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Fluorescence and Photostability of Organic Photoswitches on 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) was investigated in a silica microstructured optical fibre. An example of each photoswitch was examined both in solution as well as physically adsorbed to the silica fibre surface. This comparison was made to determine any fluorescence behavioral differences as a result of each solution and the optical fibre fluorescence sensing platform, and to determine which photoswitch has the best performance in this light intense microenvironment. It was found that the azobenzene and the spiropyran showed the most favorable behavior; showing a stronger fluorescence response and the least degradation of the fluorescence signal.

Keywords: Fluorescence; Photochromism; Photostability; Microstructured Optical Fibre; Optical Fibre Sensors; Azobenzene; Spiropyran

Highlights:

- Photostability of photoswitches investigated with Microstructured Optical Fibre.
 - Comparison of the fluorescence of four photoswitches when adsorbed to a surface
 - Photoswitching of spiropyran using MOF in solution and on a surface
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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 endeavor.[1-4] These materials must possess at least two functional states, the relative activity of which is defined 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 (Figure 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-liter sample solutions. However, a major limitation of optical sensing devices, such as optical fibres, 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, 21]

The use of a fluorescent photoswitch in these systems offers some advantage over simply detecting absorbance changes. Fluorescence spectroscopy is more versatile for signal acquisition as the instrumentation for analyte excitation and detection needs only to be on one 'side' of the sample, since the fluorescent signal can travel back along the fibre, which allows a wider range of applications; such as, fibre optic tip based sensing.[22] 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. This paper addresses this shortfall by comparing and contrasting the fluorescence and photostability of four common photoswitches. This is done by using a MOF, as this allows this comparison to be done under the high intensity light conditions that would typically be found within fibre sensors. . Conclusions can then be drawn regarding the suitability of each photoswitch for use in MOF based sensors and which could be transferrable to 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 (Figure 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,[23-27] 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 visible-red region.[28-30] In this context, we recently reported the use of 3-carboxy-5,2',4'-trimethoxy azobenzene (**Azo1**) in combination with a MOF for the sensing of aluminium ions.[21, 25] Also we recently reported the use of the spiropyran **SP1** within a MOF for the sensing of zinc ions.[26] This

spiropyran exhibited good switchability in solution, a feature common to all spiropyrans.[31-33] The trifluorinated indolylfulgide (**CF₃-fulgide**), first reported by Yokoyama,[28] 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.[34-36] However, 3-indolylfulgides such as **CF₃-fulgide** are not known to have a strong fluorescence, which limits their readout capacity.[37] The last example, the diarylalkene 1,2-bis(2,4-dimethyl-5-phenylthiophen-3-yl)-perfluorocyclopentene (**DA1**)[29, 38] has high thermal stability and high photofatigue resistance (>850 cycles) in hexane, demonstrating the potential of diarylalkenes for devices applications.

Figure 1. Structures of the photoswitches investigated.

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**,[25] **CF₃-fulgide**,[39, 40] and **SP1**[26].

The wagon wheel suspended core optical fibres (MOF) (Figure S1) used in these experiments were made from high purity silica F300 glass by the fibre drawing technique, and fabricated in-house.[41] 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 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 Figure 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 (Figure 2, blue box) the filled MOF with a mercury lamp (UVP, 8 W, 352 nm (filtered BLB) or 254 nm (shortwave) tube).

Figure 2. Optical set-up for measuring the fluorescence with a Microstructured Optical Fibre.

2.3 Fibre Fluorescence and Photostability

Solutions containing each photoswitch (**Azo1**, **SP1**, **CF₃-fulgide** or **DA1**, Figure 1) in DMSO or acetonitrile (1×10^{-3} mol L⁻¹) were drawn into separate 20 cm lengths of MOF fibre by capillary action over a 1 min period (filled length of approx. 14cm). The sample was then exposed to 50 x 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 fibre was visually inspected under an Olympus BX51 optical microscope with a 20x objective to check for obstructions in the fibre holes, fluorophore precipitation, and complete drying. For analysis, each 15 cm section was coupled to the optical setup in Figure 2 and fluorescence signal was measured as described in Section 2.3.

3. Results and Discussion

The absorbance and fluorescence spectra of each of the four photoswitch species (**Azo1**, **SP1**, **CF₃-fulgide** and **DA1** (Figure 1)) were determined in both DMSO and acetonitrile using a commercial benchtop spectrometer as defined in the experimental Section 2.2.1. These polar aprotic solvents provided sufficient solubility to allow detection of absorbance and fluorescence spectra, while also being biologically relevant and compatible. This then allowed for a comparison of the effect of the different solvents on the spectra at each photoswitched state. A solution of each photoswitch was added to a Microstructured Optical Fibre (MOF) to investigate the effect of a MOF microenvironment, i.e. irradiation brightness and surface proximity, on properties such as the emission spectra and the stability of the respective photoswitches on repeated exposure to the excitation light source. 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 systems.

3.1. Azobenzene

The fluorescence spectra of solutions of **Azo1** (Figure 1) in DMSO and acetonitrile, from excitation at 532 nm, were recorded using a bench top fluorometer in order to compare with the fluorescence spectra obtained using a MOF. **Azo1** showed a weak fluorescence signal, with an emission max at 595 nm in DMSO and 572 nm in acetonitrile (see Figure 3A, blue and red). The DMSO fluorescence signal intensity was four times more intense, reflective of a stronger observed absorbance (ϵ_{450} DMSO = 265000 L mol⁻¹ cm⁻¹ whereas ϵ_{450} acetonitrile = 84000 L mol⁻¹ cm⁻¹). Irradiation of **Azo1** with 352 nm light from a UV black light, to promote *trans* to *cis* photoisomerisation, of the azobenzene did not change either the fluorescence or absorbance (Figure S2). This may be due to the poor absorption and photoswitching yield at 352 nm, or possibly a fast thermal isomerisation back to the initial *trans* isomer on the experiment timescale.[42]

The weak signal observed for **Azo1** is consistent with the general observation that azobenzenes have poor fluorescence yields.[43, 44] However, the fluorescence and photostability are still relevant properties of some azobenzenes; i.e. as some azobenzenes, such as **Azo1**, are used as fluorescence based sensors due to a fluorescence turn-on upon ligand interaction, also, as photoswitchable compounds, azobenzenes are routinely exposed to light to induce photoswitching. The fluorescence signal of **Azo1** in a MOF and the fluorescence decay over 50 x 8 ms pulses was obtained after filling a fibre with a 1 mM solution of **Azo1** in DMSO or acetonitrile as outlined in Section 2.3. The fluorescence spectrum of **Azo1** in a MOF was then determined, shown in Figure 3A. From these experiments, several observations were made. The fluorescence of **Azo1** in the MOF is broader and red shifted compared to that determined in the cuvette spectrometer, with emission maximum at 630 nm and 600 nm in DMSO and acetonitrile, respectively (Figure 3A, orange and purple). This fluorescence was similar to that previously reported for **Azo1** in water and on poly(allylamine hydrochloride) coated fibre surfaces.[25]

Figure 3. (A) Fluorescence of **Azo1** in cuvette in acetonitrile (10 μ M, blue) and DMSO (1 μ M, red); and normalized fluorescence within a MOF in acetonitrile (purple), DMSO (orange) and adsorbed to fibre surface (green). (B) Integrated fluorescence signal of the azobenzene in a MOF during pulsing with 532 nm light in DMSO (blue) and acetonitrile (black), fitted with a second order exponential decay model (red).

The photodecay study showed that in DMSO solution the fluorescence intensity of **Azo1** decreased by 33% over the first ten pulses relative to the initial intensity (Figure 3B). This rapid decrease in fluorescence is likely due to photobleaching rather than from *trans* to *cis* photoisomerisation, as the original fluorescence spectrum was unable to be regenerated thermo- or photochemically after prolonged exposure with white or UV light; as would be expected if photochromism was occurring.

