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Biphenyl derivatives containing trimethylsilyl benzyl ether or oxime groups as probes for NO₂ detection†

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Four probes based in the use of a biphenyl moiety and functionalized with trimethylsilyl benzyl ether (P1 and P3) and oxime (P2 and P4) groups have been prepared and tested as optical probes for the detection of NO₂. Reaction of NO₂ with acetonitrile solutions of P2–P4 resulted in the formation of aldehydes 7 and 8 with a concomitant redshift of the absorption bands. Probe P2 displayed a bathochromic shift of 45 nm upon reaction with NO₂ and was able to detect this poisonous gas at concentrations as low as 0.02 ppm. P2 was highly selective against NO₂ and other gases (*i.e.* NO, CO₂, H₂S, SO₂) and vapours of organic solvents (*i.e.* acetone, hexane, chloroform, acetonitrile or toluene) had no effect in the optical properties of the probe.

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Introduction

Nitrogen oxides (NOx) are formed in large quantities from fuel combustion in cars, trucks and power plants;¹ they are a major problem in urban areas and are linked to many respiratory diseases.² From a chemical point of view NOx mainly refers to the sum of nitric oxide (NO) and nitrogen dioxide (NO₂), although other nitrogen species can also be included, such as nitrous and nitric acids. Together with the adverse effects of direct exposure to NOx on human health, it is also remarkable its contribution to ground level ozone and fine particle pollution. Hence, strict regulations regarding levels of nitrogen oxides are currently applied by governments and the monitoring of NOx levels based in reliable analytical methods is of great interest.³

Among NOx species, NO₂ causes a range of harmful effects on lungs such as increased inflammation of the airways, worsened cough and wheezing, reduced lung function, increased asthma attacks and increased susceptibility to respiratory infection.⁴ All these problems are more important for children and older adults.⁵ Due to the ubiquitous presence of NO₂, the development of selective and sensitive sensing methods for its detection is a hot

area of research.⁶ 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 NO₂ in outdoor air.⁷ However, NO₂ levels in certain cities and at certain hours can reach even higher values (near 100 ppm).

Laser-based photoacoustic spectroscopy,⁸ surface acoustic wave (SAW),⁹ transition metal oxide devices,¹⁰ carbon quantum dot-functionalized aerogels,¹¹ or ozone treated graphene¹² are some reported analytical techniques used to detect/monitor NO₂ levels. However, some of these methods show certain limitations such as lack of specificity, limited selectivity, operational complexity, non-portability, difficulties in real-time monitoring and false positive readings. As an alternative to these instrumental procedures, the development of molecular chemosensors, constructed under the chemodosimeter paradigm, has been gaining interest in recent years. However, the number of publications related with optical probes for NO₂ detection is still relatively scarce.¹³

Bearing in mind our interest in the development of chemical sensors for gas detection,¹⁴ we report herein the synthesis and sensing behavior towards NO₂ of four new chemodosimeters based on the biphenyl chromophore. Among the different organic reactions involving NO₂ we decided to explore the utility of the generation of aromatic aldehydes from trimethylsilyl benzyl ethers¹⁵ and oximes¹⁶ in order to prepare suitable chemodosimeters for the detection of this poisonous and pollutant gas. These are reactions with quantitative yields, working at room temperature and at ambient pressure. The synthesized biphenyl probes (*vide infra*) possess electron donor groups (such as methoxide electronically connected with trimethylsilyl) or oxime (weak electron acceptor) moieties. The

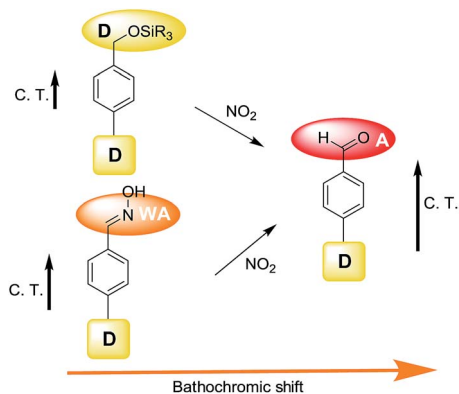
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Scheme 1 Sensing protocol used for NO₂ detection.

underlying idea is that, upon NO₂ reaction, the formed aldehyde (an electron acceptor moiety) would change the electronic properties of the chemodosimeter with subsequent shifts of the absorption bands (see Scheme 1).

