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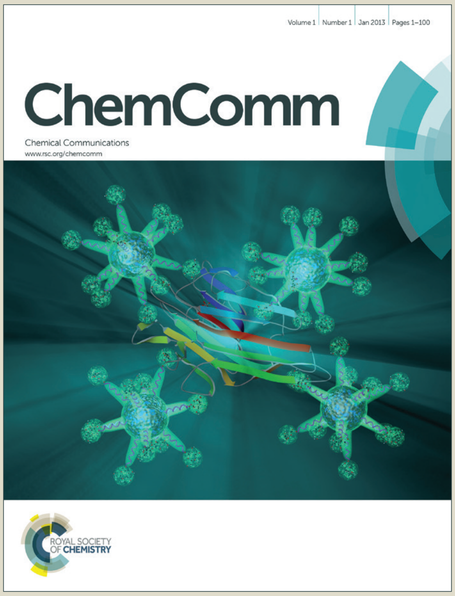

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A new chromo-fluorogenic probe based on BODIPY for NO_2 detection in air

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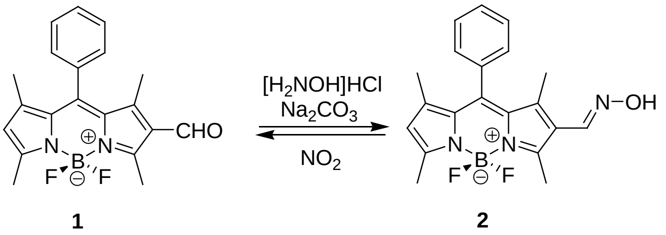
A novel colorimetric probe for the selective and sensitive detection of NO_2 in solution and in air based in a BODIPY core containing an oxime group has been prepared.

The selective and sensitive detection of toxic gases is one of the most promising applications of optical probes and the search of new sensing systems has been investigated with increasing intensity in last years. In this context nitrogen dioxide (NO_2) is one of the most prevalent and dangerous gases. There are several sources of this pollutant which are mainly related with un-vented gas stoves and heaters in addition to tobacco smoke.[1] Nitrogen dioxide is a highly reactive oxidant and corrosive and it acts mainly as an irritant affecting the mucosa of eyes, nose, throat, and respiratory tract.[2] Moreover extremely high-dose exposure to NO_2 may result in pulmonary edema and diffuse lung injury, whereas continued exposure to high NO_2 levels can contribute to the development of acute or chronic bronchitis. Even low level NO_2 exposure may cause increased bronchial reactivity in some asthmatics, decreased lung function in patients with chronic obstructive pulmonary disease and increased risk of respiratory infections, especially in young children.[3] No standards have been agreed upon for nitrogen oxides in indoor air, moreover ASHRAE and the US EPA National Ambient Air Quality Standards list 0.053 ppm as the average 24-hour limit for NO_2 in outdoor air.[4] However NO_2 levels in certain cities and at certain hours can reach much higher values of near 100 ppm.

Traditionally electrochemical sensors are usually used for detection of NO_2 in real labor environments, however interference from coexisting gases have been reported to be a problem in these devices. Moreover recent alternative approaches for detecting NO_2 such as laser-based photoacoustic spectroscopy,[5] surface acoustic wave (SAW),[6] transition metal oxide devices[7] carbon quantum dot-functionalized aerogels,[8] or ozone treated graphene have been reported.[9] In fact there is an interest in the design of new sensors capable of selectively detect NO_2. In this context chromo-fluorogenic probes are highly appealing for real-time monitoring and because they require of very inexpensive instrumentation. Moreover, in certain circumstances colour modulation can even be observed to the naked eye making chromo-fluorogenic approaches highly attractive for certain applications. However, despite the inherent advantages of optical probes the number of publications related to the design of molecular chemodosimeters for NO_2 detection is very scarce.[10]



Scheme 1. Structure of the BODIPY derivatives **1** and **2**.

