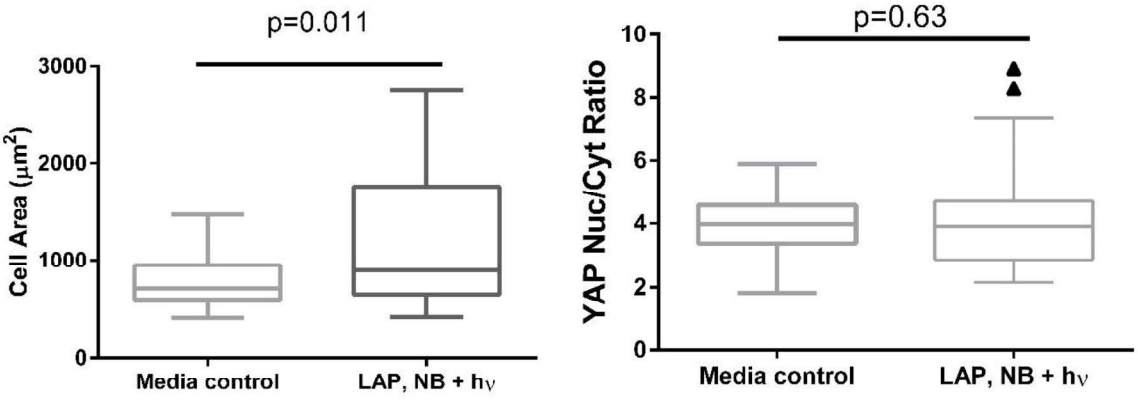


Figure S6 We synthesized hydrogels of comparable moduli that are inert to the photoinitiated thiol-ene by replacing 8 arm 20 kDa PEG thioester norbornene with an 8 arm 20kDa PEG norbornene. Elastic thiol-ene gels were then seeded with NIH 3T3 fibroblasts, treated at 24 hr, and fixed at 48 hr. Samples were then stained for the nucleus,

actin cytoskeleton and YAP/TAZ. n=30 cells. Cell area and YAP nuclear to cytoplasmic ratio are visualized by a Tukey boxplot. Reported p value is for a student's t-test.