# Adsorption of cationic organic dyes in suspended-core fibres

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We report on the absorption measurements of the liquid-filled pure-silica microstructured optical fibres. The measurements concentrate on spectroscopic analysis of the water solutions of cationic dye, oxazine 725 perchlorate which, when filling the fibre, demonstrates much stronger absorption signals than observed in bulk with regular cuvettes. Our investigations reveal that the effect originates from the adsorption of the dye molecules on the fibre inner walls. This effect also significantly enhances the sensitivity of spectroscopic measurements enabling detection of molecules at very low concentrations. In particular, the detection of 1-nM concentration of the dye was demonstrated. © 2013 Optical Society of America

Microstructured optical fibres (MOFs) attract interest of many research groups as an efficient platform for spectroscopic experiments [1]. The geometry of MOFs allows filling the fibres with liquids or gases, enabling the interaction between the introduced media and the light confined within the fibres. Consequently, the MOFs became interesting candidates for chemical [2,3] and biological sensing [4,5]. The great advantages of MOF-based sensors over the regular cuvettes are low volumes of liquids needed for detection (on the order of a few nanoliters) and a long interaction path resulting in high detection sensitivity (even in the pM range [1]).

Among many different MOF structures, the suspended- core fibres (SCFs) appear very useful for chemical sensing thanks to their wide spectral ranges covering many absorbers. The SCFs consist of a solid core of a diameter comparable to the wavelength of propagating light, surrounded by several air channels (cross section of >10 $\mu m^2$) arranged in such a way that the core is suspended at several thin struts [see Fig. 1(a)]. In such fibres, the light confined in the core penetrates the air channels as an evanescent wave and thus interacts with the fibre-filling medium. The overlap between light and the medium makes it possible to observe absorption and fluorescence spectra. Moreover, for most liquids, the size of the air channels allows introducing a foreign medium using capillary forces, which significantly facilitates the filling process.

The interactions between the fibre-filling medium and the fibre glass have been used for chemical functionalization of the fibre inner surfaces [6,7]. The mechanism of this phenomenon could be explained by chemical and/or physical adsorption. The adsorption of the compound to the glass surface could change its absorption spectra [8] resulting in interesting analytical applications. On the other hand, the liquid-glass interaction might be detrimental if the filling process is disturbed by aggregation of the dissolved substance inside the fibre channels [9].

In the present work, we investigated the adsorption of organic dye molecules to the fibre glass and its effect on the observed absorption spectra. Although the interpretation of absorption data is, by far, not trivial for SCFs, the absorbance is a conveniently measurable parameter suitable for characterization of the observed effects. The effect may be applied for detection of very low concentrations of the investigated molecules; SCFs may offer detection sensitivities significantly exceeding the limits of standard UV-Vis spectroscopy.

In the experiment, pure silica SCFs, fabricated at the Maria Curie-Skłodowska University in Lublin, Poland, were used. The outer diameter of the fibre was 80 $\mu m$ and three channels of roughly elliptical shape (with semiaxes of 13 $\mu m$ and 9 $\mu m$) were incorporated in its structure. The core was suspended on three thin (~0.1 m) struts and had a diameter of 0.8 $\mu m$ [Fig. 1(a)]. The measurements were performed with about 20 cm long fibre pieces with the setup depicted in Fig. 1(b).
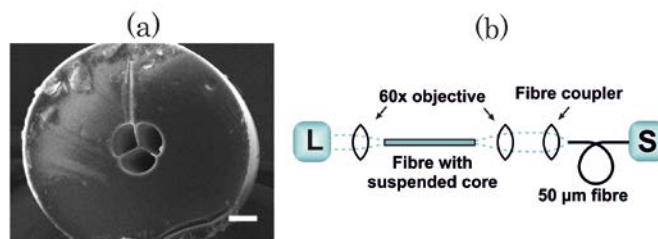


Fig. 1 (a) Scanning electron micrograph of the SCF used in the experiment (scale bar corresponds to 10 $\mu m$). (b) Scheme of the experimental setup used for absorption measurements in SCFs, L marks a halogen lamp and S a spectrometer.

Light from a halogen lamp, of a spectral range of 500-1000 nm, was delivered to the investigated SCF through a collimation setup consisting of a set of concave mirrors and a classical optical fibre (1 mm core). Two 60x microscope objectives were used for coupling the beam to and from the investigated fibre. Light decoupled from the SCF was delivered to a spectrometer operating in the 300-1100 nm spectral range with a resolution of 2.4 nm with a standard multimode optical fibre (50 μm core).

