Highly CO2 sensitive extruded fluorescent plastic indicator film based on HPTS


Published in:
The Analyst

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
© Royal Society of Chemistry 2016

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Download date: 08. Dec. 2018
This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

This article can be cited before page numbers have been issued, to do this please use: A. Mills and Y. Dilidaer, Analyst, 2015, DOI: 10.1039/C5AN02239H.
Highly CO$_2$ sensitive extruded fluorescent plastic indicator film based on HPTS

Andrew Mills and Dilidaer Yusufu
Queens University Belfast, David Keir Building, Stranmillis Road, Belfast, BT9 5AG, UK
Email: andrew.mills@qub.ac.uk

Abstract

Highly-sensitive optical fluorescent extruded plastic films are reported for the detection of gaseous and dissolved CO$_2$. 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/SiO$_2$/TBAH) with a high CO$_2$ sensitivity (%CO$_2$(S=1/2) = 0.16%) and fast 50% response ($t_{50\downarrow}$) = 2 s and recovery ($t_{50\uparrow}$) = 5 s times. Highly CO$_2$-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 %CO$_2$ in the ambient gas phase increases. The HPTS plastic film exhibits a high CO$_2$ sensitivity, %CO$_2$(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 CO$_2$.

1. Introduction

The continuous and accurate monitoring of carbon dioxide (CO$_2$) 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 CO$_2$ are the infrared (IR) detector [6], used almost exclusively for sensing gaseous CO$_2$, and the Severinghaus electrode [7], used mainly for sensing dissolved CO$_2$; neither device is inexpensive, nor easy...
to maintain or use [8-9]. In recent years, there has been a growing interest in the
development of optical CO₂ sensors [10]. Such sensors are usually based on fluorescence
intensity [11-13], or UV/Vis absorbance, changes [14-16] exhibited by encapsulated pH
indicators upon exposure to CO₂. Interest in such optical sensors is not surprising given that
optical sensors in general have many attractive features including: electrical isolation, low
noise interference, easily miniaturised, remote sensing, rapid-in-response, and usually low
cost.

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

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

\[ Q^+D^- \cdot xH_2O + CO_2 \leftrightarrow Q^+HCO_3^- \cdot (x - 1)H_2O \cdot DH \]  

(1)

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

Various groups have reported on such phase-transfer CO₂ indicators using a variety of
different Q'D·xH₂O-encapsulating materials, such as: ethyl cellulose [18-19], silicone [20-
22], polystyrene [23], and sol-gel-derived matrices [24–26]. The dynamic operational range
of these CO₂ sensors depends on various factors, including the nature of the encapsulating
medium and the pKₐ value of of the pH-indicator [27]. A major drawback exhibited by many
of these reported (usually solvent-based) CO₂ indicators is a very limited shelf life (1-2 days
in the open air) probably due to the presence of other acidic gases such as SO$_2$ or NO$_2$ 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 CO$_2$ indicators.

<table>
<thead>
<tr>
<th></th>
<th>D-</th>
<th>DH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{abs}$ (nm)</td>
<td>$\lambda_{em}$ (nm)</td>
</tr>
<tr>
<td>HPTS aqueous solution</td>
<td>455</td>
<td>510</td>
</tr>
<tr>
<td>HPTS/TOAH/EC ink film*</td>
<td>467</td>
<td>517</td>
</tr>
<tr>
<td>HPTS- pigment</td>
<td>470</td>
<td>512</td>
</tr>
<tr>
<td>HPTS- film</td>
<td>475</td>
<td>515</td>
</tr>
</tbody>
</table>

*A Accessed from ref [31].

A particularly popular pH-sensitive fluorescence dye, for use in CO$_2$ 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 $\lambda_{em} = 510$ 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 commercially availability and low cost [30]. A list of some of the reports of CO$_2$ 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.](image-url)
Table 2: Details of previous HPTS based luminescent CO$_2$ sensors.

