

# Optical thin film polymeric sensors for the determination of aqueous chloride, bromide and iodide ions at high pH, based on the quenching of fluorescence of two acridinium dyes

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## Abstract

Two halide sensitive acridinium fluorophores have been synthesised and immobilised in a hydrophilic copolymer. Thin films of the copolymers swell in aqueous media allowing dye fluorescence to be dynamically quenched by the diffusion of halide ions. The new sensor films have been characterised in terms of their sensitivity and selectivity towards halide and are compared to films containing both bound and unbound Rhodamine B. The sensor films are reversibly capable of determining halide ions at mildly alkaline pH with typical 90% response times of  $\approx 1$ –2 min. The sensor films are cheap to produce, can readily be coated on disposable glass microscope slides or on the tip of a fibre optic bundle and have a shelf life in excess of 2 years. © 2000 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* Fluorescence quenching; Halide; Chloride; Bromide; Iodide; Thin film; Sensors

## 1. Introduction

The detection of halide is becoming ever more important, especially in some industrial processes [1,2] and in medicine [3,4] and quick, cheap, reliable quantification is required. One approach in recent years has been to use polymeric or glass type halide sensors based on the quenching of fluorescence of a heterocyclic indicator/s immobilised within/on the support, by halide ions [5–8]. However, the practical use of most such sensors has been hindered because of a lack of sensitivity towards halide ions, the leaching of the dye from the sensor

support when immersed in the analyte solution, or the interference of the sensors response from other aqueous anions [8]. In this paper five new halide sensors based on the diffusional quenching of fluorescence of acridinium and rhodamine dyes immobilised in a hydrophilic copolymer are presented. These sensors offer improvements in terms of halide sensitivity, dye leaching and response times, as compared to some previous sensors [8].

For collisional quenching, the decrease in fluorescence intensity of a fluorophore in the presence of aqueous halide ions is described by the well-known Stern–Volmer equation [9]:

$$\frac{F_0}{F} = 1 + K_q\tau_0[Q] = 1 + K_{sv}[Q] \quad (1)$$

where  $F_0$  and  $F$  are the fluorescence intensities in the absence and presence of halide, respectively,

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$K_q$  is the bimolecular quenching constant,  $\tau_0$  is the unquenched lifetime,  $[Q]$  is the halide concentration and  $K_{SV}$  is the Stern–Volmer quenching constant. The magnitude of  $K_{SV}$  depicts both the sensitivity of the sensor towards halide, and the detectable halide concentration range.

A hydrophilic copolymer, “Quattro” [10,11] has been chosen as the polymeric support for the halide sensitive fluorophores. The copolymer ( $\approx 50 \mu\text{m}$  dry) typically swells  $\approx 100\text{--}200 \mu\text{m}$  in aqueous media, which is ideal for aqueous anion sensors. This copolymer is readily coatable onto a variety of surfaces and can be crosslinked in situ. It is cheap to produce and easily disposed of; an important consideration in “throw away type sensors”. More importantly, the dyes and dye counter-ions are readily soluble in this copolymer. The importance of each comonomer unit in the Quattro copolymer has been discussed in detail [10,11].

Early unbound<sup>1</sup> dye sensor film studies, where the dye is simply mixed with copolymer and crosslinking agent and the mixture then cast and cured, showed small amounts of dye leaching from the films during fluorescence quenching measurements. To address this problem, the dyes have been covalently attached to the Quattro copolymer to give bound dye sensor films. The sensitivity of both bound and unbound sensor films is discussed.

## 2. Experimental

### 2.1. Materials

All chemicals were used as-received, and obtained from the Aldrich Chemical Company except for the monomers 3-chloro-2-hydroxypropyl methacrylate (Yg), 2-hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA), purchased from Poly Sciences. Oxygen was removed from all monomers by nitrogen purge prior to polymerisation.

<sup>1</sup> Unbound dye refers to dye mixed in the copolymer solution before casting and crosslinking as compared to bound dye, where dye is covalently attached to copolymer.

