

Title: Tracking a photo-switchable surface-localised supramolecular interaction *via* refractive index

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Abstract: As supramolecular chemistry evolves, from the design of interactions in the solution and the solid state to applications at surfaces, there is a need for the development of analytical techniques capable of directly interrogating surface-localised supramolecular interactions. We present a proof-of-concept integrated optical Bragg grating sensor, capable of evanescently detecting small changes in refractive index at infrared wavelengths within a microfluidic system. The high spectral fidelity of the Bragg gratings combined with precise thermal compensation enables direct monitoring of the surface throughout the experiment, enabling the sensor to probe changes *in situ* and in real-time during surface preparation and chemical modification, and then to follow the progress of a dynamic surface-localised supramolecular interaction. In this study the sensor is assessed through the investigation of a photo-switchable inclusion complex between an azobenzene-functionalised surface and cyclodextrin in aqueous solution. The ability to investigate supramolecular interactions directly in real-time upon a planar surface *via* refractive index offers a valuable new tool in the understanding of complex dynamic supramolecular systems.

Summary of available data

Data is provided in support of the article and comprises the spreadsheet and corresponding graphs used to generate Figure 2, 3 and 4 in the manuscript. This is provided as both in excel (.xlsx) and open document (.pdf) formats.

Figure 2(a,b)

The integrated optical device consisted of four spectrally distinct Bragg gratings; an un-etched physical reference ($\lambda_B = 1538\text{nm}$) and three 'sensor' gratings ($\lambda_B \approx 1546, 1556, 1566\text{ nm}$) distributed along a linear waveguide. The reflected spectrum of the integrated optical device is plotted in air ($n = 1.00$, solid line) and in water ($n = 1.33$, dashed line) both (a) logarithmically and (b) as an extract of the data on a linear scale, showing the Gaussian profile of the Bragg peaks and low optical noise. The red line in (a) represents the background reflection spectrum from the erbium emission of the broadband source alone and it is this profile combined with reduced scattering loss that leads to the increase in the peak height in (b).

The data consists of the reflected power as a function of wavelength as measured directly in μW by the Optical Spectrum Analyser and after conversion to dBm.

Figure 2c

*The sensitivity to bulk analyte refractive index (n_{anal}) as measured by the average Bragg wavelength shift of the 'sensor' gratings resulting from changes in the effective refractive index (Δn_{eff}) of the waveguide, for the transverse electric (**X**, sensor) and the orthogonal, transverse magnetic (**O**) optical modes. The dashed-lines correspond to the bare sensor, illustrating the enhancement from the deposition of an 80 nm thin film of tantalum pentoxide (solid line); loss of guidance of the optical mode at a lower analyte refractive index is the cost of this increased sensitivity.*

The data consists of the Bragg wavelength shift, averaged over the three sensor gratings (co2-4) and referenced to air ($n=1.000$) for each Cargille oil tested. The Bragg wavelength shift for each grating was calculated by taking the average of 10 scans while immersed in the oil, with the device cleaned with acetone upon changing oils. This process was repeated for TM and TE polarisations, both before and after sputtering with a thin-film of tantalum pentoxide.

Figure 3

The Bragg wavelength shift for the azobenzene-APTES modified sensor surface in the presence of a 10 mM α -cyclodextrin solution (black circles, guideline traces the five-point moving average). Reversible photo-switching was observed upon alternating exposure to light at 370 nm ('UV') and 464 nm wavelength ('blue'). Thermal compensation was achieved through a first order approximation, derived from differential analysis of the two orthogonal polarizations of the waveguide. For comparison, the corresponding Bragg wavelength shift for the unetched reference Bragg grating is shown in red, where $d\lambda_{ref}/dT = 10 \text{ pm}/^\circ\text{C}$.

The data consists of the Bragg wavelength shift of the reference grating, in picometres and offset to an initial shift of 8 pm (red circles). The time-resolved sensor trace (black circles) was calculated by averaging the Bragg wavelength shift of the TE mode of the three sensor grating as a function of time. This was then referenced against the corresponding average TM mode data-set to remove the effect of temperature and finally an offset of 9 pm was applied to improve clarity. N.b. as this is presented as a shift rather than the absolute wavelength/refractive index, the position of the origin is arbitrary and does not translate between figures.

Figure 4a

*The average Bragg wavelength differential, $\delta(\Delta\lambda_B)$, between the α -CD/trans-azobenzene complex and *cis*-azobenzene surfaces, as a function of α -cyclodextrin concentration, plotted on a logarithmic x-axis. This average was calculated from the independent, simultaneous measurement of three Bragg gratings in thermal equilibrium over three light cycles, with the error bars representing the standard error.*

The data consists of the Bragg wavelength differential (measured in picometres), as calculated by measuring the average peak to peak difference in Bragg wavelength over three light cycles for the three sensor gratings (cf. Figure 3). This was repeated for each concentration of α -cyclodextrin. The error was estimated as $\pm 1 \text{ pm}$.

Figure 4b

*The difference in analyte refractive index, $\delta(\Delta n_{anal})$, between the α -CD/trans-azobenzene complex and *cis*-azobenzene surfaces, after correction for the sensitivity change arising from dn/dc of aqueous α -CD, plotted on linear axes.*

The data consists of the dataset in Fig.4a, as expressed as the difference in analyte refractive index and after correction for the dn/dc of the α -cyclodextrin solutions. This was achieved by calculating the refractive index, n_{anal} , of each solution from the measured value of dn/dc of $0.141 \text{ cm}^3/\text{g}$ and the refractive index of water ($n = 1.33$). Having determined n_{anal} for each solution, the sensitivity ($d\lambda/dn_{anal}$) was then calculated at each concentration from the differential of a polynomial trendline applied to the calibration dataset, shown in black in Figure 2c of the manuscript. It was found that the large increase in concentration from 330 nM to 50 mM resulted in an increase in $d\lambda/dn_{anal}$ from 49.8 to 56.7 nm/RIU for this device. The measured Bragg wavelength differential was then converted using the calculated sensitivity at each measured concentration to give the difference in analyte refractive index between the α -CD/trans-azobenzene complex and *cis*-azobenzene surfaces. Error bars were calculated by applying the specific sensitivity for each concentration to the estimated error of $\pm 1 \text{ pm}$.