After the initial rapid decrease the fluorescence signal degrades at 0.05% per pulse. Interestingly the decrease in fluorescence trended to a non-zero value, this could possibly be due to diffusion within the fibre, as only the photoswitch close to the fibre core will undergo photoexcitation and bleaching. The photobleaching rate of **Azo1** in acetonitrile is lesser than in DMSO, here the signal decayed by 12% of the initial intensity over the whole 50 pulses (0.24% per pulse). Because of the slower rate of photodecay a linear decay was not observed within the experiment timescale, unlike with the DMSO sample. This experiment demonstrates that the excitation laser light used to provide the fluorescence signal promotes photodegradation of **Azo1**. The extent of degradation is solvent dependent, with acetonitrile giving a reduced rate of decay compared to DMSO.

3.2. Spiropyran

The fluorescence spectrum of spiropyran **SP1** (Figure 1) in a MOF were obtained as described in Section 2.3. The DMSO and acetonitrile samples gave only a small difference in fluorescence peak shape; with maximum fluorescence observed at 640 nm in both solvents (Figure 4B orange/purple). This is red shifted from the 620 nm fluorescence peak observed in cuvette using the benchtop spectrometer (Section 2.2, Figure 4A). Photoswitching of **SP1** to **MC1** was induced on exposing the filled fibre to UV black light (a process first confirmed in cuvette as a colouration at 562 nm in the UV-vis absorbance spectra. (Figure S2B)). The **MC1** isomer gives a significant increase in the emission intensity at 650 nm, as would be expected from its more fluorescent cyanine structure.[45] Pulsing of the **MC1** solution with the excitation light source led to a rapid decrease in the 650 nm merocyanine peak to give the previously observed **SP1** like fluorescence spectra within four pulses (Figure 4C, insert). Irradiation of this ‘bleached’ solution with UV light caused an increase in the fluorescence due to regeneration of **MC1**, although to a reduce intensity than previously observed. This suggests that the 532 nm excitation light induced rapid reverse **MC1** to **SP1** photoswitching. This is not ideal for continuous and repetitive measurements involving a photoswitchable state, highlighting the requirement to have a non-destructive readout capability for use in optical devices. Non-destructive readout has previously been shown to be achievable by carefully selecting an appropriate excitation wavelength which causes little or no change in the photostationary state.[29, 46] A solution of **SP1** in either DMSO or acetonitrile was exposed repeatedly to the pulsing excitation light source in order to determine its photostability over time. For DMSO this produced a gradual decrease in the intensity of fluorescence at 640 nm and the appearance of a new peak at 740 nm. This second peak was not photochromic on exposure to UV or white light and it is likely due to a product of photodegradation induced by the 532 nm light. Exposure of **SP1** to the laser pulses reduced fluorescence rapidly over the first five pulses in both solvents; by 27% in DMSO and by 11% in acetonitrile. A reduced linear decay rate of 0.13% per pulse was observed in acetonitrile over the next 40 pulses (Figure 4B).

Figure 4. Fluorescence of **SP1** and **MC1** in cuvette (**A**) in acetonitrile (dark blue/light blue) and DMSO (red/pink); and normalised fluorescence within a MOF (**B**) in acetonitrile (purple), DMSO (orange) and adsorbed to fibre surface (green) and photoswitched on the

surface (black). C) Integrated fluorescence signal of the **SP1** in a MOF during pulsing with 532 nm light in; DMSO (blue), acetonitrile (black), and after UV photoswitching to the **MC1** isomer (insert), fitted with a second order exponential decay model (red).

A comparison of light induced decay of fluorescence of both **Azo1** and **SP1** shows that the two photoswitches showed a similar trend, in that the two solvent systems produce a different response to repetitive irradiation. Both of the photoswitches show increased stability in acetonitrile compared to in DMSO; manifest as a decreased rate of fluorescence signal loss and reduced formation of fluorescent side products.

3.3. Indolyfulgide

To the best of our knowledge, there are currently no reports on the fluorescence of an 3-indolyfulgide, such as **CF₃-fulgide** (Figure 1). One possible reason could be attributed to a low quantum yield of fluorescence. This therefore limits the application of fulgides within devices with fluorescence readout capabilities. However, this limitation may be overcome by the use of a MOF, which has a long optical path length, effectively concentrating the sample within the region where the fibre guides light and, therefore, enhances the detection of any weak fluorescence emission. This would then provide an opportunity to use fulgides, and potentially other weak fluorophores, in sensing applications. To investigate the fluorescence of **CF₃-fulgide**, it was first dissolved in DMSO or acetonitrile and studied using a benchtop cuvette fluorometer, this revealed a weak signal with a peak at 580 nm or 600 nm, respectively, but was only evident at high concentrations (>1 mM) (Figure 5A blue and red). The emission of the **CF₃-fulgide** solution in DMSO interestingly gave differing spectra within the MOF with a 600 nm peak and a broad 650 nm emission peak (Figure 5B orange). Irradiation of this sample with either UV light or white light, to switch the molecule to the photocyclised closed state, (see Figure 1) (a method previously confirmed by UV-vis absorption spectroscopy and ¹H NMR spectroscopy (see supporting info Figure S2C)) did not produce a change in the emission spectra when investigated in either MOF or cuvette. The acetonitrile solution of **CF₃-fulgide** within the MOF gave a different fluorescence spectra compared to in DMSO; with a similar peak at 600 nm, 630 nm and a broad peak around 770 nm (Figure 5B purple). Irradiation of the acetonitrile sample with UV light caused a large change in the spectrum with the loss of the 600 nm and 630 nm peaks. Recovery of the initial spectrum was not achieved with either 532 nm or white light, indicating that the spectral change was not due to UV induced photoswitching. Investigation of the in-MOF fluorescence of older samples known to have decomposed (by ¹H NMR spectroscopy and UV-vis absorption spectroscopy) showed only the 770 nm peak suggesting that this fluorescence is a result of degradation of **CF₃-fulgide**. **CF₃-fulgide** appears to degrade in both solvent mixtures. This thermal degradation may reflect some hydrolysis of **CF₃-fulgide**, caused by trace amounts of water in the DMSO.[35] Further photobleaching of **CF₃-fulgide** and its degradation products was observed upon pulsing with the 532 nm excitation source.

Figure 5. Fluorescence of **CF₃-fulgide** (1 mM) in cuvette (**A**) in acetonitrile (blue) and DMSO (red); and within a MOF (**B**) in acetonitrile (purple), DMSO (orange) and adsorbed to fibre surface (green).

3.4. Diarylalkene

The fluorescence spectra of a diarylalkene, **DA1**, (Figure 1) in DMSO or acetonitrile were obtained using a benchtop cuvette fluorometer as well as using a MOF as described earlier. Photoswitching of **DA1** from the uncyclised uncoloured state to the cyclised coloured state was performed by irradiation with 256 nm UV lamp (The change in the UV-vis absorption spectra after 60 min irradiation is shown in Figure S2D.) **DA1** showed no fluorescence using the benchtop fluorometer in either the uncyclised state or the photocyclised state (Figure 6, red and blue). This was expected as the uncyclised form does not absorb at the 532 nm excitation wavelength, (Figure S2D, red and blue) and other diarylalkenes which have only thiophene substituents are also known not to be fluorescent.[29, 47] However, as shown earlier for **CF₃-fulgide**, the possibility exists for molecules with very low fluorescence quantum yields to give a measureable signal in a suspended core MOF, due to the increased sensitivity provided by this architecture. Initially the **DA1** solutions in the uncyclised form, as expected, gave no fluorescence signal in the MOF (Figure 6 orange/purple). Photoswitching to the cyclised coloured state by exposing the filled fibre to 254 nm UV light resulted in a broad fluorescence signal with a maximum at 590 nm and a sharp feature at 634 nm. These emissions were not photo-reversible on exposure to photoswitching white light, and the 634 nm peak increased in a time dependent manner when within the fibre. Therefore these signals are believed to be due to the products of either oxidative degradation or photodegradation.[48, 49] A relative photodegradation rate, for comparison to the other photoswitches, was not obtained due to the lack of fluorescence signal.

Figure 6. Fluorescence of **DA1** in cuvette in acetonitrile (blue) and DMSO (red); and within a MOF in acetonitrile (purple), DMSO (orange) and adsorbed to fibre surface (green).