### 2.2. Instrumentation

Number average molecular weights,  $\overline{M}_n$ , of copolymers were determined by size exclusion chromatography, using Polymer Laboratories poly methylmethacrylate standards, covering the range 1.21 k–1.4 M. <sup>1</sup>H NMR spectra were recorded on a Varian Unity plus (400 MHz) spectrometer. IR spectra were recorded on a Perkin–Elmer PE2000R NIR FT-Raman spectrometer. Absorption measurements were performed using a Philips Unicam PU8620 UV/VIS/NIR spectrophotometer. Steady-state emission and excitation spectra for dye solutions and sensor films were recorded on a Jobin–Yvon JY3D spectrofluorimeter. Excitation maxima are corrected with respect to the xenon arc lamp profile. Glass transition temperatures,  $T_g$ , were recorded by Kodak Ltd, Harrow, London, using Differential Scanning Calorimetry (DSC), in the following manner. Both film and uncured samples were initially heated from 25 to 150°C at a heating rate of 20°C per min. The samples were then held at this temperature for 3 min before rapidly cooling at 200°C per min to 25°C. The samples were subsequently heated a second time from 25 to 150°C at 20°C per min and the  $T_g$  determined from the trace. Samples were typically measured three times and an average  $T_g$  determined.

### 2.3. Dye synthesis

It is generally known that the fluorescence of certain heterocyclic indicators, such as those based on quinine [12,13], 6-methoxyquinoline [14,15], anthracene [16], coumarins [17–19] and rhodamines [20] are quenched by halides and some pseudohalides and hence have been used in previous sensor fabrications [8]. In this paper two halide sensitive acridinium dyes (Fig. 1), have been synthesised and studied. The Stern–Volmer kinetics of these dyes in mildly alkaline conditions,  $\approx$  pH 10, are reported since the particular interest of these plastic halide sensors lies in their potential use in photographic processing solutions, where halide concentration is an important control parameter. The synthesis of dye 1 was first described by Wolfbeis and Urbano in 1982 for use as a fluorescent standard in the near neutral pH range

[14] and was achieved by fusing acridine with 1,3-propane sultone at 120°C for 2 h with moisture excluded, followed by extraction with DMF and recrystallisation from alcohol. The *intermediate* for dye 2 was described as early as 1926 by Jensen and Howland [21] (Fig. 2) and its quaternisation with methyl iodide (step 2) followed by counterion exchange with sodium tetraphenylboron to produce the borate salt, in 1984 by Urbano et al. [5]. Both dyes were successfully synthesised giving similar reaction yields and spectroscopic characterisation.

#### 2.4. Preparation of Quattro

The synthesis of the Quattro copolymer poly(2-hydroxyethyl methacrylate)<sub>16</sub>-co-(methacrylic acid)-co-(methyl methacrylate)<sub>1</sub>-co-(3-chloro-2-hydroxypropyl methacrylate)<sub>2</sub>, ratios (16:1:1:2) (Fig. 3) has been described previously [10,11]. The glass

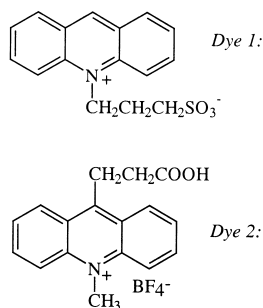


Fig. 1. Acridinium dyes 1 and 2. Dye 1 is sometimes referred to as SPA [23,28].

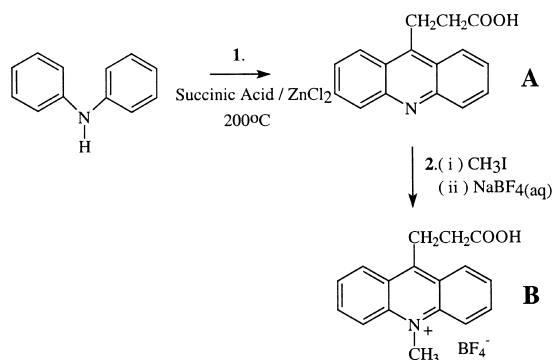


Fig. 2. Reaction scheme for the synthesis of dye 2: A. the intermediate product 3-(9-acridinyl) propionic acid; B. 3-(10-methylacridinium-9-yl) propionic acid tetrafluoroboron.

transition temperature ( $T_g$ ) was 122°C,  $\overline{M}_n = 91.8$  k, and  $\overline{M}_w/\overline{M}_n = 1.66$ .

