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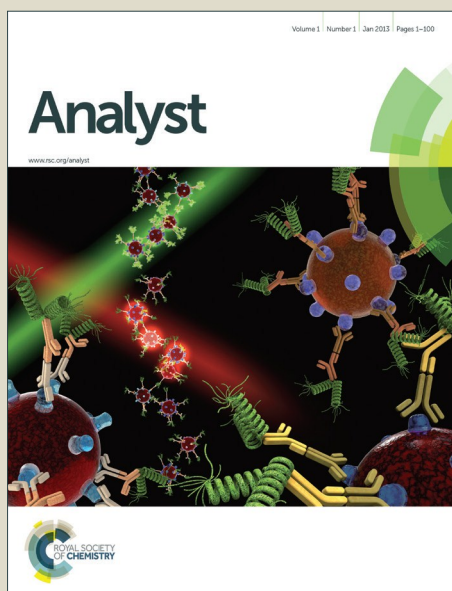
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Highly CO₂ sensitive extruded fluorescent plastic indicator film based on HPTS

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Abstract

Highly-sensitive optical fluorescent extruded plastic films are reported for the detection of gaseous and dissolved CO₂. The pH-sensitive fluorescent dye used is 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (HPTS, PTS⁻) coated on the surface of hydrophilic fumed silica and the base is tetrabutylammonium hydroxide (TBAH). The above components are used to create an HPTS pigment (*i.e.* HPTS/SiO₂/TBAH) with a high CO₂ sensitivity (%CO₂(S=1/2) = 0.16%) and fast 50% response (t_{50↓}) = 2 s and recovery (t_{50↑}) = 5 s times. Highly CO₂-sensitive plastic films are then fabricated, *via* the extrusion of the HPTS pigment powder in low-density polyethylene (LDPE). As with the HPTS-pigment, the luminescence intensity (at 515 nm) and absorbance (at 475 nm) of the HPTS plastic film decreases as the %CO₂ in the ambient gas phase increases. The HPTS plastic film exhibits a high CO₂ sensitivity, %CO₂(S=1/2), of 0.29%, but a response time < 2 min and recovery time < 40 min, which is slower than that of the HPTS pigment. The HPTS plastic film is very stable under ambient conditions, (with a shelf life > six month when stored in the dark but under otherwise ambient conditions). Moreover, the HPTS-LDPE film is stable in water, salt solution and even in acid (pH=2), and in each of these media it can be used to detect dissolved CO₂.

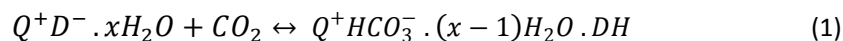
1. Introduction

The continuous and accurate monitoring of carbon dioxide (CO₂) levels in both gaseous and dissolved forms is of fundamental importance in a wide number of applications, including: chemical [1], clinical analysis [2], food industry [3] and environmental monitoring fields [4-5]. The two most common devices employed for the detection of CO₂ are the infrared (IR) detector [6], used almost exclusively for sensing gaseous CO₂, and the Severinghaus electrode [7], used mainly for sensing dissolved CO₂; neither device is inexpensive, nor easy

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2
3 to maintain or use [8-9]. In recent years, there has been a growing interest in the
4 development of optical CO₂ sensors [10]. Such sensors are usually based on fluorescence
5 intensity [11-13], or UV/Vis absorbance, changes [14-16] exhibited by encapsulated pH
6 indicators upon exposure to CO₂. Interest in such optical sensors is not surprising given that
7 optical sensors in general have many attractive features including: electrical isolation, low
8 noise interference, easily miniaturised, remote sensing, rapid-in-response, and usually low
9 cost.

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11 The principle behind most of the optical CO₂ sensors reported to-date [17] is based on the
12 acidic nature of dissolved CO₂ and the different colours/luminescence intensities exhibited
13 by a pH indicator dye when in its deprotonated (D⁻) or protonated (DH) form. Thus, such pH-
14 dye-based CO₂ indicators exhibit a change in absorbance/luminescence intensity upon
15 exposure to a change in the level of CO₂.

16
17 In the last decade, solid-state, *i.e.* apparently dry, optical CO₂ sensors have dominated the
18 literature and usually utilise a quaternary hydroxide salt, Q⁺OH⁻.xH₂O, (a phase transfer
19 agent) to create a solvent-soluble version of D⁻, *i.e.* Q⁺D⁻.xH₂O, which can be incorporated
20 in a solvent-based ink. The dried ink then functions as a CO₂-indicator *via* the following
21 equilibrium:



Colour A

Colour B

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23 Thus, in the absence of CO₂, the indicator exhibits the colour associated with the
24 deprotonated form of the pH indicator dye, *i.e.* colour A for D⁻ in reaction (1), and in the
25 presence of CO₂ it changes to colour B, due to the formation of DH as indicated in reaction
26 (1), which is usually reversible.

27
28 Various groups have reported on such phase-transfer CO₂ indicators using a variety of
29 different Q⁺D⁻.xH₂O-encapsulating materials, such as: ethyl cellulose [18-19], silicone [20-
30 22], polystyrene [23], and sol-gel-derived matrices [24-26]. The dynamic operational range
31 of these CO₂ sensors depends on various factors, including the nature of the encapsulating
32 medium and the pK_a value of the pH-indicator [27]. A major drawback exhibited by many
33 of these reported (usually solvent-based) CO₂ indicators is a very limited shelf life (1-2 days
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in the open air) probably due to the presence of other acidic gases such as SO₂ or NO₂ in the atmosphere that irreversibly protonate the indicator [28], although ambient humidity and film water content appear to also play an important part [29].

Table 1: Optical properties of HPTS in water and HPTS –based CO₂ indicators.

	D-		DH	
	λ_{abs} (nm)	λ_{em} (nm)	λ_{abs} (nm)	λ_{em} (nm)
HPTS aqueous solution	455	510	403	436
HPTS/TOAH/EC ink film*	467	517	394	440
HPTS- pigment	470	512	410	436
HPTS- film	475	515	404	441

*Accessed from ref [31].

A particularly popular pH-sensitive fluorescence dye, for use in CO₂ optical sensors work, is the 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (also known as pyranine or HPTS (see Fig. 1)) which shows distinctly different absorption and emission bands in the visible region, for DH and D⁻. For example, in aqueous solution, depending upon the pH, HPTS displays absorption bands associated with the protonated or deprotonated forms of the dye at wavelength of 403 nm or 455 nm, respectively (see Table 1). The protonated form of HPTS emits in the blue region, 436 nm, whereas the deprotonated form emits in the green $\lambda_{\text{em}} = 510$ nm. HPTS also has many distinguishing features like low toxicity, an almost ideal pK_a for making physiological measurements (*i.e.* pK_a = 7.3 – 8.1), a large Stoke's shift, high water solubility, ready commercial availability and low cost [30]. A list of some of the reports of CO₂ sensors based on HPTS is given in Table 2 [30-41].

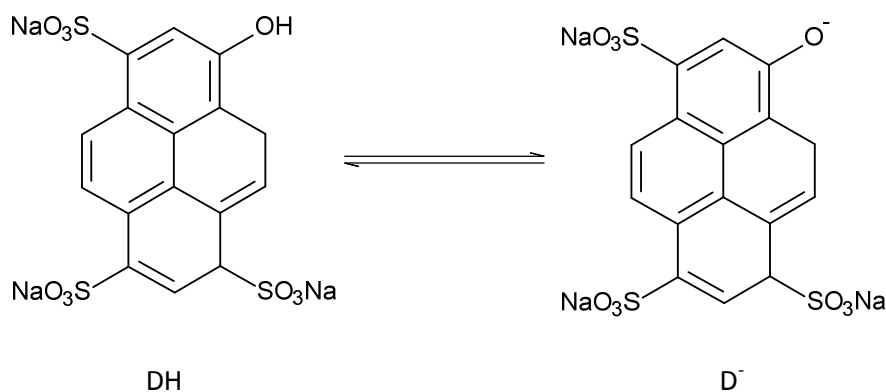


Fig. 1: Structure of the protonated (DH) and deprotonated (D⁻) forms of the pH-sensitive dye HPTS.

