



Spiropyran-based reversible, light-modulated sensing with reduced photofatigue

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ABSTRACT

Switchable materials have tremendous potential for application in sensor development that could be applied to many fields. We are focusing on emerging area of wireless sensor networks due to the potential impact of this concept in society. Spiropyran-based sensors are probably the most studied type of photoswitchable sensing devices. They suffer from many issues but photofatigue, insufficient selectivity and lack of sensitivity are probably the most important characteristics that hinder their wider application. Here, we address these issues and demonstrate that covalent attachment of modified spiropyran into a polymeric film significantly reduces photodegradation. The observed signal loss after 12th cycle of switching between the spiropyran and merocyanine forms is only about 27% compared to the loss of 57% of the initial signal in an equivalent experiment based on non-immobilized spiropyran. This has enabled us to demonstrate at least five reversible cycles of detection of an ion of interest (in our case H⁺) with minimal signal loss. Furthermore, we demonstrate that the sensitivity can be increased by incorporation of additional binding groups in the parent spiropyran molecule. Using molecular modelling to calculate the relevant bond lengths as a measure of interaction between MC and H⁺, the calculated increase of H-bond strength is approximately an order of magnitude for a derivative containing a methoxy group incorporated in the *o*-position of the parent spiropyran in comparison to the equivalent unsubstituted phenol. This theoretical result was found to correspond very well with experimental observation. As a result, we have increased the sensitivity to H⁺ by approximately one order of magnitude.

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1. Introduction

Recently, the area of wireless sensor networks (WSNs) has emerged as a topic of considerable importance, under which it is envisaged that in the near to medium term, many millions of sensors will feed data into a ubiquitous communications infrastructure, providing information on personal health indicators, the status of the environment, the quality of our food, or the presence of a threat or hazard [1]. However, despite the obvious importance of information that can be provided by chemo/bio-sensors, there is still very limited activity in the literature that convincingly demonstrates the application of these devices in a WSN [2]. A major inhibiting factor to the widespread deployment of chemical sensors/biosensors within WSNs is the need to perform regular calibration, due to changes occurring at the active sensing surface of the device [3]. Calibration involves integrating liquid control features

which, with current technologies, results in a much more complex and expensive device than would be desirable for WSN deployments. A conceptually intuitive solution to this problem could be provided by the use of 'adaptive materials' that can switch between a passive form that is relatively unaffected by exposure to the real world, and an active, sensing form that can be occasionally invoked when a measurement is required, after which the surface is switched back to the passive form [4].

A way to demonstrate aspects of this concept may be found through materials that are known to undergo light induced switching between two or more isomers, only one of which undergoes complexation with the target species [5,6]. One of the oldest and possibly the most studied group of photochromic chelating agents is the family of spiropyrans. Upon irradiation with UV light, spiropyran switches from an uncharged, passive, colourless spiropyran (SP) isomer to a zwitterionic, highly coloured, merocyanine (MC) isomer that possesses an electron-rich phenolate oxygen atom capable of serving as a binding site for certain metal ions [7,8]. Conversely, irradiation with visible (green) light causes the ejection of bound metal ions from the MC-complex and regeneration of the passive SP form [9]. This very interesting behaviour stimulated us to

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investigate whether SP could be used to make systems that exhibited photo-reversible ion-binding behaviour hence becoming the serious candidates for design of self-regenerated, “calibrationless” sensors.

Ion-binding behaviour of transition [10–12] and alkali metal ions [13] by the SP/MC system is relatively well-studied; however a number of challenges must be addressed before a fully functioning devices can be produced for real-life applications [14]. For example, the equilibrium between SP and MC is not only driven by light but also by the temperature and the polarity of the environment. The latter does not allow simple integration of SP in non-polar polymer matrixes as it is done in typical optical sensors [15] since the polar MC may easily leach out of the membrane. Covalent attachment of SP to the surface [16], polymer backbone [17] or to beads [18] is therefore seen as general solution for such type of issues. Furthermore, phenolate group in MC is a sole binding centre and with its not overly strong binding of metal ions, it does not express exceptional sensitivity and selectivity. The major limitation for using SP in reversible sensing system as regarded by many researchers is the photodegradation of SP [14]. In addition to issues arising from the chemical nature of SP, size, cost, simplicity of construction and usage of power are all issues that should not be overlooked while thinking of developing and deploying a large number of sensor in a WSN. In our work we are systematically addressing all of the aforementioned issues. For example, we have earlier developed a system based on light emitting diodes (LEDs) as both light emitters and detectors [19]. This allowed us not only to develop very simple, low cost, low power sensing platform [20] but it somewhat surprisingly resulted in reducing the photodegradation of SP [14].

