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Highly selective optical monitoring of O₂ via multiplechannels[†]

Anup Kumar,^a Rinkoo D. Gupta^b and Tarkeshwar Gupta^{*a}

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An optical probe for the detection of O_2 is outlined. The multiresponsive, redox-based sensor system is highly selective and response can be monitored optically either with conventional spectroscopic techniques, such as UV-Vis, IR or fluorescence, or by eye as a result of contrast colour changes from light yellow to dark red.

Molecular recognition¹ at low concentration is one of the most promising research areas in supramolecular chemistry² and sensor industries.³ Various host-guest interactions based molecular receptors⁴ have been developed for the detection of different analytes in solid, liquid or gas phases. Detection of gaseous analytes such as N2, CO, CO2, NO, NO2, O2 etc. have gained tremendous interest⁵ in environmental monitoring, green house effect monitoring and in scientific laboratories. A range of techniques have been reported for the detection of such analytes including titrometric, electrochemical, microscopic and optical. Optical detection is reported to be an ideal method, as it is simple to use, does not suffer from electrical interference and can be integrated in remote sensing devices.⁶ Recent, state-of-the-art optical detection of gaseous molecules is based on quenching of either emission or absorption intensity.⁷ However, "signal-on" detection of gases is relatively rare.8

Monitoring of molecular oxygen (O_2) is mandatory in various fields such as deep-sea environment, clinical analysis, ecosystem, atmosphere and diagonostic.⁹ Additionally, detection of O_2 levels in airtight containers such as glove boxes is crucial to carry out several O_2 /air sensitive reactions, where presently fume/flamebased O_2 detectors, such as dialkyzinc, are utilized. The existing O_2 detection approaches are principally based on traditional methods *i.e.*, the single signalling technique for a single sensory unit that too often suffers from selectivity and storage/stability problems.¹⁰ Therefore, there is continuous interest to formulate an efficient oxygen detection probe. To the best of our knowledge, multiplechannel analyses for O_2 using single molecules has not been reported so far.¹¹ Here, we aimed to construct a simple diaminebased optical probe to specifically detect the presence of molecular oxygen over wide range of other gases. Our strategy takes advantage of multiple-channel analyses for O_2 using a single organic molecule.

The rigorous catalytic hydrogenation reaction of 2-methoxy-4nitro-pheneylamine (1) under a H₂ atmosphere with added PtO₂ as the catalyst affords compound 2 in good yield (85%). Reaction of 2 with acetic anhydride in pyridine yields 3 that can be again easily converted to target compound 2 under acidic conditions (Scheme 1). Interestingly, 2 quickly transforms to 4 when exposed to air/O₂, whereas 1 and 3 do not respond to O₂ as judged by ¹H NMR and UV-Vis spectroscopy (Fig. S1,† S2†).

The ¹H NMR spectrum of 2 displays peaks at δ = 3.83 and 4.25 ppm due to the NH₂ proton; upon exposure to O₂ (300 ppm) it transforms to δ = 4.05 ppm, which could be assigned to the NH proton of 4 (Fig. 1a). Similarly, the peaks observed at *v* = 3352 and 3476 cm⁻¹, due to the NH₂ group of 2, transformed to *v* = 3385 cm⁻¹ in the FTIR spectrum of 4 (Fig. 1b). In addition, a new peak appears at *v* = 3186 cm⁻¹, which could be due to the formation of H₂O as a result of consecutive redox reactions. Interestingly, the successive intensity changes (decrease of NH₂ and increase of NH, H₂O peaks) as a function of O₂ concentration can be monitored with infrared and NMR spectroscopy (Fig. S3†). These data specify



 $\mbox{Scheme 1}$ Synthesis of optical probe (2), acylated product (3) and oxidative product (4).

