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A turn-on fluorescence-based fibre optic sensor for the detection of cadmium

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ABSTRACT

A stable, compact and portable optical fibre sensor for the real time detection of cadmium ions in dilute aqueous media has been designed, developed and evaluated. The sensing mechanism was based on fluorescence turn-on of a coumarin (acting as the fluorophore) bearing a dipicolylamine moiety (acting as the metal ion receptor) in the presence of metal ions *via* photoinduced electron transfer (PET). The fluorophore was covalently immobilized onto the fibre surface by polymerisation and exhibited a significant increase in fluorescence intensity in response to Cd^{2+} in the µM concentration range. A referencing scheme allowing for corrections due to fluctuations of the excitation light and transmission properties of the optical fibre or environmental perturbation to the sensor system has been introduced using a highly stable perylene red based material as the internal reference. A high selectivity, excellent photo-stability and reversibility have also been demonstrated, making this type of sensor potentially well suited for *in-situ* monitoring of the metal in the environment.

Keywords: Optical fibre sensor, fluorescent sensor, cadmium sensor, photoinduced electron transfer, coumarin dye.

1. INTRODUCTION

Metal contamination in soil due to mining and industrial activities poses a serious problem across the world both from an economic and health perspective[1]. Common methods for the remediation of metal-contaminated soil include excavation and disposal but these methods are often costly and crude. Cadmium can be released to the environment in a number of ways[2], including natural activities, human activities and remobilization of historic sources, such as the contamination of watercourses by drainage water from metal mines. Atmospheric deposition of cadmium on arable soils often outstrips its elimination, resulting in higher levels of cadmium in soils and crops. In addition, agricultural soil cadmium pollution can significantly rise through application of municipal sewage sludge. The effects of cadmium exposure on the individual are both serious and well documented: cadmium exerts toxic effects on the kidney, the skeletal system and the respiratory system and is classified as a human carcinogen[2, 3].

Conventional methods for the detection of Cd^{2+} such as atomic absorption spectrometry, voltammetry and inductively coupled plasma mass spectrometry, despite having achieved good results, are generally expensive, time consuming and cumbersome for real-time measurements outside the laboratory. In recent years, a number of fluorescent probes for the detection of Cd^{2+} have been reported[4-9]. However, there are weaknesses with them and their applications, where most are not suitable for use in the field. Commercial heavy metal sensors for use in soil are very limited and are typically either very expensive or require the extraction of soil prior to its manipulation and analysis, which could allow sample degradation to occur prior to measurement. There is a need, therefore, for the development of low-cost, portable, sensitive and selective sensing systems which are capable of real time detection of the target metal.

In this work, a stable, compact and portable fibre optic sensing system which is capable of real time detection of Cd^{2+} has been developed. A novel fluorescent polymeric material based on a derivative of coumarin (acting as the fluorophore) and dipicolylamine (acting as the cadmium ion receptor) has been designed, synthesized and covalently attached to the distal end surface of an optical fibre. In this system, the presence of the amine significantly reduces the fluorescence of the fluorophore due to the quenching of its fluorescence by the nitrogen lone pair electrons through PET. Upon complex formation with Cd^{2+}, the nitrogen lone pair electrons are donated to Cd^{2+}, which therefore abolishes or tremendously reduces the fluorescence quenching. Consequently, binding of Cd^{2+} switches on fluorescence as illustrated in Fig.1.

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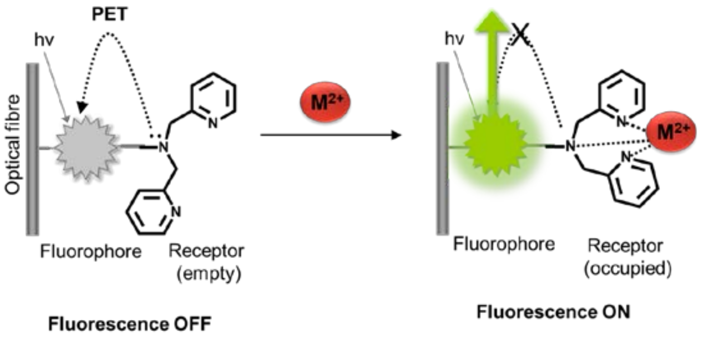