Table 2: Details of previous HPTS based luminescent CO₂ sensors.

Type	Encapsulation medium	Base (Phase Transfer Agent)	%CO ₂ (S=1/2)	Response time (s)	Recovery time (s)	E _a (kJ/mol)	Ref
Hydrogel	Agarose	Sodium bicarbonate	14.7	t _{90↓} = 15	t _{90↑} = 34	-	31
Organic polymer	Ethyl cellulose (EC)	TOAH	0.26	t _{90↓} = 4.3	t _{90↑} = 7.1	21	30, 31
		TOAH	ca. 0.25	t _{90↓} < 24	t _{90↑} = 282	-	33*
		TOAH	1.5	-	-	-	34
Silicone rubber	silicone	CTMAH	0.25	t _{90↓} = 42	t _{90↑} = 120	-	35
	Silicone plus cellulose derivatives*	TOAH	10	t _{100↓} = 420	t _{100↑} = 720	-	36*
Ormosil	Silica sol gel	CTMAH	10	t _{50↓} < 60	t _{50↑} < 180	21.9	37
		TOAH	9.1	t _{90↓} < 60	t _{90↑} < 60	-	38
		TOAH	3.5	t _{90↓} = 1.7	t _{90↑} = 38.5	-	39
	Silica sol-gel doped with silica particles	TOAH	3.8	t _{90↓} = 9.8	t _{90↑} = 195.4	-	40
	Silica sol-gel plus PTFE cover	CTMAH	5%	t _{90↓} = 420	t _{90↑} = 720	-	41*

TOAH: tetraoctylammonium hydroxide; TBAH: tetrabutylammonium hydroxide; CTMAH: cetyltrimethylammonium hydroxide; *: used for making dissolved CO₂ measurements (all other entries are for gas phase CO₂ measurements)

At this point it is useful to define the general parameter, R, based on experimentally measured luminescence intensity values, for a fluorescence-based CO₂ sensor, made at the wavelength of maximum emission for D⁻ alone, *i.e.* λ_{max}(D⁻), as a function of different %CO₂. From reaction (1), it follows:

$$R = (I_0 - I) / (I - I_\infty) = [HD] / [D^-] \quad (2)$$

where [HD] and [D⁻] are the concentrations of the protonated and deprotonated forms of the dye, respectively. I₀ is the value of intensity of the dye at λ_{max}(D⁻) when %CO₂ = 0 (*i.e.*

when all the dye is in its deprotonated form) and I_{∞} is the luminescence intensity of the film when all the dye has been converted into D^{-} , *i.e.* when $\%CO_2 = \infty$. Parameter R is a measure of the transformation of the dye from the deprotonated to protonated forms and it follows from reaction (1), that:

$$R = [HD]/ [D^{-}] = \alpha \times \%CO_2 \quad (3)$$

where α is a proportionality constant. Other work shows that the value of α is inversely dependent upon the background base concentration, $[Q^{+}OH^{-} \cdot xH_2O]$.

A useful and quick measure of the sensitivity of a CO_2 optical sensor is provided by the value of the $\%CO_2$, hence referred to as $\%CO_2(S=1/2)$, at which the normalised optical signal, S, is equal to $1/2$, *i.e.*, the point which the concentrations of the protonated and deprotonated forms of the dye are the same and $R = 1$. It is more convenient to use $\%CO_2(S=1/2)$ values to compare the sensitive of different CO_2 indicators, than refer to their values of ' α ' ($= 1/ \%CO_2(S=1/2)$). The examples of CO_2 -sensitive HPTS indicators, summarised in Table 2, illustrates the significant variation in the CO_2 sensitivity, *i.e.* $\%CO_2(S=1/2)$ value, reported for HPTS-based CO_2 sensors, that can be achieved by using different encapsulation media, such as: hydrogel [32], solvent-soluble organic polymer [30-34], silicone rubber [35,36] and silica sol gel/ormosil [37-41]. One of the earliest studies reported in Table 2, used agarose as the encapsulation medium [32], but required a gas-permeable membrane to stop the film drying out and also to allow its use for making dissolved CO_2 measurements. More recently, the literature has been dominated by phase-transfer agent sensors, using: an organic polymer, such as ethyl cellulose, EC, silica-sol gel or silicone as the encapsulation medium. These films usually suffer from poor stability unless used and stored either in water or under high humidity conditions [35,37].

In a recent paper [28] we reported on a colourimetric-based CO_2 sensor (where D = *meta*-cresol purple) in which the dye and base (tetrabutyl ammonium hydroxide, TBAH, in methanol) were first coated onto hydrophobic silica to create a CO_2 -sensitive pigment, and then extruded with low density polyethylene (LDPE) to create a CO_2 -sensitive, colour-based extruded plastic film ($\alpha = 0.185 \pm 0.02 \%^{-1}$. *i.e.* $\%CO_2(S=1/2) = 5.4\%$). Here we extend this work to the fluorescence dye HPTS and, by improving on the pigment preparation method, create both a colour and (mainly) fluorescence-based CO_2 indicator that is remarkably stable and sensitive for mainly gas phase (but also dissolved) CO_2 measurements, even when used in aqueous, acidic solution.

2. Experimental

2.1 Material and instrumentation

The 8-Hydroxypyrene-1,3,6-trisulfonic acid trisodium salt, HPTS, was purchased from Sigma-Aldrich (97%, H1529-1G) and used as received. In this work hydrophilic (not hydrophobic) silica was used to create the HPTS-pigment for subsequent extrusion in LDPE. Previous work carried out by this group [42] reported that water-based CO₂ indicators (comprising a pH dye encapsulated in hydroxyethyl cellulose with a water-based base, TBAH) were much more stable, when stored under ambient conditions, than their solvent-based counterparts (i.e. dye encapsulated in EC, with methanol-based TBAH). Thus, in this work hydrophilic (not hydrophobic) silica, and water-based TBAH (not MeOH-based TBAH) were used to create the HPTS-pigment for subsequent extrusion in LDPE. The hydrophilic silica was more compatible with the aqueous base (Q⁺OH⁻ · xH₂O) and produced brighter, more reproducible and much more stable film sensors. The hygroscopic nature of hydrophilic SiO₂ also probably plays an important role in increasing film storage stability, since it will help ensure the surface-adsorbed dye-base ion pair layer remains hydrated and, as noted by others [35,37], CO₂-indicators appear much more stable when stored under humid conditions, or in water.

The SiO₂ (Aerosil 130 hydrophilic fumed silica) was a gift from Evonik (BET surface area = 130 ± 25 m²/g). The aqueous base, tetrabutylammonium hydroxide solution (40% in water), TBAH, (86854-100ML) was purchased from Sigma-Aldrich. The low-density polyethylene, LDPE, powder (melt flow index, MFI, 20) was supplied by PW Hall UK and the LDPE pellets (MFI = 4) were provided by Ultrapolymers UK. Microscope slides were purchased from Academy Science (clear glass, 76×26 mm, thickness 1.0-1.2 mm).

All gases used were high purity CO₂ and Argon. 5% CO₂-air mixture and 1% CO₂-air mixture were purchased from BOC gases. Gas steams with other loadings of CO₂ percentages were generated using a Cole Parmer gas blender using Ar as the inert carrier gas. All fluorescence work was carried out using a PerkinElmer LS45 Fluorescence Spectrometer. All UV/Vis absorbance measurements were made using CARY 300 UV-vis spectrometer. Diffuse reflectance spectra were measured using a KONICA MINOLTA Spectrophotometer (CM-2500d). The pigmented polymer film was extruded using a Rondol Microlab Twin Screw Extruder.