#### 2.5. Dye 2 and rhodamine B attachment to the Quattro copolymer (bound dye sensor films)

Dye 2 and rhodamine B (Table 1) were covalently bound to Quattro through an ester linkage formed between the hydroxyl groups of HEMA and the carboxylic acid functional groups of the dyes (Fig. 3). The chemistry of this simple attachment process using both DCC (dicyclohexylcarbodiimide) and DMP (4-dimethylaminopyridine) has been reviewed many times [22]. It was observed that solely activating the dye with DCC/DMP followed by slow addition to the respective copolymer solution typically gave greater attachment. Whilst the percentage dye attachment could simply be increased by increasing the concentrations of DCC/DMP, percentage dye attachments were kept low to both minimise the potential change in copolymer characteristics and also eliminate the possibility of dye-dye energy transfer [23]. Table 1 shows the quantities of dye, DCC and DMP in 50 ml DMF (dimethylformamide) added to 5 g of Quattro/trio in 50 ml DMF. The mixtures were heated under reflux and argon at 70°C for 2 days. The mixtures were then drowned into H<sub>2</sub>O, the precipitate dissolved in warm ethanol and reprecipitated into diethyl ether. This procedure was repeated several times to remove any unbound dye. The dyed copolymers were then dried under vacuum at 40°C for 12 h and powdered using a blender. Elemental analysis, X-ray fluorescence spectroscopy and <sup>1</sup>H NMR indicate that the bound dye:polymer ratio for both dye 2-Quattro and rhodamine B-Quattro was < 1% w/w. DMF did not crosslink the copolymer. The crosslinking, casting and curing of dye-bound copolymers for use as sensors is described below.

#### 2.6. Unbound dye sensor films

Uncrosslinked Quattro copolymer (0.5 g) was dissolved in 2.5 ml of ethanol by stirring for ≈ 2 h at room temperature, followed by the addition of 0.01 g dye (2 parts per hundred of copolymer, pph) and a further 2 h stirring. The sensor film

