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Functionalization of Exposed Core Fibers with Multiligand Binding Molecules for Fluorescence Based Ion Sensing

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ABSTRACT

The results of functionalizing exposed-core optical fiber with multiligand binding sensor molecules for ion detection is presented. We show that the capacity of the sensor molecules to bind multiple ligands is negated when the sensor molecules are covalently bound, making the method ineffective where multiligand binding fluoroionophores are needed. An alternate functionalization method using thin film polymer doped with multiligand binding fluoroionophores is shown, demonstrating the ability for ion detection in a case where multiligand binding is needed. This one step functionalizing process for optical fiber sensing applications does not require surface attachment functional groups and has the potential to be inline with fiber drawing so that long lengths of functionalized fiber can be fabricated.

Keywords: Fiber Optic Sensor, Microstructured Fiber, Multiligand Binding Fluorophore, Fluorescence Sensing

1. INTRODUCTION

Exposed-core microstructured optical fibers (MOFs) made from silica open up new opportunities for the development of optical fiber-based sensors requiring long term and/or harsh environmental applications while providing real time analysis anywhere along the fiber length.¹ The portion of guided light protruding into the holes of the structure, often described as ‘evanescent field’, is affected by the refractive index and absorption characteristics of the medium within these holes.² This light-matter overlap provides opportunities for exploiting the interaction of light with gases and liquids, where absorption and fluorescence can be used to determine the composition and concentration of the analyte.^{3,4}

The detection of aluminium ions (Al^{3+}) is of particular interest as it provides a marker of aluminum corrosion⁵ and is also a hazard in the environment.⁶ To enable direct sensing measurements it is necessary to immobilize sensor molecules on the glass surface of the MOF exposed core. Some of the functionalization methods typically used to achieve this include silane⁷ or polyelectrolyte⁸ which provide a functional group on the surface to which the sensor molecules can be covalently attached. Fluoroionophores such as 8-Hydroxyquinoline (8-HQ) react with Al^{3+} to form a rigid multiligand complex which is strongly fluorescent when excited at the correct wavelength.⁵ These multiligand complexes provide positive indication of the presence of Al^{3+} when the analyte is mixed with the fluoroionophore. However, it is not clear if multiligand binding to Al^{3+} can occur when such molecules are covalently bonded to the core of a MOF.

Here we present recent work on the design, synthesis and operation of a novel photo-responsive, reversible fluoroionophore based on a known monoazacrown bearing spiropyran (SP) for Al^{3+} detection that is covalently bonded to the MOF core. We use this SP to test whether multiligand binding to Al^{3+} is possible when the sensing molecule is covalently bound to the glass surface. As an alternative method where the sensing molecule is not covalently bound to the surface, we also present studies on functionalizing exposed-core MOFs with a thin film (~ 50 nm) poly(methyl methacrylate) polymer (PMMA) doped with 8-HQ in free form for Al^{3+} detection by measuring the fluorescence from the 8-HQ – Al^{3+} multiligand complex. This has the potential to solve some of the practical issues¹ involved in packaging an exposed-core MOF so that it is sensitive to the chosen analyte but protected from the applied sensing environment without the need for surface attachment functional groups.

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2. EXPERIMENTAL RESULTS AND DISCUSSION

2.1 Development and characterization of switchable spiropyran sensing molecule

We have recently developed sensors for the detection of environmentally and biologically relevant metal ions by modifying photochromic molecules such as spiropyrans with suitable ionophores.⁹ These spiropyran-based ion sensors are also modified for attachment onto surfaces. By integrating ion-binding spiropyran molecules with MOF, we were able to obtain regenerable sensors that can sense the respective metal ions on-demand using light. The spiropyran-based ion sensor (SP) described here was synthesized from aza-crowned nitrosalicylaldehyde* and 3,3-Dimethyl-2-methyleneindoline-5-carboxylic acid with slight modifications to previous work.⁹

When SP is exposed to UV ($\lambda = \sim 365$ nm) it binds to Al^{3+} in the form of a multiligand complex (Fig. 1(a)) and fluoresces at $\lambda_{em} = \sim 630$ nm when excited with $\lambda_{ex} = \sim 532$ nm. The ion is released in the presence of white light or 560 nm irradiation. The sensing molecule was also designed for single-ligand binding with calcium ions (Ca^{2+}) having similar fluorescence properties as the SP- Al^{3+} multiligand complex. This provides a single-ligand binding comparison when the sensing molecule is covalently bound to the MOF core surface. Fig. 1(b) shows in solution cuvette measurements using 532 nm excitation of SP- Ca^{2+} and SP- Al^{3+} complexes, where the blue, red, and green spectra are the SP free form, SP- Ca^{2+} after UV, and SP- Al^{3+} after UV respectively.

