



'Rough guide' evanescent wave optrode for colorimetric metalloporphyrine sensors



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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 metalloporphyrin 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 μ M 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 μ M, 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 sensitizers 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 'sensitizer' 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 sensitizer, by coating a thin sensitizer 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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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 μ L, 25 μ L, 30 μ L, 35 μ L, 40 μ L and 45 μ L octylamine stock solution to 6 separate plastic cuvettes each containing 700 μ L of acetone and topped up with acetone to a total volume of 750 μ L such that the concentrations of octylamine in each cuvette are 0 μ M, 50 μ M, 60 μ M, 70 μ M,

80 μ M, and 90 μ M respectively. We finally introduced 75 μ L of ZnTPP stock solution to each cuvette and measured their spectra between 400 nm and 600 nm against a blank (same cuvette containing 825 μ L 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 μ M (measured pH =7.1). We filled the sprayed cuvettes with 700 μ L of 50 μ M PBS and then added 75 μ L 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 μ L 1-octylamine from stock solution stepwise in 10 min intervals, this resulted in 145 μ M, 187.5 μ M, 227 μ M and 265 μ M octylamine solutions in water. We recorded the absorption spectrum using an unsprayed cuvette filled with 850 μ L of 50 μ M PBS buffer as reference.

2.3. Evanescent wave fibre optics

We stripped the cladding of the central section of a multimode optical fibre of 400 μ m 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 μ M (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 μ M 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.

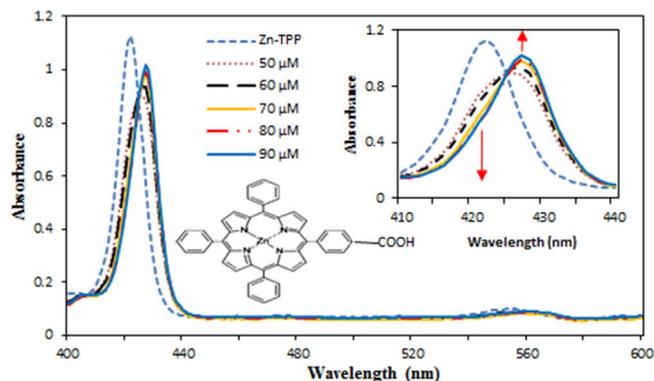


Fig. 1. UV/Vis absorption spectra for 90 μ M ZnTPP dissolved in pure acetone, and after addition of different concentrations of 1-octylamine. Insets: Soret band on expanded scale, and molecular structure of ZnTPP.

