Section 1: Figures

ESI Fig. 1 Nuclear magnetic resonance spectrum of the conjugation product of norbornene (NB) to poly(ethylene glycol) amine (PEG), where (a) indicates the spectrum of the PEG backbone with resonance between ~3.4-3.85 ppm and (b) indicates the spectrum for the allylic proton closest to the NB bridged cyclic hydrocarbon group with resonance between ~3.1-3.2 ppm. A 99% conjugation percentage was found using the ratio of the two peak areas combined with the molecular weight of the PEG and NB molecules.

ESI Fig. 2 Projection SLA-AM system diagram, where the programmable digital micromirror device (DMD) projects a 2D cross-section using a cytocompatible light source through a series of relaying optics, through an interchangeable objective, and into a photopatternable material.
**ESI Fig. 3** Surface plot of the photopattern intensity variation across the exposure field with the dashed lines indicating the region at which the intensity variation was probed, where yellow = top, gray = center-horizontal, orange = bottom, blue = left, green = center-vertical, and purple = right. The plots to the right display the percent change in intensity as a function of distance across the photopattern at the probed regions described previously, with the inset image displaying the 2D intensity output on the sample plane where the dashed lines further highlight the regions probed.

**ESI Fig. 4** Fluorescence intensity calibration curves with the power fit analyses plotted over the observed intensity values at each fluorophore concentration (blue=0.1 mM, orange = 0.05 mM, gray=0.01 mM, yellow=0.001 mM, and green=0.0001 mM), where the dashed line indicates the power model and the error bars indicate one standard deviation.

**ESI Fig. 5** Power fit analyses used to extrapolate from the observed fluorescence intensities at a given DG to include values beyond the gray level range of the confocal photodetector with $R^2$ to represent the goodness of fit.
ESI Fig. 6 Power fit analyses used to extrapolate from the observed fluorescence intensities at a given DG to include values beyond the gray level range of the confocal photodetector with $R^2$ to represent the goodness of fit.

<table>
<thead>
<tr>
<th>DG Value</th>
<th>Fit Analysis</th>
<th>$R^2$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>$C_{\text{flow}} = 0.0952 I_{\text{flow}}$</td>
<td>0.994</td>
</tr>
<tr>
<td>641</td>
<td>$C_{\text{flow}} = 0.0473 I_{\text{flow}}$</td>
<td>0.996</td>
</tr>
<tr>
<td>674</td>
<td>$C_{\text{flow}} = 0.0346 I_{\text{flow}}$</td>
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<tr>
<td>736</td>
<td>$C_{\text{flow}} = 0.0199 I_{\text{flow}}$</td>
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</tr>
<tr>
<td>843</td>
<td>$C_{\text{flow}} = 0.0085 I_{\text{flow}}$</td>
<td>0.999</td>
</tr>
<tr>
<td>900</td>
<td>$C_{\text{flow}} = 0.0057 I_{\text{flow}}$</td>
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<tr>
<td>1000</td>
<td>$C_{\text{flow}} = 0.0029 I_{\text{flow}}$</td>
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</table>

ESI Fig. 7 Working curve calibration equations used to determine the fluorophore and thus thiol concentration in the photopatterned region of each sample, where $R^2$ was used to validate the model as a representative curve for the data.

ESI Fig. 8 Plot displaying the predicted relationship between increased thiol concentration in the photopattern ($[\text{SH}]_p$) and increased modulus, where the arrow indicates the elastic modulus and thiol concentration for bulk hydrogel samples fabricated using equivalent precursor solution formulation to the photopatterned samples (10wt% monomer, 0.5:1 thiol: norbornene, indicated by ‘x’).
ESI Fig. 9 Characteristic distance molecules can diffuse before reacting plotted as a function of incident intensity for species diffusing into the photopattern, [CC] and [SH], and out of the photopattern, [C·]_S and [S·]_C. Because the characteristic distances for the radical species, [C·]_S and [S·]_C, are significantly shorter than that of unreacted species, [CC] and [SH], the characteristic distance is labelled.

ESI Fig. 10 The peak photopatterned thiol concentration, [SH]_pat, normalized by the thiol concentration of the hydrogel precursor, [SH]_soln, plotted versus exposure dose.
ESI 11 Photopattern of the resolution pattern with the subsequent confocal fluorescent microscope images of the photopatterned hydrogel, demonstrating both the high-fidelity features. The scale bar designates 100 µm. (inset) Confocal fluorescent microscope image of hydrogel photopatterned for 25s at I=20 mW/cm² demonstrating high-fidelity photopatterning capability with pixel-limited resolution. The inset scale bar designates 50 µm.