^aDepartment of Chemistry, University of Delhi, New Delhi-110 007, India. E-mail: tgupta@chemistry.du.ac.in; Fax: +91-11-27662642; Tel: +91-11-27662642 ^bFaculty of Life Sciences and Biotechnology, South Asian University, New Delhi-110 021. India

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Fig. 1 Comparative ¹H-NMR (a) and FTIR (b) spectra of **2** (black color) and **4** (red color), showing changes after exposure to 300 ppm of O_2 for 10 min.

transformation of 2 (benzonoid form) into 4 (quinoid form)¹² upon exposure to O_2 (Scheme 1). This transformation was estimated at ~60% based on NMR data.

The UV-Vis spectrum of **2** in dry acetonitrile solution displays an intense peak in the UV region at $\lambda = 315$ nm ($\varepsilon = 30.245$ M⁻¹ cm⁻¹), which can be assigned as a π - π * transition of the "benzonoid" ring.¹³ Exposing the acetonitrile solution of **2** (degassed with N₂ for 15 min) with N₂ containing 100 ppm of O₂ for 10 min resulted in an increase of absorption intensity along with a slight red shift ($\Delta\lambda = 5$ nm) at $\lambda = 315$ nm. In addition, a new band appeared in the visible region at $\lambda = 502$ nm (Fig. 2). This optical behaviour can be rationalized by the formation of a "quinoid" ring promoted through oxidation of **2** by O₂.¹³

The response time of the sensor relies on the concentration of O₂. For instance, the saturation plateau for 100 ppm of O₂ was observed after ~90 min (Fig. 2, inset). However, a pronounced increase in absorption intensity was already marked after only 10 min (35% with respect to saturation values), which can be used as a response time of the sensor for this concentration of O₂. Further, precise determination of absorption intensity as a function of time or concentration is possible by integrating the entire absorption window ($\lambda = 275$ -600 nm). Apparently, the observed concentration

dependent response may make it possible to quantify the amount of O₂ present in a medium (Fig. 2, inset). The observed absorption intensity is proportional to the concentration of O₂ up to 300 ppm for 10 min exposure time (Fig. 2, inset) and shows a linear correlation ($R^2 = 0.99$), which is an important characteristic of sensors.

Notably, fluorometric detection of O2 is also possible with 2. In fact, 2 display an emission peak at $\lambda = 456$ nm (excitation $\lambda = 320$ nm) that shows interesting successive "turn-on" (wrt intensity) coupled with "turn-off" (wrt wavelength) optical responses upon exposure to O2 in the 50-300 ppm range (Fig. 3). The emission intensity of 2 increases (2.9 fold) along with a large blue shift ($\Delta \lambda$ = 45 nm) upon exposure to 300 ppm of O2 for 10 min. It is noteworthy that generally O_2 acts as a quencher for the electronically excited state of the luminescence molecules.¹⁴ In contrast, our sensor shows enhancement of emission properties after interaction with O₂ that could be due to positive inductive effects of the methoxy group along with increased conjugation in the oxidative product. Further, the variation of emission intensity or wavelength display linear behaviour upon stepwise increases of the concentration of O₂ in the detection range of 50-300 ppm (Fig. 3, inset) that is common for fluorescent probes.¹⁵ The detection limit was found at 15 ppm using the detection limit equation¹⁶ 3S. D./ σ , where S. D. is standard deviation of ten blank measurements and σ is the slope of emission intensity.

In order to have a practical application, the sensor should exhibit some sort of selectivity, which is normally based on hostguest interactions, ligand coordination, chemical reactivity, conformation change, *etc.* In the present case, the gas sensor **2** exhibits selectivity based on redox properties. Indeed, **2** displays a high degree of selectivity for O_2 since no considerable response was observed in both absorption (Fig. 4a) and emission (Fig. 4b) spectra upon exposure to pure CO, CO₂, Ar, N₂, H₂, CH₄ and C₂H₄ for 30 min each. Alternatively, a mixture of any of the above test



Fig. 2 Absorption intensity changes of **2** (1 × 10^{-5} M in CH₃CN) as a function of time upon exposure to O₂ (100 ppm in N₂). Saturation was reached after ~90 min. Inset shows: the enhancement of the peak area in the visible region ($\lambda = 275$ –600 nm) as a function of time at 100 ppm of O₂ (black dots) and as a function of concentration of O₂ at 10 min exposure time (blue dots).



