

Supporting Information

Highly selective optical monitoring of O₂ via multiple-channels

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Experiment Section

Materials and Methods. All reactions involving air sensitive compounds were carried out under a N₂ atmosphere using Glove Box or schlenk line technique. All glassware was oven-dried at 120°C, evacuated and purged with N₂ gas for 15 min. Solvents were dried by standard methods before use. 2-amino-5-nitroanisole and PtO₂.H₂O (Adam's catalyst) was obtained from Sigma Aldrich and was used without further purification. Acetic anhydride (received from Department of Chemistry, University of Delhi) and pyridine were purchased from s. d. fine chemical Ltd (India). Catalytic hydrogenation was performed in a shaker type hydrogenator brought from Popular Traders (Hr). The high purity dinitrogen, argon, dioxygen, carbon dioxide, dihydrogen, methane, ethene and carbon mono-oxide gas cylinders were obtained from Sigma Gases and Services (Delhi). The exact volume measurement was performed using highly precise 1.0 litre and 500 ml round bottom flask (Schott Duran) and an airtight Hamilton syringe with the capacity from 50 to 2500 µl for required concentration of test gases in nitrogen. During the time of gas-estimation experiment, the cuvette was made air-tight using homemade rubber cork for the interference free detection. All ¹H NMR spectra were recorded on Jeol NMR ECX 400p spectrometer at room temperature using DMSO-d₆ and CDCl₃. All chemical shifts (δ) are recorded in ppm with reference to TMS. IR spectra were taken on Perkin-Elmer FT-IR spectrophotometer in range 400-4000 cm⁻¹ using KBr as medium. UV-Vis spectroscopy experiments were carried out on JASCO UV-Vis-NIR spectrometer (670D) using quartz cuvettes (path length, 1cm, volume 3 mL). Fluorescence spectroscopy experiments were executed on Varian Cary eclipse fluorescence instrument, with a quartz cuvette (path length, 1 cm and slit width, 10 nm). CHI 660D electrochemical analyzer was used to carry out electrochemical measurements. Electrochemical workstation with a conventional three electrode configuration consisting of glassy carbon as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode. The cyclic voltammetry (CV) measurements were carried out in CH₃CN solutions of the compound (ca. 10⁻² M), and the concentration of the supporting electrolyte (TBAP) was maintained at 1.0 M. All of the potentials reported in this study were referenced against the Ag/AgCl electrode, which under the given experimental conditions gave a value of 370 (± 5 mV) for the ferrocene/ferrocinium couple (ΔE= 60 mV). The pH of the solution was maintained with Metrex digital pH-meter, which was calibrated with buffer solution of pH 4.00 and 9.00 before the experiments. De-oxygenation of the solutions was achieved by bubbling dinitrogen

for 15 min. Water used in the experiment was double distilled and degassed by purging N₂ for 15 min.

Synthesis of 2-methoxy-1, 4 phenylene-diamine (2)^{S1}. 2-amino-5-nitroanisole (**1**) (5.52g, 0.0325 mmol) in 1, 4-dioxane (45 ml) was treated with PtO₂.H₂O (0.05g, 0.2 mmol). The mixture was stirred under hydrogen (3 bar) for 20 h. The catalyst was separated by filtration through celite under N₂, subsequently solvent was evaporated to dryness. A light pinkish colour solid product was obtained, which was stored under inert atmosphere (Yield, 85%). ¹H NMR (400 MHz, DMSO-d₆): δ/ppm 6.35 (d, *J* = 8.0 Hz, 1H), 6.17 (d, *J* = 2.2 Hz, 1H), 5.96 (dd, *J* = 2.2, 8.1 Hz, 1H), 4.25, 3.83 (br, s, 4H, NH₂), 3.65 (s, 3H, OCH₃). IR (KBr, cm⁻¹): ν = 3478 (NH₂), 3348 (NH₂), 1626 (C=C_{Ar}), 1268, 1232 (C-O-C). ES MS: m/z (%): 139 (100) [M + 1], 124 (55) [M-NH₂⁺], 108 (10) [M-2NH₂⁺]. UV-Vis (CH₃CN; λ, nm; ε, M⁻¹ cm⁻¹): 216 (107990), 248 (66571), 314 (28355). CV (vs Ag/AgCl): +0.32V, -0.20V.