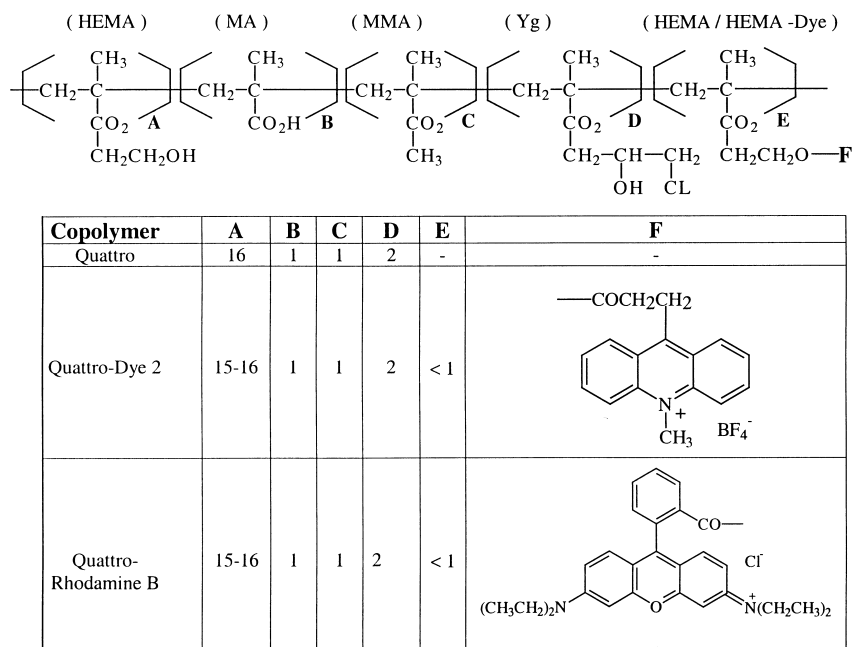


Fig. 3. The structural formulae of the Quattro copolymer poly(2-hydroxyethyl methacrylate)<sub>16</sub>-co-(methacrylic acid)<sub>1</sub>-co-(methyl methacrylate)<sub>1</sub>-co-(3-chloro-2-hydroxypropyl methacrylate)<sub>2</sub>, ratios (16:1:1:2), and dye 2 and rhodamine B bound to the Quattro copolymer.

Table 1

Quantities of dye, DCC and DMP in 50 ml DMF added to 5 g Quattro in 50 ml DMF<sup>a</sup>

Dye	Amount of dye used	Amount of DCC used	Amount of DMP used	Reaction yield
Dye 2	0.336 g (0.95 mmol)	0.196 g	0.012 g	3.21 g (60.2%)
Rhodamine B	0.456 g (0.95 mmol)	0.196 g	0.012 g	3.48 g (63.8%)

<sup>a</sup> The reaction mixtures were continuously stirred under argon for 2 days at 70°C. Dye 1 was not attached to Quattro.

formulation, in which the % copolymer, dye and crosslinking agent have been optimised, has been previously discussed by the author and is approximately the same for both bound and unbound sensor films [11]. The copolymer crosslinking mechanism has also been discussed previously [24].

To minimise dye–dye energy transfer [23] within sensor films optical densities were kept very low,  $\leq 0.01$ . The crosslinking of unbound sensor films is described below.

### 2.7. Polymer crosslinking, casting and curing

For both bound and unbound dye sensor films, crosslinking was carried out by the addition of

0.125 g (25 pph) TPA (tripropylamine), a polymer crosslinking agent, dropwise with rapid stirring to 0.5 g of copolymer, (uncrosslinked polymer for unbound and dyed polymer for bound dye films), dissolved in 2.5 ml ethanol. Films were then rapidly cast by sliding a drop of copolymer mixture between two glass slides, the resulting films on the separated slides being then cured in a Gallenkamp BS2 fan assisted oven at 140°C. After curing, films were washed in distilled water to remove excess crosslinking agent. The crosslinking agent did not quench the fluorescence of dyes 1 and 2 or rhodamine B.

The 3-chloro-2-hydroxypropyl methacrylate (Yg) (Fig. 3) affords the base-induced crosslinkability of

the Quattro copolymer [11]. Crosslinking, when polymer chains are linked and the polymer network effectively becomes more “dense”, decreases the polymer free volume, where the free volume is the “empty space” between polymer molecules. This reduction in free volume can influence the diffusional properties of analytes within the polymer and the polymer’s swelling properties when immersed in a suitable solvent [11]. Free volume is typically measured to determine polymer  $T_g$ s, although in the differential scanning calorimetry used in this work it is the change in enthalpy ( $\Delta H_m$ ) during polymer melting that enables the  $T_g$  to be determined.

### 2.8. Dye leaching

pH 10 buffers were made by mixing 50 ml of 0.025 mol dm<sup>-3</sup> borax, 18.3 ml of 0.1 mol dm<sup>-3</sup> NaOH and 31.7 ml of doubly distilled deionised water [25]. Sensor films cast on glass microscope slides were immersed in 1 litre of water thus buffered at 20°C. The percentage dye remaining in films was calculated from the decrease in optical density of films as a function of time. Initial optical densities were typically  $\leq 0.01$ .

