**SUPPORTING INFORMATION**

# Controlled Core-to-Core Photo-polymerisation – Fabrication of an Optical Fibre-Based pH Sensor

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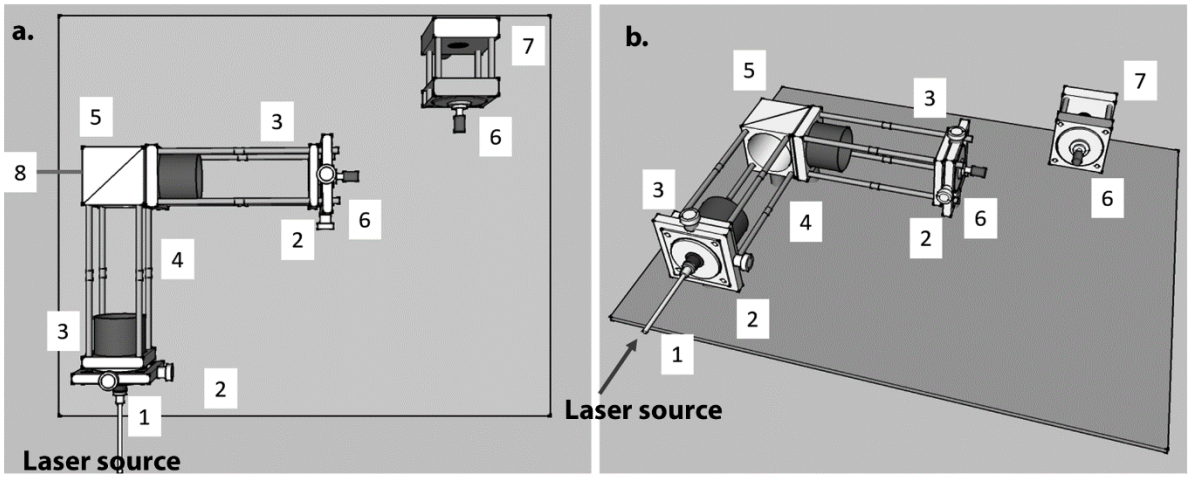


**Figure S-1.** Transverse view (a) and lateral view (b) of the optical set-up for photo-polymerisation and fluorescence measurement. Table S1 shows the list of the components used to assemble the set ups.

**Table S-1.** List of the components used to assemble the optical set-ups.

| **No.** | **Component** |
|---|---|
| 1 | Single mode fibre patch cable (1m, 405 – 532nm) |
| 2 | 5 mm travel XY translation mounts, connected to Z-axis translation mount |
| 3 | Molded glass aspheric lenses (350 – 700nm broadband antireflective (AR) coating) |
| 4 | 30 mm cage system – includes rods, and adaptors for fibres and lenses |
| 5 | Beam-splitter with dichroic mirror and bandpass filters<br>For 485 nm laser, the bandpass filter has the cut-on wavelength > 510 nm |
| 6 | Bare fibre terminator |
| 7 | Compact USB 2.0 CMOS cameras (resolution of 1280 X 1024 pixels, color sensor), connected to a display |
| 8 | Spectrometer collection (Ocean Optics USB2000+VIS-NIR-ES or Ocean Optics QE Pro). |