In this work, we demonstrate the reversible, light-modulated sensing that is a step in the direction of achieving sensing with reduced need for calibration. We also describe our effort to strengthen the binding of metal ion by introducing secondary binding centre within the molecule of SP while employing molecular modelling as a powerful tool for predicting the effect of introducing new groups within a molecule. Finally, we address the photodegradation and demonstrate that it is possible to significantly reduce the degree of photodegradation of SP through covalent attachment to a polymer surface.

2. Experimental

2.1. Materials and instruments

6-Nitro-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] 98% (spiropyran), ethylene diamine 99% (redistilled), 1,8 diamino octane 99%, methacrylic acid 99% (redistilled), omega,omega-dimethoxy-omega-phenylacetophenone (DMPA), NaOH, boric acid, citric acid and potassium dihydrogenphosphate (KH_2PO_4) were purchased from Aldrich. Polymethyl methacrylate (PMMA) was purchased from Goodfellow. 1-Ethyl-3-(3-dimethylamino propyl) carbodiimide hydrochloride (EDC) was purchased from Fluka Scientific. Aqueous solutions were made with deionized Nanopure water (18 M Ω cm). The UV irradiation source BONDwand UV-365 nm was obtained from Electrolite Corporation. The white light source was obtained from Chiu Technical Corporation. Spectra were recorded on a UV-vis-NIR PerkinElmer Lambda 900 spectrometer. The thickness of $\sim 130 \mu\text{m}$ of the SP-polymer film was measured using a PARISS imaging spectrometer coupled to a Nikon eclipse E800 microscope.

2.2. Synthesis

Two derivatives of SP have been synthesized according to the procedure outlined below [21].

2.3. 1-(3-carboxypropyl)-3,3-dimethyl-6-nitrospiro-[2H-1]-benzopyran-2,2-indoline

The solution of 5-nitrosalicylaldehyde (0.7 g, 2 mmol) in ethanol (10 ml) was added drop wise to a solution of 1-(3-carboxypropyl)-3,3-dimethyl-2-methyleneindolinium bromide (0.34 g, 2 mmol) in ethanol (10 ml) over 30 min. The reaction mixture was refluxed over 1 day. The resulting yellow precipitate was filtered off and washed using cold ethanol. The yellow product was recrystallised from ethanol two times to obtain yellow crystals 0.7 g, yield –83%.

2.4. 1-(3-carboxypropyl)-3,3-dimethyl-8-methoxy-6-nitrospiro[2H-1]-benzopyran-2,2-indoline

The solution of 3-methoxy-5-nitrosalicylaldehyde (0.5 g, 1.45 mmol) in ethanol (10 ml) was added drop wise to a solution of 1-(3-carboxypropyl)-3,3-dimethyl-2-methyleneindolinium bromide (0.28 g, 1.45 mmol) in ethanol (10 ml) over 30 min. The reaction mixture was refluxed over 1 day. The resulting brown solution was cooled down and the product was precipitated out by adding ethyl acetate. The yellow precipitate was filtered and washed with cold ethanol. The crude product was purified by column chromatography, silica/ethyl acetate, to obtain pure crystal ester-spiropyran 0.3 g, yield-46%.

Fig. 1 depicts the two compounds used in this work and their transformation from neutral and passive “spiro” form (SP) to zwitterionic and active merocyanine form (MC).

2.5. Experiments

1,8-Diaminooctane was covalently attached to the PMMA surface as a linker group of the requisite length for the carboxylated spiropyran derivative as described elsewhere [16]. Universal buffer (30 mM of boric acid, citric acid and KH_2PO_4) in water was prepared and stored in the dark. Prior to each measurement, a small piece of the film of approximately 1 cm \times 0.5 cm was cut out, immersed in deionized water if required, exposed to visible light for 1 min and the spectrum of the closed form (SP) was recorded. The reference spectrum of the opened form (MC) was obtained after the same film was exposed to UV light for 1 min. When required, the active film (MC) was exposed to buffer solution with appropriate pH adjusted using NaOH and new spectra were recorded.

3. Discussion

3.1. Reversible ion detection

Doping of traditional, hydrophobic plasticized polymeric membranes by SP intuitively seems as the simplest solution for its utilization in chemical sensors. Unfortunately, the MC form is significantly more polar than SP [22] which makes it prone to leaching out of the membrane. Over the years, covalent attachment of sensing components emerged as an attractive solution for the problem of their insufficient retention [23]. We have earlier demonstrated that modified SP can be attached to activated polymethylmethacrylic (PMMA)-based surface binding sites with full preservation of the ability of SP to switch between the active and passive form and detection of Co^{2+} while in active form [16]. In light of our attempts for simplification of sensing platform, it is important to note that the switching can be achieved using simple LEDs [24]. In order to use SP in the vision of simple, self-regenerated sensors, it is critical to demonstrate the reversibility of switching between the active and passive form as well as the complete regeneration of sensing film and return to the original, pre-sensing state.

The typical absorbance spectrum of the film used in this work is given in Fig. 2A. Dotted line depicts the spectrum of SP-modified

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