<table>
<thead>
<tr>
<th>Type</th>
<th>Encapsulation medium</th>
<th>Base (Phase Transfer Agent)</th>
<th>%CO$_2$ (S=1/2)</th>
<th>Response time (s)</th>
<th>Recovery time (s)</th>
<th>$E_a$ (kJ/mol)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogel</td>
<td>Agarose</td>
<td>Sodium bicarbonate</td>
<td>14.7</td>
<td>$t_{90,\downarrow} = 15$</td>
<td>$t_{90,\uparrow} = 34$</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>Organic polymer</td>
<td>Ethyl cellulose (EC)</td>
<td>TOAH</td>
<td>0.26</td>
<td>$t_{90,\downarrow} = 4.3$</td>
<td>$t_{90,\uparrow} = 7.1$</td>
<td>21</td>
<td>30, 31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TOAH</td>
<td>ca. 0.25</td>
<td>$t_{90,\downarrow} &lt; 24$</td>
<td>$t_{90,\uparrow} = 282$</td>
<td>-</td>
<td>33*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TOAH</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>Silicone rubber</td>
<td>silicone</td>
<td>CTMAH</td>
<td>0.25</td>
<td>$t_{90,\downarrow} = 42$</td>
<td>$t_{90,\uparrow} = 120$</td>
<td>-</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silicone plus cellulose derivatives*</td>
<td>TOAH</td>
<td>10</td>
<td>$t_{100,\downarrow} = 420$</td>
<td>$t_{100,\uparrow} = 720$</td>
<td>-</td>
</tr>
<tr>
<td>Ormosil</td>
<td>Silica sol gel</td>
<td>CTMAH</td>
<td>10</td>
<td>$t_{90,\downarrow} &lt; 60$</td>
<td>$t_{90,\uparrow} &lt; 180$</td>
<td>21.9</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TOAH</td>
<td>9.1</td>
<td>$t_{90,\downarrow} &lt; 60$</td>
<td>$t_{90,\uparrow} &lt; 60$</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TOAH</td>
<td>3.5</td>
<td>$t_{90,\downarrow} = 1.7$</td>
<td>$t_{90,\uparrow} = 38.5$</td>
<td>-</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silica sol-gel doped with silica particles</td>
<td>TOAH</td>
<td>3.8</td>
<td>$t_{90,\downarrow} = 9.8$</td>
<td>$t_{90,\uparrow} = 195.4$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Silica sol-gel plus PTFE cover</td>
<td>CTMAH</td>
<td>5%</td>
<td>$t_{90,\downarrow} = 420$</td>
<td>$t_{90,\uparrow} = 720$</td>
<td>-</td>
</tr>
</tbody>
</table>

TOAH: tetraoctylammonium hydroxide; TBAH: tetrabutyrammonium hydroxide; CTMAH: cetyltrimethylammonium hydroxide; *: used for making dissolved CO$_2$ measurements (all other entries are for gas phase CO$_2$ measurements)

At this point it is useful to define the general parameter, $R$, based on experimentally measured luminescence intensity values, for a fluorescence-based CO$_2$ sensor, made at the wavelength of maximum emission for D$^-$ alone, i.e. $\lambda_{\text{max}}$ (D$^-$), as a function of different %CO$_2$.

From reaction (1), it follows:

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

where [HD] and [D$^-$] are the concentrations of the protonated and deprotonated forms of the dye, respectively. $I_0$ is the value of intensity of the dye at $\lambda_{\text{max}}$ (D$^-$) when %CO$_2$ = 0 (i.e.
when all the dye is in its deprotonated form) and $I_\infty$ 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:

$$R = \frac{[HD]}{[D^-]} = \alpha \times \%CO_2$$  \hspace{1cm} (3)

where $\alpha$ is a proportionality constant. Other work shows that the value of $\alpha$ 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 $\frac{1}{2}$, 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 ‘$\alpha$’ (= 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 highhumidity 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 (tetramethylammonium 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 HTPS-pigment for subsequent extrusion in LDPE. Previous work carried out by this group [42] reported that water-based CO$_2$ 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 HTPS-pigment for subsequent extrusion in LDPE. The hydrophilic silica was more compatible with the aqueous base (Q$^+$OH$^-$, xH$_2$O) and produced brighter, more reproducible and much more stable film sensors. The hygroscopic nature of hydrophilic SiO$_2$ 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], CO$_2$-indicators appear much more stable when stored under humid conditions, or in water.

The SiO$_2$ (Aerosil 130 hydrophilic fumed silica) was a gift from Evonik (BET surface area = 130 ± 25 m$^2$/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 CO$_2$ and Argon. 5% CO$_2$-air mixture and 1% CO$_2$-air mixture were purchased from BOC gases. Gas steams with other loadings of CO$_2$ 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-SiO$_2$ pigment (i.e. ‘HPTS-pigment’) appeared bright yellow in the absence of CO$_2$, and pale yellow/colourless in the presence of CO$_2$, 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 CO$_2$.](image)

2.3 Preparation of the HPTS-LDPE film
The CO$_2$-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$^\circ$C here, so as avoid the thermal degradation of the dye, which occurs at temperatures > 180$^\circ$C. Thus, other work carried out using the higher molecular weight polyolefin, polypropylene, which requires a much higher, > 200$^\circ$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 CO$_2$, namely: $9.8\times10^{-13}$ cm$^3$/(273 K; $10^5$ Pa). cm/(cm$^2$.s.Pa), although this is ca. 10x's less than ethyl cellulose [43]. More importantly, LDPE has a water vapour permeability ($68\times10^{-13}$ cm$^3$/(273 K; $10^5$ Pa). cm/(cm$^2$.s.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 CO$_2$ indicator film [30-
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 improves 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 HTPS-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 CO$_2$ 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 CO$_2$ exposure, (lower row, from left to right) under UV irradiation with or without CO$_2$ 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 CO$_2$/Ar gas blend under test. In this work with the wavelength
of excitation, $\lambda_{\text{ex}}$, was always set at 470 nm. The desired argon and CO$_2$ mixtures were generated using a Cole-Parmer gas blender.

2.5 Variation in relative humidity (RH)
A 100% relative humidity ($T = 21^\circ C$) humid gas, which was either: 5% CO$_2$ 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 $T = 21^\circ C$. 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 CO$_2$/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 %CO$_2$ 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% CO$_2$) and 100% CO$_2$ 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 CO$_2$, 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 CO$_2$ (i.e. due to its yellow D$^-$ form- the blue line in figure) and (ii) at 410 nm in the presence of CO$_2$ (due to its colourless DH form, the red line in Fig. 4).
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, $\lambda_{em}$ 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 %CO$_2$, as a series of different Ar/CO$_2$ gas mixtures.

Fig. 6: Plot of the relative fluorescence intensity from the HPTS-pigment (taken from Fig. 5) as a function of the %CO$_2$. Insert data reveals an α value of $6.4 \pm 0.3\%^{-1}$ ($R^2 = 0.9924$), where $\frac{(I_0-I)}{(I-I_{\infty})} = R = \alpha%CO_2$. 
The results of this work showed that the initial high level of emission exhibited by the deprotonated form of the HPTS-pigment, D', (λ = 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.

![Graph showing variation in luminescence intensity](image)

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 (t₅₀↓) = 2 s, and a 50% recovery time (t₅₀↑) = 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(CO₂) = 0.14 cm²s⁻¹) [46].
3.2 The HPTS-LDPE film CO\textsubscript{2} 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 CO\textsubscript{2} (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 %CO\textsubscript{2}. A R vs %CO\textsubscript{2} plot of the data revealed a %CO\textsubscript{2}(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 CO\textsubscript{2} sensor film, when compared to many of the other reported HPTS-based CO\textsubscript{2} 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 %CO\textsubscript{2}(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 CO\textsubscript{2} sensitivity as their solvent-based EC ink CO\textsubscript{2} sensor counterparts.