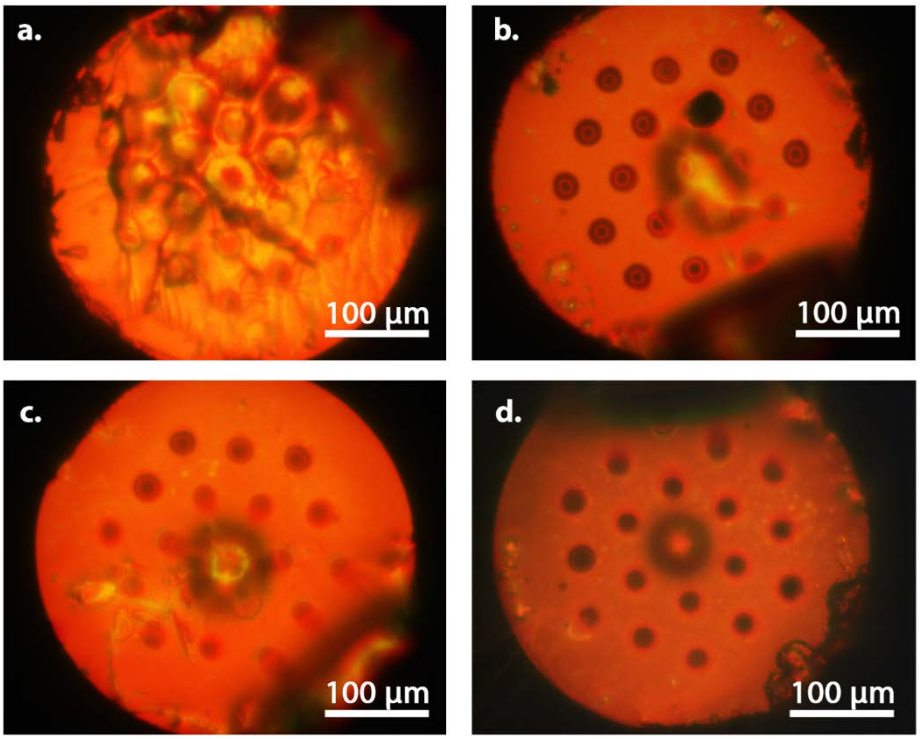


**Figure S-2.** Photo-polymerisation of fluorescein *O*-methacrylate and PEG diacrylate into etched-silanized optical fibres with variation of laser power, time of irradiation, and polymerisation solution composition: (a) 2.1 mW and irradiated for 1 minutes – large global polymer deposition. Polymerisation solution consisted of fluorescein *O*-methacrylate (0.025 M), TPO (0.025 M) and PEG-diacrylate (2.0 M). (b) 3.0 mW and irradiated for 5 seconds. (c) 1.1 mW and irradiated for 5 seconds. Polymerisation solution for (b) and (c) consisted of fluorescein *O*-methacrylate (0.07 M), TPO (0.01 M) and PEG-diacrylate (0.60 M). (d) 100 µW and irradiated for 5 seconds. Polymerisation solution consisted of fluorescein *O*-methacrylate (0.17 M), TPO (0.05 M) and PEG-diacrylate (1.37 M)). Fresh polymerisation solution used for every polymerisation.