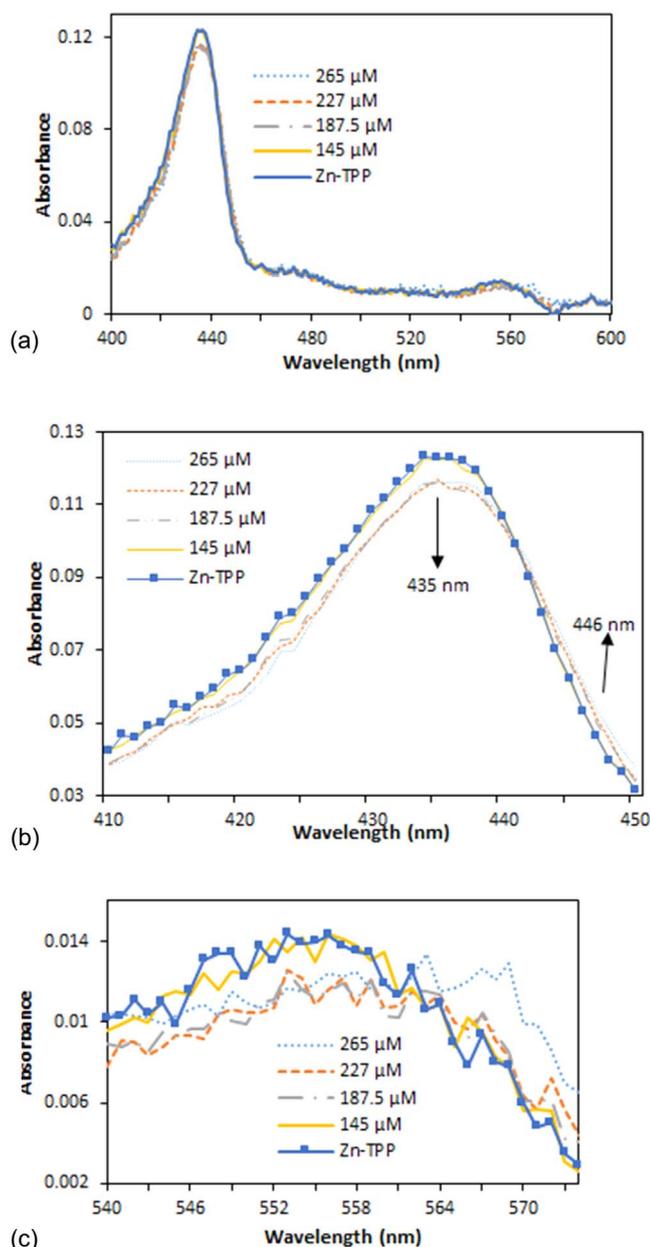


Fig. 2. a. Absorption spectra of cuvettes with sprayed ZnTPP film on the inner walls filled with PBS buffer, adding increasing amounts of 1-octylamine. b, c: Same spectra on expanded wavelength scales, showing Soret band (b) and Q- band (c).

3.2. ZnTPP coated cuvette

To make contact between a waterborne amine, and water-insoluble ZnTPP, we have therefore spray-coated the insides of spectroscopic cuvettes with a thin ZnTPP film, filled the cuvettes with 50 μM PBS buffer, and titrated with 1-octylamine. The result is shown in Fig. 2:

Absorbance is very low due to the low thickness of sprayed films, giving noisy spectra. In the Soret band, Fig. 2b, a slightly reduced absorbance is visible for high (187.5 μM and more) 1-octylamine concentrations. The Q band, 2c, is even weaker and at 567 nm, an increase in absorbance due to amine is only barely visible for 265 μM above a significant noise level. Coating the inside of cuvettes with water-insoluble sensitizers can sometimes lead to useful optrodes for waterborne analytes when analyte/sensitizer interactions, and absorbance bands, are particularly strong [29], *i.e.* sensitizers are 'stoichiometric' rather than 'indicating' [30]. Usually, however, like here, thin films give insufficient absorbance for low LoD, while thicker films

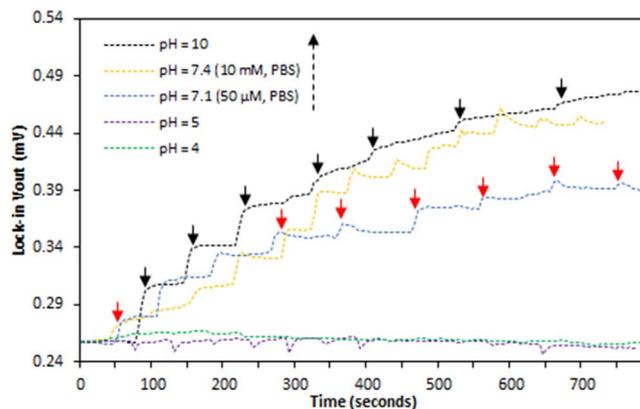


Fig. 3. Fibre optic response V_{out} vs. time for ZnTPP-coated fibres running through different buffers. Amine addition is indicated by arrows (+5 μM per arrow). The probing LED wavelength was 567 nm, overlapping the Q- band.

would be impenetrable to waterborne analyte. Traditionally, the contact between water-insoluble sensitizers and waterborne analytes is mediated by embedding sensitizers into PVC membranes or sol-gel matrices, giving far longer optical path length in the sensitive medium, but also leading to slow response times.

