



A comparative study of the fluorescence and photostability of common photoswitches in microstructured optical fibre



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ABSTRACT

The fluorescence spectra and photostability under 532 nm laser excitation of four different common photoswitches (an azobenzene, spiropyran, indolyfulgide, and a diarylperfluorocyclopentene) were investigated in a silica microstructured optical fibre. An example of each photoswitch was examined in solution and physically adsorbed to the silica fibre surface. This comparison was made to define fluorescence behaviour in these two states and to determine which photoswitch has the best performance in this light intense microenvironment. The azobenzene and the spiropyran switches demonstrated the strongest fluorescence response and the least degradation of the fluorescence signal.

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1. Introduction

The study and development of smart materials and sensors that can be switched on and off or modulated in some way, is an important area of current endeavour [1–4]. These materials must possess at least two functional states that can be interconverted by an external stimulus such as heat, electric potential or light. Of particular interest in this context is the use of an organic photochromic dye that can be attached to a solid support such as polymer, nanoparticles, or bulk surfaces; providing materials where surface properties such as hydrophobicity, charge, conductivity, colour, molecular recognition, and material size can be easily controlled. Such photoswitchable materials have been proposed for many applications; for example in data storage [5], nano-electronics [6,7], switchable polymers [8,9], nano-machines [10,11], gas storage [12], drugs [13,14], and sensor devices [15–17].

Microstructured Optical Fibres (MOFs) show particular promise as a new material for smart sensor devices [18]. The holes surrounding the micron sized waveguide core in wagon-wheel MOFs

(Supporting Fig. S1) allow interaction between an analyte within the holes and the evanescent field of guided light to allow the absorbance and fluorescence (through light recapture) of the analyte to be detected [19]. A MOF provides a very sensitive sensing platform due to its large light interaction path length and ability to sample nano-litre quantities; and combined with its small size, biocompatibility and ability to sense remotely allows for use within an in vivo environment [20]. Chemical detection at pico-molar sensitivity has previously been demonstrated in such systems [21,22]. However, a major limitation of such optical sensing devices is that the sample can be exposed to high intensity light, which can result in bleaching. As such, the organic sensing molecule needs to be photostable, especially if required over extended periods and repeated use, and particularly if fixed to the photon rich waveguide surface [20,23].

MOFs are particularly promising for fluorescence based applications, rather than absorbance, as the fluorescence spectrum is measurable at either end of the fibre. Therefore, all instrumentation required for analyte excitation and detection can be located at one end of the fibre; freeing the other end for sample interaction, such as for fibre tip based sensing [24]. However, while the absorption and photoswitching properties of common photoswitches for use in such devices are well studied and reported, the associated fluorescence spectra are typically not, possibly due to a tendency to have poor fluorescence yields [25]. However, this is of lesser

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importance for MOF sensors due to enhanced sensitivity. This paper addresses this shortfall by comparing and contrasting the fluorescence and photostability of four common photoswitches within a common MOF sensing system under high intensity light conditions broadly found within fibre sensors. Conclusions are drawn regarding the suitability of each photoswitch for use in MOF based sensors, and potentially other devices that utilize high intensity light.

Four examples of photoswitches, each representing a different class of organic photoswitch were chosen for study, i.e. an azobenzene, spiropyran, indolyfulgide, and diarylalkene (Fig. 1). Members of these classes are known to have high fatigue resistance, an ability to operate at biologically compatible wavelengths, and well-defined switching states that exhibit large conformational differences; making them suitable for applications in devices. Azobenzenes and spiropyrans have already found use in MOF devices [26–30], while the indolyfulgide (**CF₃-fulgide**) and diarylalkene (**DA1**) show promising properties in terms of high photoswitching fatigue resistance, a large spectroscopic change upon photoswitching, and tunable absorption profiles within the biologically viable visible-red region [31–33]. The photochemical properties of unsubstituted spiropyran [34] and azobenzenes [35] on optical fibre have been reported. In addition, we have found little spectral differences between substituted and non-substituted azobenzenes (supporting Fig. S4) and spiropyrans [22,29,30,36,37] particularly in the absence of ion binding. Therefore, for this study, we focused on the characterization of 3-carboxy-5,2',4'-trimethoxy azobenzene (**Azo1**) [20,28] and spiropyran **SP1** [29]. These compounds have been reported in applications for sensing of Al ions with respect to corrosion detection and sensing of zinc ions in biology. Importantly, **Azo1** and **SP1** can be attached to a surface, which makes them ideal candidates for this study in the context of sensor development. The trifluorinated indolyfulgide (**CF₃-fulgide**), first reported by Yokoyama [31], has high fatigue resistance, high thermal stability (no thermo-isomerisation) and large separation between ring opening and closing photoisomerisation wavelengths, and as such shows much promise for applications in data storage [38–40]. However, 3-indolyfulgides, such as **CF₃-fulgide**, do not have a strong fluorescence, which limits their readout capacity [41]. Diarylalkene, 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)-perfluorocyclopentene (**DA1**) [32,42], has high thermal stability and high photofatigue resistance (>850 cycles) in hexane, demonstrating the potential of diarylalkenes for devices applications.

