Talanta 164 (2017) 228–232

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

‘Rough guide’ evanescent wave optrode for colorimetric metalloporphyrine sensors

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ARTICLE INFO

Keywords:
Optrode
Evanescent wave
Amine
Metalloporphyrin
Lock-in

ABSTRACT

When films of zinc 5-(4-carboxyphenyl),10,15,20-triphenyl porphyrin (ZnTPP) are exposed to waterborne amine in pH- neutral or alkaline media, both Q- band and Soret band respond with a change of absorbance due to the donation of amine ‘lone pair’ electrons to the metalloprophyrin π orbital. However, this is difficult to reveal with a conventional spectrometer even under high amine concentration. We therefore introduce optical fibres coated with ZnTPP into a bespoke ‘light balance’ evanescent wave absorbance meter [doi:10.1016/j.snb.2016.05.065]. The light balance makes absorbance changes clearly visible under only 5 μM aqueous amine, making PVC membranes redundant. We find sensitivity is higher, and limit- of- detection lower, in the Soret band rather than the Q- band, reflecting the stronger Soret band absorbance. Also, we find that sensitivity is higher, and limit- of- detection approximately two times lower, when rough rather than smooth fibres are used. We believe the rough fibre surface leads to enhanced evanescence, and therefore better overlap of the wave propagating in the fibre with the ZnTPP fibre cladding. We find a limit of detection to waterborne amines below 1 μM, which compares well to other sensors for waterborne amines [Korent, S.M. et.al. Anal. Bioanal. Chem. 387 (2007) 2863–2870; Algarni, S. A. et.al. Talanta 153 (2016) 107–110]. We therefore recommend ‘rough guide’ evanescent wave optrodes, in combination with sensitive ‘light balance’ detector, to succeed membrane-embedding of colorimetric sensitisers such as metalloporphyrines.

1. Introduction

Fibre optic wave guides are often used to take light towards, and away from, the sensitive element of optrode sensors, commercial equipment is available for that purpose [1]. The sensitive element itself typically consists of an analyte- specific chromophore (called ‘sensitiser’ or ‘receptor’) that is insoluble in water, embedded into a plasticised PVC membrane [2,3], or a sol- gel matrix [4,5], to mediate contact with waterborne analyte. However, plasticisers in PVC membranes contaminate the sample under study due to leaching [6] and evaporation [7]. Moreover, PVC membranes are thick [7] and suffer from slow diffusion. Sol- gel matrices are prepared using harsh chemicals [5].

A more elegant approach is to directly combine optical waveguide, and sensitiser, by coating a thin sensitiser film directly onto the unclad core of an optical fibre. The evanescent wave of light propagating in the fibre core probes the absorbance of the chromophore, absorbance changes in response to analyte lead to a detectable change of the intensity of propagating light. PVC membranes and sol-gel matrices can be avoided altogether, although they are sometimes retained [8]. Despite of the simplicity and elegance of evanescent wave fibre optic transducers, there is only a limited number of reports on such sensors in the literature [8–10]. This may be because dedicated equipment to detect the intensity loss of the propagating wave is not commercially available, and researchers used conventional spectrometers or simple photodiode circuits. Some of us have therefore designed a bespoke LED- driven self-referenced ‘light balance’ fibre optic absorbance meter with Lock-in detection specifically for evanescent wave absorbance measurement [11]. Assembled only from generic and affordable electronic and fibre- optic components, this instrument enables highly sensitive evanescent wave absorption measurement, which we demonstrated on a generic chromoionophore [12] to detect waterborne

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http://dx.doi.org/10.1016/j.talanta.2016.11.057
Received 26 September 2016; Received in revised form 22 November 2016; Accepted 24 November 2016

cations.

Here, we apply this instrument to the detection of organic solutes in water, *e.g.* amines. Amines are released when proteins degrade *e.g.* under bacterial action, which makes amines an indicator of food spoilage [13], and they may be toxic if consumed [14–16]. As sensitiser, we used a water insoluble Zinc porphyrin derivative designed for good adhesion on glass, Zinc 5-(4-carboxyphenyl),10,15,20-triphenyl) porphyrin (ZnTPP) [17]. It has been shown previously that metalloporphyrins show colorimetric [16,19,20] or gravimetric [18,21–23] sensitivity to odours *e.g.* of amines [16,18], alcohols [18,19], or aromatic compounds [18]. Sensitivity and selectivity are influenced by the core metal and peripheral ligands [18].

We here show that ZnTPP shows absorbance response to amine when both are dissolved in organic solvent, but this becomes marginal when ZnTPP is coated as a film inside a cuvette to sample waterborne amine. However, when ZnTPP is coated onto an optical fibre, and transduced with our evanescent wave absorbance meter, we find absorbance response to waterborne amines with low limit- of- detection (LoD). Finally, we take evanescent waveguide sensing to a new level by introducing an optical fibre that was deliberately roughened before coating with sensitiser. Previous workers [24,25] have already used curved waveguides to enhance evanescent wave coupling to the analyte medium. The many curvatures at a rough surface also enhance evanescent wave coupling, leading to reduced LoD.

2. Experimental

2.1. Synthesis

The synthesis of Zinc 5-(4-carboxyphenyl),10,15,20-triphenyl porphyrin (ZnTPP) was reported previously [17]. Reagents and solvents (Sigma-Aldrich, Fluka, and Carlo Erba Reagenti) for synthesis and purification of ZnTPP were of synthetic grade and used as received. The structure of ZnTPP is shown as inset to Fig. 1, the single carboxylic acid group on the molecule's periphery will promote adhesion on glass.