Results and discussion

Probes **P1–P4** were prepared following the synthetic pathway depicted in Scheme 2. Pd(0) catalyzed cross-coupling reaction of the appropriate boronic acids (**1** and **2**) with 4-bromohydroxymethylbenzene (**3**) or 4-bromobenzaldehyde (**4**) yielded the corresponding biphenyl derivatives bearing hydroxyl (**5** and **6**) or aldehyde (**7** and **8**) moieties.¹⁷ Transformation of the hydroxyl group into the corresponding trimethylsilyl ether (probes **P1** and **P2**) was carried out using hexamethyldisilazane (HMDS) in dry CH₂Cl₂,¹⁸ whereas the probes containing oximes (**P3** and **P4**) were obtained with hydroxylamine hydrochloride in H₂O/MeOH mixed with sodium carbonate.¹⁹ All compounds were characterized by ¹H NMR, ¹³C NMR and MS (see ESI[†]). Acetonitrile solutions of the four probes (1.0 × 10⁻⁴ M) showed intense absorption bands in the 260–300 nm region with ε values ranging from 6000 to 15 000 M⁻¹ cm⁻¹.

In a first step, the absorption changes of probes **P1–P4** (1.0 × 10⁻⁴ M in acetonitrile) after bubbling 1 ppm of NO₂ during 5 min (obtained from a commercial cylinder), was tested.

Acetonitrile solutions of **P1** showed an absorption band centered at 277 nm that was redshifted to 285 nm upon

bubbling air containing 1 ppm of NO₂ (see Fig. 1). Interestingly, the same absorption band centered at 285 nm was observed upon bubbling NO₂ into acetonitrile solutions of probe **P3** (see also Fig. 1). The new absorption band, formed upon NO₂ bubbling, was ascribed to the formation of aldehyde **7** as a consequence of the oxidative deprotection of the trimethylsilyl ether moiety in **P1** and of the rupture of the oxime group in **P3**. In fact both, the UV and ¹H NMR spectra of aldehyde **7**, were fully coincident with that obtained after treatment of probes **P1** and **P3** with NO₂. Optically, the transformation of an electron donor (trimethylsilyl ether in **P1**) or a weak electron acceptor (oxime in **P3**) group into an aldehyde (with a marked ability to attract electronic density) yielding **7**, resulted in a bathochromic shift of the absorption band of **P1** and **P3**. A similar redshifts of the absorption bands of acetonitrile solutions of **P2** and **P4** was observed upon bubbling NO₂ (1 ppm in air) (see Fig. 1). These changes were ascribed to the reaction of NO₂ with the probes that yielded in both cases aldehyde **8**. Also in this case it was found that the UV and ¹H NMR spectra of aldehyde **8**, were fully coincident with that obtained after treatment of probes **P2** and **P4** with NO₂. The best sensing performance, in terms of a larger shift of the absorption band, was obtained for probe **P2**, for which a redshift of 45 nm (from 264 to 309 nm) was observed upon bubbling 1 ppm of NO₂. For this reason, further detailed studies with **P2** were carried out in order to assess the sensitivity and selectivity of this probe toward NO₂.

The limit of detection (LOD) using **P2** for NO₂ was determined by UV measurements by bubbling increasing amounts of NO₂ into an acetonitrile solution of the probe. As shown in Fig. 2, the absorbance at 309 nm was gradually enhanced when the concentration of NO₂ increases. From the titration profile a LOD as low as 0.02 ppm was calculated.

In a second step, the selectivity of **P2** was assessed. This is an important issue in the design of probes for pollutant gases in order to overcome potential interferents or false-positive readings produced by other species. Taking this into account, the potential reactivity of probe **P2** with other hazardous gases (*i.e.* NO, CO₂, H₂S, SO₂) or organic vapors (*i.e.* acetone, hexane, chloroform, acetonitrile, toluene) was tested by bubbling the selected species into acetonitrile solution of **P2** (1.0 × 10⁻⁴ M). None of the gases tested, at concentrations up to 100 ppm, induced changes in the UV

