Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Pulsed laser writing of holographic nanosensors

A. K. Yetisen,†[a]* M. M. Qasim,†[b]* S. Nosheen, [b] T. D. Wilkinson,[b] and C. R. Lowe [a]

[a] Department of Chemical Engineering and Biotechnology, University of Cambridge, Tennis Court Road, Cambridge, CB2 1QT, UK

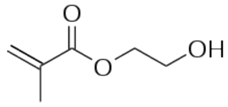
[b] Centre of Molecular Materials for Photonics and Electronics, Department of Engineering, University of Cambridge, 9 JJ Thomson Avenue, Cambridge, CB3 0FA, UK

* Corresponding authors: qmm20@cam.ac.uk and ay283@cam.ac.uk

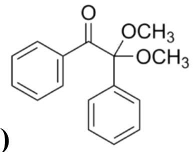
† Equal contribution

Preparation of the Recording Medium

Composition: HEMA (99.5 mol%), TACPP porphyrin (0.5 mol%) and DMPA hydrogel.



Hydroxyethylmethacrylate (HEMA)
(99% - liquid)



2,2-Dimethoxy-2-phenylacetophenone (DMPA)
(photoinitiator)
(99% solid)

Porphyrin (TACPP 2) (in DCM, 80 mg/mL)

The initial solvent was DCM, and it was evaporated and replaced by THF.

Total volume needed to make a full microscope slide of hydrogel: 200µL

Table. Composition of the polymer

Material	MW (g/mol)	Molarity (mol)	Molarity (%)
HEMA	130.14	0.00995	99.5
TACPP	1495.62	0.00005	0.5
DMPA	256.30		

In total, 0.0005 mol of monomer mixture was prepared.

Required weight

0.0004975 moles of HEMA, M * mw = mass; therefore 0.0004975 [mol] x 130.14 [g/mol] = 0.06474465 g
0.0000025 moles of TACPP, M * mw = mass; therefore 0.0000025 [mol] x 1495.62 [g/mol] = 0.00373905 g

Required volume

V = m / ρ, therefore for HEMA, V = 0.06474465 [g] / 1.07 [g/ml] = 60.51 µl
V = m / ρ, therefore for TACPP, V = 0.00373905 [g] / 0.08 [g/ml] = 46.74 µl

Photoinitiator: DMPA (0.001 g)

Total volume: ~107 µl

Porphyrin-based Holographic Sensor and its Bragg diffraction

The fabricated sensor showed visible-light Bragg diffraction (Figure S1).

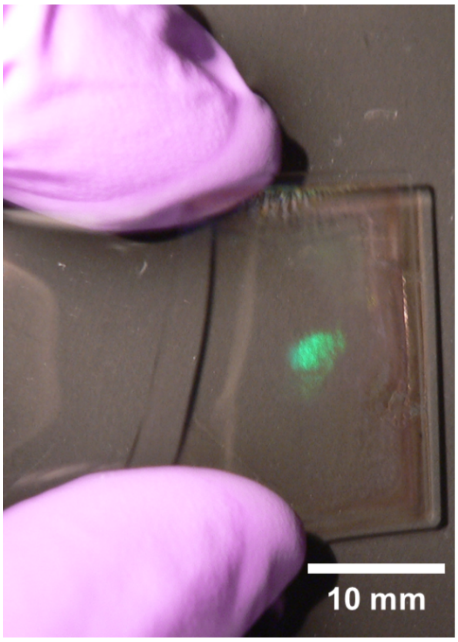


Figure S1. Tunable holographic sensor

Characterisation of the Porphyrin

UV-Vis measurements were taken to characterise the compound (Figure S2a) and polymer matrix before and after laser exposure (Figure S2b).

