A dual detecting polymeric sensor: chromogenic naked eye detection of silver and ratiometric fluorescent detection of manganese

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ABSTRACT

Polymer **1**, a poly(olefin) with pendant Schiff base units is prepared by reacting poly(allylamine) and 2-hydroxynapthaldehyde in methanol. The optical properties of **1** are investigated in THF:H_2O (9:1) solvent system buffered at pH 7.0 ± 0.1 using HEPES. When tested against a range of physiological and environmentally relevant cations **1** displays selectivity for Ag^+ from changes in the UV–vis spectra with linearity established in the range of 10–60 μM. The addition of Ag^+ to a solution of **1** also causes a colour change from colourless to dark yellow meaning Ag^+ is also detectable by the naked eye. In contrast, selectivity is observed for Mn^{2+} from changes in the emission spectra again with good linearity observed in the range of 0–50 nM. This is the first reported polymeric sensor capable of detecting both Ag^+ and Mn^{2+} using two different detection modes.

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The development of new synthetic sensing assemblies for the recognition and detection of physiologically and environmentally important analytes is of considerable interest.[1] UV–vis and fluorescence spectroscopy remains the most frequently used modes of detection in these sensors due to their high sensitivity, adaptability and relative inexpense. As selectivity is a major priority of any sensor, most are designed to show high specificity for a single target, and as such, are limited to reporting on the concentration/location of one analyte per sensor. More recently however, there has been a shift towards the development of sensors capable of simultaneously recognising more than one analyte.[2] Molecular logic, a concept pioneered by de Silva and co-workers is one such example, where two (or more) analytes are required to bind with a probe at predefined levels before a single fluorescence signal is observed.[3] Semi-selective receptors that enable the binding of two guests with distinct spectral responses have also been reported.[4] Such sensors have benefits over their single analyte analogues as many physiologically deleterious conditions are indicated by the abnormal concentration of more than one analyte.[5] In addition, the ability to screen solutions for more than one target at a time leads to faster analytical processing times and potential cost reduction. Both silver and manganese can produce adverse health effects in humans if present in sufficient quantities. For example, silver in any form is a bioaccumulative toxic heavy metal and in extreme cases, accumulation in humans can cause Argyria, a condition characterised by a bluish-grey colouration of the skin.[6] The increased use of silver nanoparticles as potential therapies[7] and biochemical labels[8] increases the likelihood of exposure to this element.

Similarly, manganese is a toxic, yet essential trace element meaning it is not only essential for human health but also can be detrimental if present in larger quantities. Therefore sensors that can monitor both silver and manganese concentrations have obvious benefits.

We have developed a polymeric sensor capable of detecting Ag^+ and Mn^{2+} by colorimetric and fluorescence detection, respectively. The sensor consisted of a poly(olefin) backbone with pendant naphthalene-containing Schiff base receptors. We have previously demonstrated that the immobilisation of Schiff base receptors on a Quantum Dot (QD) surface led to an enhancement in the selectivity of the resulting QD-Schiff base conjugate relative to the receptor alone.[9] Similarly, we demonstrate here that immobilisation of this class of receptors on a polymeric backbone results in selectivities not observed for the receptor alone. To the best of our knowledge, this is the first reported example of a polymeric sensor for the dual detection of both Ag^+ and Mn^{2+}.

The sensor **1**, was synthesised in one step from commercially available precursors by reacting 15 kDa poly(allylamine) (PAA) with an excess of 2-hydroxy-1-naphthaldehyde in dry methanol. After stirring for 18 hours a product was observed to precipitate from solution and was collected by filtration. It was further purified by redissolving in chloroform and by precipitating with methanol. Control compound **2** was prepared by reacting 2-hydroxy-1-naphthaldehyde with aniline in methanolic solvent as detailed by us in a previous communication.[10]

The successful grafting of 2-hydroxy-1-naphthaldehyde onto PAA was confirmed by ^{1}H NMR spectroscopy, with Figure 1 showing the stacked spectra of 2-hydroxy-1-naphthaldehyde (top) and sensor **1** (bottom). The aldehyde proton, observed at 10.80 ppm in 2-hydroxy-1-naphthaldehyde was absent in the spectrum of **1**