This investigation into the fulgide **CF₃-fulgide** and diarylalkene **DA1** highlights that although some photoswitches or fluorophores may be suitable for a variety of applications, due to favorable thermal- and photo- stability in controlled, deaerated, non-polar solvents, their use may be limited in situations involving real world applications, such as in high intensity optical devices or biological samples, due to enhanced degradation.

3.5. Solid State Fibre Fluorescence Measurements

In finding applications in switchable devices the photoswitchable compounds may often be covalently attached to a surface, suspended in a matrix, dried to a powder, or physically adsorbed to a support rather than dissolved in a solution. Each environment might be expected to influence the way the photoswitchable compounds interacts with light and its associated spectral and photoswitching properties. In this section, differences in fluorescence of the photoswitches **Azo1**, **SP1**, **CF₃-fulgide** and **DA1** in the solid state when they are physically adsorbed to the core of a MOF, is investigated and the results compared to the solution observations discussed above.

Microstructured optical fibres were coated separately with each photoswitch using a modified “drip method”[50, 51] (see Section 2.4) prior to coupling to the fluorescence setup; fluorescence and photostability measurements were then performed as described in Section 2.4. Optimization of the alignment of the MOF core to the excitation light source is typically determined by maximizing the fibre transmittance; however, this was not possible with the fluorophores pre-attached to the core as this could cause photobleaching, and the fluorophores caused an increase in fibre transmission loss due to increased absorption and scattering of the light. Therefore to minimize light exposure the dry photoswitch coated fibres were coupled to the laser setup as quickly as possible using filtered laser light and the relative optical power and photobleaching rates of the samples were compared based on relative changes in fluorescence intensities. The initial fluorescence signals from each of the four photoswitches prior to prolong exposure to 532 nm light is shown in Figures 3A, 4B, 5B and 6 comparing to their respective solution fluorescence and the integrated signal decay due to photobleaching is shown in Figure 7.

Figure 7. The integrated fluorescence of each photoswitch coated onto the inner surface of a MOF during irradiation with 532 nm light (black) then after subsequent switching with UV light (blue) fitted with two component exponential decay function (red). (A) **Azo1**. (B) **SP1**. (C) **CF₃-fulgide**. (D) **DA1**.

The azobenzene **Azo1** showed a broad peak with a maximum around 600 nm (Figure 3A green), similar to what was observed in the solution-based fibre experiment described in Section 3.1. Pulsing with the 532 nm laser caused a reduction in the signal intensity by 26% over the 50 pulses (0.5% per pulse) (Figure 7A). This is twice as fast as that observed when **Azo1** was dissolved in acetonitrile. The fluorescence from the dried **Azo1** was still decreasing after the monitored 50 pulses, unlike in the DMSO and acetonitrile dissolved sample which plateaued within the 50 pulses. Thus further indicating that the plateauing of signal intensity in the solution state may be due to diffusion of the fluorophore solution near the light exposed surface mixing within the MOF: no such equilibrium can be formed with a fixed fluorophore. Subsequent UV exposure, to induce photoswitching from the native *trans* isomer to the *cis* isomer, gave no change in the fluorescence peak shape, however, a small recovery of the signal intensity was observed.

The spiropyran, **SP1**, showed a broad emission, with peak maximums at 580 nm and 620 nm in these experiments (Figure 4B green). Bleaching occurred to the extent of 22% of the initial intensity over the 50 pulses (0.4% per pulse) (Figure 7B black). Irradiation of the fibre with UV 352 nm light

for 10 min photoswitched **SP1** to **MC1** resulting in an increase in the fluorescence with a new emission at 647 nm (Figure 4B black). Pulsing of the **MC1** with the 532 nm excitation light quickly bleached this new peak, reproducing the original spectrum within ten pulses; the photobleaching then continued at the same rate as was observed with the unswitched **SP1** (Figure 7B blue). Photoswitching between the different **SP1** and **MC1** emissions with UV 352 nm and green 532 nm light was able to be reproduced at least three times with a gradual decrease in the intensity between switching cycles as a result of the photodegradation (see supporting Figure S3). The fluorescence spectra of **SP1** in the solid state was similar to that in the DMSO and acetonitrile solutions (Section 3.2). The formation of a new fluorescence at 740 nm, as observed in the solution studies, was not observed in the solid state, even after multiple photoswitching cycles; indicating that, this degradation in the solid state is dominated by a different pathway than which occurred in the solution.

The indolylfulgide, **CF₃-fulgide**, adsorbed to the fibre core gave a similar spectrum to that observed in the cuvette benchtop fluorometer experiment (see Section 3.3), with a main peak at 590 nm and a shoulder peak at 630 nm (Figure 5B, green). No other emission peaks above 650 nm were observed, unlike compared to **CF₃-fulgide** in solution in fibre. Photobleaching caused a 10% decrease in the signal intensity over the 50 pulses (0.2% per pulse) (Figure 7C). Irradiation of **CF₃-fulgide** in the fibre using UV light or halogen white light to induce photoswitching, again, gave no change in the fluorescence spectrum. Meaning that either photoswitching was not occurring in the adsorbed state or, as the same observation was made in solution, the closed fulgide is not fluorescent from excitation at 532 nm.

The adsorbed diarylalkene, **DA1**, in the MOF showed a very different strong emission spectrum compared to the lack of fluorescence observed in the previous DMSO and acetonitrile solutions. The initial spectrum showed a fluorescence signal with a maximum at 627 nm (Figure 6 green). After exposure to pulsing of the 532 nm excitation light the signal decreased by 54% (1% per pulse) (Figure 7D) and broadened. After exposure to UV light the peak intensity at 627 nm increased, indicating photoswitchability in the solid state. Repeated exposure to 532 nm light decreased the 627 nm peak intensity and the formation of a new higher wavelength emission became evident. This new peak at approx. 660 nm did not appear to change with UV, or white light irradiation suggesting that this was not photochromic and possibly due to a photodecay product.

The above investigation shows that the fluorescence of each of the four photoswitches was observable in the solid state; fluorescence spectral features were comparable to in solution, apart from for **DA1** which did not show fluorescence in solution. In the solid state photoswitching was observed for **SP1**. A greater photodegradation was observed on the surface. However, this could be attributed to higher intensity light due to the fluorophore concentrated within the evanescent field, as well as no diffusion of the fluorophores. Also, as spectral changes associated with solution based degradation was not observed it is believed that an alternative degradation pathway is dominant.

4. Conclusions/Outlook

The photostability of organic photoswitches is important for their incorporation into switchable smart materials for optical systems. The fluorescence and photostability of four types of photochromic molecules (**Azo1**, **SP1**, **CF₃-fulgide** and **DA1**) was investigated when dissolved in DMSO, or

acetonitrile, or adsorbed to a MOF silica surface. It was observed that **Azo1** and **SP1** had stronger fluorescence in solution compared to **CF₃-fulgide** and **DA1**. A difference in the rate of photodecay was observed between the two solutions investigated, with degradation of **Azo1** and **SP1** occurring 2-3 fold slower in acetonitrile than in DMSO. When adsorbed to the silica surface a fluorescence signal was observed for all photoswitches. Photodegradation of this signal appeared to proceed faster than in solution, possibly a result of the concentration of the photoswitch on the light intense fibre surface as well as a lack of diffusion within the fibre air-holes. Therefore, of the four photoswitches investigated in this study the most suitable for fibre device applications were found to be azobenzene, **Azo1**, and spiropyran, **SP1** due to their higher fluorescence yield, and solution stability.

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Vitae

Daniel Stubing completed his BSc (Hons) in synthetic drug design at the University of Adelaide in 2010, where he is currently pursuing a PhD under the supervision of Prof. Andrew Abell in photoswitchable surfaces for optical sensors.

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Conflicts of Interest

The authors declare no conflict of interest.