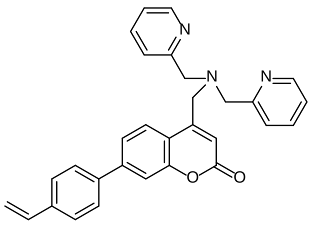

Coumarin dipicolylamine 1

Figure 1. Illustration of fluorescence switching on by Cd^{2+} binding via a PET mechanism

The main disadvantage of fluorescence intensity detection schemes is that they are affected by various potential interfering factors such as the fluctuation of excitation light source used, the aging of optical fibres and environmental condition changes. Therefore, a regular calibration is usually required in order to increase the reliability of measurements. In this work, a new stable polymer based on perylene red has been introduced into the system as the internal reference to eliminate the need for regular calibrations due to fluctuations of instrumental parameters, which is very important in remote sensing measurements where the sensors are not accessible after installation.

2. EXPERIMENTAL

2.1 Sensor probe fabrication

The fabrication of the sensing probe requires a multi-step process which has been previously described[10]. The pre-polymerization mixture was prepared by mixing a solution containing coumarin dipicolylamine **1** (1.5 mg, 0.0032 mmol), PRP reference polymer (5 mg) and poly(ethylene glycol) diacrylate (Mn = 575) (30 mg) in *N,N*-dimethylacetamide (500 µL) with a 40% acrylamide solution in water (500 µL) and a 25 mM phosphate buffer pH 7 solution (500 µL). Ammonium persulfate initiator (10 mg) was then added. The solution was purged thoroughly with argon for 2 min. A small volume of the solution was placed into a capillary tube *via* a syringe and the distal end of the fibre was inserted. They were sealed quickly with PTFE tape and polymerized in an oven at 75 ^{o}C for 15 min. A typical probe prepared by this procedure is shown in Fig. 2. The sensor tip was placed in a 25 mM phosphate buffer pH 7 solution overnight, followed by washing repeatedly with distilled water to remove all unreacted materials as well as the excess amount of polymer formed which was not directly bound to the fibre. The probe was then stored in a cool and dark place until use.

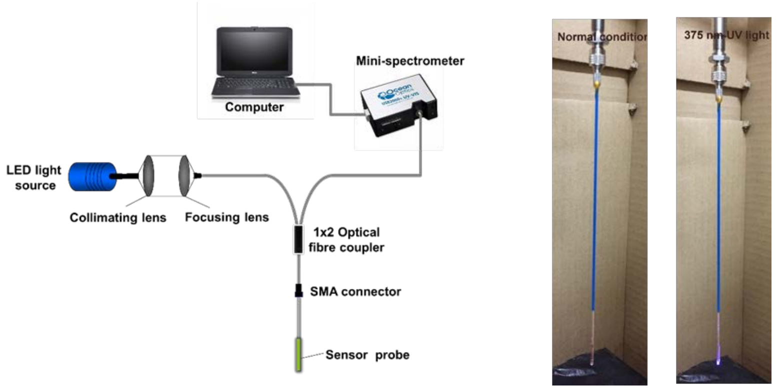

Figure 2. Left: experimental set-up used in the evaluation of the performance of the probe designed. Right: the sensing probe prepared in this work under normal conditions and when 375 nm UV light was launched to the end of the fibre.

2.2 Experimental set-up

The set-up used for the measurements undertaken to calibrate the probe is as presented in Fig. 2, where light from a 3 mW LED (Roithner Lasertechnik), emitting at a center wavelength of 375 nm is coupled through a multimode UV/Visible fibre (Thorlabs), using collimation and focusing lenses (Comar), into one branch of a 2x1 multimode fiber coupler (Ocean Optics). The other end of the fibre coupler is connected, through a SMA connector, to the sensor probe with the active sensing region being located at the distal end of the fibre. Following interaction of Cd^{2+} with the active region, a portion of the total light emitted from the sensing layer is collected and guided through the other end of the fibre coupler to an Ocean Optics USB2000 spectrometer, the output from which is then displayed on a computer screen.