2.2 Preparation of the HPTS-pigment

0.2 g HPTS acid trisodium salt were fully dissolved in the mixture of 3.1 ml of a 40% TBAH aqueous solution and 100 ml of ethanol. 2 g hydrophilic silica were then added, and the mixture stirred for 2.5 h, after which the solvent was evaporated under reduced pressure using a rotary evaporator. The final, dry yellow pigment powder was scraped out and then ground into a fine powder using a mortar and pestle. The HPTS-TBAH-SiO₂ pigment (*i.e.* 'HPTS-pigment') appeared bright yellow in the absence of CO₂, and pale yellow/colourless in the presence of CO₂, as illustrated by the photographs of the two different forms in Fig. 2. The wavelengths of the absorption and emission maxima of the D⁻ and DH forms of the HPTS-pigment are given in Table 1.



Fig. 2: Photographs of HPTS- pigment (from left to right) in the absence and presence of CO₂.

2.3 Preparation of the HPTS-LDPE film

The CO₂-sensitive plastic films were fabricated *via* the extrusion of a mixture of the HPTS-pigment powder in low-density polyethylene (LDPE), with a final pigment loading of 5 wt.%, using a Rondol Microlab 10 mm twin screw extruder (barrel L/D 25/1). LDPE was primarily chosen as the encapsulation matrix because it can be extruded at low enough temperatures, ca. 140°C here, so as avoid the thermal degradation of the dye, which occurs at temperatures > 180°C. Thus, other work carried out using the higher molecular weight polyolefin, polypropylene, which requires a much higher, > 200°C, extrusion temperature, only yielded films in which the dye was thermally degraded. LDPE, is attractive as an encapsulation medium for other reasons, such as its reasonable permeability towards CO₂, namely: $9.8 \times 10^{-13} \text{ cm}^3 \cdot (\text{273 K}; 10^5 \text{ Pa}) \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$, although this is ca. 10x's less than ethyl cellulose [43]. More importantly, LDPE has a water vapour permeability ($68 \times 10^{-13} \text{ cm}^3 \cdot (\text{273 K}; 10^5 \text{ Pa}) \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{Pa})$) that is 100 times less than that of EC [43] and so encourages much greater water retention (by the silica particles), which leads to a much greater stability under ambient storage conditions, when compared to an EC-based CO₂ indicator film [30-

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35]. In addition, LDPE is much less (ca. 10x's) permeable towards acid gases, such as SO₂, than EC [43,44] and this also helps improve the film's stability, since ambient levels of the latter, typically ca. 100 ppb in many towns and cities, have been suggested [1,45] as a likely additional cause of the reported poor stability exhibited by most solvent-based CO₂ indicators. In support of this, no change in colour or response characteristics were observed when an HPTS-LDPE film was exposed to either ca. 100 ppb NO₂ or SO₂ for 20 min, whereas, in both cases, the solvent-based, HPTS-EC film was bleached.

The extrusion process is summarised as follows: 2 g HPTS-pigment and 18 g LDPE powder (melt flow index, MFI, 20) were mixed to produce 10 wt.% pigmented powder. The extruder was then used to create 10 wt.% of HPTS pigmented LDPE 'master-batch' pellets using a processing temperature that increased gradually from 90°C at the feed zone, to 140°C at the die, using a feed hopper rate of 41 rpm, extruder screw speed of 80 rpm and a pelletizer speed of 0.5 m min⁻¹. These pellets were then 'diluted' to 50% w/w using virgin LDPE pellets (MFI 4), to produce the final 5wt.% pigment loading required for the extruded HPTS-LDPE film product. The thermal processing conditions for producing the (HPTS/TBAH/SiO₂) pigmented LDPE extruded film, *i.e.* the 'HPTS-LDPE film', were: 90°C (at the feed zone), increasing to 110–125–135°C (across the barrel) and finally 140°C (at the die zone). The feed hopper rate was 20 rpm, extruder screw speed was 80 rpm, and take-off speed was 1.7 m min⁻¹. The final product, a 5 wt.% pigmented HPTS-LDPE film (central thickness 55-60 μm) appeared pale yellow under daylight, as the dye is in its deprotonated, D⁻, form, and emitted a bright green luminescence, due to D⁻, under UV irradiation as illustrated by the photographs in Fig. 3.

The level of pigment chosen, 5 wt%, was an optimised value, in as much that a much higher level (> 20%) leads to a significant loss in the performance characteristics of the polymer, such as elasticity and tear resistance, whereas a pigment level of << 5%, produces a film that is insufficiently coloured to allow the necessary absorbance and luminescence spectral characteristics to be recorded for this work. In polymer extrusion in general, a 5 wt% pigment loading is not unusual.

The specific surface area of the hydrophilic silica is 150 m² g⁻¹, which suggests a fundamental particle size of ca. 15 nm, which is beyond optical resolution and difficult to see even using

SEM. However, EDX analysis for Si of a typical image of the edge of a HPTS-LDPE film reveals a fine, and uniform dispersion of particles, for example: see image in supplementary information, S1, suggesting the HPTS-coated silica particles are uniformly distributed throughout the extruded film.

Upon exposure to CO₂ the film became colourless, as the dye was in its protonated, DH, form, and emitted a bright blue turquoise luminescence, due to DH. The wavelengths of the absorption and emission maxima exhibited by the HPTS-LDPE film in its D⁻ and DH forms are given in Table 1.

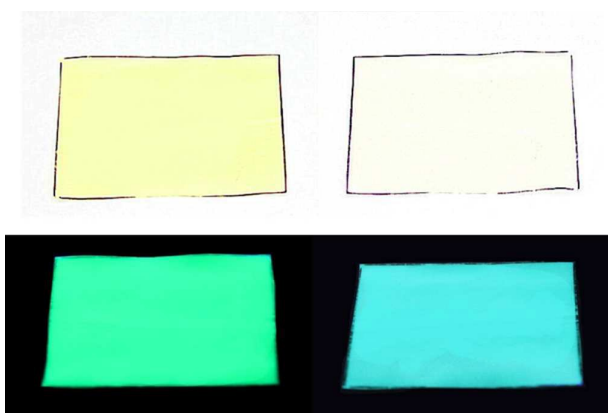


Fig. 3: 5 wt.% HPTS- film (upper row, from left to right) under daylight with or without pure CO₂ exposure, (lower row, from left to right) under UV irradiation with or without CO₂ exposure.

2.4 Fluorescence measurements

In making luminescence intensity measurements, the HPTS-pigment or HPTS-LDPE film, was mounted on a microscope slide using double-sided tape. The width of the slide was cut to fit the diagonal of a typical 1 cm quartz fluorescence cell (*i.e.* width ca. 1.4 cm). In order to maximise the measured luminescence intensity from the sample, the slide was placed in a fluorescence cuvette, and positioned so that the edge of the slide was directly in line with the emission detector of the fluorimeter and so square on, with respect to the excitation beam. Positioning the film in this way, allowed the luminescence from the sample, which was mostly gathered by the glass substrate, *via* total internal reflection, to exit from the edges of the microscope slide and so be easily detected and measured. The emission spectrum of any sample (pigment or film) on the microscope slide was typically recorded after 5 min purging with the CO₂/Ar gas blend under test. In this work with the wavelength

of excitation, λ_{ex} , was always set at 470 nm. The desired argon and CO₂ mixtures were generated using a Cole-Parmer gas blender.

2.5 Variation in relative humidity (RH)

A 100% relative humidity (T = 21°C) humid gas, which was either: 5% CO₂ in Ar, or just Ar, was generated by purging the gas under test through two Dreschel bottle half filled with water connected in series; the relative humidity (RH) of the gas was measured using a hair-hygrometer.