The absorbance and fluorescence spectra of each of the four photoswitches (**Azo1**, **SP1**, **CF₃-fulgide** and **DA1** (Fig. 1)) were determined in both DMSO and acetonitrile (polar aprotic solvents) and also within a MOF. The effect of solvent, irradiation brightness and surface proximity on the emission spectra and the stability of the respective photoswitches on repeated exposure to the excitation light source was then defined. These two solvents were chosen for comparison as they provided sufficient solubility of all photoswitches, while also being biologically relevant; the photoswitches were found to have poor solubility in water or mixed acetonitrile:water (1:9) solutions. Finally, the fluorescence, photostability and photoswitchability of each photoswitch was investigated in the solid state, by physically adsorbing them onto the fibre surface, in order to compare to the solvated systems and to approximate surface functionalized behaviour.

2. Experimental section

2.1. Materials

All solvents used were HPLC grade obtained from Sigma-Aldrich and were used as supplied. The diarylalkene, **DA1**, was obtained

from TCI co. (Tokyo). The purity of this compound was confirmed by ¹H NMR spectroscopy and was used as supplied. All other photoswitches were synthesized following published methods; **Azo1** [28], **CF₃-fulgide** [43,44], and **SP1** [29].

The wagon wheel suspended core optical fibres (MOF) (Fig. S1) used in these experiments were made from high purity silica F300 glass by the fibre drawing technique, and fabricated in-house [45]. The fibres have hole diameters of 27.7 μm, providing a total fill volume of 18 nL/cm. The core size is 1.5 μm.

2.2. Apparatus

2.2.1. Cuvette measurements

Bulk solution absorbance and fluorescence measurements of the photoswitches in acetonitrile and DMSO (10 μM–1 mM) were obtained using a CARY 5000 UV-vis spectrometer and a CARY Eclipse fluorometer respectively. Measurements were conducted in a quartz cuvette, path length 10 mm, volume 700 μL. Fluorescence emission measurements were obtained after excitation at 532 nm, emission slit width 5 mm, excitation slit width 10 mm, and at 20 °C. Switching experiments were performed in the cuvette using a mercury lamp (UVP, 8 W, 352 nm (filtered BLB) or 254 nm (shortwave tube) or with a halogen white light.

2.2.2. Fibre fluorescence optics setup

The optics setup for determining the fluorescence of fluorophores within a MOF is shown in Fig. 2. An attenuated 25 mW fibre coupled laser light source (CrystaLaser) with an excitation wavelength of 532 nm was coupled into the core of the MOF. Optimal alignment and calibration of the MOF to the optics setup was achieved by monitoring the optical power transmitted by the fibre at the 'fill' end using a power meter (Thorlabs). The fluorophores fluorescence emission is captured by the fibre and its propagation in the backward direction [19] was recorded with a Horiba iHR550 spectrometer with Synapse CCD detector (100 g/mm grating, 0.5 mm entrance slit width). Photoswitching was performed by externally irradiating (Fig. 2, blue box) the filled MOF with a mercury lamp (UVP, 8 W, 352 nm (filtered BLB) or 254 nm (shortwave tube)).

2.3. Fibre fluorescence and photostability

Solutions containing each photoswitch (**Azo1**, **SP1**, **CF₃-fulgide** or **DA1**, Fig. 1) in DMSO or acetonitrile (1 mM) were drawn into separate 20 cm lengths of MOF fibre by capillary action over a 1 min period (filled length of approx. 14 cm). The sample was then exposed to 50 × 8 ms pulses of 532 nm light of either approx. 0.017 mW for the **SP1** or 0.17 mW for the other photoswitches (**Azo1**, **CF₃-fulgide** or **DA1**) (determined by the optical power transmitted by the empty fibre) and the resulting fluorescence was measured after each pulse. This excitation power provided a significant fluorescence signal for detection and analysis. The change in integrated peak intensity over the 50 pulses was calculated to compare the relative rates of photobleaching.

2.4. Solid state fluorescence measurements

Solutions of photoswitches **Azo1**, **SP1**, **CF₃-fulgide** or **DA1** in acetonitrile (1 mL, 1 mM) were each separately flowed through 40 cm lengths of MOF by external positive pressure supplied by a nitrogen source. Each fibre was then cleared of solution and dried by flowing nitrogen through the holes overnight. A 3 cm length was removed from each end of each fibre to remove possible end-facet damage that may have occurred during the filling process and the remaining fibre was split into two 15 cm sections for analysis. Each

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