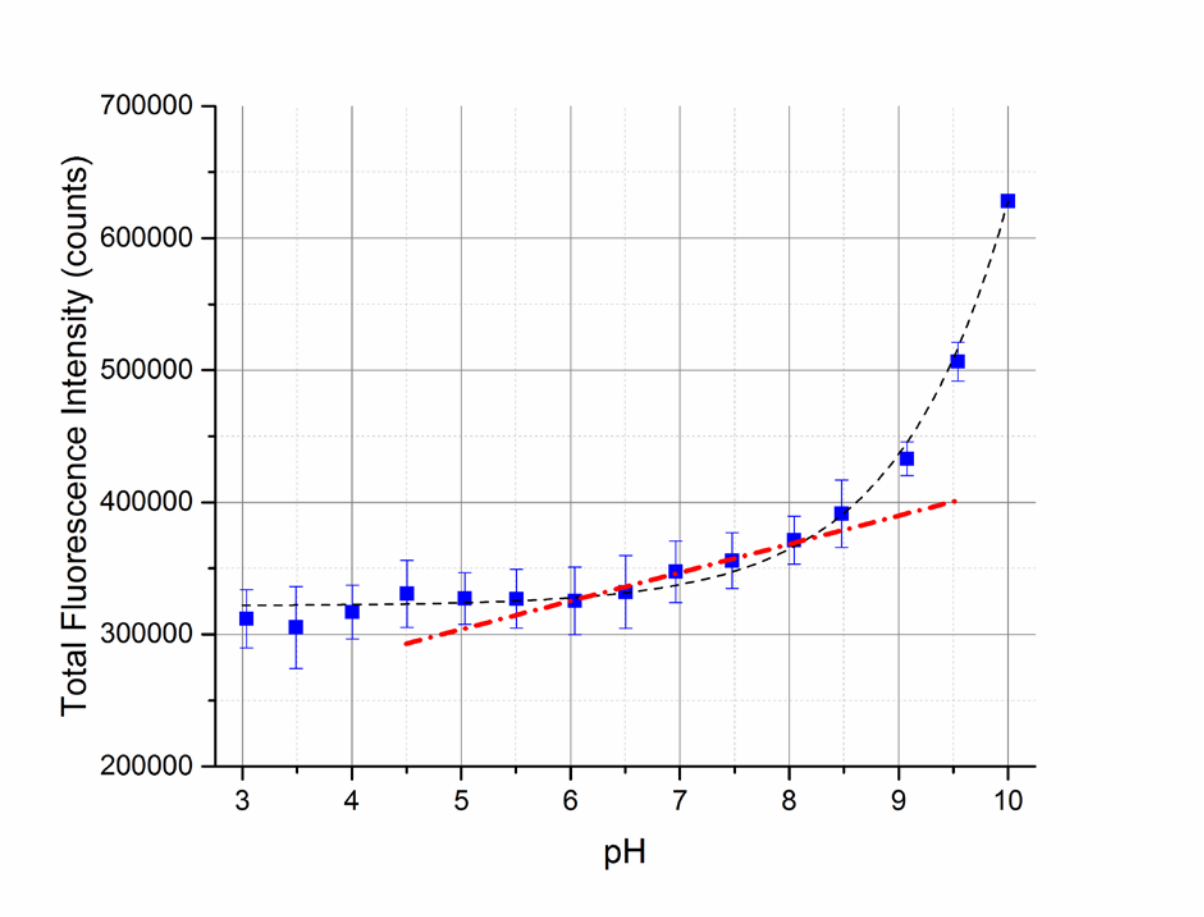


**Figure s-3.** pH response of the fluorescein-based sensor from pH 3 to pH 10 (n = 3). The sensor was excited at 485 nm, operating at 1.0 µW. The black dotted line showing the trend for the whole pH, and the red dotted line showing the linear trend from pH 6 to pH 8. The linear trend from pH 6 and pH 8 was plotted by considering only the data within their standard deviations at those pH's only (pH 6 – pH 8). All pH solutions were prepared in distilled water from the appropriate buffer system; citric acid (0.2 M) and sodium citrate (0.2 M) for pH range 3.0 – 5.5, $Na_2HPO_4$ (0.2 M) and $NaH_2PO_4$ (0.2 M) for pH range 6.0 – 8.0, and sodium carbonate (0.2 M) and sodium bicarbonate (0.2 M) for pH range 8.5 – 10.0. The pH values were measured using a glass-electrode pH meter (Mettler Toledo), and where necessary adjusted using the appropriate acid or base.

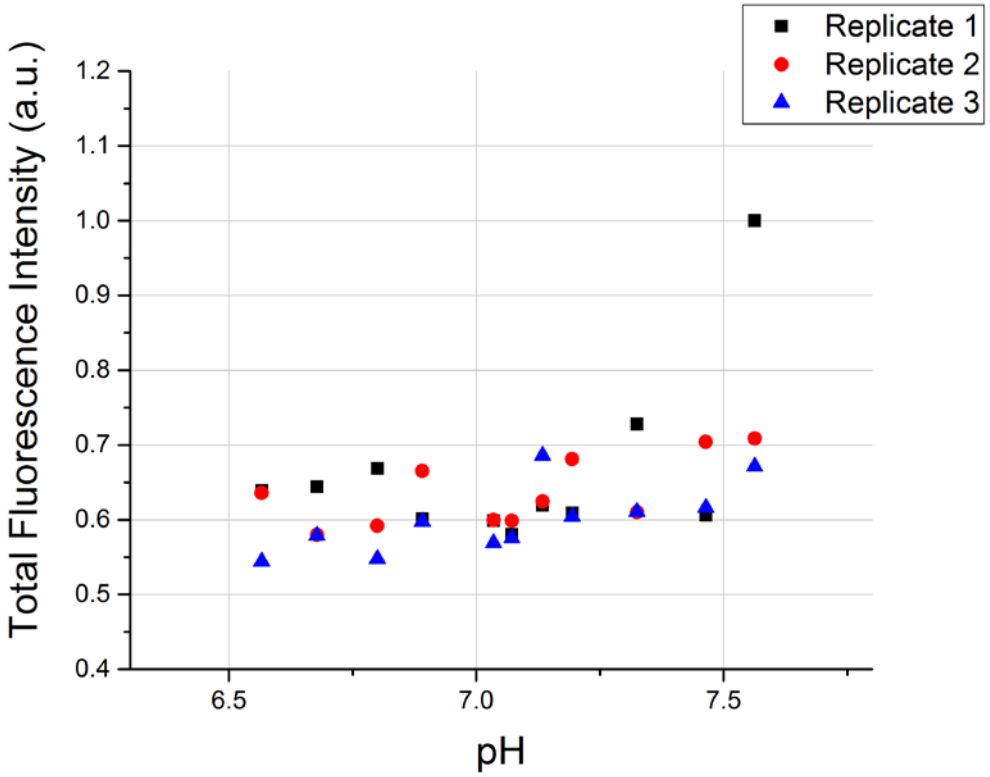


**Figure S-4.** Three replicates of integrated fluorescence spectra of the fluorescein o-methacrylate-based sensor at 0.1 pH increments from pH 6.6 to 7.6. For pH 6.6 to 7.5, all three points (black, red, and blue) were used to calculate the average total fluorescence intensity at each pH. Due to the anomaly, black point (Replicate 1) of pH 7.6 was not used to calculate the average fluorescence intensity at pH 7.6.