While absorption of light is generally described by the Lambert-Beer law, which relates the transmitted light intensity to the absorption coefficient and the optical path length, in the considered case this relation needs to be modified to account for the fact that light transmitted through a fibre core penetrates the liquid-filled channels only in the form of an evanescent wave [2]. This modification can be expressed by the factor $\Phi(\lambda)$ which represents the fraction of the total optical power present in the liquid-filled channels. That reduction of the signal amplitude relative to a cuvette of identical length is very important for any spectroscopic application of MOFs. For the investigated SCF filled with water, $\Phi(\lambda)$ equals 10 -15% in the wavelength range from 600 to 700 nm, increasing for larger wavelengths. In fact, we did observe such a reduction when the SCFs were filled with water or water solutions of bromophenol blue sodium salt (BB), being an anionic organic dye [10]. This situation changed, however, when the SCFs were filled with a water solution of oxazine 725 perchlorate (OX), the 3,7-bis (diethylamino) phenoxazin-5-ium perchlorate [Fig. 2(a)], in which case the opposite effect was observed, i.e., absorption increased with respect to the cuvette [11].

Oxazin is a popular laser dye, soluble in water, with its absorption properties determined by the cationic part of the molecule (henceforth in this article OX is called a cationic dye). In a cuvette, the absorption spectrum of the OX water solution consists of a strong absorption band at 655 nm partially overlaying with a weaker band at 610 nm [see Fig. 2(b)].

Motivated by the discrepancy of our observation and predictions of Ref. [2], we have performed systematic studies of the transmission of light through OX-filled SCFs. First, the transmission spectrum of an empty SCF was recorded to identify effects related to structural or material properties of the fibre and to determine the reference spectrum for further measurements. Next, the fibre was dipped in the water solution of OX for about 15 minutes which enabled filling up the whole fibre due to capillary forces. Finally, the transmission spectrum of the liquid-filled SCF was recorded and analysed. It was verified with a CCD camera that the detected transmission spectrum originated only from the light guided through the core and was not related with light transmitted in the cladding of the fibre. The comparison of the OX spectra measured in the SCF and a 1 cm cuvette is shown in Fig. 2(b). The two spectra reveal similar shapes, particularly, the two bands are present in OX-filled SCF but the position of the 655 nm band is slightly red-shifted (to about 662 nm). Much more dramatic, however, is the difference in the amplitudes of the spectra (even after normalization to the same optical path length by dividing absorbance recorded in both systems by corresponding lengths). This result appears to be in contradiction to the previous observations with water or anion-dye BB solutions [10]. According to those, the transmission spectrum of the SCF uniformly filled with an absorbing substance should have the same shape as the absorption spectrum measured in the cuvette but its intensity should be lower by the factor $\Phi(\lambda)$ due to interaction via evanescent wave. Thus, the reported observations indicate existence of an additional process that increases the absorbance of the OX solution filling the SCFs that was not included in the former description.
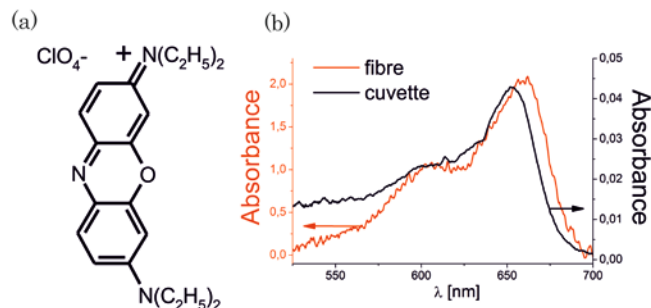


Fig. 2 (a) Structural formula of OX. (b) The absorption spectra of a 200 nM water solution of OX measured in a 1-cm cuvette (black line) and in the fibre (red line). The OX solutions were prepared from the powder (Exciton) and distilled water.

To investigate the distribution of the OX molecules within the SCF, the absorption spectrum of the filled fibre was recorded after cutting off a 1 cm piece of the fibre from its dipped end. Figure 3 depicts the spectra measured before and after cutting the piece off. As shown, before shortening of the fibre both the OX (655 nm) and water (~1000 nm) absorption bands were visible in the spectrum. Shortening of the fibre from 23.1 cm to 22.2 cm resulted in the disappearance of the OX band while the water band was still presented in the observed spectrum. This observation indicated that the OX absorption signal comes from the fibre part shorter than 1 cm from its dipped end.
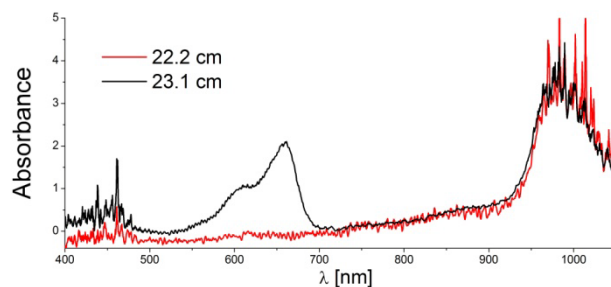


Fig. 3 Absorption spectra of the SCF filled with a 200 nM water solution of OX. The 23.1 cm long fibre (black line) was shortened to 22.2 cm (red line).