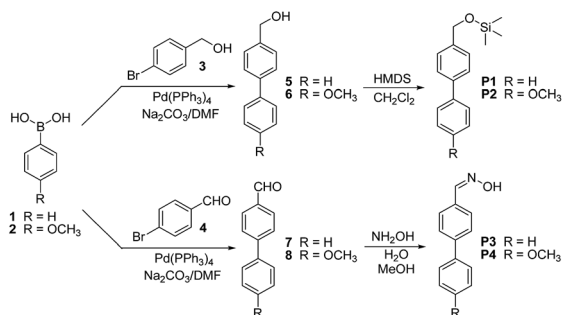
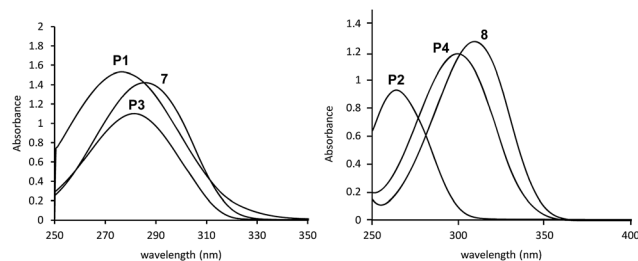
Scheme 2 Synthetic pathways used for the preparation of probes **P1–P4**.

Fig. 1 (Left) UV spectra of probes **P1** and **P3** (1.0 × 10⁻⁴ M in acetonitrile) alone and after bubbling 1 ppm of NO₂ during 5 min. (Right) UV spectra of probes **P2** and **P4** (1.0 × 10⁻⁴ M in acetonitrile) alone and after bubbling 1 ppm of NO₂ during 5 min. The reactions gave aldehydes **7** and **8**, respectively.

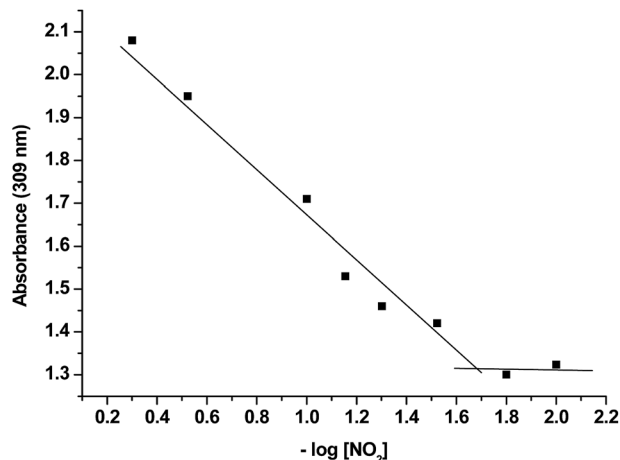


Fig. 2 Absorbance at 309 nm measured after bubbling increasing quantities of NO_2 into acetonitrile solutions of probe **P2** (1.0×10^{-4} M).

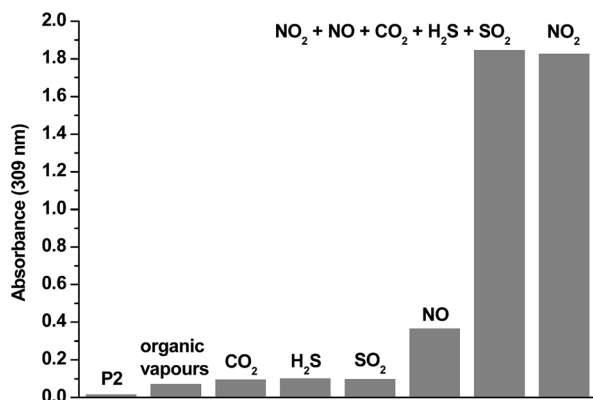


Fig. 3 Absorbance at 309 nm of probe **P2** alone and in the presence of selected potential interferents (all compounds at a concentration of 100 ppm).

spectra of probe **P2** indicating a high selective reaction of **P2** with NO_2 (see Fig. 3).

Competitive studies were also carried out. Thus, Fig. 3 shows that the absorption of the band at 309 nm of probe **P2** in the presence of a complex gas mixture ($\text{NO}_2 + \text{NO} + \text{CO}_2 + \text{H}_2\text{S} + \text{SO}_2$) was the same than that observed when NO_2 was used alone. This result demonstrated a high selective response of probe **P2** toward NO_2 and suggested its possible use for the detection/monitoring of this poisonous gas.