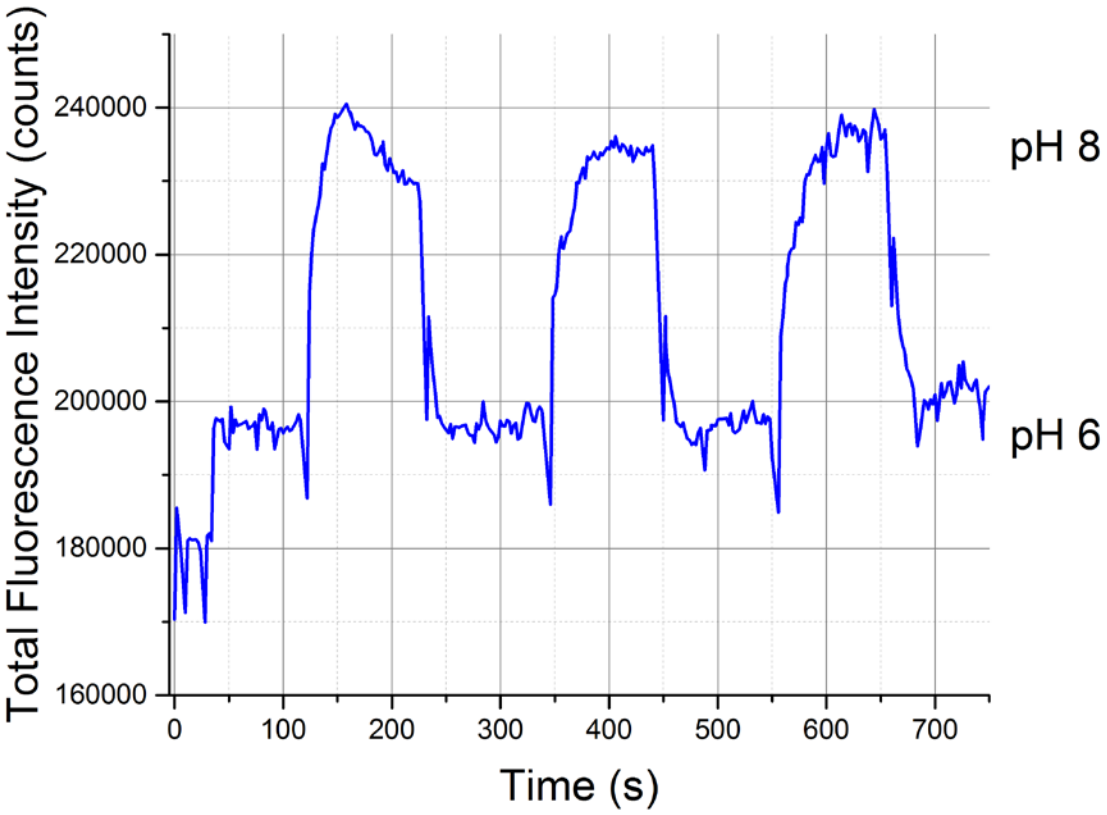


**Figure s5.** Time response of the sensor was found to be 31 + 3 seconds, measured by measuring changes in fluorescent intensity following movement of the sensor from pH 6 to pH 8 and back to pH 6.

## Experimental.

**Chemicals.** All chemicals were purchased from Sigma Aldrich Co. and were used without further purification, unless otherwise stated.

**Optical Fibre.** The multicore fibre was fabricated using the "stack and draw" process commonly used to fabricate photonic crystal fibres.[1] Initially, a Ge-doped optical fibre preform (ø = 32 mm, numerical aperture = 0.3, Draka-Prysmian) with a parabolic refractive index profile and a thin pure silica jacket was drawn down to rods (ø = 5.75 mm). To increase the core-to-core separation in the final fibre, each of the rods was then further jacketed with a pure silica tube (outer ø = 10 mm), and drawn down again to 19 rods (ø = 2.4 mm). The rods were then stacked in a hexagonal close-packed array, placed into a jacket tube, and drawn down under a vacuum to form the final fibre. The final diameter of the cores was 20 μm, with a center-to-center separation of 46 μm.