Synthesis of N, N'-Diacetyl-2-methoxy-1, 4-phenylenediamine (3)^{S2}. 2-methoxyphenylene-1, 4-diamine (5.0 g) was dissolved in dry pyridine (15 ml) and stirred slowly for 30 min, subsequently 20 ml of acetic anhydride was added drop wise and the resulting mixture was stirred for 3h. The resultant solution was cooled, poured onto ice, and the crude product collected by filtration. The crude product was purified by recrystallization from ethanol and stored in air (Yield, 60%). ¹H NMR (400 MHz, DMSO-d₆): δ/ppm 8.34 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.22 (br, s, 1H), 6.5 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.87 (s, 3H), 2.19 (s, 3H), 2.17(s, 3H). IR (KBr, cm⁻¹): ν = 3304 (N-H), 1672 (C=O), 1626 (C=C_{Ar}), 1298, 1252 (C-O-C). ES MS: m/z (%): 223 (100) [M + 1], 181 (82) [M-COCH₃⁺]. UV-Vis (CH₃CN; λ, nm; ε, M⁻¹ cm⁻¹): 231 (32704), 266 (64732), 293 (36535).

Transformation of 3 into 2. To a stirring solution of N, N'-Diacetyl-2-methoxy-1, 4-phenylenediamine (110 mg, 50 mmol) in ethylene glycol, 2.5 ml of conc. HCl was added drop wise until 15 min. The reaction mixture was refluxed and then extracted with ethyl acetate and double distilled degassed water (3×). The organic layer was dried over anhydrous Na₂SO₄ and finally under vacuum (Yield, 65 %). The purity has been checked with ¹HNMR and Mass data. Notably, **2** is stable in degassed acetonitrile solution for at least more than 6 h and **3** is stable in open air for at least 1 months as judged by ¹HNMR and UV-Vis spectroscopy.

Preparation of ppm level samples. The ppm level concentration was maintained using a gas balloon fitted with vacuum septum for gas introduction into one litre R.B flask, equipped with two gas needles for gas inlet and outlet. The flask was filled with dinitrogen gas and 300 μl of dioxygen was introduced through syringe via septum. Subsequently, gas mixture was mixed by sacking for ~ 10 min and passed through the sample via inlet needle while keeping outlet needle open. Likewise, the lower ppm dioxygen gas sample was prepared by injecting the 50, 100, 150, 200, 250 μl dioxygen gas in flask which is previously filled with one litre of dinitrogen.

Sensing experiment with ppm level of O_2 . The acetonitrile solution of **2** (1×10^{-5} M) was carefully degassed by purging N_2 for 30 min in air-tight cuvette, subsequently, 50 ppm concentration of O_2 in N_2 was passed through the solution of **2** for 10 min. Thereof the UV/Vis and Fluorescence spectra were recorded. Similarly, O_2 sensing experiment with other concentrations was carried out.

Selectivity experiment with test gases. The reactivity of **2** was tested with other gases including CO , CO_2 , C_2H_4 , CH_4 , Ar , N_2 , H_2 , Air and O_2 . In one set of experiment, 300 ppm of O_2 in each test gases were passed through solution of **2** for 10 min before recording UV-Vis and Fluorescence spectra. In another set of experiment, pure test gases were passed through acetonitrile solution of **2** for 10 min. Notably, both experiments were performed using afresh acetonitrile solution of **2** (1×10^{-5} M), which was degassed with pure N_2 for 15-30 min.

pH dependent O_2 sensing experiment. The pH of the solution was maintained using 0.01 M HCl and 0.01 M NaOH in ethanol. A number of solutions of **2** were made having pH = 1.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0. The O_2 sensing experiment in each pH solution was carried out by passing 300 ppm of O_2 in N_2 for 10 min. Notably, both experiments were performed using afresh acetonitrile solution of **2** (1×10^{-5} M), which was degassed with pure N_2 for 15-30 min.

Monitoring of O_2 using test paper. A strip of whatman paper was purged with N_2 and then, dipped in 10^{-3} M acetonitrile solution of **2** and dried under N_2 gas. The resulting test strip was exposed with 100 ppm O_2 for 10 min. Subsequently, new test strip was taken and purged with 200 ppm O_2 for 10 min. Similarly, experiment was preceded by exposing with higher concentration of O_2 for 10 min using different test strip and data are presented in Fig. S4.