References and Notes

- [1] R. Klajn, Immobilized azobenzenes for the construction of photoresponsive materials, *Pure and Applied Chemistry*, 82(2010) 2247+.
- [2] A. Bianco, S. Perissinotto, M. Garbugli, G. Lanzani, C. Bertarelli, Control of optical properties through photochromism: a promising approach to photonics, *Laser & Photonics Reviews*, 5(2011) 711-36.
- [3] M.L. Bossi, P.F. Aramendía, Photomodulation of macroscopic properties, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 12(2011) 154-66.
- [4] L. Florea, D. Diamond, F. Benito-Lopez, Photo-Responsive Polymeric Structures Based on Spiropyran, *Macromolecular Materials and Engineering*, 297(2012) 1148-59.
- [5] X. Sun, S. Park, D.S. Shin, W. Dong, B. Zhao, K. Jang, Multi-level recording of photochromic indolyfulgide, *Optical Materials*, 30(2007) 652-6.
- [6] X. Guo, D. Zhang, G. Yu, M. Wan, J. Li, Y. Liu, et al., Reversible Photoregulation of the Electrical Conductivity of Spiropyran-Doped Polyaniline for Information Recording and Nondestructive Processing, *Advanced Materials*, 16(2004) 636-40.
- [7] D. Sysoiev, A. Fedoseev, Y. Kim, T.E. Exner, J. Boneberg, T. Huhn, et al., Synthesis and Photoswitching Studies of Difurylperfluorocyclopentenes with Extended π -Systems, *Chemistry – A European Journal*, 17(2011) 6663-72.
- [8] Q. Luo, H. Cheng, H. Tian, Recent progress on photochromic diarylethene polymers, *Polymer Chemistry*, 2(2011) 2435-43.
- [9] H. Nishi, T. Namari, S. Kobatake, Photochromic polymers bearing various diarylethene chromophores as the pendant: synthesis, optical properties, and multicolor photochromism, *Journal of Materials Chemistry*, 21(2011) 17249-58.
- [10] V. Balzani, G. Bergamini, P. Ceroni, Light-powered Molecular Devices and Machines, in: S. Bellucci (Ed.) *Nanoparticles and Nanodevices in Biological Applications - the Infn Lectures - Vol I*, Springer-Verlag Berlin, Berlin, 2009, pp. 131-58.
- [11] G. Vives, J.M. Tour, Synthesis of Single-Molecule Nanocars, *Accounts Chem Res*, 42(2009) 473-87.
- [12] R. Lyndon, K. Konstas, B.P. Ladewig, P.D. Southon, P.C.J. Kepert, M.R. Hill, Dynamic Photo-Switching in Metal–Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release, *Angewandte Chemie International Edition*, (2013) n/a-n/a.
- [13] I. Tochitsky, A. Polosukhina, Vadim E. Degtyar, N. Gallerani, Caleb M. Smith, A. Friedman, et al., Restoring Visual Function to Blind Mice with a Photoswitch that Exploits Electrophysiological Remodeling of Retinal Ganglion Cells, *Neuron*, 81(2014) 800-13.
- [14] I. Willner, S. Rubin, Control of the Structure and Functions of Biomaterials by Light, *Angewandte Chemie International Edition in English*, 35(1996) 367-85.
- [15] L. Florea, A. Hennart, D. Diamond, F. Benito-Lopez, Synthesis and characterisation of spiropyran-polymer brushes in micro-capillaries: Towards an integrated optical sensor for continuous flow analysis, *Sensors and Actuators B: Chemical*, 175(2012) 92-9.
- [16] Q. Zou, J. Jin, B. Xu, L. Ding, H. Tian, New photochromic chemosensors for Hg²⁺ and F⁻, *Tetrahedron*, 67(2011) 915-21.
- [17] J. Wang, C.-S. Ha, A colorimetric and fluorescent turn-on chemosensor for Zn²⁺ based on an azobenzene-containing compound, *Tetrahedron*, 65(2009) 6959-64.
- [18] A.M. Cubillas, S. Unterkofler, T.G. Euser, B.J.M. Etzold, A.C. Jones, P.J. Sadler, et al., Photonic crystal fibres for chemical sensing and photochemistry, *Chem Soc Rev*, 42(2013) 8629-48.

- [19] S. Afshar V, Y. Ruan, S.C. Warren-Smith, T.M. Monro, Enhanced fluorescence sensing using microstructured optical fibers: a comparison of forward and backward collection modes, *Opt Lett*, 33(2008) 1473-5.
- [20] S. Afshar V, S.C. Warren-Smith, T.M. Monro, Enhancement of fluorescence-based sensing using microstructured optical fibres, *Opt Express*, 15(2007) 17891-901.
- [21] T.M. Monro, S. Warren-Smith, E.P. Scharfner, A. Francois, S. Heng, H. Ebendorff-Heidepriem, et al., Sensing with suspended-core optical fibers, *Optical Fiber Technology*, 16(2010) 343-56.
- [22] B. Valeur, I. Leray, Design principles of fluorescent molecular sensors for cation recognition, *Coordination Chemistry Reviews*, 205(2000) 3-40.
- [23] S. Heng, M.-C. Nguyen, R. Kostecky, T.M. Monro, A.D. Abell, Nanoliter-scale, regenerable ion sensor: sensing with a surface functionalized microstructured optical fibre, *RSC Advances*, 3(2013) 8308-17.
- [24] G.O.S. Williams, J.S.Y. Chen, T.G. Euser, P.S.J. Russell, A.C. Jones, Photonic crystal fibre as an optofluidic reactor for the measurement of photochemical kinetics with sub-picomole sensitivity, *Lab on a Chip*, 12(2012) 3356-61.
- [25] S.C. Warren-Smith, S. Heng, H. Ebendorff-Heidepriem, A.D. Abell, T.M. Monro, Fluorescence-Based Aluminum Ion Sensing Using a Surface-Functionalized Microstructured Optical Fiber, *Langmuir*, (2011) null-null.
- [26] S. Heng, C.A. McDevitt, D.B. Stubing, J.J. Whittall, J.G. Thompson, T.K. Engler, et al., Microstructured Optical Fibers and Live Cells: A Water-Soluble, Photochromic Zinc Sensor, *Biomacromolecules*, (2013).
- [27] X. Zhang, S. Heng, A.D. Abell, Photoregulation of α -Chymotrypsin Activity by Spiropyran-Based Inhibitors in Solution and Attached to an Optical Fiber, *Chemistry – A European Journal*, (2015) n/a-n/a.
- [28] Y. Yokoyama, K. Takahashi, Trifluoromethyl-substituted photochromic indolylfulgide. A remarkably durable fulgide towards photochemical and thermal treatments, *Chem Lett*, (1996) 1037-8.
- [29] M. Irie, Diarylethenes for Memories and Switches, *Chem Rev*, 100(2000) 1685-716.
- [30] M. Irie, T. Lifka, K. Uchida, S. Kobatake, Y. Shindo, Fatigue resistant properties of photochromic dithienylethenes: by-product formation, *Chem Commun*, 0(1999) 747-50.
- [31] M. Natali, L. Soldi, S. Giordani, A photoswitchable Zn (II) selective spiropyran-based sensor, *Tetrahedron*, 66(2010) 7612-7.
- [32] M. Kubinyi, O. Varga, P. Baranyai, M. Kállay, R. Mizsei, G. Tárkányi, et al., Metal complexes of the merocyanine form of nitrobenzospiran: Structure, optical spectra, stability, *J Mol Struct*, 1000(2011) 77-84.
- [33] R. Klajn, Spiropyran-based dynamic materials, *Chem Soc Rev*, 43(2014) 148-84.
- [34] M.A. Wolak, N.B. Gillespie, C.J. Thomas, R.R. Birge, W.J. Lees, Optical properties of photochromic fluorinated indolylfulgides, *Journal of Photochemistry and Photobiology A: Chemistry*, 144(2001) 83-91.
- [35] M.A. Wolak, C.J. Thomas, N.B. Gillespie, R.R. Birge, W.J. Lees, Tuning the Optical Properties of Fluorinated Indolylfulgimides, *The Journal of Organic Chemistry*, 68(2002) 319-26.
- [36] Y. Yokoyama, Fulgides for Memories and Switches, *Chem Rev*, 100(2000) 1717-40.
- [37] Y.C. Liang, A.S. Dvornikov, P.M. Rentzepis, Fluorescent photochromic fulgides, *Research on Chemical Intermediates*, 24(1998) 905-14.
- [38] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, Photochromism of Dithienylethenes with Electron-Donating Substituents, *The Journal of Organic Chemistry*, 60(1995) 8305-9.
- [39] C.J. Thomas, M.A. Wolak, R.R. Birge, W.J. Lees, Improved Synthesis of Indolyl Fulgides, *The Journal of Organic Chemistry*, 66(2001) 1914-8.
- [40] F. Strübe, S. Rath, J. Mattay, Functionalized Fulgides and Fluorophore-Photoswitch Conjugates, *European Journal of Organic Chemistry*, (2011) n/a-n/a.
- [41] A.S. Webb, F. Poletti, D.J. Richardson, J.K. Sahu, Suspended-core holey fiber for evanescent-field sensing, *OPTICE*, 46(2007) 010503--3.