**Optical Instruments.** The 405nm laser was purchased from CVI Melles Griot, and the 485nm from PicoQuant. All other optical instrumentation was purchased from Thorlabs. The input and output powers of all light sources were measured using a power meter (Thorlabs).

**Sensor Fabrication.** A 5 cm length of coating at each end of a 1 m length of fibre optic (19 cores, ø = 20 μm) was removed using a sharp razor blade, followed by cleavage of each end (~ 1cm) to give a smooth surface. The cleaved fibres were cleaned using deionized water in an ultrasonic bath for 3 minutes. The fibre facets were etched in 40% hydrofluoric acid (HF) for 60 seconds before sonication in deionized water for 5 minutes. For surface activation, the etched fibres were dipped in methanol for 30 minutes, which was followed by dipping the fibres into a 20% (v/v) solution of 3-(trimethoxysilyl)propyl methacrylate in acetone overnight. The fibre was then washed in deionized water, and dried prior to polymerisation.

The transverse and lateral views of the optical set-up used for photo-polymerisation and fluorescence measurement are shown in the Figure S-1. The illuminating laser light was launched from a single mode fibre with alignment of the fibre controlled relative to the first (launch) lens to provide a collimated on axis beam into the fibre coupling system. The light was passed through a laser line filter (to ensure a clean laser spectrum of the desired wavelength) and the light reflected by a dichroic mirror onto the desired core of the optical fibre. The collimated beam was focused onto a single core of the optical fibre with XY and Z control of the optical fibre using a translational stage. The position of the core was noted through imaging the distal end of the fibre.

For fluorescence measurements, light emitted from the optical fibre (sensor) was roughly collimated by the coupling lens, and passed straight through the dichroic mirror, with an additional filter to remove any remaining laser excitation light. The fluorescent light was coupled into a spectrometer collection fibre with the same lens arrangement.

In all cases, compact aspheric lenses were used, where identical lenses were used in all locations to give unity magnification of the laser source (single mode fibre, MFD ~ 5um) onto the test optical fibre (19 cores, ø = 20

μm), and imaging of the test fibre core onto the spectrometer collection optics (50 μm collection fibre) for efficient coupling.

Dichroic and filters: A beam-splitter cube was used to mount the dichroic mirror and both the excitation and emission filters. During polymerisation, the set used was optimal for 405nm pump light, while for fluorescence measurements, the cube was replaced with a one containing a filter set for 485nm laser illumination and collection of wavelengths > 510nm into the spectrometer.

All stock solutions were prepared in *N*,*N*-dimethylacetamide (DMA). For the optimised polymerisation, the polymerisation solution comprising of fluorescein *O*-methacrylate (0.17 M), poly(ethylene glycol) diacrylate (PEG diacrylate, $M_n$ 250) (1.37 M) and diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) (0.05 M). After successful core-laser coupling, the distal end of the fibre was placed into the polymerisation solution. The power of the laser was optimized to be 100 μW from the 405nm laser.

**Absorbance and Fluorescence.** The absorbance spectrum of TPO was recorded using a UV-Vis spectrophotometer (UV-1800 Shimadzu). The fluorescence set-up was the same as the polymerisation set-up but using a laser emitting at 485 nm operated at 1.0 μW with a >510nm band-pass filter, unless otherwise stated. Fluorescence spectra were captured on a spectrometer (Ocean Optics USB2000+VIS-NIR-ES or QE Pro). For pH response (pH 3 to pH 10 (Figure S3), and time response (Figure S5) studies), the 485 nm laser in combination with a pulsed laser driver (PDL 800-D, Picoquant) was used, and the fluorescence spectra was recorded with an integration time of 500 ms. For sensor analysis between pH 6.6 to pH 7.6 (Figure 2d) and photo-stability studies (Figure 2e), measurements were performed by manually opening a shutter and recording the fluorescence spectrum with an integration time of 1 second. The manual shutter was closed between measurements to avoid any unnecessary photo-bleaching. Fluorescence imaging on the distal tip was captured through a fluorescent microscope (EVOS Fl, Bothell, WA) equipped with a GFP filter set (excitation wavelength = 470/22 nm).

**References.**

1. P. Russell, *Scienc*e 2003, **299** (5605), 358–362