2.6 Variation in temperature

Most experiments were conducted under an ambient condition with T = 21°C. However, in one set of experiments the effect of temperature on the sensitivity of the HPTS- film was probed over the range 21-36°C. In this work HPTS-LDPE film was attached to a microscope slide and placed on a thermostatically controlled electric heater block. The HPTS-LDPE film was then covered with a cuvette, with one of its faces removed, so as to allow different CO₂/Ar gas mixtures to be purged through the cuvette and so pass over the HPTS-LDPE film surface. This set-up allowed the luminescence spectra of the HPTS-LDPE film to be recorded as a function of %CO₂ in the gas phase, whilst the HPTS-LDPE film was maintained at a fixed, known temperature.

3 Result and discussion

3.1 HPTS-pigment

The diffuse reflectance spectra of a sample of the HPTS-TBAH coated on hydrophilic silica particles (*i.e.* the 'HPTS-pigment') under an argon (*i.e.* 0% CO₂) and 100% CO₂ were measured using a Minolta spectrometer. In order to make these measurements, 3 g of the HPTS-pigment were placed in a 14 ml glass vial sealed with a plastic cap, and the gases under test, *i.e.* either pure argon or CO₂, were then sequentially purged through the vial for 2 min before recording the diffuse reflectance spectra of the pigment. The results of this work are illustrated in Fig. 4 and reveal that the HPTS-pigment has UV/Vis absorption peaks at: (i) 410 and 470 nm in the absence of CO₂ (*i.e.* due to its yellow D⁻ form- the blue line in figure) and (ii) at 410 nm in the presence of CO₂ (due to its colourless DH form, the red line in Fig. 4).

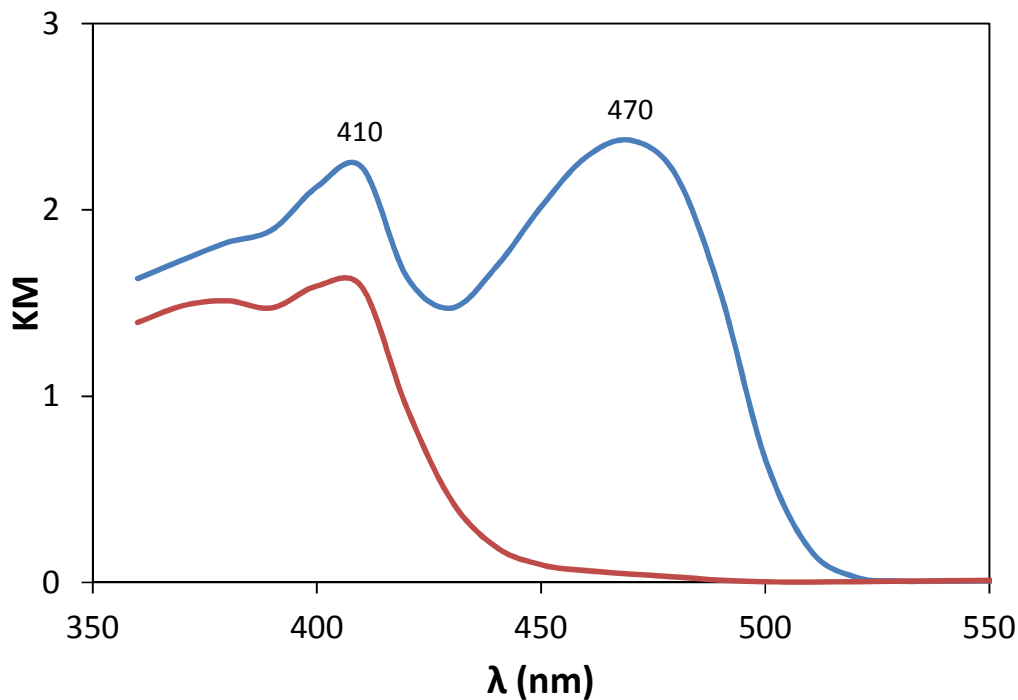


Fig. 4: Kubelka Munk plots of the HPTS- pigment under 0% (blue line) and 100% (red line) of CO_2 .

These results are consistent with the known UV/Vis absorption spectra of the D^- and DH forms of HPTS (see Table 1) and show clearly that the presence of CO_2 promotes the protonation of HPTS (initially in its deprotonated, D^- , yellow form) to its largely colourless, DH form, as indicated by reaction (1).

In terms of luminescence, the spectra of the HPTS-pigment was first recorded in the absence of CO_2 and revealed a wavelength for the maximum in the emission spectrum, λ_{em} of 512 nm, as illustrated in Figure. 5. The changes in this luminescence spectrum, upon exposure to a series of different levels of CO_2 , were then recorded and the results are also illustrated in Fig. 5.

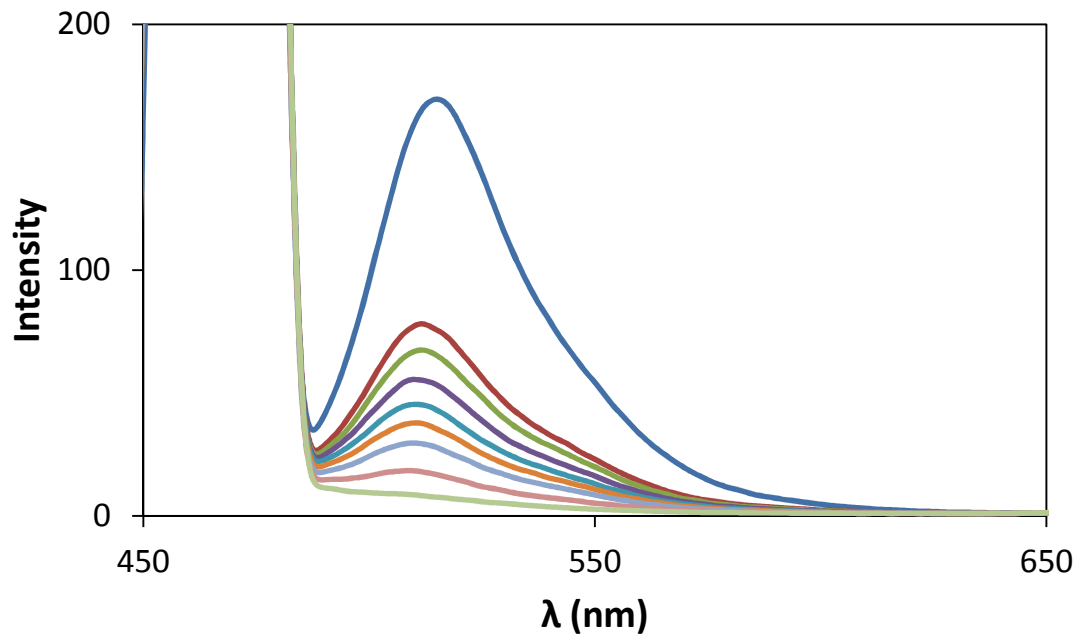


Fig. 5: Emission spectra of the HPTS-pigment upon exposure to (from top to bottom): 0, 0.17, 0.21, 0.28, 0.43, 0.58, 1, 5 and 100 %CO₂, as a series of different Ar/CO₂ gas mixtures.

