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Additional Information

# A new simple chromo-fluorogenic probe for NO<sub>2</sub> detection in air

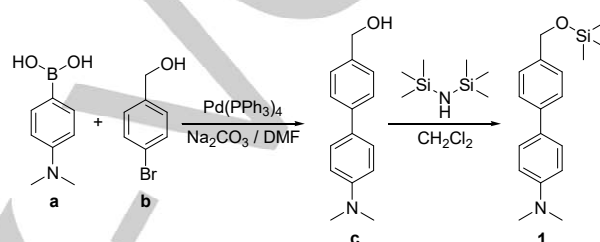
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**Abstract:** A new chromo-fluorogenic probe, consisting on a biphenyl derivative containing both a silylbenzyl ether and a *N,N*-dimethylamino group, for NO<sub>2</sub> detection in gas phase has been developed. A clear color change from colorless to yellow together with an emission quenching was observed when the probe reacted with NO<sub>2</sub>. A limit of detection to the naked eye of ca. 0.1 ppm was determined and the system was successfully applied to the detection of NO<sub>2</sub> in realistic atmospheric conditions.

Nitrogen dioxide, (NO<sub>2</sub>) is formed when fossil fuels such as coal, oil, gas or diesel are burned at high temperatures. On-road sources like cars, trucks, and buses are the largest sources of emissions, followed by power plants, diesel-powered heavy construction equipment and other movable engines, and industrial boilers. NO<sub>2</sub> can also form indoors when fossil fuels such as wood or natural gas are burned. Moreover when heaters or stoves are not vented fully to the outside, higher levels of NO<sub>2</sub> can be reached indoor. Due to the ubiquitous presence of this gas in the atmosphere the development of selective and sensitive detection methods is a timely area of research. However, in spite of the well-known NO<sub>2</sub> toxicity, no standards have been agreed upon for nitrogen oxides in indoor air. ASHRAE and the US EPA National Ambient Air Quality Standards list 0.053 ppm as the average 24-hour limit for NO<sub>2</sub> in outdoor air.<sup>1</sup> However it has been found that NO<sub>2</sub> levels in certain cities and at certain hours can reach values near 100 ppb. Nitrogen dioxide causes a range of harmful effects on the lungs such as increased inflammation of the airways, worsened cough and wheezing, reduced lung function, increased asthma attacks and increased susceptibility to respiratory infection.<sup>2</sup>

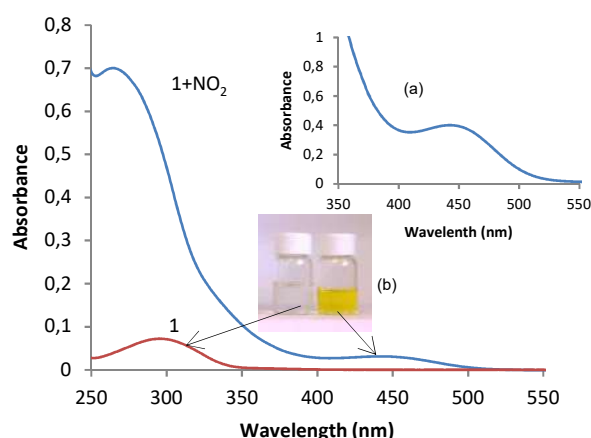
Different approaches for NO<sub>2</sub> detection such as laser-based photoacoustic spectroscopy,<sup>3</sup> surface acoustic wave (SAW),<sup>4</sup> transition metal oxide devices<sup>5</sup> carbon quantum dot-functionalized aerogels,<sup>6</sup> or ozone treated graphene<sup>7</sup> have been described in the literature. However some of these methods

show certain limitations such limited selectivity, operational complexity, non-portability, difficulties in real-time monitoring and false positive readings. As an alternative to these protocols, the development of easy-to-use fluorogenic and chromogenic chemosensors has been gaining interest in recent years. Still, the number of publications related to the design of probes for NO<sub>2</sub> sensing is very scarce.<sup>8</sup>



**Scheme 1.** Synthetic procedure used to prepare probe 1.

Following our interest in the design of colorimetric probes for hazardous gases, we report herein a new probe for NO<sub>2</sub> detection both in solution and in gas phase. The probe consists of a biphenyl derivative containing a silylbenzyl ether and a *N,N*-dimethylaminophenyl group (compound 1, see Scheme 1). The sensing protocol relies in the well-known NO<sub>2</sub>-induced transformation of silylbenzyl ethers into the corresponding aromatic aldehydes which is a solvent-free oxidative deprotection procedure that occurs in practically quantitative yields and under very soft reaction conditions.<sup>9</sup> Moreover, an unexpected nitration of the *N,N*-dimethylaminobenzene ring was also observed (*vide infra*).