2.2. Conventional absorption spectroscopy

For conventional spectroscopy, we used a commercial spectrophotometer (UV550 Spectrophotometer, Thermo Scientific) with 1 cm path length plastic cuvettes (CVD-UV1S, Ocean Optics). For spectroscopic detection of amine in organic solvent, we prepared 1 mM stock solution of ZnTPP and 1.5 mM stock solution of 1-octylamine (74988, Sigma Aldrich, UK), in acetone. We then transferred 0 μL, 25 μL, 30 μL, 35 μL, 40 μL and 45 μL octylamine stock solution to 6 separate plastic cuvettes each containing 700 μL of acetone and topped up with acetone to a total volume of 750 μL such that the concentrations of octylamine in each cuvette are 0 μM, 50 μM, 60 μM, 70 μM, 80 μM, and 90 μM respectively. We finally introduced 75 μL of ZnTPP stock solution to each cuvette and measured their spectra between 400 nm and 600 nm against a blank (same cuvette containing 825 μL of acetone). To attempt spectroscopic detection of amine in aqueous solution with conventional spectroscopy, we sprayed the inside walls of cuvettes with 1 mM ZnTPP solution in acetone using a hand pumped fragrance sprayer and dried under vacuum for 12 h. 10 mM phosphate buffered saline (PBS, pH 7.4) was prepared by dissolving a PBS tablet (P4417, Sigma Aldrich, UK), in 200 mL of DI water. To simulate food effluent, we further diluted PBS with DI water to 50 μM (measured pH =7.1). We filled the sprayed cuvettes with 700 μL of 50 μM PBS and then added 75 μL of octylamine from 1.5 mM stock solution of 1-octylamine in water (note, 1-octylamine saturates in water at 1.54 mM [26]), and recorded the absorption spectrum with UV550 Spectrophotometer. We then added 3 more aliquots of 25 μL 1-octylamine from stock solution stepwise in 10 min intervals, this resulted in 145 μM, 187.5 μM, 227 μM and 265 μM octylamine solutions in water. We recorded the absorption spectrum using an unsprayed cuvette filled with 850 μL of 50 μM PBS buffer as reference.

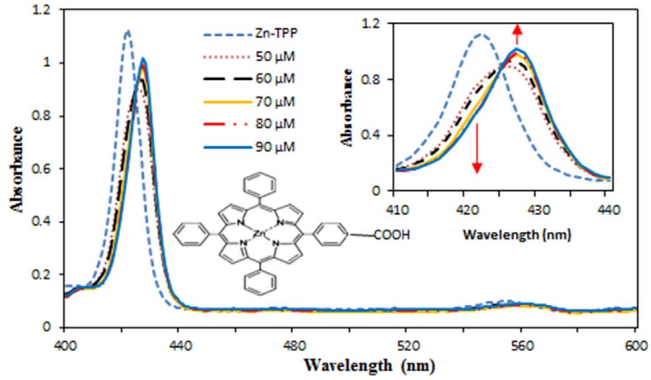

Fig. 1. UV/Vis absorption spectra for 90 μM ZnTPP dissolved in pure acetone, and after addition of different concentrations of 1-octylamine. Insets: Soret band on expanded scale, and molecular structure of ZnTPP.

2.3. Evanescent wave fibre optics

We stripped the cladding of the central section of a multimode optical fibre of 400 μm diameter (FT400UMT, Thorlabs) as described earlier [11]. For 'rough guide' experiments, the unclad fibre was roughened using diamond- coated glass engraving bits mounted on a Dremel 'Corded Multi- Tool 3000' rotary tool. The Dremel was clamped into fixed position, and a fibre was strapped onto a table that could be moved sideways on ball bearings. The table was mounted on a telescopic platform that we raised to bring the fibre into touch with the rotating Dremel bit, then slid the table sideways to roughen the unclad section of the fibre. The fibre was then unstrapped, rotated around its long axis by 90°, and the procedure was repeated until the entire surface of the fibre was roughened. To sensitise fibres, we then sprayed them with 1 mM ZnTPP in the same way as the insides of cuvettes. We ran sprayed fibres through a sample vessel *via* feed-throughs that we fitted into our evanescent wave fibre optic 'light balance' with Lock- in detection, as described previously [11]. The instrument was equipped with either a green (567 nm) or blue (446 nm) LED to match the ZnTPP Q- band, or Soret band, respectively [27,28]. The vessel was filled with 3 mL buffer. We used 10 mM (pH 7.4) and 50 μM (pH =7.1) PBS from Aldrich, and (potassium hydrogen phthalate / HCl), pH 4; (potassium hydrogen phthalate / NaOH), pH 5; and (Disodium tetraborate / NaOH), pH 10 from APC Pure. We titrated with 1-octylamine aliquots in 5 μM steps. The resulting Lock-In output voltage, V_{out}, was recorded in real time with a bespoke LabView routine as a measure of evanescent wave absorbance. For control experiments, we repeated the same procedure using non-sensitised fibres.

3. Results and Discussion

3.1. Dissolved ZnTPP

In Fig. 1, we show absorption spectra for the Zn porphyrin derivative, ZnTPP, dissolved in acetone in the presence of different concentrations of 1-octylamine.

Under addition of amine, the absorbance peak of the ZnTPP Soret band does undergo bathochromic shift from 422 nm to 427 nm and slightly drops in intensity. No clearly visible change can be observed in the Q band. ZnTPP can therefore in principle be used for amine detection. However, even in the Soret band, change of absorbance is small. More importantly, the experiment illustrated in Fig. 1 had to be conducted in acetone because ZnTPP is insoluble in water- yet the practical interest is in the aqueous medium.