Following our interest in the development of chromo-fluorogenic probes for toxic gases, we show herein a new chemosensor able to detect selectively the presence of NO_2 both in solution and in air (see Scheme 1). The design of the probe is based in the ability of NO_2 to react with oximes and give the corresponding carbonyl group under very soft conditions.[11] Moreover we have used as dye a BODIPY core which are a class of well-known fluorophores with widespread applications as fluorescent probes due to their valuable characteristics, such as high molar absorption coefficients and high quantum yields leading to intense absorption and fluorescence bands.[12]

Probe **2** was easily prepared from the corresponding aldehyde 2-formyl-8-phenyl-1,3,5,7-tetramethylboron-dipyrromethene (**1**). Moreover compound **1** was readily prepared 8-phenyl-1,3,5,7-tetramethylboton-dipyrromethene[13] by oxidation with DMF and $POCl_3$.[14] Probe **2** was then obtained by reaction of **1** with hydroxylamine hydrochloride under mild basic conditions in

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ethanol:water.[15] Compound **2** was fully characterized by ^{1}H NMR, ^{13}C NMR and MS (see Supporting Information for details). The oxime in **2** is electronically connected to the BODIPY core and it was expected that its transformation to the corresponding aldehyde in the presence of NO_2 would result in a significant optical change.

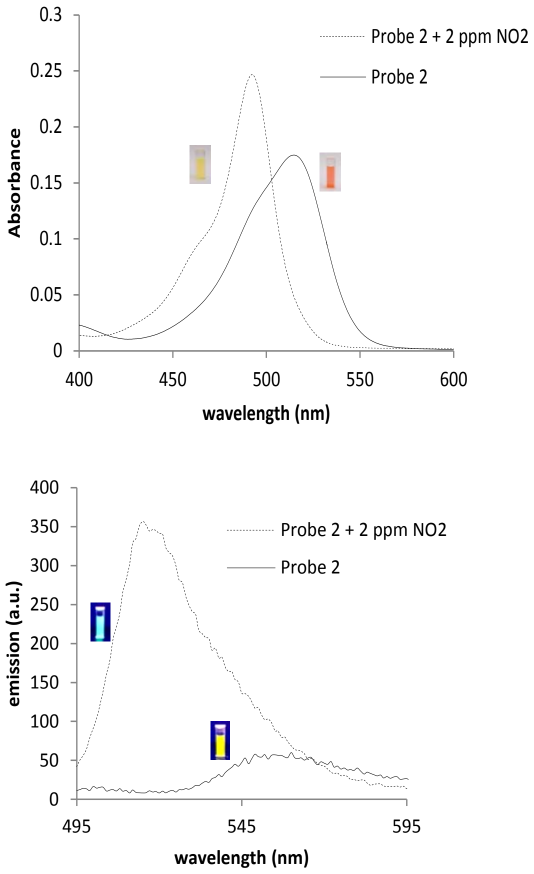

Figure 1. a) UV (a) fluorescence (b) spectra and spectra of probe **2** (acetonitrile, 10^{-5} M) alone and after bubbling air containing NO_2 at a concentration of 2 ppm. Insets display the visual changes both in color and fluorescence.

Acetonitrile solutions of probe **2** showed a visible absorption band at 515 nm (log $\varepsilon = 4.2$). Moreover the probe was weakly fluorescent due to C=N isomerization[15] with an emission band centered at 560 nm ($\lambda_{exc} = 500$ nm) and a quantum yield of only 0.19 (relative to Rhodamine B in EtOH ($\lambda_{exc} = 500$ nm)). Bubbling of air containing NO_2 at a concentration of 2 ppm to acetonitrile solutions of probe **2** immediately resulted in clear optical response. In particular a hypsochromic shift of the absorption band from 515 nm to 492 nm (log $\varepsilon = 4.4$) was observed (see Figure 1a). Moreover a remarkable emission change was also found (see Figure 1b); in the presence of NO_2 the weak emission at 560 nm disappeared and a new highly emissive band at 515 nm ($\lambda_{exc} = 485$ nm, $\phi = 0.77$) evolved. This remarkable chromo-fluorogenic response was visible to the naked eye (see also Figures 1 and 2). Optical changes were attributed to the transformation of the oxime **2** into the corresponding aldehyde **1** that is strongly fluoresecent[14] ($\phi = 0.77$ relative to Fluorescein at pH=8.06 ($\lambda_{exc} = 490$ nm)). This was clearly demonstrated via a simple comparison between ^{1}H NMR and UV spectra of the reaction product between **2** and NO_2 and these of aldehyde **1**. From additional titration experiments of **2** with NO_2 limits of detection (LOD) of 0.56 ppm (from UV-vis) and 0.46 ppm (from fluorescence) were determined.