3. RESULTS AND DISCUSSION

3.1 Spectral properties and fluorescence response of the fluorophore to metal ions in solution

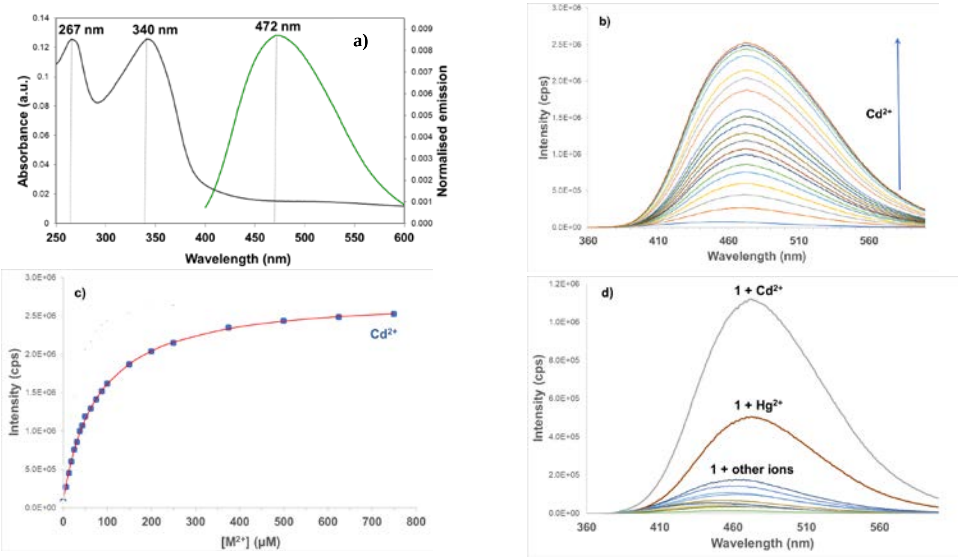

Figure 3. a) Absorption (left) and emission (right) spectra of **1** (5 µM) in H_2O/MeCN (7:3, v/v). Emission spectra recorded with λex = 340 nm. b) Emission spectra of **1** (50 µM, λex = 345 nm) in H_2O/MeCN (7:3, v/v) with the addition of Cd^{2+} (0 to 750 µM). c) Titration plots at 472 nm. The red solid lines show the computer fits. d) Emission spectra of **1** (50 µM, λex = 345 nm) in H_2O/MeCN (7:3, v/v) in the presence of 1 equiv of different metal ions.

The absorption spectrum of **1** performed in H_2O/MeCN (7:3, v/v) shows two main bands in the UV region, at about 267 nm and 340 nm (Fig. 3a). The emission spectrum for the compound recorded in the same solvent using excitation at the absorbance maximum includes only one band at 472-474 nm. The quantum yield of **1** was calculated to be about 0.5%, which is very low as the fluorescence of the compound is quenched by the nitrogen lone pair through PET. Adding Cd^{2+} to **1** in solution resulted in a significant increase in fluorescence intensity of the fluorophore (Fig. 3b). It can be seen that the emission intensity at 472 nm increases nearly 15-fold after the addition of 50 µM (1 equiv) of Cd^{2+} and continues to increase until an approximate saturation is reached at around 33-fold (Fig. 3c). The sharper increase in fluorescence intensity when the addition of Cd^{2+} is less than 0.5 equiv suggests that the interactions of the fluorophore with the metal ions may not be on a 1:1 basis, rather on a 2:1 basis. The titration data were then fitted to the 2:1 association model, giving binding constants $K_{1:1}$ of $2.56 \pm 1.20 \times 10^3$, $K_{2:1}$ of $3.85 \pm 0.15 \times 10^4$. This indicates that the association between **1** and Cd^{2+} is relatively strong and **1** is an excellent receptor for Cd^{2+}. The selectivity of **1** for the metal ions was studied in H_2O/MeCN (7:3, v/v). It can be observed from Fig, 3d that **1** shows no response to the other metal ions except for Hg^{2+} where there is a small increase in intensity. However, the change for Hg^{2+} is significantly less than that for Cd^{2+}, indicating that **1** is reasonably selective for the detection of Cd^{2+}, which is a matter of necessity for an excellent chemosensor.