**Figure 1.** UV spectra of 1 (acetonitrile, 1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>) before and after exposure to air containing NO<sub>2</sub> at a concentration of 2 ppm for 10 min. Inset: (a) changes in the visible zone of probe 1 (acetonitrile, 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>) in the absence and (b) in the presence of NO<sub>2</sub> and visual colour changes.

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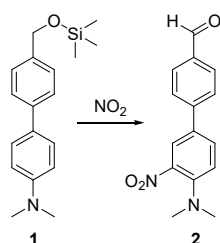
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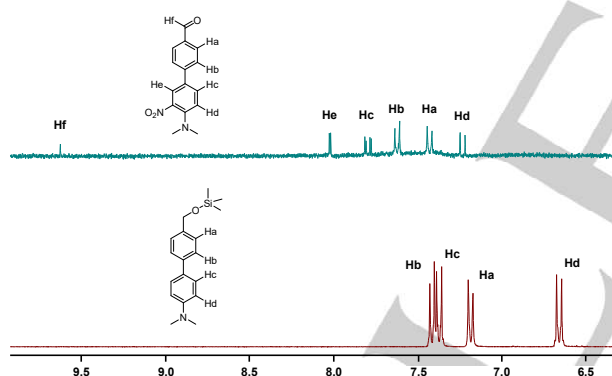
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Probe **1** was prepared following the synthetic pathway shown in Scheme 1. Pd(0) catalyzed cross-coupling reaction of the boronic acid derivative **a** with 4-bromohydroxymethylbenzene (**b**) gave rise to the corresponding hydroxymethyl biphenyl derivative (**c**).<sup>10</sup> Silylation of the hydroxyl group in **c** to obtain probe **1** was carried out using hexamethyldisilazane in dry CH<sub>2</sub>Cl<sub>2</sub>.<sup>11</sup> All compounds were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS (see Supporting Information).

In a first assay, the optical response of acetonitrile solutions of probe **1** was tested by putting them in contact with air containing 2 ppm of NO<sub>2</sub> from a commercial cylinder (10 minutes). Acetonitrile solutions of probe **1** showed an intense absorption band at 303 (log ε = 4.7). Upon exposure to NO<sub>2</sub> (g) a hypsochromic shift of the UV band from 303 to 253 nm (log ε = 5.2) was observed and a new absorption appeared in the visible region at 450 nm (log ε = 3.2) (see Figure 1). This band was responsible for the clear color change from colorless to yellow.



**Scheme 2.** Sensing NO<sub>2</sub> mechanism for probe **1**.

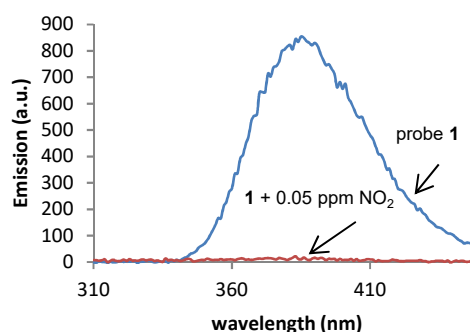


**Figure 2.** <sup>1</sup>H NMR spectra (CD<sub>3</sub>CN) of free **1** (down), and **1** after exposure to a nitrogen atmosphere containing NO<sub>2</sub> (g) (2 ppm) for 10 minutes (up).

In order to assess the mechanism of the chromogenic response, <sup>1</sup>H NMR studies with probe **1** in the absence and in the presence of NO<sub>2</sub> in CD<sub>3</sub>CN were carried out (see Figure 2). The aromatic zone of the <sup>1</sup>H NMR spectrum of probe **1** showed two pair of doublets at 7.18 (Ha) and 7.40 (Hb) ppm and at 6.65 (Hd) and 7.35 (Hc) ppm ascribable to the 1,4-disubstituted benzene rings. Upon NO<sub>2</sub> contact all the aromatic signals underwent a marked downfield shifts and a new singlet appeared at 9.65 ppm (Hf). Also the aromatic protons of the *N,N*-dimethyl aminobenzene moiety changed from a pair of doublets to three signals centered at 7.20 (d, Hd), 7.80 (dd, Hc) and 8.05 (d, He) ppm typical of an aromatic ring with a 1,2,4 tri-substitution pattern. Both facts suggested that, upon NO<sub>2</sub>

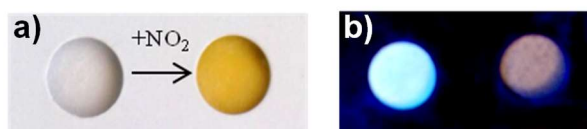
addition two reactions occurred, (i) an oxidative deprotection of the silyl ether and (ii) a nitration of the *N,N*-dimethyl aminobenzene ring to yield compound **2** (see Scheme 2). HRMS studies confirmed the formation of product **2** (*m/z* = 271.1068 corresponding to [2+H]<sup>+</sup>, see supporting information). It is important to remark that the presence of the trimethyl silyl moiety in **1** was mandatory in order to observe a clear colour modulation. Thus similar experiments with 4-dimethylamino-4'-hydroxymethyl biphenyl in the presence of NO<sub>2</sub> resulted in a complex mixture of products with no clear colour changes (data not shown).