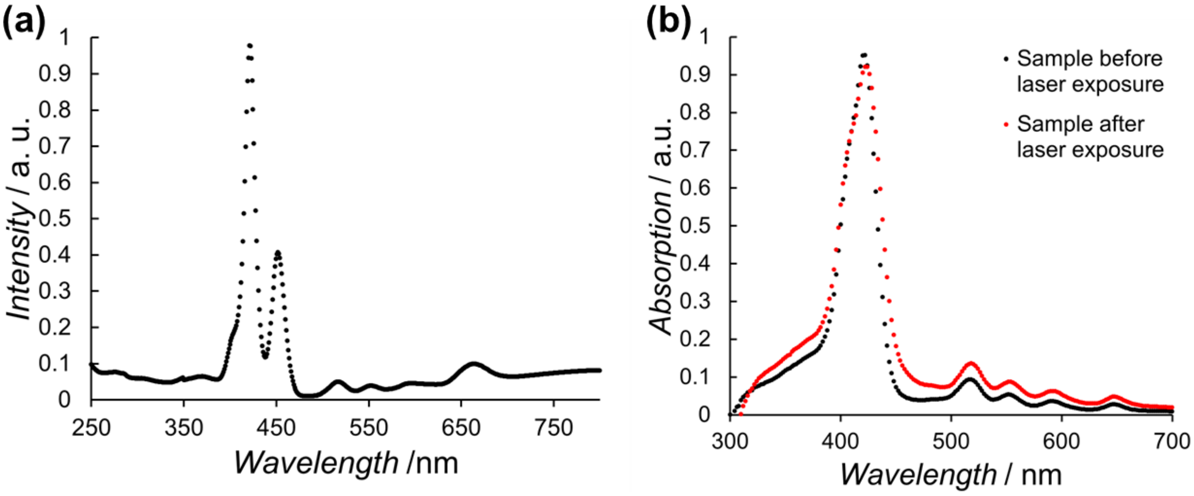


Figure S2. Ultraviolet-visible spectroscopy of (a) TACPP **2** in solution showing peaks at 422 nm (soret band) and 453 nm, (b) sample before and after laser-light exposure.

The system’s response to pure organic solvents

Wavelength shifts were recorded at -38, -24 and 37 nm deviated from ~320 nm for pure dichloromethane, chloroform and tetrahydrofuran, respectively (Figure S3).

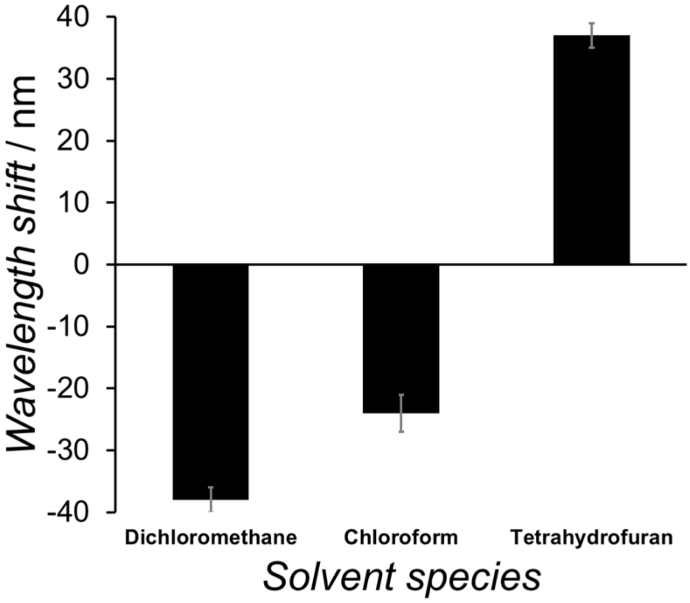


Figure S3. The response of the sensor to various organic solvents.

The influence of pH change on the absorption characteristics of the hologram

Upon changing the pH of the pHEMA-TACPP system from 7.0 to 3.0, the absorption showed a shift from 420 nm (pH 7.0) to 425 nm (pH 3.0) (Figure S4).

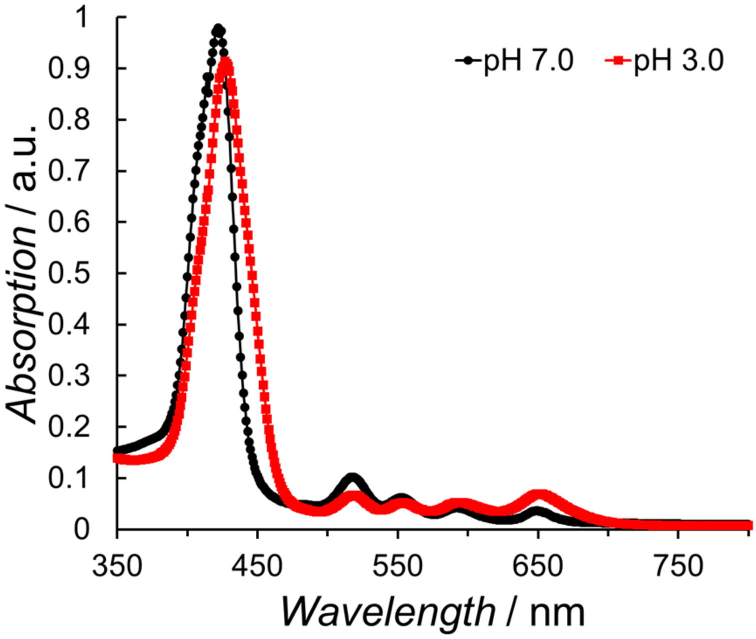


Figure S4. Ultraviolet-visible spectroscopy of pHEMA-TACPP system

The influence of low ionic strength on the sensor response

Different ionic strengths at low concentrations were tested with the fabricated sensor. Figure S5 shows the diffraction measurements.