3.3. ZnTPP coated 'evanescent wave' fibres in different aqueous media

3.3.1. Q band on 'smooth' fibres

To avoid the need for membranes or matrices, we have recently demonstrated an evanescent-wave fibre optic absorbance meter [11], which we here apply to amine sensing with ZnTPP. The procedure is described in the experimental section under 'evanescent wave fibre optics'.

First, we record the amine response of ZnTPP-sprayed fibres when immersed in different buffers, *i.e.* working at different pH. This work probed the ZnTPP Q band (green LED), and we used smooth fibres (*i.e.*, unclad, but not roughened). In Fig. 3 we show output voltage, V_{out} , for a titration series where 1-octylamine was added in steps of 5 μM from aqueous stock solution to different aqueous buffer media, as detailed in the experimental section.

For neutral or alkaline media ($\text{pH} > 7$), Fig. 3 shows a clear Q-band response to amine titration in steps of 5 μM , while only a marginal Q-band response is visible in Fig. 2c (coated cuvette) even at 265 μM . Response may initially overshoot as amine droplets are added near the fibre, leading to high local concentration. Readings for further evaluation are taken after stirring and equilibration. Fibre optic response is a stepwise increase of absorbance in response to increasing octylamine concentration, *i.e.* 'indicating' rather than 'stoichiometric' [30]. This is explained by the donation of electrons from the amine nitrogen's lone pair to the porphyrine's π orbital, *i.e.* the amine acts as Lewis base, the porphyrine as Lewis acid. Response is stronger for higher pH, but absent in acidic media (pH 4, pH 5). Note the pK_a of alkane amines is approximately 10.6 [31], hence octylamine becomes increasingly protonated in all but rather alkaline media, and can no longer act as Lewis base. In other words, the Lewis acid ZnTPP cannot successfully compete for amine with H_3O^+ in acidic (low pH) media.

Fig. 4 shows the response characteristics, extracted as previously reported [32] from Fig. 3, against analyte concentration for media above pH 7.

Fig. 4 shows response characteristics reminiscent in shape to typical indicating chromophoric optrode characteristic [33], which can be approximated [34] by the Langmuir adsorption isotherm, Eq. (1):

$$\Delta V_{\text{out}}/\Delta V_{\text{out}}(\text{sat}) = Kc/(Kc + 1) \quad (1)$$

Wherein K is the equilibrium constant of the sensitizer/analyte complex; the characteristic analyte concentration $c_{1/2}$ where half of

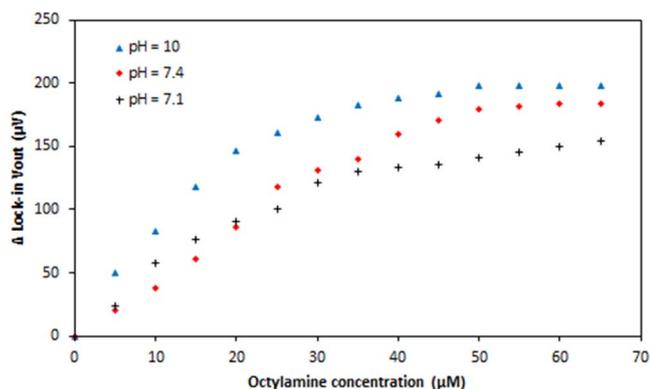


Fig. 4. Calibration chart of fibre optic response ΔV_{out} vs. octylamine concentration c for spray-coated fibres probed at 567 nm (Q-band) in different buffers.

available sensitizers are complexed with analyte is given by $c_{1/2} = 1/K$. Quantitative analysis of Fig. 4 allows determination of $c_{1/2}$, sensitivity, and limit-of-detection; a detailed technical account is given in the supplementary section. Results are summarised in rows 1–5 in Table 1 below. Note results for concentrated (10 mM) and dilute PBS (50 μ M) are very similar, while sensitivity in pH 10 buffer is higher. Hence, sensitivity is controlled by pH (*via* degree of amine protonation), but not by ionic strength.