Despite this interesting optical response of probe **2** in solution, the detection of NO_2 in gas phase is of greater importance. Therefore, and encouraged by the sensitive response observed with **2** in acetonitrile, in an attempt to extend the application of **2** to real-time monitoring, we decided to take a further step and developed test strips for the colorimetric detection of NO_2 in air. To this end, hydrophobic polyethylene oxide films containing probe **2** were prepared. Sensing films were readily obtained by mixing **2** and polyethylene oxide (Mw 400,000 Dalton) in dichloromethane. The mixture was then poured into a glass plate and kept in a dry atmosphere for at least 24 h (see Supporting Information). In a typical assay, films were placed into a container holding air and NO_2 (1 ppm). Immediately a clear color modulation from pink to pale yellow was observed (see Figure 2). From additional experiments using the polyethylene oxide membrane containing **2** and different amounts of NO_2 in air a visual limit of detection of 0.1 ppm was determined after ten minutes exposure. Moreover Figure 2 also show a photograph of the emission changes (excitation using a conventional UV lamp) of the sensing polyethylene oxide membrane in the absence and presence of NO_2 also at a concentration of 1 ppm. Using emission changes a visual LOD of 0.1 was determined for the detection of NO_2 in air after ten minutes exposure. These LOD are lower than the alarm threshold of 400 µg/m^3 (ca. 0.2 ppm) established by the European Community for nitrogen dioxide.

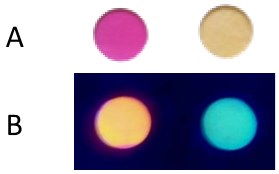

Figure 2. Sensing polyethylene oxide membranes containing probe **2**. A) Colour modulation of the sensing film in absence (left) and presence (right) of NO_2 (1 ppm) in air. B) Emission of the sensing film (excitation at 254 nm) in absence (left) and presence (right) of NO_2 (1 ppm) in air.

One important issue in relation to the design of probes for pollutant gases is the role played by potential interferents or false-positive outcomes produced by other species. Bearing this concept in mind, the reactivity of probe **2** with other hazardous gases (i.e. NO, CO_2, H_2S, SO_2) was also studied. Moreover the probe was also tested in the presence vapours of acetone, hexane, chloroform, acetonitrile and toluene. Polyethylene oxide films containing probe **2** were prepared and the films were placed into a container holding the corresponding gas. In all cases probe **2** displayed a remarkably selective response for NO_2 in air. In particular no reaction was detected in the presence of NO, CO_2, H_2S and SO_2 at very high concentrations (up to 100 ppm). Moreover, no colour or emission changes were observed in the presence of the volatile organic

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compounds such as acetone, hexane, chloroform, acetonitrile and toluene (up to 100 ppm in air). In addition it was also observed that no colour changes of the probe were observed in the presence of water vapour. Such behaviour indicated that there was no reaction between **2** and these gases tested, thus rendering **2** a suitable selective probe for the detection of NO_2. In a final experiment the membrane containing **2** was introduced into a container with all the studied vapours for 24 h yet no change in the colour of the probe was observed. In contrast, when the same experiment was carried with the additional presence of NO_2 the expected colour change took place.

In summary, we reported herein a simple probe based on a BODIPY derivative that was able to chromo-fluorogenically detect the presence of NO_2 both in solution and in air. In particular, the reaction of probe **2** with NO_2 induced in the transformation of the oxime to an aldehyde. The conversion of **2** in **1** resulted in a hypsochromic shift of the absorption band concomitantly with a colour change from pink to orange. In addition a strong enhancement of the fluorescence emission together with a blue shift of the band was also observed rendering **2** a fluorimetric off-on sensing method for NO_2. Notably the signalling ability of **2** was also retained when incorporated onto polyethylene oxide membranes, which allowed the development of simple test strips for the chromo-fluorogenic sensing of NO_2 in air with a limit of detection of ca. 0.1 ppm. In addition, probe **2** was highly selective and allowed the optical detection of NO_2 in presence of other pollutant gases, water vapour and volatile organic compounds.

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Notes and references

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