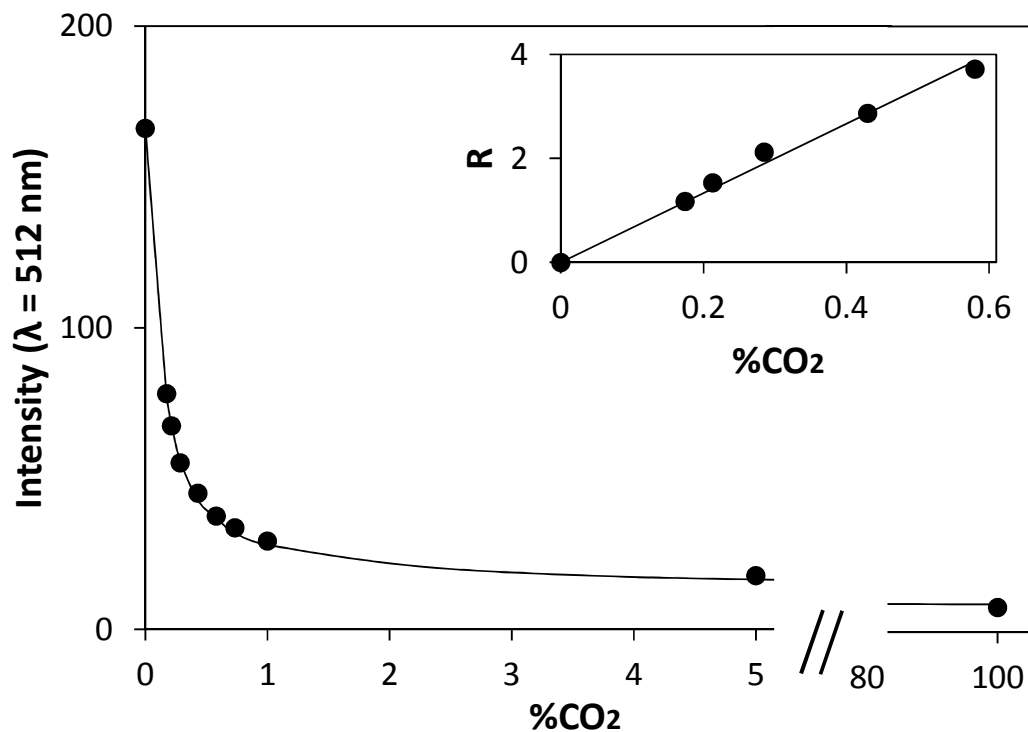


Fig. 6: Plot of the relative fluorescence intensity from the HPTS-pigment (taken from Fig. 5) as a function of the %CO₂. Insert data reveals an α value of $6.4 \pm 0.3\%^{-1}$. ($R^2 = 0.9924$), where $(I_0 - I) / (I - I_\infty) = R = \alpha \%CO_2$.

The results of this work showed that the initial high level of emission exhibited by the deprotonated form of the HPTS-pigment, D^- , ($\lambda = 512$ nm) decreased with increasing %CO₂ in the purging gas, as D^- is converted to DH, *via* reaction (1). A plot of the intensity of emission at 512 nm as a function of %CO₂, gleaned from the spectra illustrated in Fig. 5, is shown in Fig. 6, along with a R vs %CO₂ plot of the data, as the insert diagram. The latter reveals a %CO₂(S=1/2) = (1/ α) value of 0.16%, which suggests that the HPTS-pigment is extremely sensitive to CO₂, and more sensitive than most of the other HPTS CO₂ sensors reported to-date, as indicated by the examples listed in Table 2.

Finally, the response and recovery times for the HPTS-pigment were measured *via* the observed variation in the luminescence intensity of the HPTS-pigment as a function of time, produced upon exposure to an alternating stream of 0% (*i.e.* Ar) and 5% CO₂. The results of which are illustrated in Fig. 7.

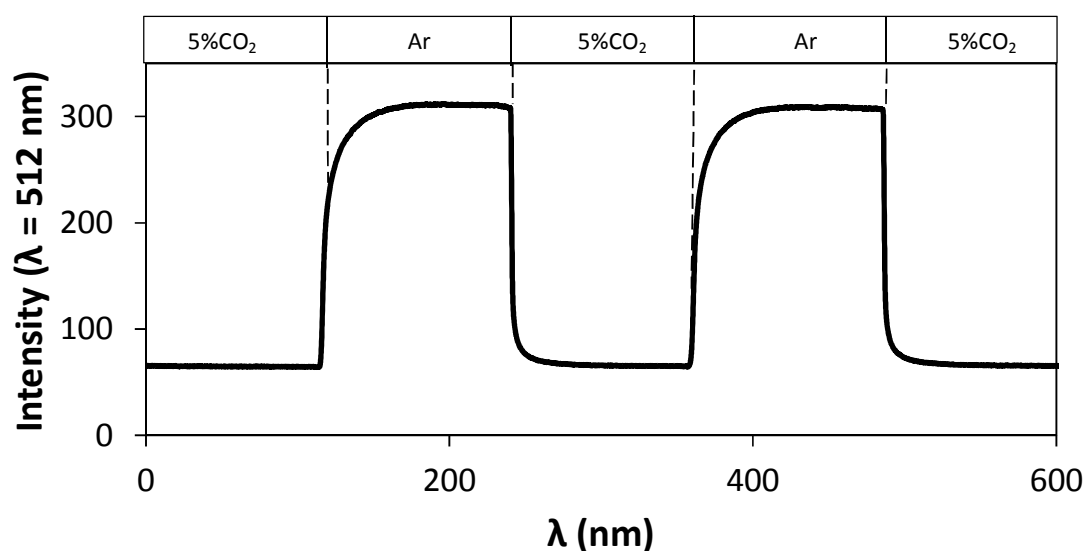


Fig. 7: Variation in the measured luminescence intensity exhibited by the HPTS pigment upon exposure to alternating streams of 5% CO₂ and Ar.

From the data illustrated in Fig. 7, a 50% response time ($t_{50\downarrow}$) = 2 s, and a 50% recovery time ($t_{50\uparrow}$) = 5 s, were calculated, and reveal that the HPTS-pigment has a quick response time and recovery time, as is likely due to the high surface area of the HPTS-pigment, and the large diffusion coefficient, D, for CO₂ in the air ($D(\text{CO}_2) = 0.14 \text{ cm}^2\text{s}^{-1}$) [46].

3.2 The HPTS-LDPE film CO₂ indicator

Upon extrusion of the HPTS-pigment in LDPE, the absorbance and luminescence properties of the polymer film (*i.e.* the 'HPTS-LDPE film') were studied and the results are summarised in Table 1. The luminescence intensity at 515 nm exhibited by the HPTS-LDPE film was measured as a function of different known levels of CO₂ (0% to 100%) in the ambient gas and the results are illustrated in Fig. 8. These results show that, as with the HPTS-pigment, the luminescence intensity of the HPTS-LDPE film decreased with increasing %CO₂. A R vs %CO₂ plot of the data revealed a %CO₂(S=1/2) value of 0.29 %, which is slightly less than that exhibited by the HPTS-pigment (see Table 3), but still represents a very sensitive CO₂ sensor film, when compared to many of the other reported HPTS-based CO₂ sensors, such as those listed in Table 2. It is interesting to note that HPTS-LDPE film has a very similar sensitivity as that of a HPTS-TOAH solvent based EC ink film [31], which has %CO₂(S=1/2) of 0.26% (see Table 2). Additional work suggests that this is a general feature of such films, *i.e.* dye-coated pigment-loaded LDPE plastic films exhibit a similar CO₂ sensitivity as their solvent-based EC ink CO₂ sensor counterparts.