Fig. 3 Monitoring of fluorescence intensity along with wavelength changes of **2** (1 $\times 10^{-5}$ M in CH₃CN) after exposure to various concentrations of O₂ in N₂ for 10 min, each ranging from 50 ppm (light grey), 100 ppm (magenta), 150 ppm (cyan), 200 ppm (yellow), 250 ppm (orange), 300 ppm (dark gray). Inset shows "turn-on" coupled with "turn-off" changes in intensity and wavelength.



Fig. 4 Representative bar chart showing % change in area under the peak for absorption (a) and emission (b) intensities of **2** (1×10^{-5} M in CH₃CN) after exposure to pure gas analytes (blue bar) and 300 ppm of O₂ in each gas analyte (black bar) for 10 min. 1, CO; 2, CO₂; 3, C₂H₄; 4, CH₄; 5, Ar; 6, N₂; 7, H₂; and 8, air.

gases with 300 ppm of O_2 show full response in both absorption and emission spectra (Fig. 4) and the colour change of the solution from pale yellow to dark red can be seen by eye.

More importantly, the O_2 detection and the simultaneous absorption/emission intensity changes of 2 were clearly followed by a gradual change in colour from pale yellow to pink and finally dark red that could be clearly seen by eye (Fig. 5). Other test gases did not induce any significant colour change of the solution. The "by-eye" detection of O_2 with contrast colour change renders this sensor suitable for practical application in scientific laboratories for the detection of O_2 level in conventional glove boxes or in organic solvents. Interestingly, the change in colour after exposure of O_2 (100–300 ppm) can also be monitored on test paper (see Fig. S4†).

Reversibility of a sensor is much sought-after in sensor engineering, but it is not necessarily a requirement. Our sensor shows partial recovery (up to 65%) upon addition of a suitable reducing agent such as Zn/NaOH (Scheme 1) under a N_2 atmosphere as judged by ¹H NMR and UV-Vis spectroscopy. The lack of full recovery could be due to the slow autopolymerisation of 4 as a function of time.¹⁷ However, the sensing assets can be



Fig. 5 Colorimetric changes of 2 upon exposure with various concentrations of O_2 . (a) no O_2 , (b) 50, (c) 100, (d) 150, (e) 200, (f) 250, and (g) 300 ppm for 10 min exposure time.



Fig. 6 Monitoring the absorption intensity changes in the area under the peak of 2 (1 \times 10⁻⁵ M in CH₃CN) as a function of pH of the solution upon exposure to 300 ppm of O₂ for 10 min each.

stored in an air-stable acetylated form, **3**, which can be converted to the active form, **2**, by refluxing in an acid (see SI[†]).

Notably, the pH of the solution considerably affects the sensing performance of **2**. As shown in Fig. 6, the optimum response was observed in the pH range 5.0–7.0. The failure of the sensor response at a pH lower than 5.0 could be due the non-availability of the lone pair on nitrogen as a result of quaternization and at a pH higher than 7.0 could be due to the non-participation of lone pairs.¹⁸

Conclusions

In conclusion, we have demonstrated a simple approach for "turnon" detection of O2 via multiple-channel analyses. The opticallyrich (both chromogenically and fluorogenically), photo-stable (see Fig. S5[†]) and redox-active (see Fig. S6,[†] S7[†]) diamine-based organic probe is highly selective toward O2 since no reactivity was observed with a variety of other test gases. A highly O2-selective fluorescence enhancing property (2.9 fold) in conjunction with a visible colorimetric change from pale yellow to dark red was observed. Most importantly, our results state that the detection of O₂ can be monitored by ¹H NMR, FTIR, absorption and emission spectroscopy or by eye using a single molecule. Further, the sensing assets have been stored in the acetylated form of the sensor that can be converted to the active form by maintaining the pH of the solution. The single input coupled with multiple output behaviour of this multi-responsive molecule opens the door for the development of molecular logic gates¹⁹ and the principle may also be extended to other optical probes in order to improve sensitivity, response time and reusability.

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