

Electronic Supplementary Information

A supramolecular two-photon-active hydrogel platform for direct bioconjugation under near-infrared radiation

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Experimental

NMR data analysis: calculation of PEI methacrylation

The extent of methacrylation of branched PEI was determined by the analysis of ¹H NMR spectra using the following formulas (Forrest *et al.*, *Pharm. Res.*, 2004):

$$\text{methacrylated secondary amines (\%)} = \left(\frac{E_{bb}}{4} \cdot \frac{3}{M'} \cdot N' \right)^{-1} \cdot 100\%$$

$$\text{methacrylated tertiary amines (\%)} = \left(\frac{E_{bb}}{4} \cdot \frac{3}{M''} \cdot N'' \right)^{-1} \cdot 100\%$$

where M' is the integration of δ 1.70-1.75 peaks corresponding to methacrylated secondary amines [$-\text{NH}-\text{COC}(\text{CH}_2)\text{CH}_3$], M'' is the integration of δ 2.0-2.1 peaks corresponding to methacrylated tertiary amines [$>\text{N}-\text{COC}(\text{CH}_2)\text{CH}_3$], and E_{bb} is the integration of δ 2.5-3.0 peaks corresponding to ethylene backbone.

N' and N'' are the mole fractions of PEI primary and secondary amines, 0.31 and 0.39 respectively, based on the analysis of the commercial PEI starting material by ¹³C NMR (von Harpe *et al.*, *J. Controlled Release*, 2000).

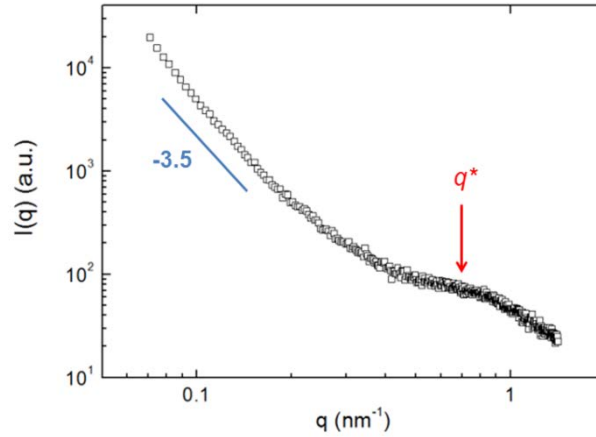


Fig. S1 Small angle X-ray scattering (SAXS) profile in log-log plot of swollen PEIMA hydrogel obtained at room temperature, showing a steep intensity decay at lower q values (slope -3.5) and a broad peak at 0.7 nm^{-1} .

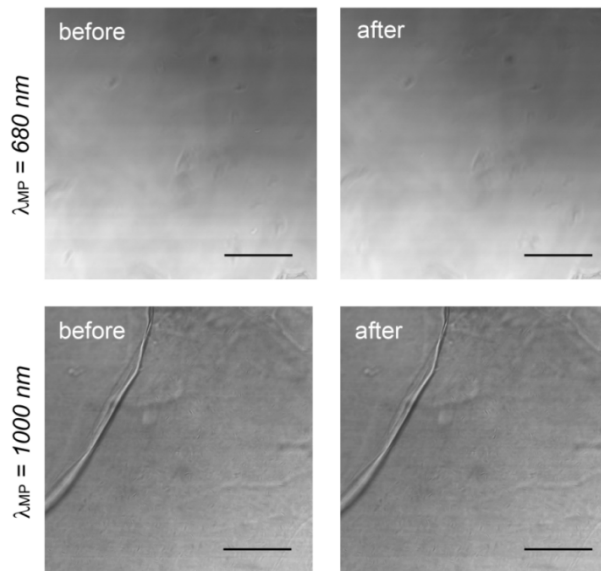


Fig. S2 Microscopy images showing control experiments for photopatterning of PEIMA supramolecular hydrogel. White light transmission images of PEIMA hydrogel in a solution without functional probes. No imprinting is visible before and after multiphoton laser irradiation at wavelengths of 680 nm (top) and 1000 nm (bottom). Scale bars are $100 \mu\text{m}$.