In addition, acetonitrile solutions of probe **1** (1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>) were fluorescent and presented a broad emission band at 385 nm (λ<sub>ex</sub> = 303 nm, Φ = 0.76). The emission was also NO<sub>2</sub>-sensitive and a quenching was found when acetonitrile solutions of **1** were exposed to 0.05 ppm of this gas (see Figure 3). From UV-visible titration profile a limit of detection of ca. 7.2 ppb was calculated (using the 3s<sub>b</sub>/m procedure, where s<sub>b</sub> is the standard deviation of blank and *m* is the slope of the linear regression plot, see Supporting Info). The linear fitting of absorbance at 450 nm versus NO<sub>2</sub> concentration between 0.01 and 0.1 ppm could be used for the quantification of nitrogen dioxide. In addition to this, a clear optical response to the naked eye was found for NO<sub>2</sub> concentrations as low as ca. 0.1 ppm.



**Figure 3.** Fluorescence spectra of acetonitrile solutions of probe **1** (1.0 × 10<sup>-4</sup> mol dm<sup>-3</sup>) before and after exposure to air containing NO<sub>2</sub> at a concentration of 0.05 ppm.

Encouraged by the sensitive response to NO<sub>2</sub> observed with **1** and in order to extend the potential applicability of the probe to real monitoring, we decided to take a step further. For this purpose probe **1** was incorporated into a hydrophobic polyethylene oxide film (see Supporting Info) and the test strips prepared were placed into a container holding 1 ppm of NO<sub>2</sub> for 5 minutes. As seen in Figure 4 the colorless films clearly turned yellow upon exposure to air containing NO<sub>2</sub> at this concentration. A gradual color change from pale yellow to orange can be clearly observed in the 0.1 to 2 ppm range (see Supporting Info). Besides, changes in fluorescence were also observed by the naked eye with a conventional 254 nm UV lamp. The limit of detection to the naked eye of NO<sub>2</sub> in air, when using the polyethylene oxide films, was ca. 0.1 ppm, with a typical response time of less than 5 minutes.



**Figure 4.** Sensing polyethylene oxide membranes containing probe **1**. (a) Color modulation of the sensing film in absence (left) and presence (right) of NO<sub>2</sub> (1 ppm) in air. (b) Emission of the sensing film (excitation at 254 nm) in absence (left) and presence (right) of NO<sub>2</sub> (1 ppm) in air.

One important issue related 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, polyethylene oxide films containing **1** were prepared and placed into a container in the presence of other hazardous gases (i.e. CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>) or some volatile organic compounds (i.e. acetone, hexane, chloroform, acetonitrile and toluene). No color or emission changes were observed in the presence of these tested compounds even at concentration of 100 ppm. In addition, it was also found that moisture was unable to induce any chromo-fluorogenic change in the films containing probe **1**.

Once demonstrated the selective response of **1** in air, the potential use of the films to monitor the presence of NO<sub>2</sub> in more realistic conditions was also tested. In particular, films containing probe **1** were placed in a car tunnel in Valencia (Spain) with heavy daily traffic and with high levels of air pollution. At the same time NO<sub>2</sub> detection was also carried out by means of two independent passive samplers exposed on a 5 days basis that gave accumulative values of NO<sub>2</sub> of 193 and 186 ppb.<sup>12</sup> It was found that after these 5 days of exposition the color of the films visibly changed from colorless to yellow clearly indicating the presence of NO<sub>2</sub>.

In summary, we have developed herein a new chromogenic probe for the selective and sensitive detection of NO<sub>2</sub>. Probe **1** contains a trimethylsilyl ether moiety that is oxidized in the presence of NO<sub>2</sub>. Besides a nitration reaction of at the *N,N*-dimethylbenzene moiety takes place. Both reactions were responsible of the chromogenic detection. NO<sub>2</sub> sensing was achieved both in solution and in gas phase. Probe **1** allowed the simple colorimetric detection NO<sub>2</sub> with limits of detection lower than the generally accepted alarm threshold. Furthermore the response of probe **1** towards NO<sub>2</sub> was selective and other common gas pollutants (such as CO<sub>2</sub>, H<sub>2</sub>S and SO<sub>2</sub>) and volatile organic compounds (acetone, hexane, chloroform, acetonitrile and toluene) were unable to induce color modulation. Moreover probe **1** in polyethylene oxide membranes were satisfactorily used for the monitoring of NO<sub>2</sub> levels in real environmental samples (a tunnel with heavy daily traffic).