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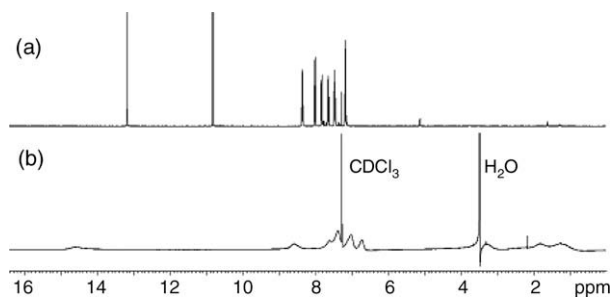*E-mail address:* j.callan@rgu.ac.uk (J.F. Callan).

Figure 1. ^{1}H NMR spectra of (a) 2-hydroxy-1-naphthaldehyde and (b) Sensor **1**, recorded in CDCl$_3$.

while the hydroxy proton, present at 13.15 ppm in the starting material was observed further downfield as a broad resonance centred at 14.75 ppm. The downfield shift of the hydroxy proton accompanied by its significant broadening suggests a hydrogen bonding interaction between neighbouring hydroxyls of adjacent receptors.[11] Formation of the Schiff base was confirmed by the presence of the imine proton at 8.60 ppm which was not present in the starting material. The aromatic region also experienced slight changes in chemical shifts relative to the monomer and the peaks were generally much broader, consistent with anchorage on a polymer backbone.[12] The backbone protons and first side-chain methylene protons were observed in the upfield region as a group of resonances centred at 1.35, 1.80 and 3.30 ppm. By comparing the relative integration of the aromatic and backbone regions the percentage incorporation was judged to be 100% from which a molecular weight of ∼50 kDa was established (Scheme 1).

The optical properties of **1** were investigated in a THF:H$_2$O (9:1) solvent system buffered at pH 7.0 (HEPES). The UV–vis spectrum was characterised by two main bands centred at 308 nm and 418 nm. The effect of a range of environmentally and physiologically important metal ions on the UV–vis spectrum was investigated by preparing solutions containing **1** (20 µM) and the ion (100 µM). A substantial enhancement of the 310 nm and 418 nm bands was observed upon addition of Ag$^+$ while the other ions produced minimal effects on the absorbance intensity at these wavelengths (see Supplementary data). When the changes at 310 nm were monitored, good selectivity was observed for Ag$^+$ with a 70% increase in absorbance when compared to the starting intensity (Fig. 2a).

The titration of Ag$^+$ ions with a solution of **1** caused a gradual increase in intensity of both the 310 nm and the 418 nm bands, the former accompanied by a slight blue shift and the latter accompanied by a slight red shift of the absorption maxima (Fig. 2b). When a plot of the absorbance intensity at 310 nm against Ag$^+$ concentration was made, good linearity was observed in the range of 10–60 µM (Fig. 2c). The effect caused by Ag$^+$ was very significant that it could be detected by the naked eye with a distinct change in colour of the solution from colourless to dark yellow while the colour of the solutions containing the other ions remained relatively unchanged (Fig. 3).
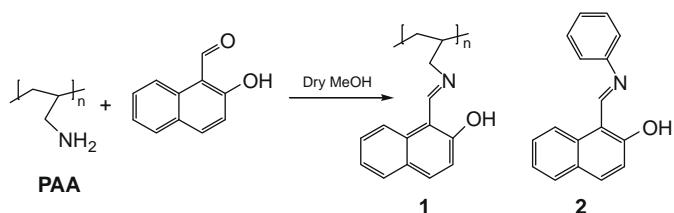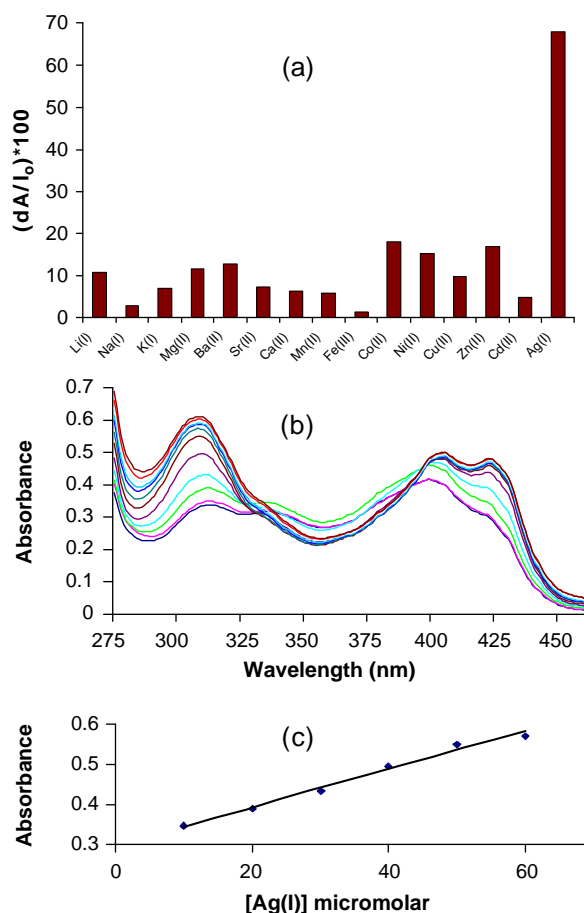