Control experiments with other electron donating analytes (alcohols, ketones) revealed similar sensitivity as to amines, even at acidic pH, as alcohols and ketones do not get protonated easily. This non-specific response characteristic agrees with observations on porphyrin-based odour sensors; if specific response to amines is desired an amine selective porphyrine with Cobalt central atom has to be used as sensitizer [18]. However, less selective ‘broadband’ response is preferred in ‘artificial nose’ sensor arrays [37].

3.3.2. Soret band and rough fibres

To enhance sensitivity and push LoD lower, we have conducted further experiments, where we either used the Soret band (rather than the Q band), or a deliberately roughened fibre, or both. We expect that the stronger absorbance in the Soret band leads to higher sensitivity, we have therefore probed absorbance with a blue LED during a titration series. Also, to enhance evanescence, previous workers have already used bent or curved waveguides [24,25]. Here, we have roughened fibres as described in the experimental section before spray coating with ZnTPP. We expect that using a rough fibre should lead to multiple curvatures at the fibre / sensitizer interface which will enhance evanescent wave overlap with the ZnTPP sensitizer. Images of a fibre before and after roughening are shown in the supplementary section, Fig. S3.

In Fig. 5, we show the response for titration experiments under different pH, using either roughened fibres, or probing in the Soret band (blue LED), or both. Overshoots are explained and accounted for as in Fig. 3. Also included is a control experiment with a smooth fibre

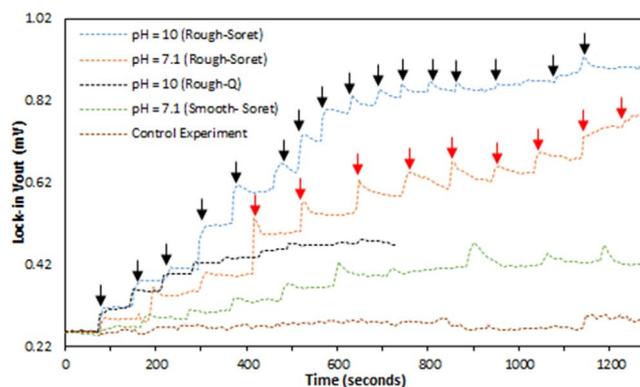


Fig. 5. Fibre optic response V_{out} vs. time for ZnTPP-coated fibres running through buffer solutions with different pH. Amine addition is indicated by arrows. The probing LED wavelength was either 567 nm, overlapping the Q-band, or 446 nm, overlapping the Soret band.

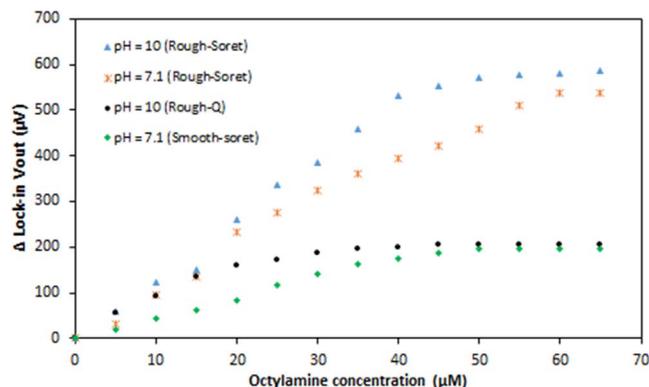


Fig. 6. Calibration chart of fibre optic response ΔV_{out} vs. octylamine concentration c in buffer solution with different pH, including rough fibre and/or Soret band results.

that was not sensitized with a ZnTPP coating, as expected showing no response to amine titration ΔV_{out} vs c characteristics are shown in Fig. 6.