### 2.9. Steady-state Stern–Volmer analysis

Steady-state Stern–Volmer analysis of dyes 1, 2 and rhodamine B solutions was carried out at 21°C, pH 10 (borax buffer), using halide concentrations in the range 1–10<sup>-4</sup> mol dm<sup>-3</sup>. The Stern–Volmer quenching constants for dyes 1, 2 and rhodamine B with aqueous halide ions were subsequently calculated using the Axum Graphics linear regression program. Whilst Stern–Volmer analysis for dye solutions was carried out on the above spectrofluorimeter, analysis of sensor films was carried out using an optical flow cell, described previously by the author and co-workers [26]. In this cell aqueous halide solutions are pumped over the surface of the copolymer films and the extent of fluorescence quenching monitored orthogonal to the plane of excitation. A step-wise increase in halide concentration allows the Stern–Volmer quenching constant  $K_{SV}$  [eq. (1)] to be determined for the particular dye–polymer combination.

### 2.10. Sensor film response times

Both bound and unbound sensor films were cast from solutions of 2.5 ml ethanol; 0.5 g copolymer; 2 pph dye (for unbound films); 25 pph TPA (tri-propylamine), cured in hot/dry environment for 12 h. Sensor film response times were determined using the optical flow cell [26]. At the point of halide injection into the flow cell the digital storage oscilloscope was triggered and the variation in fluorescence intensity measured with time.

### 2.11. Sensor film swelling measurements

Swelling measurements using a “swellometer” [24] were performed on the copolymer sensor films to give an indication of the extent of dye attachment and the degree of crosslinking. Dry films were mounted in the sample holder of the swellometer and the dry film thickness measured, effectively zeroing the instrument. Lowering the sample into the swelling media activated a small tappet that continually moved up and down probing the surface of the copolymer film, providing swelling data as a function of time. The temperature of the solution during a measurement was  $19 \pm 0.5^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. Dye attachment

Table 1 shows the quantities of dye, copolymer, DCC and DMP and the dye–polymer yields for the dye attachment procedure. Approximately 10–18% w/w of the HEMA comonomer units were targeted for attachment using these quantities, but less than 1% w/w of the dye was actually bound to Quattro. Percentage dye attachments were estimated from <sup>1</sup>H NMR, FTIR, X-ray fluorescence spectroscopy, mass spectroscopy and nitrogen elemental analysis, where the dye was the only source of nitrogen in the recovered polymer. It was found that using smaller concentrations of either dye or DCC/DMP resulted in no detectable attachment, whilst using larger quantities resulted in copolymers with larger molecular weight distributions that

were difficult to cast. As a consequence, Stern–Volmer quenching constants for these films were too small for practical sensor use. It was thought that the ability of the methacrylic acid co-monomer units to compete for HEMA hydroxyl groups during the dye attachment process caused the low percentage dye attachment, and may also be a cause of self-crosslinking within the Quattro copolymer. The  $T_g$  and  $\overline{M}_n$  for both polymers increased after dye attachment,  $T_g$  increasing from 122 to 141°C and  $\overline{M}_n$  increasing from 91.8 to 95.0 k for the rhodamine B polymer. The % increase in polymer volume, i.e. the final swollen volume, decreased to 150 and 135% for the dye 2 and rhodamine B bound films, respectively, as compared to 157% for the virgin polymer. The rates of sensor film swelling were greater at higher temperatures, consistent with previous findings [11].

### 3.2. Dye Leaching

A typical problem of polymeric-based sensors is that of dye leaching when a sensor film is immersed in solution. Unbound dye sensor films

soaked in buffered water (pH 10, 20°C), for 5 h, typically showed only a few percentage dye loss. However, bound dye sensor films showed no dye loss, even after very long immersion times (Fig. 4). Notably, at very low pHs ( $\approx$  pH 1) dye leaching is significantly greater, possibly due to hydrolysis of the dye-polymer ester linkage and the subsequent unbinding of the dye.