Scheme 1.

Figure 2. (a) Bar chart illustrating the % change in absorbance at 310 nm for **1** upon addition of various metal ions (b) UV–vis spectra of **1** upon increasing concentration (0–125 µM) of Ag$^+$ (c) plot of absorbance intensity of **1** at 310 nm against concentration for Ag$^+$. [**1**] = 20 µM, solvent: THF:H$_2$O (9:1) HEPES buffer solution at pH 7.0 ± 0.1.

The fluorescence spectrum of **1** was characterised by three weakly emissive bands centred at 357, 454 and 518 nm when excited at 275 nm. As in the UV–vis study the effect of adding ions on the emission profile of **1** was investigated (see Supplementary data). Significant changes were observed upon addition of Mn^{2+}, with substantial enhancements for the peaks at 357 and 454 nm, the former being accompanied by a red shift (∼19 nm) of the emission maximum. The weak fluorescence observed for **1** in the absence of metal ions is most likely due to a rapid isomerisation about the C=N bond leading to non-radiative decay of the excited state. Binding of Mn,$^{2+}$ however, locks one particular conformation (i.e., cis or trans) in place resulting in an enhancement of fluorescence.[13] Of the remaining ions only Co^{2+} and Sr^{2+} produced any significant effect on the emission profile of **1** with enhancements of 48% and 55% when compared to the starting intensity, and much lower than the 195% enhancement observed for Mn^{2+} (Fig. 4a).

