

## Supporting Information

### **(-)-Riboflavin and Flavin mononucleotide as visible light photo initiators in the thiol-ene polymerisation of PEG-based hydrogels**

#### **Experimental**

##### **Materials**

All materials were purchased from Sigma Aldrich and used as received unless otherwise stated. Four arm PEG (20kDa) was purchased from JenKem Technology USA.

##### **Methods**

##### **Synthesis of Norbornene-functionalised PEG (PEG-4-NB)**

5-norbornene-2-carboxylic acid (11.5mol, 1.595g) was dissolved in dichloromethane (10mL). N,N'-dicyclohexylcarbodiimide (5.8mol, 1.19g) was added to the solution and stirred for 30 min. Four arm PEG (0.3mol, 6g), dimethylaminopyridine (0.6mol, 0.07g) and pyridine (5.8mol, 0.465mL) were dissolved in dichloromethane(10mL) then added to the acid solution. The mixture was stirred at room temperature for 72 hours. The mixture was filtered, then dialysed (MWCO 6-8kDa) against methanol. The polymer was precipitated twice into diethyl ether to obtain the pure product as a white solid. (5.4g, 90%). <sup>1</sup>H NMR was used to determine the functionalisation as 85%.

##### **Hydrogel fabrication and swelling**

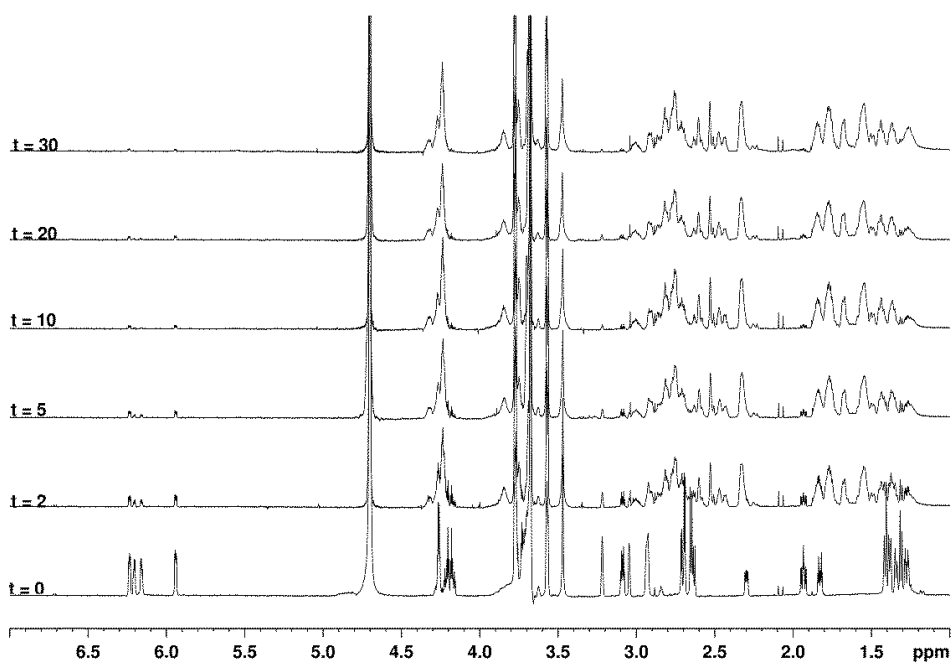
The step growth thiol-ene hydrogels were formed by radical mediated photopolymerisation using 1.3mM or 0.26mM of initiator under visible light at an intensity of 27mW/cm<sup>2</sup> at 455nm. 7wt% of polymer solution was used with DTT added at 1 equivalent of thiol to norbornene functionality. To quantify the hydrogel swelling, 150uL samples were prepared by irradiating between two glass slides at a thickness of 1mm. After gelation, the gels were incubated at 25°C in distilled water (milli Q) for 24hrs to remove the sol fraction. They were lyophilized to obtain their dry weights, and then incubated in distilled water for 72hrs to achieve equilibrium swelling. The gels were removed, blotted dry with a Kim wipe and weighed to obtain a swelling profile and swollen mass.

##### **HRMAS NMR spectroscopy**

For NMR measurements, the hydrogel precursor solution in D<sub>2</sub>O was syringed into several 40uL HRMAS inserts and irradiated for specific times under 455nm light at 30mW/cm<sup>2</sup>. <sup>1</sup>H NMR spectrum was recorded on a Bruker 700MHz spectrometer with TXI HRMAS probe at 3000Hz with 32 scans and pre-saturation on the PEG peak at 3.67ppm. The extent and monitoring of the reaction was determined using the disappearance of the norbornene alkene peaks at 5.6-6ppm.

## Rheology

A Discovery HR-1 Hybrid Rheometer (TA Instruments) was used for rheological measurements. In-situ rheology was performed using parallel plate geometry with a quartz upper plate (50mm) at 25°C. All measurements were conducted with a 400 $\mu$ m gap. A stress sweep was performed beforehand to find the linear viscoelastic region. To obtain the gel point, we performed time sweep by setting the stress at 50Pa, conducted in the viscoelastic region. All gel point measurements were taken at frequency of 1Hz.