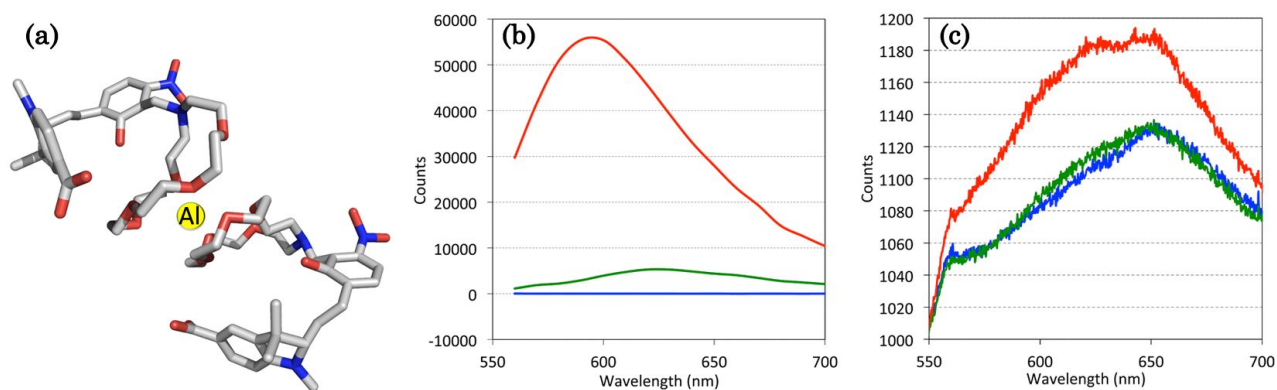


Figure 1. (a) SP- Al^{3+} multiligand complex fluorescent form. (b) Cuvette measurements using 532 nm excitation, where the blue, red, and green spectra are the (●) SP free form, (●) SP- Ca^{2+} after UV, and (●) SP- Al^{3+} after UV respectively. (c) Back reflected spectra of SP functionalized fiber using 532 nm excitation, where the blue, red, and green spectra are (●) acetonitrile after UV, (●) $10 \mu\text{M}$ Ca^{2+} after UV, and (●) $10 \mu\text{M}$ Al^{3+} after UV respectively.

2.2 Silane functionalization of spiropyran to MOF exposed core

The fiber used for these experiments was an exposed-core silica MOF, fabricated¹⁰ with $7.5 \mu\text{m}$ effective core diameter. In order to couple the SP molecules to the exposed core surface, 3-aminopropyltriethoxysilane (APTES) was used which covalently bonds to hydroxyl groups on the silica core surface to provide free amine groups for covalent bonding with the SP carboxylic acid group.⁷ The fiber was prepared for APTES functionalization by flame sealing the holes at each end, then clean and hydroxylate the outer surface by immersion in 70% nitric acid for 16 hrs followed by 2 hrs in 70/30 piranha solution (concentrated sulfuric acid and hydrogen peroxide). After rinsing and drying, the prepared fiber was immersed in 5% APTES-toluene solution for 2 hrs then rinsed with toluene and acetonitrile. This silane functionalized fiber was then immersed in a solution of SP-acetonitrile-HATU[†] for 20 hrs and rinsed with acetonitrile.

A 600 mm long SP functionalized fiber was coupled to a 532 nm (15 mW) laser and the back reflected spectra was measured with a 100 mm long central section immersed in acetonitrile, $10 \mu\text{M}$ Ca^{2+} , and $10 \mu\text{M}$ Al^{3+} shown by the blue, red, and green spectra respectively in Fig. 1(c). In each case the fiber was first irradiated with white light for 2 minutes, and then irradiated for 5 minutes with UV ($\lambda = 365$ nm) before recording the spectra.

*unpublished results

[†]1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU)

The cuvette measurement (Fig. 1(b)) results showed strong fluorescence from the SP- Al^{3+} multiligand complex (green) and a order of magnitude higher fluorescence measured for the SP- Ca^{2+} single-ligand complex (red). For the functionalized fiber case (Fig. 1(c)), the Ca^{2+} solution peak (red) is clearly higher than the acetonitrile reference (blue), however there is no response when the fiber is exposed to Al^{3+} solution. This demonstrates that the SP molecule is functionalized on the exposed core of the MOF and is able to bind to ions on a one-to-one basis, however the ability for two SP molecules to bind to Al^{3+} is limited.