Conclusions

Four new biphenyl-based probes **P1–P4** have been synthesized and used for the selective recognition of NO_2 . For all four probes a bathochromic shift of the absorption bands was observed in the presence of the NO_2 and ascribed to the generation of an aromatic aldehyde upon reaction of NO_2 with trimethylsilyl benzyl ether or oxime groups contained in **P1–P2** and **P3–P4**, respectively. Among the prepared chemosensors, **P2** showed the higher shift of the absorption band and for this probe a LOD as

low as 0.02 ppm was determined for NO_2 detection. Moreover, the response of **P2** was highly selective and no reaction was found in the presence of NO , CO_2 , H_2S , SO_2 or organic vapors of acetone, hexane, chloroform, acetonitrile or toluene. We believe that these, or similar probes based in the same chemical reaction, can display a large potential as optical probes for the selective detection of NO_2 .

Experimental section

General remarks

Dichloromethane and acetonitrile were distilled from P_2O_5 under Ar prior to use. Silica gel 60 F254 (Merck) plates were used for TLC. Column chromatography was performed on silica gel. ^1H and ^{13}C NMR spectra were determined on a Bruker AV 300 spectrometer. Chemical shifts are reported in parts per million (ppm), calibrated to the solvent peak set. High-resolution mass spectra were recorded in the positive ion mode with a VG-AutoSpec mass spectrometer. Absorption and fluorescence spectra were recorded using a Shimadzu UV-2600 spectrophotometer.

Synthesis of biphenyl alcohols 5 and 6

In a typical run, the corresponding boronic acid (**1** for the synthesis of **5**; **2** for the preparation of **6**) (2 mmol) was added, to a solution of **3** (1 mmol) in DMF (20 mL) in the presence of sodium carbonate (6 mmol). Afterward, the flask was evacuated and refilled with argon. Then, tetrakis(triphenylphosphine) palladium(0) was added and the crude obtained heated at 100°C for 30 minutes with vigorous stirring. The resultant mixture was diluted with H_2O (10 mL) and Et_2O (10 mL), followed by extraction twice with Et_2O . The ethereal extract was collected and the solvent evaporated under vacuum. The final product was isolated by column chromatography on silica, with hexane/ethyl acetate (8 : 2) as eluent, yielding a colourless solid (65%).

5

(65%), colourless solid. ^1H NMR (300 MHz, DMSO) δ (ppm): 7.68–7.60 (m, 4H), 7.50–7.32 (m, 5H), 5.21 (t, $J = 5.7$ Hz, 1H), 4.54 (d, $J = 5.7$ Hz, 2H). ^{13}C NMR (75 MHz, DMSO) δ (ppm): 142.2, 140.5, 138.9, 129.3, 127.6, 127.4, 126.9, 126.7, 62.9.

6

(67%), colourless solid. ^1H NMR (300 MHz, DMSO) δ (ppm): 7.50–7.43 (m, 4H), 7.37 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 5.20 (t, $J = 5.7$ Hz, 1H), 4.53 (d, $J = 5.7$ Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ (ppm): 159.1, 132.9, 132.8, 132.7, 127.9, 127.4, 126.2, 114.7, 63.0, 55.6.

Synthesis of probes **P1** and **P2**

HDMS (40 mmol) was added to the corresponding alcohol (20 mmol) in dry dichloromethane (20 mL). The mixture was stirred at room temperature for 22 h (full conversion) under argon atmosphere. The solvent was evaporated and the crude was purified by column chromatography on silica using hexane/

ethyl acetate (8 : 2) as eluent, to give the probes **P1** (90%) or **P2** (93%) as white solids.

P1

(90%), white solid, mp 158–160 °C. ¹H NMR (300 MHz, DMSO) δ (ppm): 7.50 (m, 4H), 7.27 (m, 5H), 4.56 (s, 2H), 0.00 (s, 9H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 140.5, 140.3, 139.2, 129.2, 127.6, 127.3, 126.9, 63.8, –0.1. UV-Vis (acetonitrile) λ_{\max} = 277 nm (ϵ = 15 300 M⁻¹ cm⁻¹).

P2

(93%), white solid, mp 170–173 °C. ¹H NMR (300 MHz, DMSO) δ (ppm): 7.45 (m, 4H), 7.22 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 4.55 (s, 2H), 3.66 (s, 3H), 0.00 (s, 9H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 139.6, 138.8, 132.6, 129.2, 127.9, 127.3, 126.2, 114.6, 63.8, 0.1. UV-Vis (acetonitrile) λ_{\max} = 264 nm (ϵ = 8000 M⁻¹ cm⁻¹).