- [42] J. Garcia-Amoros, A. Sanchez-Ferrer, W.A. Massad, S. Nonell, D. Velasco, Kinetic study of the fast thermal cis-to-trans isomerisation of para-, ortho- and polyhydroxyazobenzenes, *Physical Chemistry Chemical Physics*, 12(2010) 13238-42.
- [43] B.-K. Tsai, C.-H. Chen, C.-H. Hung, V.K.S. Hsiao, C.-C. Chu, Photoswitchable fluorescence on/off behavior between cis- and trans-rich azobenzenes, *Journal of Materials Chemistry*, 22(2012) 20874-7.
- [44] E. Wagner-Wysiecka, T. Rzymowski, M. Szarmach, M.S. Fonari, E. Luboch, Functionalized azobenzocrown ethers as sensor materials—The synthesis and ion binding properties, *Sensors and Actuators B: Chemical*, 177(2013) 913-23.
- [45] B. Seefeldt, R. Kasper, M. Beining, J. Mattay, J. Arden-Jacob, N. Kemnitzer, et al., Spiropyran as molecular optical switches, *Photochemical & photobiological sciences : Official journal of the European Photochemistry Association and the European Society for Photobiology*, 9(2010) 213-20.
- [46] G.M. Tsivgoulis, J.-M. Lehn, Photonic Molecular Devices: Reversibly Photoswitchable Fluorophores for Nondestructive Readout for Optical Memory, *Angewandte Chemie International Edition in English*, 34(1995) 1119-22.
- [47] K. Matsuda, M. Irie, Diarylethene as a photoswitching unit, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 5(2004) 169-82.
- [48] H. Taniguchi, A. Shinpo, T. Okazaki, F. Matsui, M. Irie, Photodegradation Mechanism of Photochromic Diarylethene Derivatives, *NIPPON KAGAKU KAISHI*, 1992(1992) 1138-40.
- [49] S. Bonacchi, M. El Garah, A. Ciesielski, M. Herder, S. Conti, M. Cecchini, et al., Surface-Induced Selection During In Situ Photoswitching at the Solid/Liquid Interface, *Angewandte Chemie International Edition*, 54(2015) 4865-9.
- [50] R. Garcia-Fernandez, W. Alt, F. Bruse, C. Dan, K. Karapetyan, O. Rehband, et al., Optical nanofibers and spectroscopy, *Appl Phys B*, 105(2011) 3-15.
- [51] U. Wiedemann, W. Alt, D. Meschede, Switching photochromic molecules adsorbed on optical microfibres, *Opt Express*, 20(2012) 12710-20.

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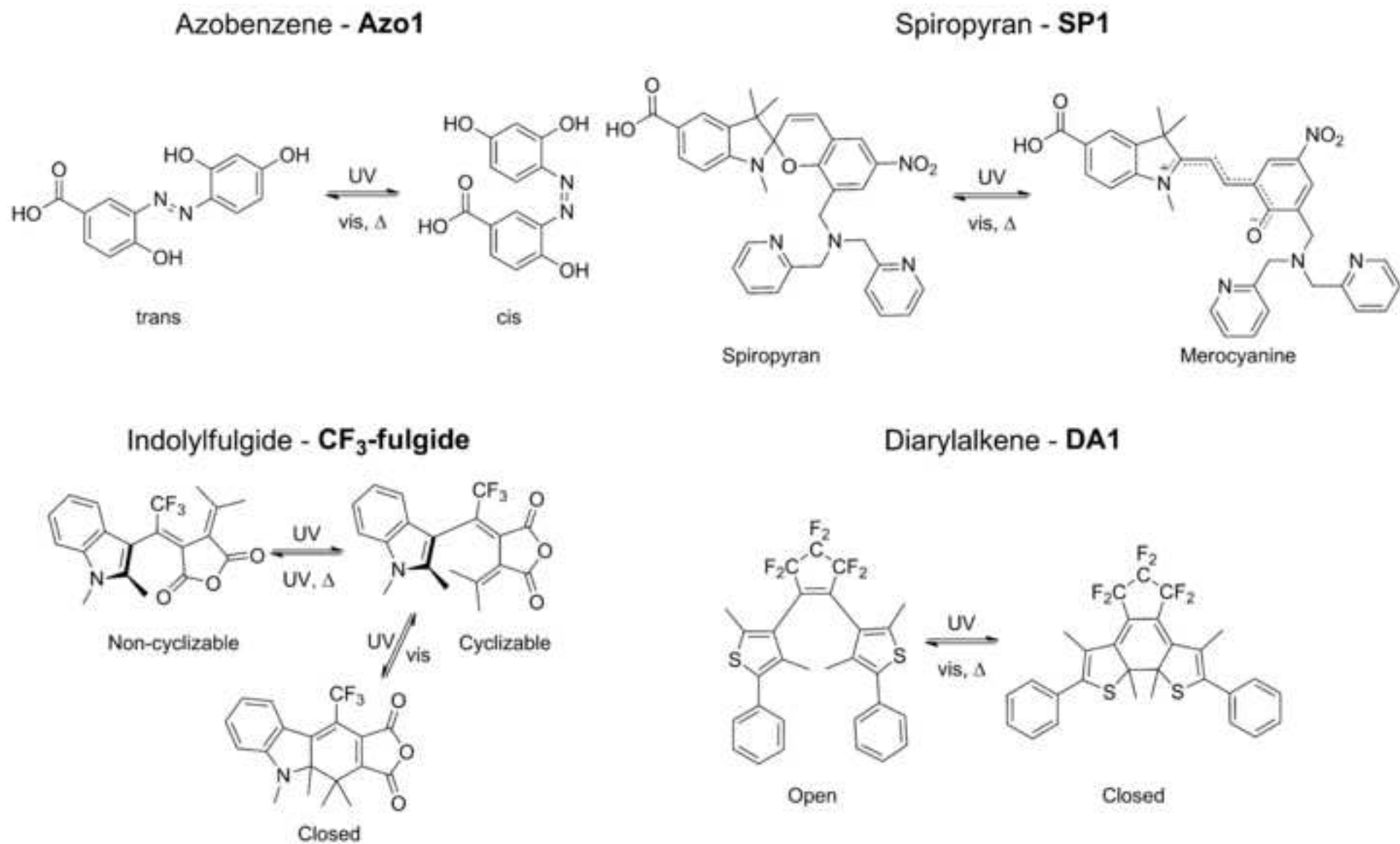