Section 2: Derivations
Thiol-ene step-growth photopolymerization employs radical photoinitiation, whose rate is defined as

\[
R_i = -\frac{d[I]}{dt} = \frac{2.303 f \epsilon I I_0 A}{N_A \hbar c},
\]

where \([I]\) is the concentration of photoinitiator (LAP) in the solution, \(f\), efficiency, and \(\epsilon\), molar absorptivity, are 0.8 and 470 L mol\(^{-1}\) cm\(^{-1}\), based on standard values for LAP.\(^1\)\(^2\) Also in Equation 1, \(I_0\) is the incident illumination intensity (mW cm\(^{-1}\)) and \(N_A\), \(\hbar\), and \(c\) are Avogadro’s number, Planck’s constant and the speed of light, respectively. The approximate concentration of the four species, \([SH],[CC],[S\bullet]\), and \([C\bullet]\), is governed by the following equations: \(^3\):

\[
\frac{d[SH]}{dt} = - k_{ct}[C\bullet][SH],
\]

\[
\frac{d[CC]}{dt} = - k_p[S\bullet][CC],
\]

\[
\frac{d[S\bullet]}{dt} = R_i - R_t(S\bullet) + k_{ct}[C\bullet][SH] - k_p[S\bullet][CC],
\]

\[
\frac{d[C\bullet]}{dt} = R_i - R_t(C\bullet) - k_{ct}[C\bullet][SH] + k_p[S\bullet][CC].
\]

Where the termination rate of thiyl and carbon-centered radicals, \(R_t(S\bullet)\) and \(R_t(C\bullet)\), are defined as

\[
R_t(S\bullet) = 2k_{i1}[S\bullet]^2 + k_{i2}[S\bullet][C\bullet]
\]
and
\[ R_t(C\bullet) = k_{t1}[S\bullet][C\bullet] + 2k_{t3}[C\bullet]^2, \] (7)

where \( k_{t1}, k_{t2}, \) and \( k_{t3} \) are the bimolecular termination rate parameters for thiol-thyl, thyl-carbon, and carbon-carbon radical recombination, respectively. The rate at which all radicals terminate, independent of species, is thus the sum of (6) and (7),
\[ R_t = R_t(S\bullet) + R_t(C\bullet) = 2k_{t1}[S\bullet]^2 + 2k_{t2}[S\bullet][C\bullet] + 2k_{t3}[C\bullet]^2. \] (8)

The polymerization rate \( R_p \) of this reaction related to individual radical concentrations is
\[ R_p = k_{ct}[C\bullet][S\bullet] = k_p[S\bullet][CC], \] (9)

given the rates of thiol and vinyl group consumption are equivalent. In steady state, the rate at which radicals are generated is equal to the rate at which radicals are terminated, \( R_t = R_t(S\bullet) = R_t(C\bullet) \), or equations (4) and (5) = 0. Solving for \([S\bullet], [C\bullet]\), and combining (1) through (9), the steady state polymerization rate, \( R_{ps} \), is found to be
\[ R_{ps} = \frac{R_t}{2k_t \sqrt{\frac{k_{t1}}{(k_p[CC])^2} + \frac{k_{t2}}{(k_{ct}[CC][S\bullet])} + \frac{k_{t3}}{(k_{ct}[S\bullet])}}} - 1. \] (10)

Reddy et al. identified that each termination mechanisms must be equivalent in thiol-norbornene chemistries \( k_{t1} = k_{t2} = k_{t3} \) and that both propagation and chain transfer polymerizations are equally likely \( k_p = k_{ct} \) thus, \( R_p \) simplifies to
\[ R_{ps} = \frac{R_t}{2k_t \sqrt{\frac{1}{[CC]^2} + \frac{1}{[CC][S\bullet]} + \frac{1}{[SH]^2}}} - 1. \] (11)

With the steady state polymerization rate of the thiol-norbornene reaction, the steady state concentrations of the carbon-centered \([C\bullet]\) and the thyl radicals \([S\bullet]\), is determined by substituting (11) into using (9) and solving for each radical species,
\[ [C\bullet]_s = \frac{R_{ps}}{k_{ct}[SH]} = \frac{R_p}{k_p[SH]}, \] (12)

where \([S\bullet]_s\) is equivalently related to \([CC]\).

For a given formulation and illumination intensity, the steady-state concentrations of the thiol-norbornene reaction are thus fully determined by the initiation rate, the polymerization rate, and the two radical concentrations \([S\bullet]_s\) and \([C\bullet]_s\). The initiation rate constants for LAP are given above and Cramer et al. and Reddy et al. gives the termination constant \( k_t = 3.5 \times 108 \) L mol\(^{-1}\) cm\(^{-3}\) and polymerization rate constant \( k_p = 0.5-3.1 \times 106 \) L mol\(^{-1}\) cm\(^{-3}\). A fourth advantage of the thiol-norbornene reaction is thus the complete, quantitative understanding of the reaction which is then used to predict patterning fidelity in gels formed from this chemistry.

Section 3: References