The effect of adsorption of OX molecules on the fibre walls was further investigated using a confocal fluorescence microscopy. The images of the end section of the SCF filled with the 200 nM solution of OX are presented in Fig. 4. The fibre dipped end was imaged in planes normal to the fibre axis at different depths (z planes). The excitation wavelength was 532 nm and the images were taken with a spatial resolution of 2 µm and spectral integration over the whole 662 nm band. Figure 4(a) shows the regular, white light optical image. The fluorescence image of the fibre recorded with the laser beam focused at the fibre centre (z = 0 µm), overlaid with the corresponding optical image [Fig. 4(b)] shows strong fluorescence from the OX-filled channels. The signal decreases very quickly along the fibre length (y axis) and vanishes approximately 60 µm after the fibre end face. The fluorescence from the z-planes outside of the channels, at 40 µm and -40 µm, [Fig. 4(c)] appears weaker than that closer to the fibre centre, at 15 µm and -15 µm, because of geometrical conditions (higher number of imaged molecules on a curved internal surface of the capillaries than on a quasi-flat external surface of the fibre). This observation confirms that all absorption comes from the molecules adsorbed close to the fibre end. This also shades light on the dynamics of the process: while filling the fibres with capillary forces, dye molecules adsorb onto the fibre wall.

Bearing in mind the complex role of dye-molecule adsorption, we also investigated absorption spectra of OX-filled SCFs for various concentration of the solution, ranging from 50 nM to 400 nM (Fig. 5). We have observed that the absorbance scales linearly with the concentration, which indicates that the desorption length increases with the concentration which reflects nearly uniform distribution of the molecules along the walls. However, specific quantitative dependences of the adsorption on such parameters as concentration remain yet to be determined.
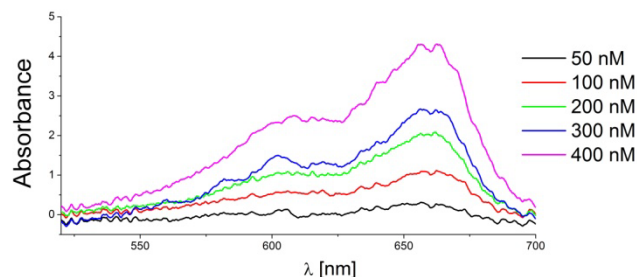


Fig.5. Absorption spectra of a water solution of OX measured in the SCF fibres in a 50 to 400nM concentration range.

The observation presented above suggested the ability to enhance the sensitivity of the spectroscopic measurements of cationic dyes. For this sake the number of the molecules interacting with light may be increased by continuous flushing of the solution through the fibre for the time enabling full coverage of the fibre inner
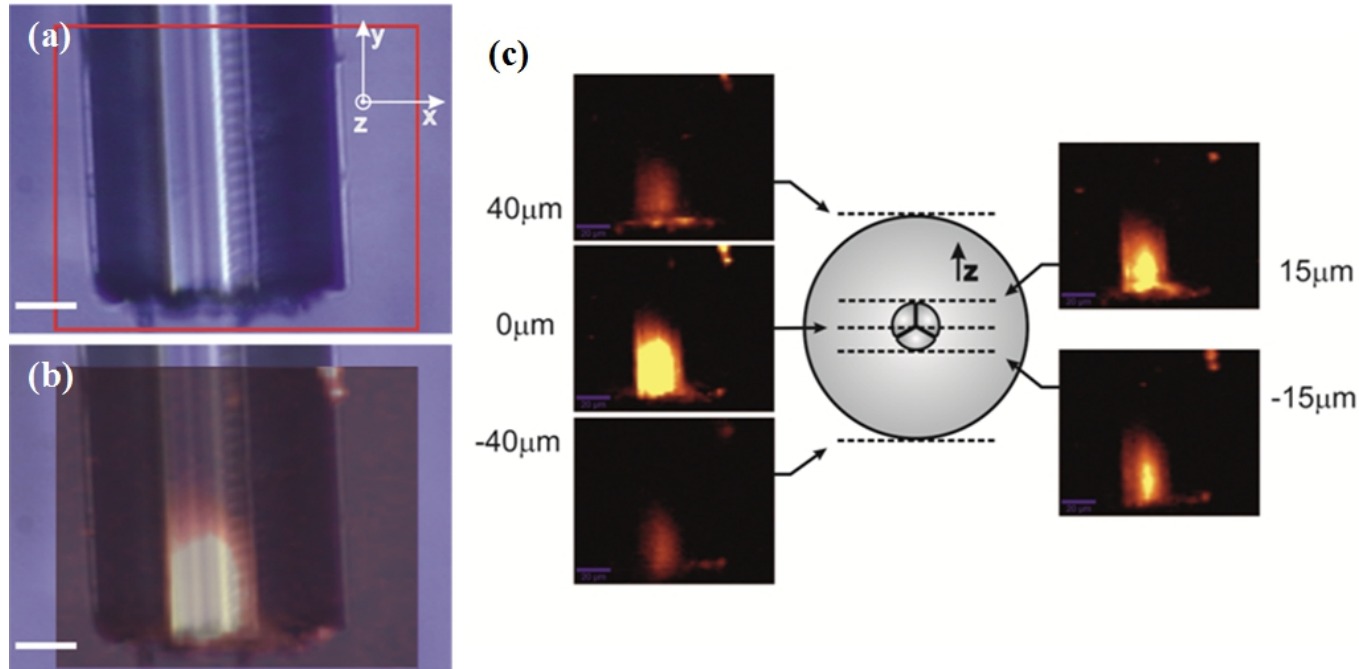