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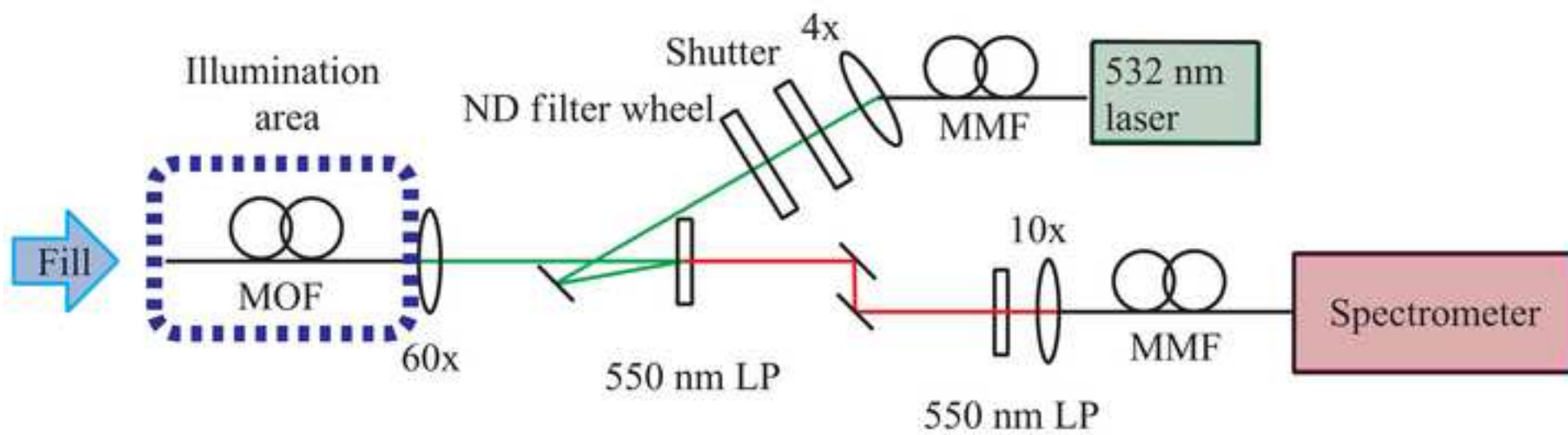


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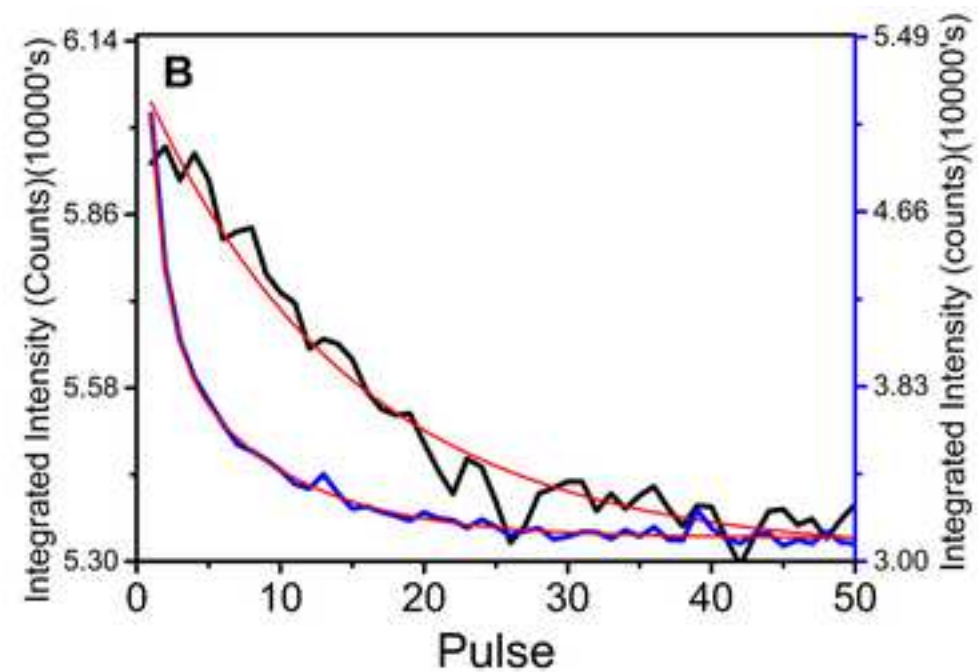
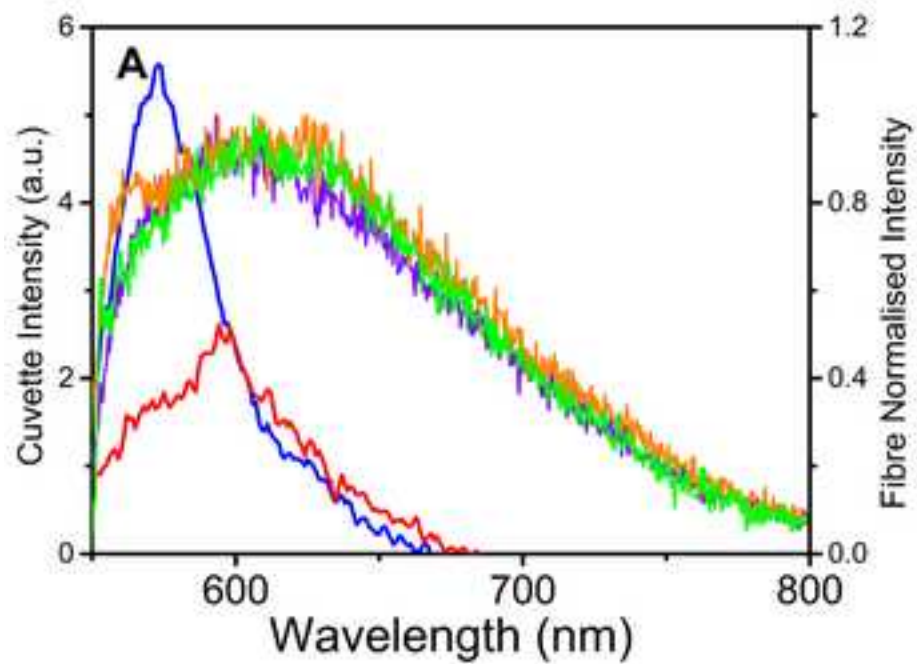