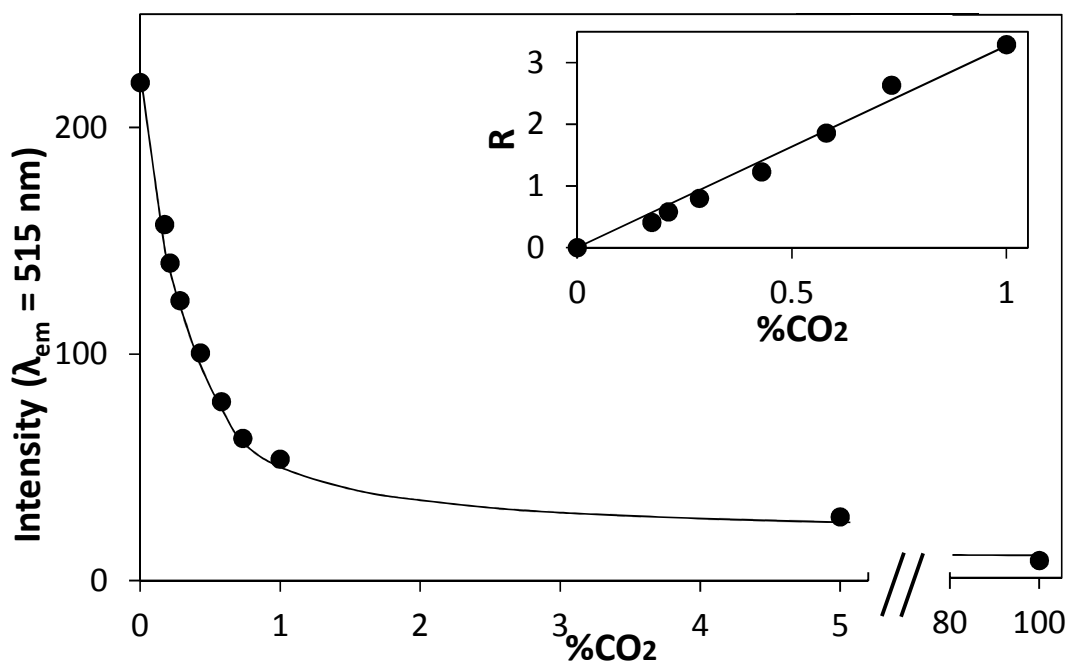


Fig. 8: Diagram of a typical plot of the relative fluorescence intensity from the HPTS-LDPE film as a function of the %CO₂. Insert data reveals an α value of $3.48 \pm 0.14\%^{-1}$. ($R^2 = 0.9898$), where $(I_0 - I) / (I - I_\infty) = R = \alpha\%CO_2$.

A study of the variation in luminescence intensity of the HPTS-LDPE film upon switching the ambient gas phase composition alternatively from 0% to 5% CO₂ and back again was carried out and the results are illustrated in Fig. 9.

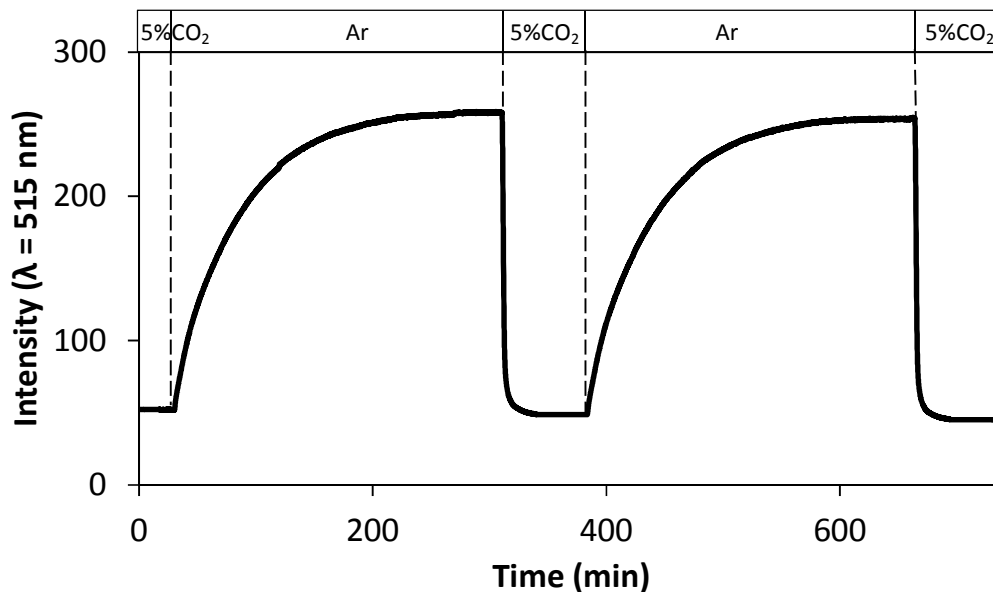


Fig. 9: Repeat response and recovery of HPTS-LDPE film was tested by purging alternative streams of 5% CO₂ and pure Ar.

An analysis of the data in Fig. 9 revealed a 50% response time ($t_{50\downarrow}$) of 120 s and 50% recovery time ($t_{50\uparrow}$) of 2340 s. As noted earlier, a film thickness, ℓ , of ca. 55-60 μm , combined with a pigment level of 5 wt%, allowed the necessary absorbance and luminescence spectral characteristics to be recorded for this work. However, a necessary consequence of this high film thickness is the long response and (particularly) recovery times exhibited the HPTS-LDPE film, see table 3. These values are much greater than those exhibited by most other reported HPTS-based CO₂ indicator ink films, see table 2, which are also generally much thinner, typically 1-8 μm [39,34]. The asymmetric nature of the response and recovery times are a direct consequence of the hyperbolic nature of the response of this, and all other pH-indicator-based CO₂ indicators, where the observed change in fluorescence intensity, or absorbance, is inversely proportional to the partial pressure of CO₂, $P(\text{CO}_2)$, which in turn is proportional to the %CO₂. In most cases, these response and recovery times depend, respectively, directly upon the rate of diffusion of the CO₂ into and out of the indicator film, with a proportionality constant that is inversely proportional to ℓ^2 [47]. Thus, it follows, by using a narrower film die in the extruder, it will

be possible to create a thinner HPTS-LDPE film, than that reported here, and that such a film will be necessarily faster to respond and recover. It also follows that, as the indicator is fluorescence-based, there would be no need to increase the pigment loading in a thinner film, above that of the current value, 5 wt%. As it is possible to extrude an LDPE film that is ca. 12.5 μm [48], i.e. the thickness of most commercial plastic wrap film, then it can be calculated that such an HPTS-LDPE film would exhibit approximate response and recovery times of 5 and 102 s, respectively – which are in line with those reported by others [34,39] for films of a similar thickness. A summary of the main properties of the CO_2 -sensitive HPTS sensor films studied here, including the associated limits of detection (LOD), is given in Table 3.

Table 3: HPTS based luminescent CO_2 sensor properties.

CO_2 sensor	α ($\%^{-1}$)	$\% \text{CO}_2$ ($S=1/2$)	r^2	Response time (s)	Recovery time (s)	LOD %
HPTS-pigment	6.4 ± 0.3	0.16	0.9924	$t_{50\downarrow} = 2$	$t_{50\uparrow} = 5$	0.007
HPTS-LDPE film	3.48 ± 0.14	0.29	0.9898	$t_{50\downarrow} = 120$	$t_{50\uparrow} = 2340$	0.01
HPTS-ink*	3.2 ± 0.1	0.26	0.9983	$t_{90\downarrow} = 4.3$	$t_{90\uparrow} = 7.1$	0.009

*From [30] and [31]; all response and recovery times were recorded purging alternatively 0% and 5% CO_2 . The correlation coefficients (r^2) were derived from the straight line plots of the R vs $\% \text{CO}_2$ data for the different sensors studied.

3.3 Effect of temperature

As might be supposed, considering the nature of reaction (1), all pH indicator based CO_2 optical sensors are temperature sensitive, and decrease in CO_2 sensitivity with increasing temperature. The HPTS-LDPE film is no different, as revealed by the results of a series of calibration curves (*i.e.* luminescence intensity vs $\% \text{CO}_2$) curves recorded at a series of different temperatures, spanning the range 21- 36°C. The latter data were then used to generate appropriate R vs $\% \text{CO}_2$ plots for the different temperatures studied and the results are illustrated in Fig. 10. The value of the gradient for each of these plots is $\alpha(T)$ *i.e.* the values of α at the associated temperature, and an Arrhenius plot of $\ln(\alpha(T))$ vs $1/T$, reveals a value for the activation energy for reaction (1) of $38 \pm 2 \text{ kJ mol}^{-1}$. This value is not too

dissimilar to the value of 21 kJ mol^{-1} reported [31] by this group for an HPTS- CO_2 sensitive solvent-based ink (polymer: ethyl cellulose, plasticizer: tributyl phosphate; base/phase-transfer agent: TOAH) and by another group using HPTS encapsulated in an organically-modified silica glass (ormosil) [33] (see Table 2).