**Figure S1 Proton spectrum showing the disappearance of the norbornene alkene groups at 5.9-6.2ppm**

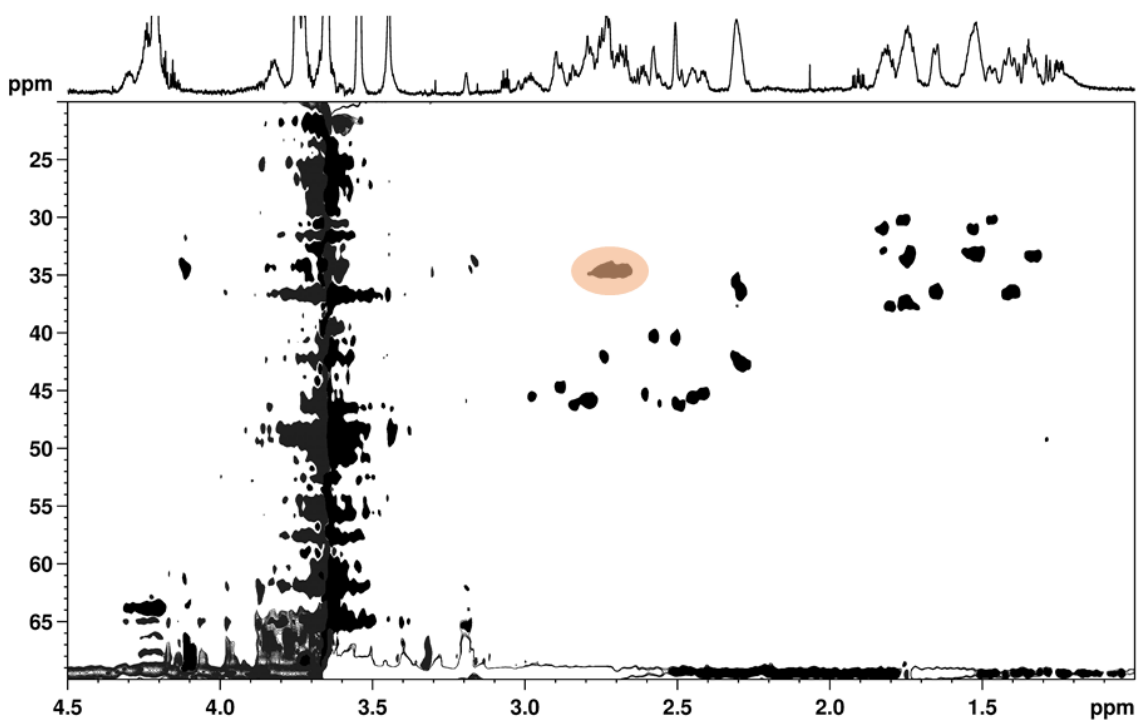


Figure S2 HSQC spectrum of fully reacted hydrogel. The red circle shows the characteristic thioether peak.

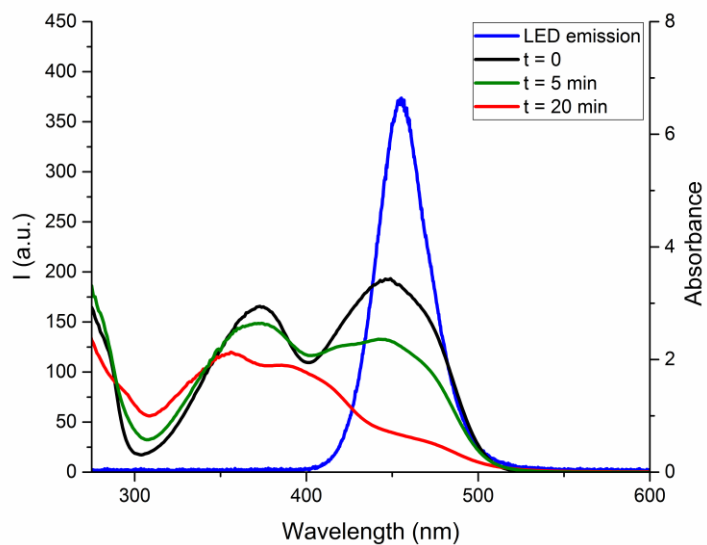


Figure S3 UV/Visible spectrum of FMN in water (1.3mM) after irradiation with light (455nm, 27mW/cm<sup>2</sup>) and the emission spectrum of the LED

## Calculation of Mesh Size

Use the Flory-Rehner Equation to determine the average MW between crosslinks

$$-\left[\ln(1 - v_2) + v_2 + \chi v_2^2\right] = \frac{V_1}{\bar{v}M_c} \left(1 - \frac{2\bar{M}_c}{M_n}\right) \left(v_2^{\frac{1}{3}} - \frac{v_2}{2}\right)$$

Calculate mesh size ( $\xi$ ) by determining the root-mean square of the end to end distance of the polymer in unperturbed state  $(\bar{r}_0^2)^{1/2}$

$$(\bar{r}_0^2)^{1/2} = lC_n^{1/2}n^{1/2}$$

$$\xi = v_2^{-1/3}(\bar{r}_0^2)^{1/2}$$