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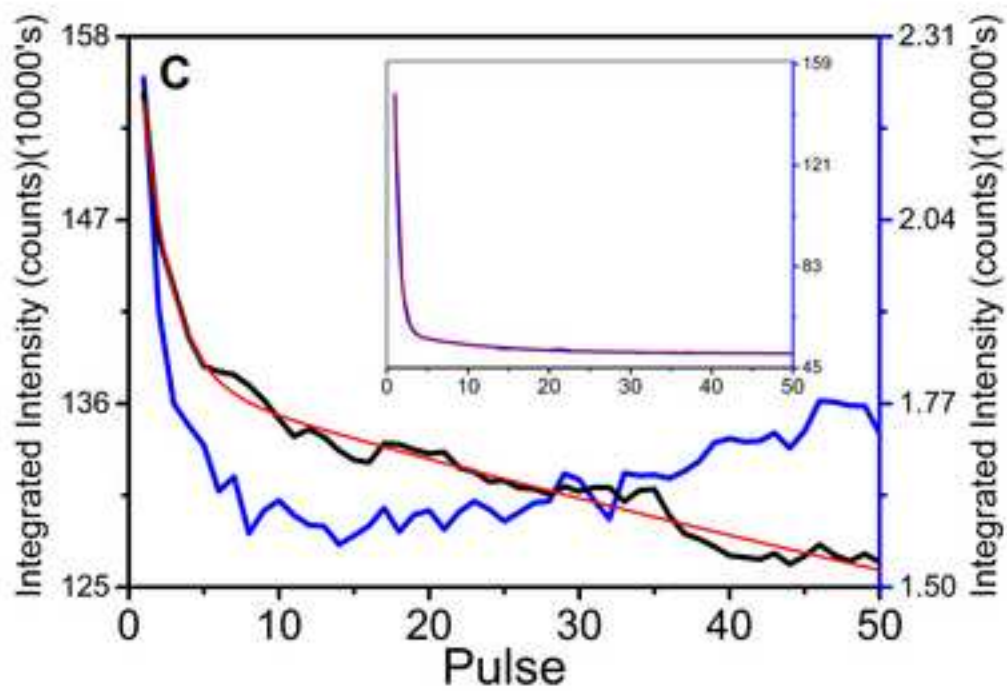
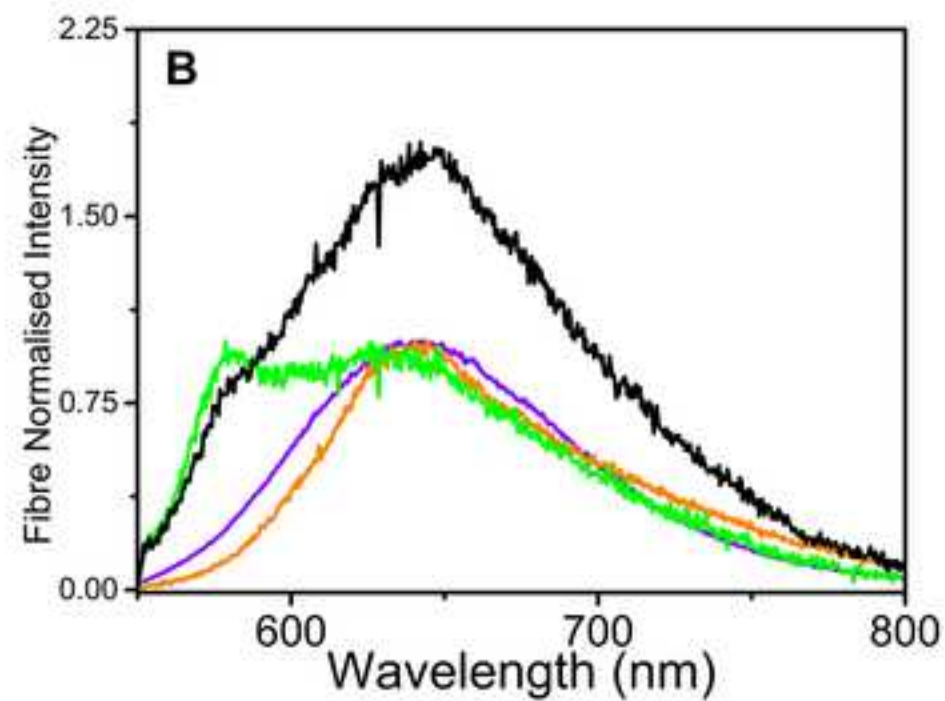
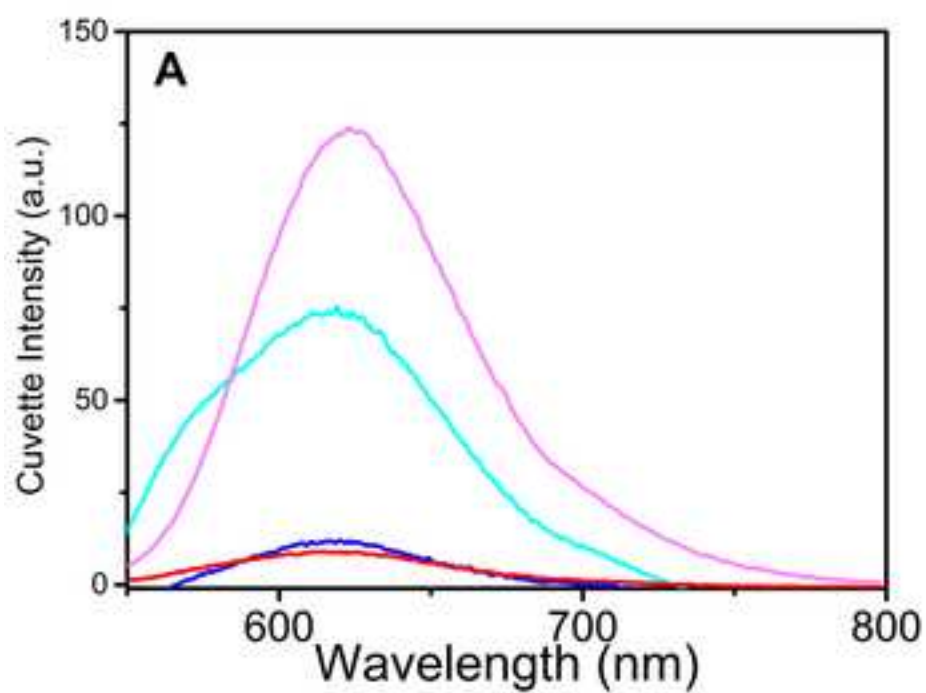


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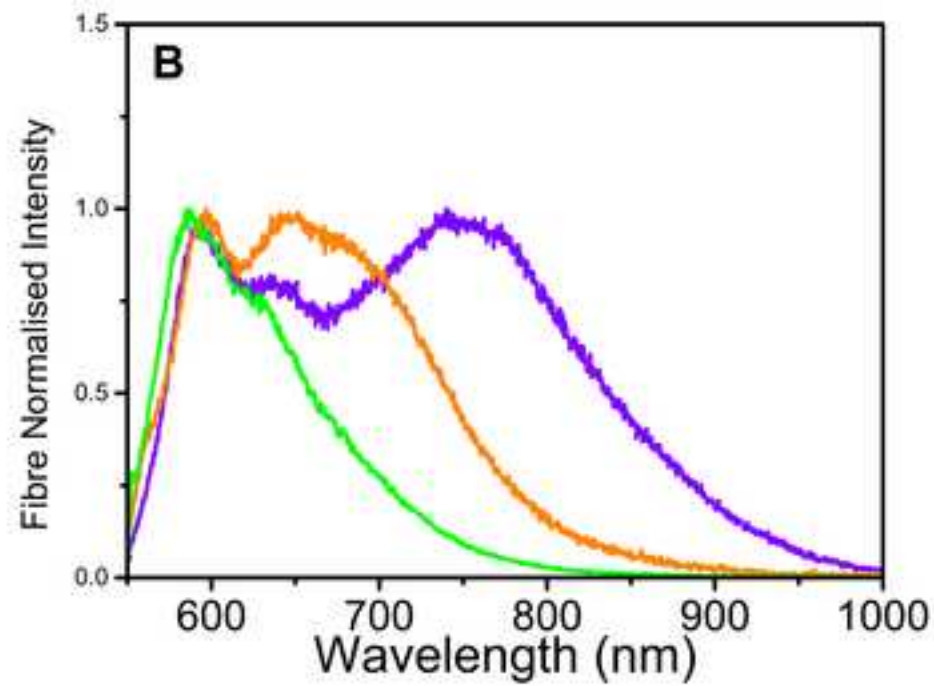
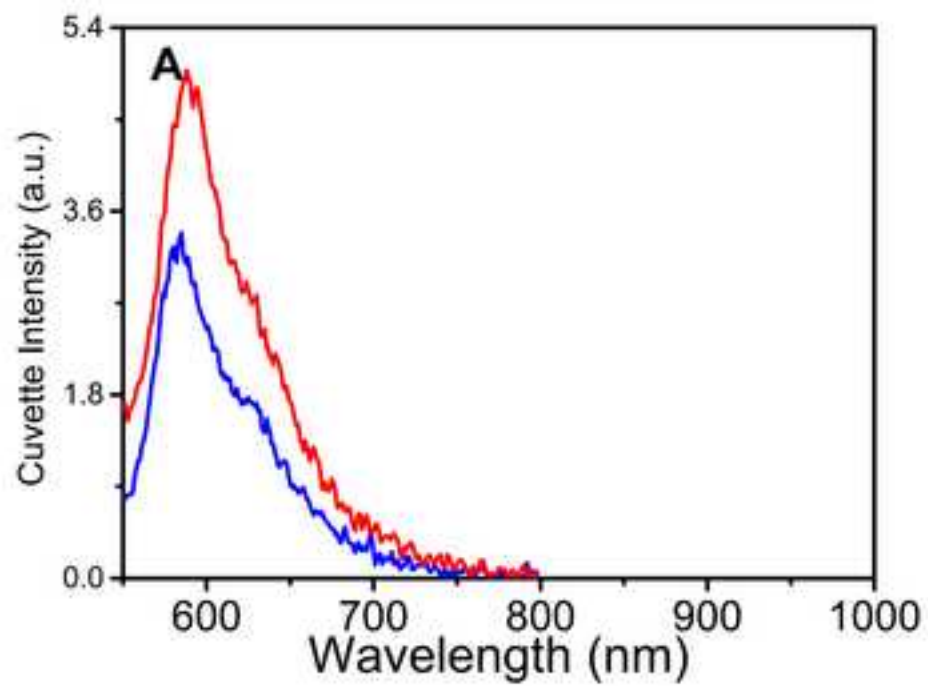