### 3.3. Stern–Volmer analysis of sensor films

The excitation and emission maxima for dyes 1 and 2 and rhodamine B in solution, unbound and bound in copolymer are shown in Table 2. All dyes demonstrated good solubility in both pH 10 solution and unbound film solution formulations. The excitation and emission spectra for the unbound and bound dyes are the same as in solution, indicating little or no electronic interaction between the copolymer support and dye molecules. Dyes 1 and 2 each show  $\lambda > 100$  nm Stokes-shifted fluorescence maximum, which combined with low (0.01) film optical densities eliminates the possibility of dye–dye energy transfer [23]. However, since

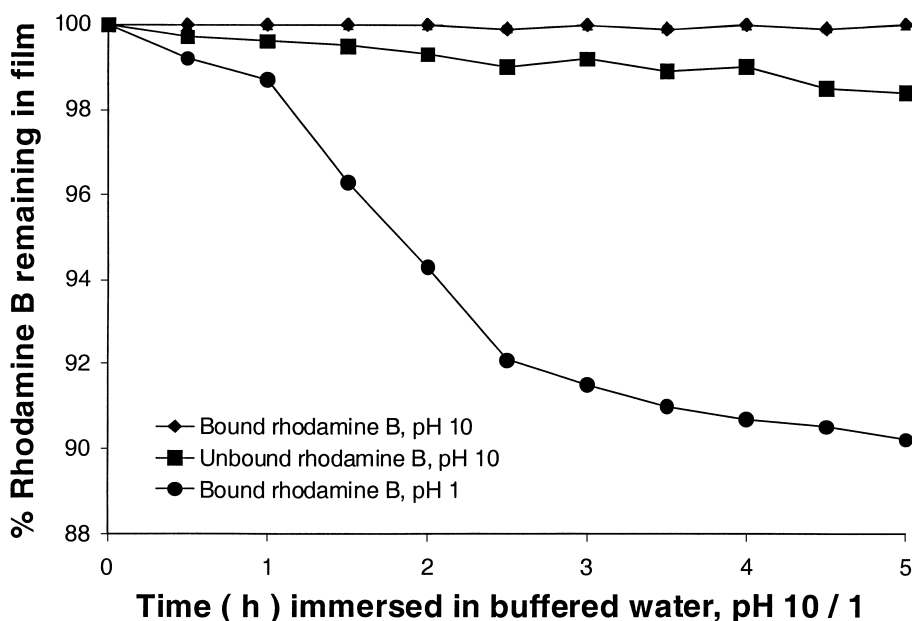


Fig. 4. Static leaching of rhodamine B unbound and bound films in buffered water, pH 10 and 1 respectively. Films were cast from solutions made up from the following: 2.5 ml ethanol; 0.5 g copolymer; 25 pph TPA and cured at 140°C for 12 h. All films had the same initial thickness,  $\approx 50 \mu\text{m}$ , and the same optical density.

dyes 1 and 2 have similar absorption and emission wavelength maxima, sensor films containing both dyes, which could allow simultaneous halide sensing [8,27], was not possible. Instead, individual sensor films were used in the Stern–Volmer analysis.

Solution Stern–Volmer plots for dyes 1 and 2 and rhodamine B are all linear with good linear regression correlation coefficients. However, Stern–Volmer plots for both unbound and bound films typically show negative deviations under conditions of very efficient quenching, i.e. at halide concentrations greater than  $\approx 0.1 \text{ mol dm}^{-3}$ . Even so, for halide concentrations in the range of most biological and technical interest, i.e.  $0.1\text{--}0.001 \text{ mol dm}^{-3}$ , both bound and unbound sensor films gave Stern–Volmer plots with good linearity. The halide concentration at which Stern–Volmer plots deviate from linearity varied from dye to dye as observed previously by the author for immobilised quinolinium and indolium dyes [7].

The Stern–Volmer constants for the dyes studied, in solution, and unbound and bound in sensor

films, are shown in Table 3. The high solution  $K_{SV}$  for dye 2 quenched by iodide is encouraging and is one of the highest reported, being slightly better than Lucigenin [28], which has a solution  $K_{SV}$  of  $750 \text{ M}^{-1}$  for aqueous iodide between pHs 4 and 9. However, dye 2 has lower chloride and bromide sensitivities than Lucigenin, 390 and  $585 \text{ M}^{-1}$  respectively [28]. It is interesting to note that 6-methoxy-*N*-(3-sulfopropyl)quinolinium (SPQ), which has been used to measure intracellular chloride levels [23] has solution  $K_{SV}$ s for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  of 118, 175 and  $276 \text{ M}^{-1}$  respectively (measured in aqueous buffers) [28].