## Acknowledgements

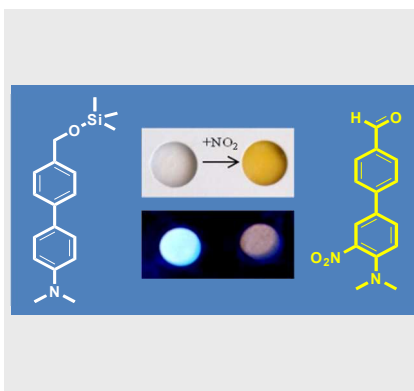
We thank the Spanish Government (MAT2012-38429-C04) and Generalitat Valenciana (PROMETEOII/2014/047) for support. SCSIE (Universidad de Valencia) is gratefully acknowledged for all the equipment employed. We thank Dr. A. Múñoz from the CEAM (Valencia-Spain) for her help for the development of the measures in real environment.

**Keywords:** NO<sub>2</sub> • detection • chromogenic • gas phase • sensing films

- [1] U.S. Environmental Protection Agency (EPA). Office of Environmental Health Hazard Assessment (OEHA). Non-cancer Health Effects (RELS). [California, DC, USA]: **1999**.
- [2] a) W. S. Tunnicliffe., P. S. Burge, J. G. Ayres, *Lancet*, **1994**, *344*: 1733-1736. b) M. Shima, M. Adachi *Int. J. Epidemiol.*, **2000**, *29*, 862-870.
- [3] A. Mukherjee, M. Prasanna, M. Lane, R. Go, I. Dunayevskiy, A. Tsekoun, C. Kumar, N. Patel, *Appl. Opt.*, **2008**, *47*, 4884-4887.
- [4] E. Nieuwkoop, M. J. Vellekoop, M. S. Nieuwenhuizen, A. W. Barendsz, *Sensor. Actuat.*, **1986**, *10*, 47-64.
- [5] a) W. K. Nomani, D. Kersey, J. James, D. Diwan, T. Vogt, R. A. Webb, G. Koley, *Sensor. Actuat. B: Chem.*, **2011**, *160*, 251-259. b) D. Zhang, Z. Liu, C. Li, T. Tang, X. Liu, S. Han, B. Lei, C. Zhou, *Nano Letters*, **2004**, *4*, 1919-1924. c) S. -W. Choi, A. Katoch, G. -J. Sun, P. Wu, S. S. Kim, *J. Mater. Chem. C*, **2013**, *1*, 2834-2841. d) X. Liang, S. Yang, J. Li, H. Zhang, Q. Diao, W. Zhao, G. Lu, *Sensor. Actuat. B: Chem.*, **2011**, *158*, 1-8.
- [6] R. Wang, G. Li, Y. Dong, Y. Chi, G. Chen, *Anal. Chem.*, **2013**, *85*, 8065-8069.
- [7] M. G. Chung, D. H. Kim, H. M. Lee, T. Kim, J. H. Choi, D. K. Seo, J. -B. Yoo, S. -H. Hong, T. J. Kang, Y. H. Kim, *Sensor. Actuat. B: Chem.*, **2012**, *166-167*, 172-176.
- [8] a) S. Ohira, E. Wanigasekara, D. M. Rudkevich, P. K. Dasgupta, *Talanta*, **2009**, *77*, 1814-1820. b) L. A. Juárez, A. M. Costero, M. Parra, S. Gil, F. Sancenón, R. Martínez-Máñez, *Chem. Commun.*, **2015**, *51*, 1725-1727. c) Y. Yan, J. Sun, K. Zhang, H. Zhu, H. Yu, M. Sun, D. Huang, S. Wang, *Anal. Chem.* **2015**, *87*, 2087-2093. d) Y. Yan, S. Krishnakumar, H. Yu, S. Ramishetti, L.-W. Deng, S. Wang, L. Huang, D. Huang, *J. Am. Chem. Soc.* **2013**, *135*, 5312-5315.
- [9] M. Javaheri, M. R. Naimi-Jamal, M. G. Dekamin, G. Kaupp, *Phosphorus Sulfur Silicon Relat. Elem.*, **2012**, *187*, 142-148.
- [10] C. M. Nunes, A. L. Monteiro, *J. Braz. Chem. Soc.*, **2007**, *18*, 1443-1147.
- [11] J. Marjan, *Tetrahedron*, **2012**, *68*, 3861-3867.
- [12] These data were submitted by Dr. A. Múñoz from the CEAM (Valencia, Spain) that were undergoing parallel experiments in the same car tunnel.

## COMMUNICATION

A new chromo-fluorogenic probe for NO<sub>2</sub> detection in gas phase has been developed



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**Page No. – Page No.**

**A new simple chromo-fluorogenic probe for NO<sub>2</sub> detection in air**