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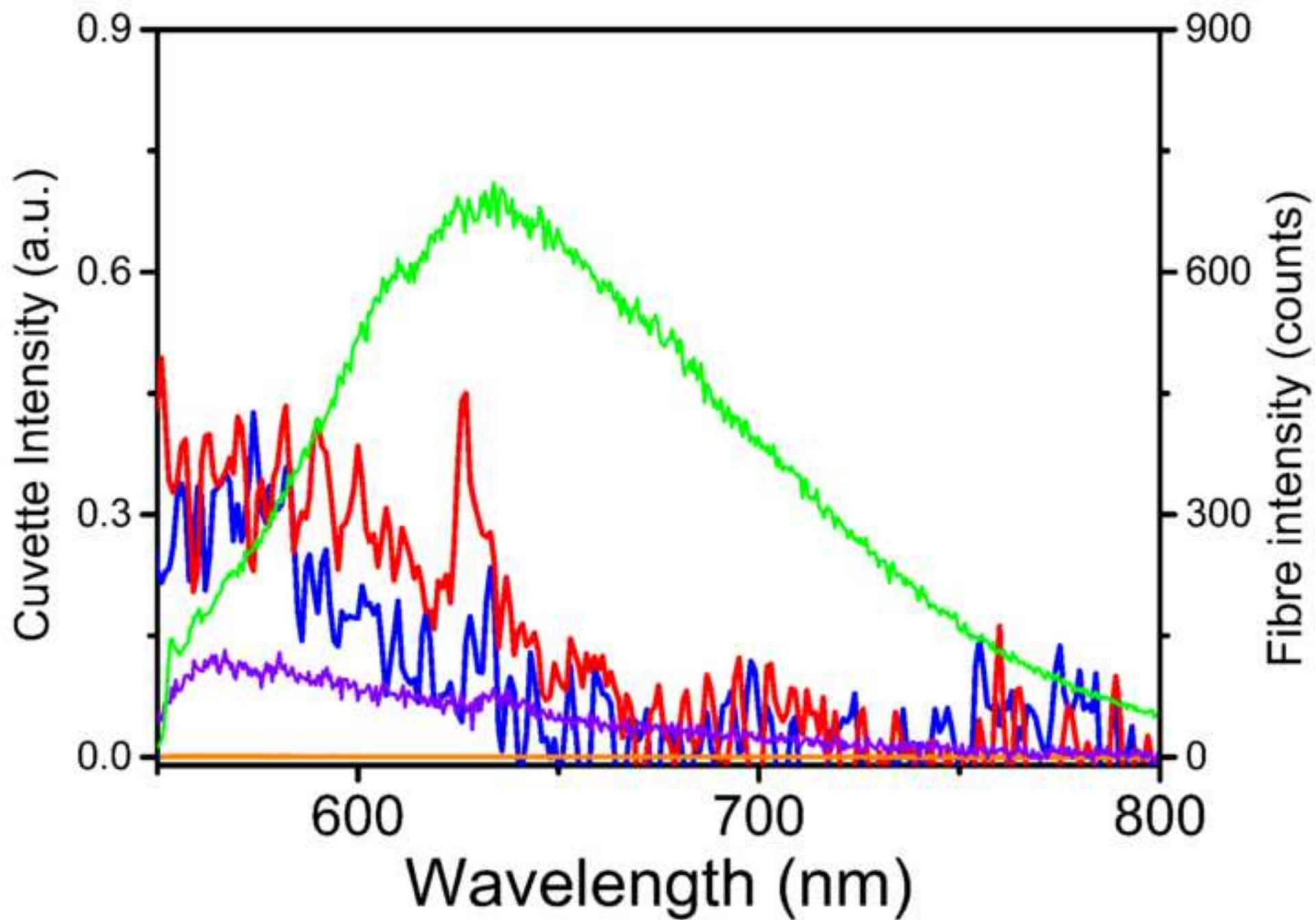
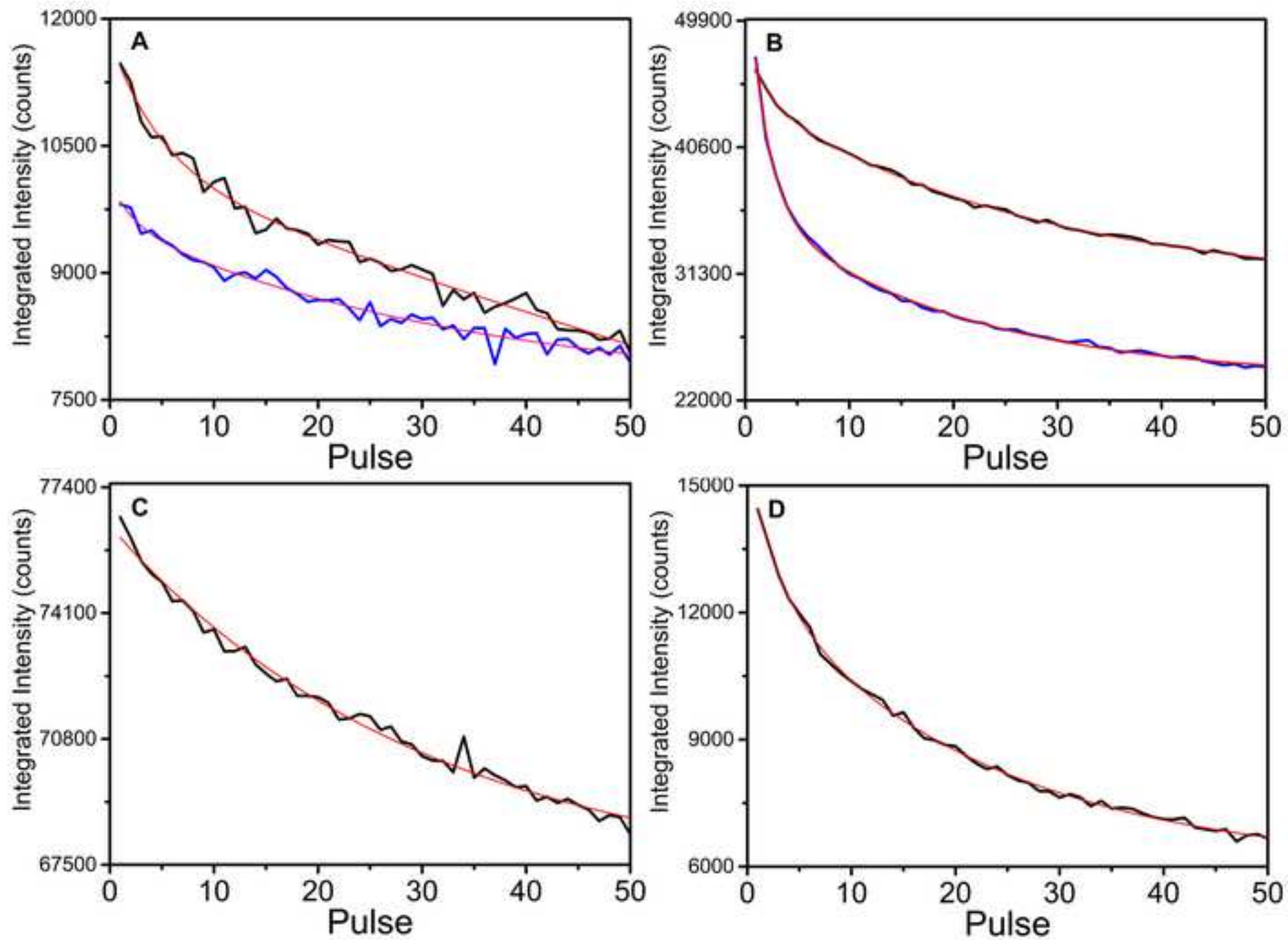


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