Synthesis of 7 and 8

4 (1.5 mmol) and **1** or **2** for **7** and **8** respectively (3 mmol) were dissolved in DMF (20 mL). Afterward, sodium carbonate (9 mmol) was added to this solution. The crude reaction was stirred under inert atmosphere for 30 min. Then, a catalytic amount of tetrakis(triphenylphosphine)palladium(0) was added and the reaction was stirred at 100 °C for 10 minutes. After this time water (10 mL) was added and the mixture was extracted with ethyl acetate (2 \times 20 mL). The organic phase was washed with brine (2 \times 20 mL), dried with MgSO₄ and evaporated to give the product.

7 was purified by silica column chromatography with hexane/ethyl acetate (9 : 1) to give a white crystalline solid (82%). ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.06 (s, 1H), 8.01 (m, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.78 (m, 2H), 7.50 (m, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ 193.20, 146.34, 139.27, 135.56, 130.62, 129.60, 129.06, 127.84, 127.60. HRMS (EI): m/z calc. for C₁₃H₁₀O 182.07 [M + 1]⁺ found: 183.0797 UV-Vis (acetonitrile) λ_{\max} = 289 nm (ϵ = 9500 M⁻¹ cm⁻¹).

8 was purified by silica column chromatography with hexane/ethyl acetate (8 : 2) to give a white crystalline solid (75%). ¹H NMR (300 MHz, DMSO-*d*₆) δ 10.03 (s, 1H), 8.01–7.93 (m, 2H), 7.91–7.85 (m, 2H), 7.74 (d, J = 9.0 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 3.82 (s, 3H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 192.9, 160.2, 145.9, 134.8, 131.3, 130.5, 128.7, 127.0, 114.9, 55.6. HRMS (EI): m/z calc. for C₁₄H₁₂O₂ 212.08 [M + 1]⁺ found: 213.0901. UV-Vis (acetonitrile) λ_{\max} = 309 nm (ϵ = 12 700 M⁻¹ cm⁻¹).

Synthesis of probes P3 and P4

The corresponding aldehyde (**7** and **8** for **P3** and **P4** respectively, 2 mmol) and hydroxylamine hydrochloride (2.2 mmol) were dissolved in methanol–water (1 : 1, 40 mL). A previously prepared solution of sodium carbonate (2 mmol) in water was slowly added and the reaction was stirred for 3 h at room temperature. Then, methanol was evaporated and the aqueous phase was extracted with ether (4 \times 40 mL). The organic phase

was washed with brine (1 \times 30 mL) and dried with MgSO₄. After evaporation of the solvent probes **P3** (99%) and **P4** (77%) were isolated as white solids.

P3

(99%), white crystalline solid, mp 142–145 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ 11.28 (s, 1H), 8.19 (s, 1H), 7.70 (m, 6H), 7.48 (m, 2H) 7.40 (m, 1H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 148.1, 141.2, 139.8, 132.6, 129.3, 128.1, 127.3, 127.3, 126.9. HRMS (EI): m/z calc. for C₁₃H₁₁NO 197.08 [M + 1]⁺ found: 198.0913. UV-Vis (acetonitrile) λ_{\max} = 282 nm (ϵ = 5800 M⁻¹ cm⁻¹).

P4

(77%), white crystalline solid, mp 165–167 °C. ¹H NMR (300 MHz, chloroform-*d*) δ 8.09 (s, 1H), 7.50 (m, 5H), 6.92 (d, J = 8.9 Hz, 2H), 5.23 (s, 1H), 3.79 (s, 3H). ¹³C NMR (75 MHz, DMSO) δ (ppm): 159.5, 148.2, 140.9, 134.8, 130.5, 128.7, 128.1, 127.0, 114.9, 55.6. HRMS (EI): m/z calc. for C₁₄H₁₃NO₂ 227.09 [M + 1]⁺ found: 228.1019. UV-Vis (acetonitrile) λ_{\max} = 300 nm (ϵ = 11 800 M⁻¹ cm⁻¹).

Limits of detection measurements

Increasing quantities of NO₂ gas from commercially available NO₂ cylinder were bubbled for 5 min through a solution of **P2** in acetonitrile. The UV spectra were recorded in 1 cm path length cells at 25 °C. Representation of the wavelength (nm) vs. concentration of NO₂ allowed the limit of detection to be calculated by using the eqn (1)

$$\text{LOD} = 3s_b/m \quad (1)$$

in which s_b is the standard deviation of blank measurements and m is the slope of the linear regression plot.

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