The changes in the fluorescence spectra of **1** upon the continuous addition of Mn^{2+} ions are shown in Figure 4b. The results show a gradual increase and red shifting of the 357 nm band, a gradual increase of the 454 nm band and a small decrease in the 518 nm band. The presence of an isoemission point at 492 nm was also observed. These significant changes offer great flexibility in selecting wavelengths for the ratiometric determination of Mn^{2+} by fluorescence. Ratiometric monitoring has benefits over single wavelength monitoring in that it is free from the errors associated with sensor concentration, photobleaching and local environmental
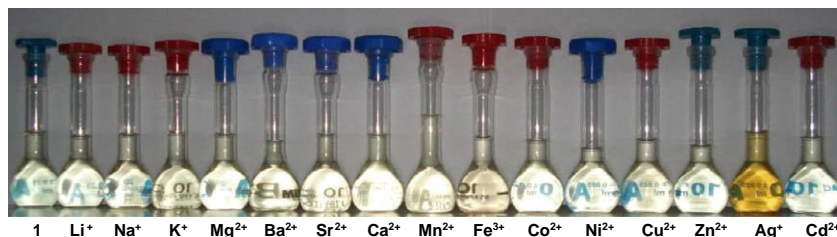
Figure 3. Photograph of **1** in the presence of various metal ions. [**1**] = 20 μM, [ions] = 100 μM in a THF:H$_2$O (9:1) HEPES buffer at pH 7.0 ± 0.1.
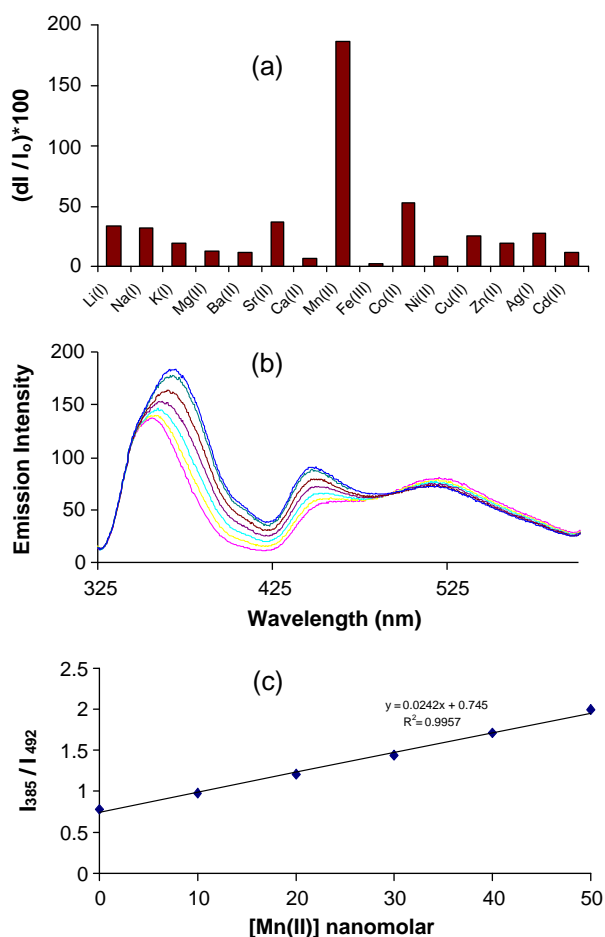

Figure 4. (a) Emission spectra of **1** in the presence of various metal ions, (b) emission spectra of **1** upon increasing the concentration of Mn^{2+} (0, 10, 20, 30, 40 and 50 nM) and (c) plot of ratiometric fluorescence intensity against Mn^{2+} concentration. [**1**] = ~20 μM. [ions] = 100 μM for (a).

and excited states was not totally unexpected as it has previously been shown by Bhardwaj et al. that tripodal Schiff base sensors containing structural motifs similar to the repeat unit present in **1** display chromogenic selectivity for Ag$^+$.[15] In addition, we have also shown that Schiff base receptors can undergo Excited State Intramolecular Proton Transfer (ESIPT) to produce keto and enol tautomers with different binding selectivities.[10] Unfortunately, as polymeric systems are characterised by non-exact molecular weight distributions we were unable to determine the binding stoichiometry occurring between **1** and Ag$^+$/Mn^{2+}.

In summary, we have reported for the first time that, by appending Schiff base receptors on a polymeric backbone, the selectivity of the resulting macromolecule can be improved significantly. Moreover, we illustrate that different selectivities were observed in the ground and excited states, with the former enabling detection of Ag$^+$ and the latter Mn^{2+}. This is, to the best of our knowledge, the first reported example of a dual detecting polymer capable of detecting both Ag$^+$ and Mn^{2+}. In addition, the greater processing ability of polymers (i.e., into films, etc.) compared to that of low molecular weight compounds is another advantage of this system. We believe this approach could be extended to many more receptors and may result in a new generation of optical sensors.

Acknowledgements

Supplementary data

Supplementary data (experimental procedures and spectral data for various compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.04.108.

effects.[14] We compared changes in the intensity at 385 nm against those at 492 nm and plotted this ratiometric change (I$_{385}$/I$_{492}$) as a function of concentration. Using this approach, linearity was established in the range of 0–50 nM as shown in Figure 4c. Linearity was also observed when the ratiometric intensity change I$_{446}$/I$_{492}$ was plotted against concentration illustrating the flexibility of this system (see Supplementary data).

In contrast to the selectivity displayed for **1**, monomer **2** (prepared as a control sample) was observed to bind to many different ions when examined by UV–vis or fluorescence spectroscopy under identical conditions to those used for **1**, suggests that for **1**, the availability of multiple binding sites from adjacent receptors is sufficient to complete the co-ordination sphere of specific metal ions. The variation in selectivity of **1** between the ground

References and notes

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