2.3 Thin film polymer doping

The method used to coat exposed-core MOFs with PMMA is an extension of the method for micron scale polymer coating in glass capillaries.¹¹ Cast PMMA was dissolved in dichloromethane (DCM) at a concentration of 12.3 g per litre. 8-HQ which is known to complex with Al^{3+} and then fluoresce strongly with UV excitation,⁵ was added to the dissolved PMMA solution making a concentration of $30_{(8-HQ)} : 100_{(PMMA)}$ by weight. The exposed-core MOF (Fig. 2(a)), with an effective core diameter of $7.5 \mu\text{m}$, was pulled through the PMMA+8-HQ DCM solution and silicon septa, to leave behind a 50 nm coating of the doped PMMA on the core surface (Fig. 2(b)). This method allows long lengths to be functionalized, with the potential to be placed inline with the draw tower during fiber fabrication.

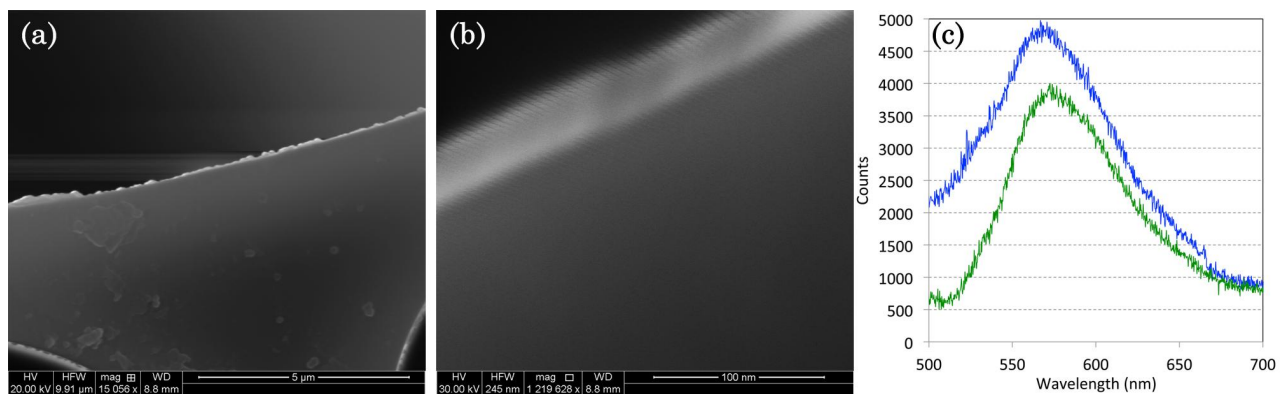


Figure 2. SEM images of (a) the core area of exposed-core MOF with PMMA+8HQ thin film on the exposed side of the core, and (b) close up of 50 nm polymer coating. (c) Back reflected spectra of the functionalized fiber directly after exposure to (●) Al^{3+} solution (green) and (●) after 1 hour (blue).

An 800 mm long PMMA+8-HQ functionalized fiber was coupled to a 375 nm (18 mW) laser and the back reflected spectra of the unexposed fiber recorded. We found that the thin film polymer functionalized exposed-core fiber optical performance was not significantly degraded. The central section, 230 mm long, was immersed in a saturated solution of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. The back reflected spectra from the fiber was measured straight after immersion and again after 1 hour of immersion for which the unexposed fiber subtracted result (Fig. 2(c)) shows the fluorescence peak of 8-HQ – Al^{3+} complex increasing over time. Apart from demonstrating the ability for thin polymer film functionalized fiber to detect Al^{3+} , with the potential for corrosion detection, this result also shows that the 8-HQ is not held too tightly within the polymer, allowing for multiligand binding so that three molecules can still complex with the Al^{3+} .

3. CONCLUSION AND FUTURE WORK

We have developed a novel photo-responsive, reversible fluoroionophore by chemically modifying a known monoazacrown bearing SP for Al^{3+} detection and covalently bonding to a MOF core. This molecule fluoresces strongly when complexed to Al^{3+} with multiligand binding in solution, and even more strongly when single-ligand binding with Ca^{2+} . When functionalized to the exposed core of a MOF the ability for multiligand binding was shown to be negated, although single-ligand binding was still achievable. An alternative functionalization method using thin film polymer doped with multiligand binding fluoroionophores was shown, demonstrating the ability for ion detection where multiligand binding is needed. This one step functionalizing process for optical

fiber sensing applications does not require surface attachment functional groups and has the potential to be inline with fiber drawing so that long lengths of functionalized fiber can be fabricated. In the future, applying the SP to the thin film polymer doping technique has the potential to create a robust and reversible ion sensor capable of multiligand binding for corrosion detection.

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