3.2 Response of the sensor probe to Cd^{2+}

The calibration of the sensor was performed using a series of solutions of the nitrate salt in deionized water. The probe was immersed in the Cd^{2+} solutions and the signals were allowed to reach constant values before being recorded. The sensor was rinsed with Tris-EDTA buffer solution (10 mM Tris-HCl; 1 mM EDTA), followed by deionized water between measurements. In a way that is similar to that seen for the free fluorophore, the sensor exhibited an increase in fluorescence intensity with increasing Cd^{2+} concentration in the micromolar range (Fig. 4). The calibration curve was constructed as a plot of the ratio of the fluorescence intensity at 442 nm (the first emission peak) to that at 611 nm (the emission peak of the reference material PRP) versus the concentration of Cd^{2+}. The plot displays a linear relationship in the concentration range of 0 – 28 μM (R2 = 0.9985) (Fig.4b). At higher concentrations of Cd^{2+}, no further change of intensity was observed due to the saturation of all available binding sites.

It can be seen from Fig.4c that the metal binding process is completely reversible and the Tris-EDTA solution restores fluorescence of the sensor back to the baseline level. The sensor can also be recovered in H_2O but the process requires a greater amount of time, almost two hours to attain a 95% recovery compared to just 15 min with the use of EDTA.

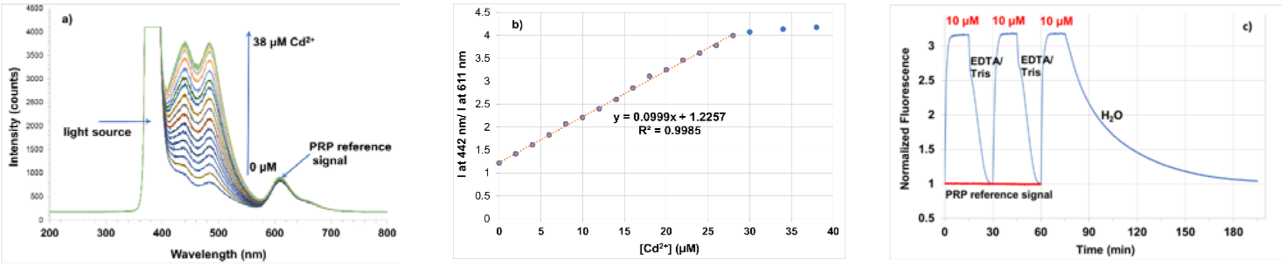

Figure 4. a) Fluorescence spectra of the sensor probe in deionised water with the addition of Cd^{2+}. b) Titration plot (I_{442nm}/I_{611nm} versus $[Cd^{2+}]$). c) Forward and reverse dynamic response of the sensor probe with the addition of Cd^{2+} and removal of Cd^{2+} using a Tris-EDTA buffer solution (λex = 375 nm, λem = 440 nm).

4. CONCLUSIONS

In this paper, a novel fibre optic sensor system for the detection of Cd^{2+} in aqueous media has been reported. The sensing mechanism was based on fluorescence turn-on of a coumarin (acting as the fluorophore) bearing a dipicolylamine moiety (acting as the metal ion receptor) in the presence of metal ions *via* photoinduced electron transfer (PET). The fluorophore was covalently immobilized onto the fibre surface by polymerisation and exhibited a significant increase in fluorescence intensity in response to Cd^{2+} in the μM concentration range. The sensor has also demonstrated a high selectivity for Cd^{2+} over other metal ions. A referencing scheme allowing for corrections due to fluctuations in the light source or environmental perturbation to the sensor system has been introduced using a perylene red based material as the internal reference. The sensor system developed is potentially suited for *in-situ* long term monitoring of the said metal ions. Further optimisation of the sensor design and packaging is on-going for the next-stage field tests and the results will be reported in future work.

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