![Diagram of a typical plot of the relative fluorescence intensity from the HPTS-LDPE film as a function of the %CO\textsubscript{2}.](image)

Fig. 8: Diagram of a typical plot of the relative fluorescence intensity from the HPTS-LDPE film as a function of the %CO\textsubscript{2}. Insert data reveals an α value of 3.48 ± 0.14%\textsuperscript{−1}. (R\textsuperscript{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% CO$_2$ and back again was carried out and the results are illustrated in Fig. 9.

![Graph](image)

**Fig. 9:** Repeat response and recovery of HPTS-LDPE film was tested by purging alternative streams of 5% CO$_2$ and pure Ar.

An analysis of the data in Fig. 9 revealed a 50% response time ($t_{50↓}$) of 120 s and 50% recovery time ($t_{50↑}$) of 2340 s. As noted earlier, a film thickness, $\ell$, of ca. 55-60 $\mu$m, 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 CO$_2$ indicator ink films, see table 2, which are also generally much thinner, typically 1-8 $\mu$m [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 CO$_2$ indicators, where the observed change in fluorescence intensity, or absorbance, is inversely proportional to the partial pressure of CO$_2$, $P$(CO$_2$), which in turn is proportional to the %CO$_2$. In most cases, these response and recovery times depend, respectively, directly upon the rate of diffusion of the CO$_2$ into and out of the indicator film, with a proportionality constant that is inversely proportional to $\ell^2$ [47]. Thus, it follows, by using a narrower film die in the extruder, it will
It is 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.

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

*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 %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 %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 %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 $\alpha$ 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 ± 2 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).

3.4 Effect of humidity

Many reported CO$_2$ optical sensors exhibit a sensitivity (as measured by the measured value for $\alpha$) 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$^\circ$C, the value for $\alpha$ 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.

Fig. 10: R versus %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 $(I_0-I)/(I-I_\infty)= R = \alpha$ %CO$_2$. 

![Graph showing R versus %CO$_2$ for HPTS-TBAH pigmented LDPE film at various temperatures](image-url)
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

<table>
<thead>
<tr>
<th>Medium</th>
<th>α (%)</th>
<th>%CO₂ (S=½)</th>
<th>r²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry gas (RH=0)</td>
<td>3.4</td>
<td>0.29</td>
<td>0.9898</td>
</tr>
<tr>
<td>Humid gas (RH =0)</td>
<td>0.85</td>
<td>1.2</td>
<td>0.9923</td>
</tr>
<tr>
<td>water</td>
<td>0.084</td>
<td>12</td>
<td>0.9847</td>
</tr>
<tr>
<td>1M NaCl aqueous solution</td>
<td>0.11</td>
<td>9.1</td>
<td>0.9997</td>
</tr>
<tr>
<td>0.01M HCl aqueous solution</td>
<td>0.091</td>
<td>11</td>
<td>0.9786</td>
</tr>
</tbody>
</table>

*: for all dissolved CO₂ measurements the HPTS-LDPE film was soaked overnight in water prior to testing and the associated error is ± 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 ≥ 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 (dop) dyes, reported recently by Schutting et al [34], which was used to create a number of different, sensitive EC-based, CO$_2$ 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: OSLON; 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 CO$_2$.

3.7 Detection of dissolved CO$_2$

Another striking advantage of the HPTS-LDPE film CO$_2$ sensor, over that of most other optical CO$_2$ 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 CO$_2$ 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 deactivated most CO$_2$ 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 CO$_2$-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 CO$_2$ sensor. A rather nice demonstration of the ability of the HPTS film to function as a CO$_2$ 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 CO$_2$-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).
If placed in 0.01 M HCl the film remains exactly as if in still water, unless CO$_2$ is bubbled through, whereupon it will decolourise, irreversibly, as shown in Fig. 11 by the film in carbonated water.