The Stern–Volmer constants for unbound sensor films are much lower than those for the corresponding dyes in solution, probably due to a lower halide diffusion rate in the copolymer films (i.e. the  $K_q$  term in  $K_{SV}$ ). Similarly, for rhodamine B bound films, the Stern–Volmer constants are significantly smaller in bound as compared to unbound films. No response towards halides is observed for dye 2 bound films, surprising since

Table 2

Excitation ( $\lambda_{ex}$ ) and emission ( $\lambda_{em}$ ) wavelength maxima for the rhodamine B and dyes 1 and 2 in solution (pH 10, borax buffer) unbound and bound to the Quattro copolymer (wet films/ $\text{H}_2\text{O}$ , pH 10)<sup>a</sup>

Dye	Solution		Dye solubility in water	Unbound dye sensor films		Dye solubility in unbound polymer	Bound dye sensor films	
	$\lambda_{ex}$ (nm)	$\lambda_{em}^a$		$\lambda_{ex}$ (nm)	$\lambda_{em}^a$		$\lambda_{ex}$ (nm)	$\lambda_{em}^a$
Dye 1 <sup>a</sup>	360	490	Very good	360	490	Very good	–	–
Dye 2	357	500	Very good	360	490	Very good	360	490
Rhodamine B	550	580	Very good	550	590	Very good	550	590

<sup>a</sup> Dye 1 was not bound to copolymer.

Table 3

Stern–Volmer constants for dyes in solution ( $\text{H}_2\text{O}/\text{pH 10}$ ) and in unbound and bound dye sensor films<sup>a</sup>

Dye in Quattro sensor films	Conditions for solution studies	Steady-state Stern–Volmer constants ( $\text{mol}^{-1} \text{ dm}^3$ )			Steady-state Stern–Volmer constants ( $\text{mol}^{-1} \text{ dm}^3$ )			Steady-state Stern–Volmer constants ( $\text{mol}^{-1} \text{ dm}^3$ )		
		Solution			Unbound films			Bound films		
		$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$
Dye 1 <sup>b</sup>	$\text{H}_2\text{O}/\text{pH 10}$	1	58	374	–	5	196	–	–	–
Dye 2	$\text{H}_2\text{O}/\text{pH 10}$	1	47	762	–	10	230	–	–	–
Rhodamine B	$\text{H}_2\text{O}/\text{pH 10}$	– <sup>c</sup>	–	5	–	–	1	–	–	1

<sup>a</sup> For all film studies, films were exposed to aqueous halide at pH 10.

<sup>b</sup> Dye 1 was not bound to Quattro.

<sup>c</sup> Indicates no detectable quenching.

Table 4  
Sensor film 90% response times to molar halide solutions

Dye in Quattro sensor films	Response time(s) to 1 mol dm <sup>-3</sup>			Response time(s) to 1 mol dm <sup>-3</sup>		
	Cl <sup>-</sup> Unbound (90%)	Br <sup>-</sup>	I <sup>-</sup>	Cl <sup>-</sup> Bound (90%)	Br <sup>-</sup>	I <sup>-</sup>
Dye 1 <sup>a</sup>	– <sup>b</sup>	70	65	–	–	–
Dye 2	–	140	150	–	–	–
Rhodamine B	–	–	35	–	–	40

<sup>a</sup> Dye 1 was not bound to copolymer.

<sup>b</sup> Indicates no response obtained

unbound dye 2 films show modest  $K_{SV}$  values for aqueous halide. It is worth noting that the reduction in the final swollen volume for bound dye 2 films was smaller than that for rhodamine B films, suggesting that rhodamine B films were cross-linked to a greater extent. It is thus unlikely that the lack of sensitivity of dye 2 bound films is a result of significant crosslinking of the polymer. Further studies on the photophysics of fluorophores within the Quattro copolymer will be reported shortly.