Each experiment in Figs. 3–6 were repeated three times and showed the same results. Quantitative analysis for Fig. 4 and is shown in detail in the supplementary section, Fig. S2. Results are shown in Table 1, rows 6–9. All else being equal, sensitivity m is slightly larger, and LoD slightly lower, in the Soret band than in the Q-band, reflecting the stronger absorbance in the Soret band (row 7 *vs.* row 3; row 9 *vs.* row 6 in Table 1). This is partially offset though by the lower intensity of blue LEDs, and the weaker response of our photodiodes in the blue [36]. Comparing smooth to rough fibres, sensitivity (m) is larger and LoD is lower for a rough fibre, all else being equal (row 6 *vs.* row 5, row 8 *vs.* row 7 in Table 1). This supports our hypothesis that a rough fibre surface leads to enhanced evanescence. When we combine all measures that lead to high sensitivity / low LoD (high pH, Soret band, rough

Table 1

Summary of all quantitative results for amine sensing with our fibre-optic transducer, as determined from Figs. 4 and 6. Details of analysis and definitions of sensitivity (m), r^2 , b , and Δb are in the supplementary information. The limit-of-detection, c_{LoD} is calculated from m and Δb *via* $c_{LoD} = 3\Delta b/m$ [35].

Row	Band	pH	Fibre	$K [(\mu\text{M})^{-1}]$	$c_{1/2} [\mu\text{M}]$	$m [\mu\text{V}/\mu\text{M}]$	r^2	$b [\mu\text{V}]$	$\Delta b [\mu\text{V}]$	$c_{LoD} [\mu\text{M}]$
1	Q	4	Smooth	$\ll 0.002$	$\gg 600$	–	–	–	–	–
2	Q	5	Smooth	$\ll 0.002$	$\gg 600$	–	–	–	–	–
3	Q	7.1	Smooth	0.0382	26	7.6	0.998	–1.02	4.05	2.10
4	Q	7.4	Smooth	0.0234	43	7.7	0.992	0.67	5.06	1.97
5	Q	10	Smooth	0.041	24	11.4	0.993	0.98	6.12	1.61
6	Q	10	Rough	0.0511	20	14.0	0.993	1.23	6.25	1.34
7	Soret	7.1	Smooth	0.0260	38	8.9	0.987	1.62	5.4	1.82
8	Soret	7.1	Rough	0.0261	38	23.6	0.991	–2.17	6.45	0.82
9	Soret	10	Rough	0.0297	34	29.2	0.988	–2.01	4.96	0.51

fibre), we find a limit- of- detection of 0.51 μM (Table 1, row 9).

4. Conclusions

When dissolved in organic solvent, the Zinc porphyrin derivative 5-(4-carboxyphenyl),10,15,20-triphenyl porphyrin (ZnTPP) shows a colorimetric response to amine in both Q- and Soret bands. This is explained by the donation of 'lone pair' electrons to the metalloporphyrin π orbital [18]. However, ZnTPP is insoluble in water, and thin ZnTPP films in contact with water only leads to marginal response to waterborne analyte in a conventional spectrometer. When ZnTPP is instead coated onto the surface of an evanescent wave fibre optode, a Lock- In 'light balance' absorbance meter [11] measurement reveals 'indicating' colorimetric response of ZnTPP to amine in alkaline or pH-neutral media, but not in acidic media as ZnTPP can not compete for amine in strongly protonating environments. Sensitivity is slightly larger, and limit- of- detection (LoD) slightly lower, in the Soret- rather than the Q- band. Sensitivity and limit- of- detection can be improved further when a roughened, rather than smooth, fibre is used to enhance evanescence. We achieve LoD of 0.51 μM octylamine in water, which is an improvement as compared to other sensors for waterborne amines [5,16,21,26]. We therefore recommend 'rough guide' evanescent wave optodes, in combination with a suitable instrument for absorbance measurement [11], to succeed membrane- embedding of non- water soluble colorimetric sensitizers such as metalloporphyrins for the detection of waterborne analytes.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2016.11.057.

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