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

It is common practice when using CO$_2$ optical indicators for the measurement of dissolved CO$_2$ to protect the dye in the indicator film from protonation through the use of top-coat, thin layer of a gas (i.e. CO$_2$ 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 CO$_2$ indicator to monitor, without interference from ions in the solution under test, the partial pressure of CO$_2$ 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 CO$_2$-based indicator reported here is highly resistant to dye leaching, which, in other CO$_2$ 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,
dissolved in the water under test and allows the film to operate as a dissolved CO$_2$ indicator in 0.01 M HCl, for at least 12 h.

In aqueous solution, be it with, or without, salt or acid, the sensitivity (i.e. the value of $\alpha$) of the HPTS-LDPE film towards CO$_2$ was found to be approximately the same but greatly reduced, (typically by a factor of ca. 37), compared to that for gaseous CO$_2$ measurements ($\text{RH} = 0$), so that the $\%\text{CO}_2(S=1/2)$ values increased from ca. 0.29% to ca. 10.7%, see table 4; although, in all cases the film exhibited a reversible response towards CO$_2$ and so recovered its initial luminescence and colour in the absence of CO$_2$, as indicated by the photographs in figure 11. Although the exact cause for the marked decrease in CO$_2$ sensitivity of the HPTS-LDPE film in aqueous solution is not clear, it is likely to be associated with the significant change in the microenvironment surrounding the encapsulated HPTS-silica pigment particles due, in turn, to an increased water content of the film. Evidence for this is provided by the observation that the absorbance $\lambda_{\text{max}}$ for the film shifts from the usual value of 475 nm for a dry film, to 455 nm for the HPTS-LDPE film in water, coupled to the fact that the absorbance $\lambda_{\text{max}}$ for HPTS dissolved in water is also 455 nm (see table 1). The effects produced by an increase in polarity of the microenvironment, signified by the negative shift in the $\lambda_{\text{max}}$ of HPTS and brought about by the immersion of the film in water, are likely to include: (i) a decrease in the $pK_a$ of HPTS [18] (for example the $pK_a$ of acetic acid is 15.5 in (non-polar) dichloroethane, but 4.8 in water) [51] and (ii) a decrease in the solubility of CO$_2$ (for example the solubility of CO$_2$ is 17 times higher in trichloromethane than it is in water [52]). Both of these effects are likely to produce a measurable decrease in the CO$_2$ sensitivity, exhibited by the HPTS-LDPE film, when the film is highly hydrated as opposed to dry. It is also worth noting that this overall loss of sensitivity, when in water, is readily reversed by returning the film to a dry atmosphere.

4 Conclusions

The highly CO$_2$ sensitive fluorescence HPTS-pigment ($\%\text{CO}_2(S=1/2) = 0.16$) and extruded plastic HPTS-LDPE film ($\%\text{CO}_2(S=1/2) = 0.29$) presented here exhibit a sensitive and reversible response to CO$_2$ over a wide range of concentration. The HPTS CO$_2$ sensitive plastic film can be used in water and acid solution ($\text{pH} = 2$) to detect dissolved CO$_2$ without the dye leaching out from the plastic. Such properties make the HPTS plastic film a
promising CO₂ sensor for detecting and measuring both gaseous and dissolved CO₂ levels. The HPTS plastic film has a shelf life over six months when stored in the dark and ambient atmospheric conditions, but, like many CO₂ optical sensors, it is sensitive to changes in humidity and temperature. This suggests that the HPTS-LDPE film optical sensor is best used in areas where no significant changes in RH and T are expected, and the measurement of the ambient level of CO₂ is important, such as in modified atmosphere food packaging [53].

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