Although the studies here are limited to halide sensor films at pH 10, the sensors are effective over a broader pH range. However, there are some small changes to Stern–Volmer constants and dye leaching occurs at very low pHs.

### 3.4. Sensor film response times

The 90% response times (the time for a 90% change in fluorescence signal) of unbound dye films to molar halide solutions are found to lie in the range 35–150 s (Table 4). The results show a longer response time for bound rhodamine B films than for unbound rhodamine B films. Again, this is thought to be due to the increased crosslinking of the copolymers after dye attachment and hence the longer diffusional time of aqueous halide. This is supported by the increase of  $\overline{M}_n$  and the decrease in final swollen volume of films after dye attachment. The response times to smaller halide concentrations were also longer.

The films were found to be reversible by washing with distilled water, the dye fluorescence returning as the halide was removed. To return film fluorescence to its original unquenched intensity required washing with 1 mol dm<sup>-3</sup> nitrate solution for

approximately 180 s: the volume of nitrate typically used was 10 times that of halide. The use of molar nitrate to maintain both a constant background ionic strength and refractive index upon halide injection into the flow cell has been discussed previously [26].

Interestingly, even when very thin sensor films and high halide concentrations were used, no sensor film fluorescence was 100% quenched. This “background fluorescence” could be due to dye buried within the polymer, and inaccessible to halide ions, and this may also account for the negative deviation of Stern–Volmer plots at high halide concentration, i.e.  $> 0.1$  mol dm<sup>-3</sup>. Films also displayed, as one would expect, a quicker response time towards halide at higher solution temperatures.

### 3.5. Sensor film selectivity and shelf life

Sensor film selectivity was studied using 0.5 mol dm<sup>-3</sup> solutions of various anions. Whilst sulphite was found to be an efficient fluorescence quencher, no interferences were observed with nitrate, sulphate, phosphate or perchlorate ions. Response times and Stern–Volmer constants for a selection of sensor films were studied during a 2-year period to ascertain the “shelf life” of the sensors. Both remained unchanged, indicating sensor film stability during the 2-year period.

## 4. Conclusions

Thin film sensors based on the hydrophilic Quattro copolymer, dyes 1 and 2 and rhodamine B



are sensitive to aqueous halide at mildly alkaline pH. Supporting the dyes, unbound, in the hydrophilic Quattro copolymer significantly reduced  $K_{SV}$  as compared to solution values. However, unbound dye 2 films still showed a good sensitivity towards iodide. Covalently binding the dyes to the polymer further reduced the  $K_{SV}$ s. This was attributed to a reduced halide diffusion rate within sensor films, a result of dye attachment, crosslinking during dye attachment and base-induced crosslinking of the polymer by TPA during casting and curing. The very nature of halide sensors, which employ the quenching of fluorescence, require the immobilisation/entrapment of fluorophores in a support and it is the entrapment which nearly always results in a significant reduction in  $K_{SV}$  and hence of the halide range detectable. Future work, to be published shortly, will address this problem by using sol-gel glasses as the support, where very large meso-pore structures allow the more rapid diffusion of aqueous halide ions and thus increase the accessibility of dye molecules to halide ions, i.e. increase  $K_{SV}$ , as compared to immobilisation in typical polymer films.

The Quattro copolymer and dyed sensor films typically have a greater swelling rate and a greater final swollen volume when immersed in a higher temperature medium. Operating these sensor films at higher temperatures may, therefore, decrease sensor response times, increase sensitivity towards halide ions and may also extend the region of linear Stern–Volmer response. Given that unbound dye films described here do not significantly leach dye when immersed and are appreciably sensitive to halide, they could be used for the *on-line* industrial monitoring of halide or the measurement of halide concentrations in blood, serum or plasma, where solution temperatures can be greater than 20 °C.

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