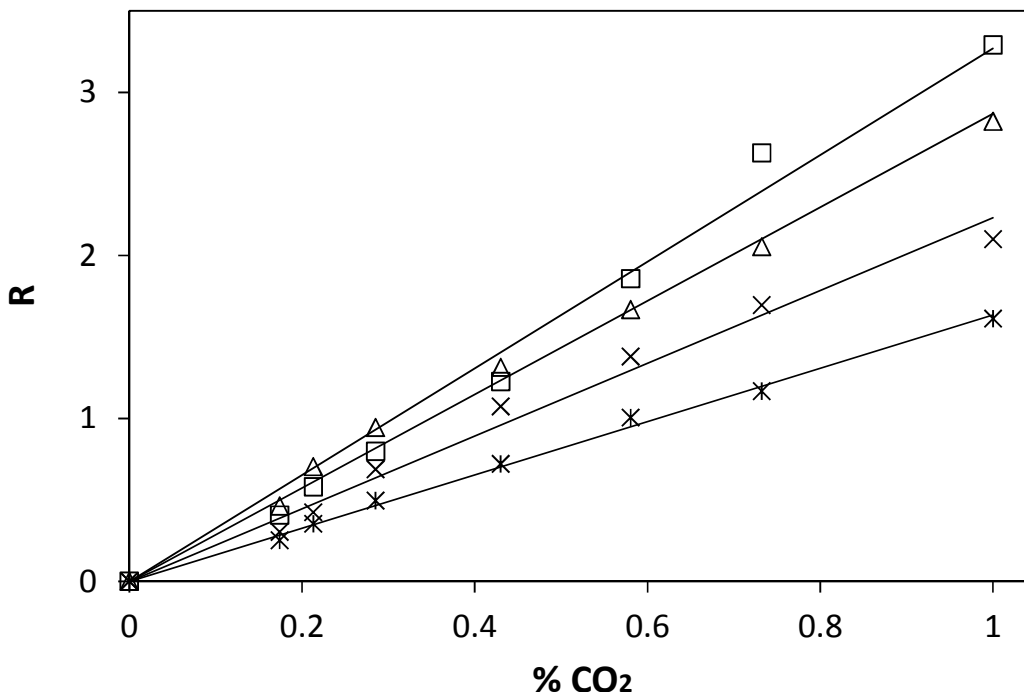


Fig. 10: R versus $\% \text{CO}_2$ plot of HPTS-TBAH pigmented LDPE film at various temperature (from top to bottom 21°C , 26°C , 31°C , and 36°C) where $(I_0 - I)/(I - I_\infty) = R = \alpha \% \text{CO}_2$.

3.4 Effect of humidity

Many reported CO_2 optical sensors exhibit a sensitivity (as measured by the measured value for α) which is humidity dependent, and this appears especially so when an organically-modified silica glass (ormosil) is used as the encapsulation medium [34]. This effect is usually reversible, enabling the use of the sensor to be used as a CO_2 sensor at any RH value, provided the latter quantity is fixed [34]. Since the HPTS-LDPE film CO_2 reported here uses hydrophilic silica, which is hygroscopic, as the inorganic core of the HPTS-pigment, *vide supra*, it is not too surprising that the HPTS-LDPE film sensor is also humidity dependent, and loses sensitivity with increasing RH. Thus, at 21°C , the value for α was found to decrease by a factor of ca. 4.0 as the RH was increased from 0 to 100%, *i.e.* from dry to wet

CO₂, see Table 4. As noted by others [33], working on ormosil-based CO₂ indicators, which exhibit a similar sensitivity, this suggests that such, humidity-sensitive, sensors need to be used in an environment where the ambient RH, and temperature also for that matter, are largely invariant. One such possible area of application would be the monitoring of the CO₂ level in modified atmosphere packed, high water content, foodstuffs, such as fish and meat, since they are usually chilled at ca. 5°C, so that any CO₂ indicator would be operating at a fixed T, and inside the pack the RH would be constant and ca. 100%.

Table 4: Summary of the characteristics of an HPTS-LDPE film as a quantitative CO₂ indicator in different media

Medium	α (% ⁻¹)	%CO ₂ (S=½)	r ²
Dry gas (RH=0)	3.4	0.29	0.9898
Humid gas(RH =0)	0.85	1.2	0.9923
water	0.084	12	0.9847
1M NaCl aqueous solution	0.11	9.1	0.9997
0.01M HCl aqueous solution	0.091	11	0.9786

*: for all dissolved CO₂ measurements the HPTS-LDPE film was soaked overnight in water prior to testing and the associated error is \pm 10%

3.5 Dark stability

One of the most striking feature of the HPTS-LDPE film CO₂ sensors is its stability. For example, when stored under ambient atmospheric conditions, in the dark, the film is stable for > 6 months, showing no loss in sensitivity or fluorescence intensity/colour. In contrast, a typical HPTS-CO₂ sensitive ink will last ca. 5-7 days under the same conditions, before losing all its (yellow) colour and sensitivity towards CO₂. Silicone and ormosil encapsulated HPTS CO₂ sensors exhibit the same poor stability when stored under ambient atmospheric conditions. In most cases this lack of stability is usually attributed [33] to loss of water (if kept in a dry atmosphere) and possible permanent reaction with common, albeit low level, acidic pollutants, such as SO₂ and NO₂ [28]. Others [35] have noted that the stability of the latter films can be improved markedly by storing them either in water, or in a very humid (usually RH \geq ca. 80%) atmosphere, although such storage conditions then limits their commercial potential. In contrast, HPTS-LDPE film sensors appear very stable when stored under ambient, dark conditions, which renders them much more viable commercially.

3.6 Photostability

The photostability of HPTS is known to be poor, especially when compared to other dyes, such as the diketo-pyrrolo-pyrrole (ddp) dyes, reported recently by Schutting et al [34], which was used to create a number of different, sensitive EC-based, CO₂ indicators. Using similar conditions as reported by these workers [34] to test the indicators photostability, in particular illumination with a high intensity 458 nm LED (Manufacturer: OSLO; 2W LED; 458 nm irradiance: 27 mW cm⁻²), the luminescence of both a HPTS-EC ink film and HPTS-LDPE film were found to decrease by ca 40% after 4 h continuous illumination. Obviously, despite this clear weakness, the employment of a ratiometric method [41] would help extend the useful lifetime of the HPTS-LDPE films, as would the use of a pulsed light source. In regard of the latter, Schutting et al [34] note that a 100 ms excitation light pulse is sufficient to access the fluorescence intensity information of such indicators and that this needs only to be carried out every few seconds in order to provide a useful real-time measurement of ambient CO₂.

3.7 Detection of dissolved CO₂

Another striking advantage of the HPTS-LDPE film CO₂ sensor, over that of most other optical CO₂ sensors, is its marked high stability in aqueous solution, even when the solution is highly acidic (pH ≤ 2) or very salty ([NaCl] = 1 M). Most other optical CO₂ sensors exhibit only a limited stability in water, due to dye leaching, ion exchange and proton permeation. Thus, for such sensors, this limited stability is usually compromised by exposure to increasing levels of electrolyte and especially by increasing levels of acidity. An aqueous solution with a pH < 3, is usually acidic enough to protonate and deactivate most CO₂ optical sensors reported to date. In contrast, the HPTS-LDPE film sensor reported here shows no loss of function, or dye, when stored in water, or 1 M NaCl for long periods of time (> 24 h), and is stable and unaffected for at least 12 h when placed in CO₂-free, 0.01 M HCl aqueous solution. In addition, under such conditions; including in 0.01 M HCl, it is still able to function as a CO₂ sensor. A rather nice demonstration of the ability of the HPTS film to function as a CO₂ sensor in aqueous solution, regardless of pH, is provided by the series of photographic images some of which are given in Fig. 11. These show, from left to right, that in CO₂-free (*i.e.* 'still') water the HPTS film retains its original yellow colour (due to the D⁻ form of the dye), but upon dipping into sparkling, *i.e.* carbonated, water this colour is totally lost (within 20 s) but, is restored upon its removal from the sparkling water (within 45 mins).