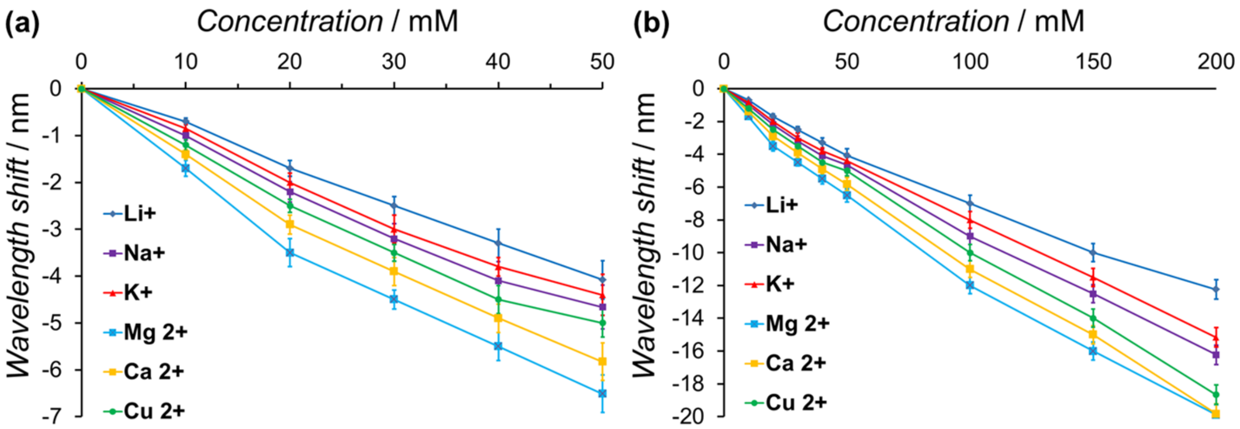


Figure S5. The effect of ionic strength on the sensor response (Donnan osmotic pressure (dominant) and the chelation effect)

The influence of high ionic strength on the sensor response

High concentrations of ionic strength cause the polymer to shrink due to the Donnan osmotic pressure (Figure S6).

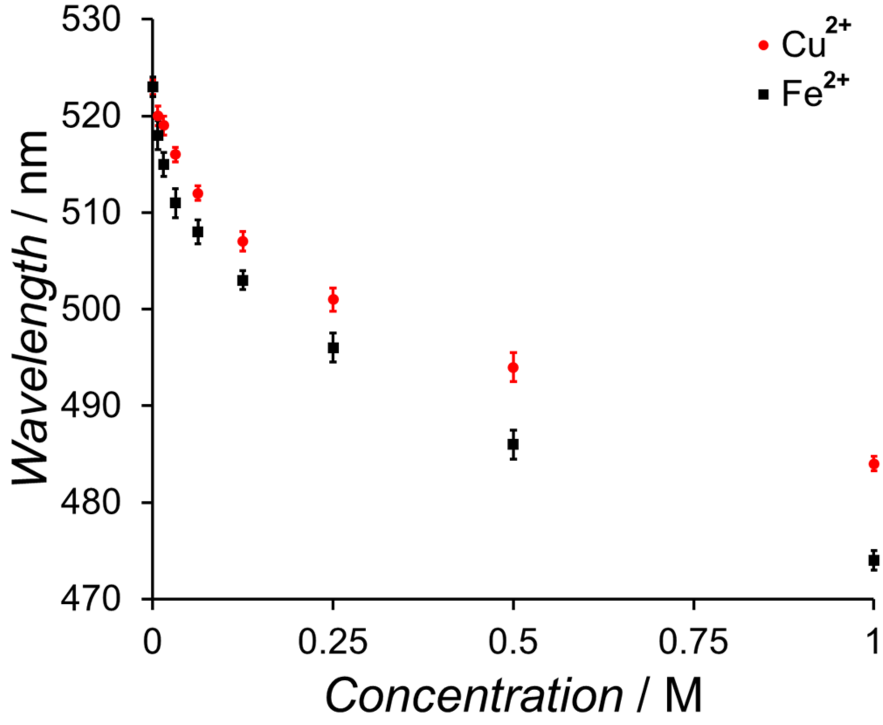


Figure S6. Shrinkage in the system due to the Donnan osmotic pressure.