Fig. 4. Images of the end section of the SCF recorded for a fibre filled with the 0.2 µM OX solution. (a) An optical white-light image of the fibre with indicated region of fluorescence confocal imaging (a red rectangle) and depicted xyz axes. (b) A typical fluorescence image (excited by a 532 nm laser focused on the fibre core) overlaid with a corresponding optical image. White bar marks a 20 µm distance. (c) Fluorescence confocal -microscope images for different in-plane depth (z planes). The dotted lines indicate imaged planes, corresponding to signals observed at 40 µm, 15 µm, 0 µm, -15 µm, -40 µm.

walls. Figure 6 illustrates such an increase of the sensitivity. In that case, 1-nM concentration of OX molecules was flushed through the fibre over 200 min using a standard medical syringe. While the concentration is 50 times lower than the lowest in Fig. 5, the OX spectrum is still clearly visible. This example demonstrates feasibility of measurements of very low molecular concentrations that are impossible to detect in a standard cuvette.
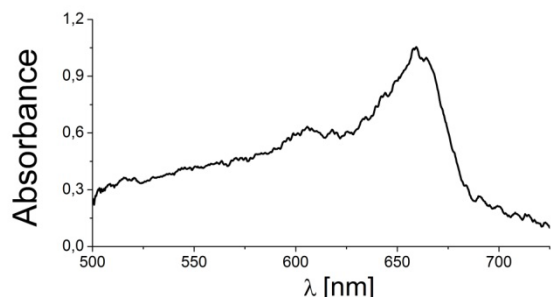


Fig. 6. The absorption spectrum of a 1-nM water solution of OX measured in in a fibre filled under pressure.

The SCFs have been recognized as an efficient platform for UV-Vis absorption measurements of liquids. In this paper, we demonstrated that physicochemical processes on the interface between fibre channels and solution have a significant impact on the interaction between light and the fibre-filling medium and may lead to significant differences in absorption spectra. In particular, we found that adsorption of cationic molecules, such as oxazine, to the fibre glass surface locally increases the concentration of the molecules, resulting in a much stronger absorption of light in the silica fibre than in a standard cuvette. The described enhancement of absorption is stable in time and occurs for various realizations of the experiment with a range of pure silica SCFs from various manufacturers and for various cationic dye (identical results were obtained with Pyridine 1). By performing fluorescence imaging, we demonstrated that dye molecules are selectively adsorbed on the inner walls of the very first part dip end of the fibre. While the detailed mechanism of this adsorption remains to be determined, it is believed to be related with chemical bonding of molecules to the glass surface by ionic interactions [12]; for example, pure silica fibre glass is negatively charged and OX molecules in water are dissociated into OX cations and perchlorate anion. In contrast, pure solvents or anionic organic dyes do not reveal this phenomenon [10,11].

With our results, we demonstrated that the absorbance scales linearly with the concentration, which is important for possible applications of the microstructured optical fibres for measurements of very low concentration liquids. Particularly, based on the observed effect, we demonstrated about a 40-fold increase of the spectroscopic signal in the SCFs relative to a 1 cm cuvette with the same concentration of the OX solution. Quantitative measurements seem feasible, although they would require further detailed studies of the mechanisms of molecular adsorption on the glass-liquid interface.

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