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3 If placed in 0.01 M HCl the film remains exactly as if in still water, unless CO₂ is bubbled
4 through, whereupon it will decolourise, irreversibly, as shown in Fig. 11 by the film in
5 carbonated water.
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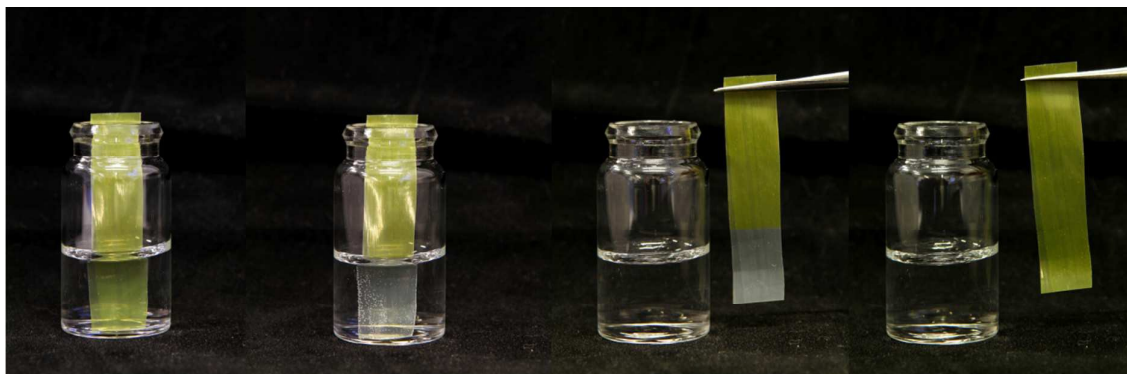


Fig. 11: Photographs of (from left to right) HPTS-LDPE film partly immersed in still water, sparkling water, removed from the sparkling water, and left in the air till recovered.

It is common practice when using CO₂ optical indicators for the measurement of dissolved CO₂ to protect the dye in the indicator film from protonation through the use of top-coat, thin layer of a gas (i.e. CO₂ in this case) -permeable, ion (i.e. proton and salt in this case)-impermeable layer, such as Teflon [17] or a hydrophobic silicone layer [1]. This layer allows the CO₂ indicator to monitor, without interference from ions in the solution under test, the partial pressure of CO₂ in an aqueous solution over a range of pH values, typically pH 4-8. Obviously, in this work the LDPE layer provides the same function as the hydrophobic silicone or Teflon layer used previously by others [1,17], i.e. it acts as a gas-permeable, ion-impermeable layer. However, unlike the latter it also acts as the sensor encapsulation medium, thus making the sensor a much simpler construction. As a consequence of its ion-impermeable nature, the LDPE CO₂-based indicator reported here is highly resistant to dye leaching, which, in other CO₂ indicators, can take place via an ion exchange mechanism when placed in concentrated solutions of electrolyte. It is also very stable at pH's as low as pH 2, which is due not only to its low ion permeability but also its low permeability towards water vapour [43], which is much less (> 500 x's) that of silicone rubber [49] and probably even lower for the more polar, slightly acidified vapour generated by the most acidic aqueous solutions, like that of HCl used here, which have a negative azeotrope [50]. As a consequence, the LDPE provides an excellent barrier to the permeation of HCl, or any acid,

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3 dissolved in the water under test and allows the film to operate as a dissolved CO₂ indicator
4 in 0.01 M HCl, for at least 12 h.
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8 In aqueous solution, be it with, or without, salt or acid, the sensitivity (i.e. the value of α) of
9 the HPTS-LDPE film towards CO₂ was found to be approximately the same but greatly
10 reduced, (typically by a factor of ca. 37), compared to that for gaseous CO₂ measurements
11 (RH = 0), so that the %CO₂(S=1/2) values increased from ca. 0.29% to ca. 10.7%, see table 4;
12 although, in all cases the film exhibited a reversible response towards CO₂ and so recovered
13 its initial luminescence and colour in the absence of CO₂, as indicated by the photographs in
14 figure 11. Although the exact cause for the marked decrease in CO₂ sensitivity of the HPTS-
15 LDPE film in aqueous solution is not clear, it is likely to be associated with the significant
16 change in the microenvironment surrounding the encapsulated HPTS-silica pigment particles
17 due, in turn, to an increased water content of the film. Evidence for this is provided by the
18 observation that the absorbance λ_{\max} for the film shifts from the usual value of 475 nm for a
19 dry film, to 455 nm for the HPTS-LDPE film in water, coupled to the fact that the absorbance
20 λ_{\max} for HPTS dissolved in water is also 455 nm (see table 1). The effects produced by an
21 increase in polarity of the microenvironment, signified by the negative shift in the λ_{\max} of
22 HPTS and brought about by the immersion of the film in water, are likely to include: (i) a
23 decrease in the pK_a of HPTS [18] (for example the pK_a of acetic acid is 15.5 in (non-polar)
24 dichloroethane, but 4.8 in water) [51] and (ii) a decrease in the solubility of CO₂ (for example
25 the solubility of CO₂ is 17 times higher in trichloromethane than it is in water [52]). Both of
26 these effects are likely to produce a measurable decrease in the CO₂ sensitivity, exhibited by
27 the HPTS-LDPE film, when the film is highly hydrated as opposed to dry. It is also worth
28 noting that this overall loss of sensitivity, when in water, is readily reversed by returning the
29 film to a dry atmosphere.
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49 **4 Conclusions**

50 The highly CO₂ sensitive fluorescence HPTS-pigment (%CO₂(S=1/2) = 0.16) and extruded
51 plastic HPTS-LDPE film (%CO₂(S=1/2) = 0.29) presented here exhibit a sensitive and
52 reversible response to CO₂ over a wide range of concentration. The HPTS CO₂ sensitive
53 plastic film can be used in water and acid solution (pH = 2) to detect dissolved CO₂ without
54 the dye leaching out from the plastic. Such properties make the HPTS plastic film a
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3 promising CO₂ sensor for detecting and measuring both gaseous and dissolved CO₂ levels.
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5 The HPTS plastic film has a shelf life over six months when stored in the dark and ambient
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7 atmospheric conditions, but, like many CO₂ optical sensors, it is sensitive to changes in
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9 humidity and temperature. This suggests that the HPTS-LDPE film optical sensor is best used
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11 in areas where no significant changes in RH and T are expected, and the measurement of
12
13 the ambient level of CO₂ is important, such as in modified atmosphere food packaging [53].

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15 A well-noted drawback of an intensity (rather than lifetime) based indicators, such as the
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17 HPTS-LDPE CO₂ indicator described here, is that they are susceptible to drift and
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19 instabilities, due to, amongst other things, source fluctuations, detector drift and dye
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21 leaching [41]. Many of these issues can be overcome through the use of ratiometric
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23 detection, where the luminescence of both the protonated and deprotonated forms of the
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25 dye are measured and ratioed, and the ratio measured as a function of %CO₂. A striking
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27 demonstration of this has been reported by Wencel et al. for an HPTS/silica sol gel film,
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29 using two low cost LEDs ($\lambda_{\text{max}}(\text{emission}) = 405$ and 450 nm, respectively) to effect dual
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31 excitation ratiometric detection [41]. Thus, it should be possible to employ this approach
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33 when using the HPTS-LDPE film reported here and so avoid many of the problems
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35 associated with non-referenced intensity-based indicators.
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