Stability Test under UV-radiation. The acetonitrile solution of **2** ($0.5 \times 10^{-5} \text{M}$) was prepared and kept under UV-radiation chamber (356 nm, 15 watt) for 5 min. Then, UV-Vis spectra was run to observe the resulting changes. After that, same solution was again kept in UV chamber for 10, 20, 30 min to check the stability under UV-radiation (see Figure S5).

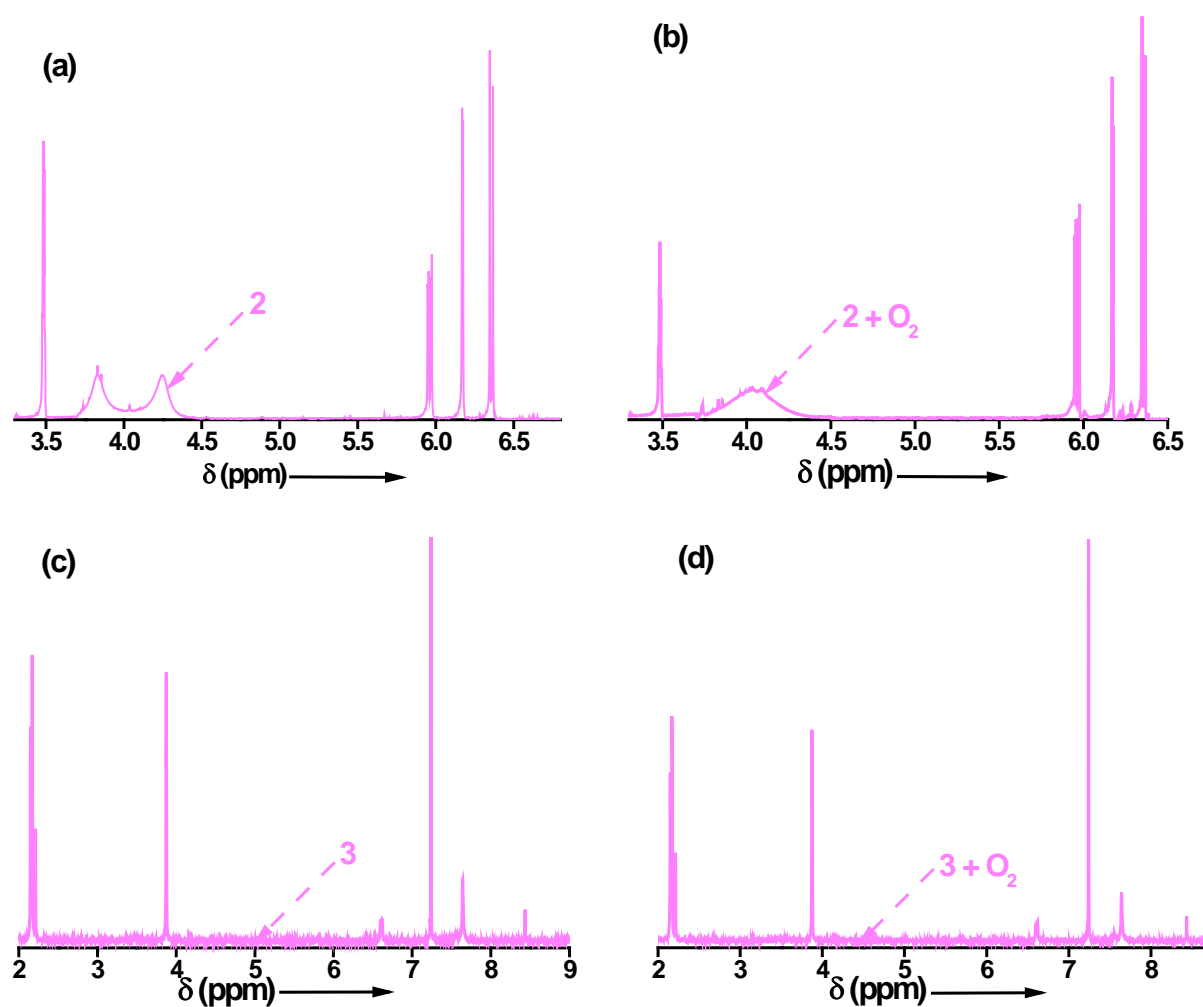


Figure S1. ^1H NMR spectra of **2** (a), **2** upon exposure of O_2 (300 ppm) for 10 min (b), **3** (c) and **3** upon exposure of pure O_2 for 10 min (d) in DMSO-d_6 solution.

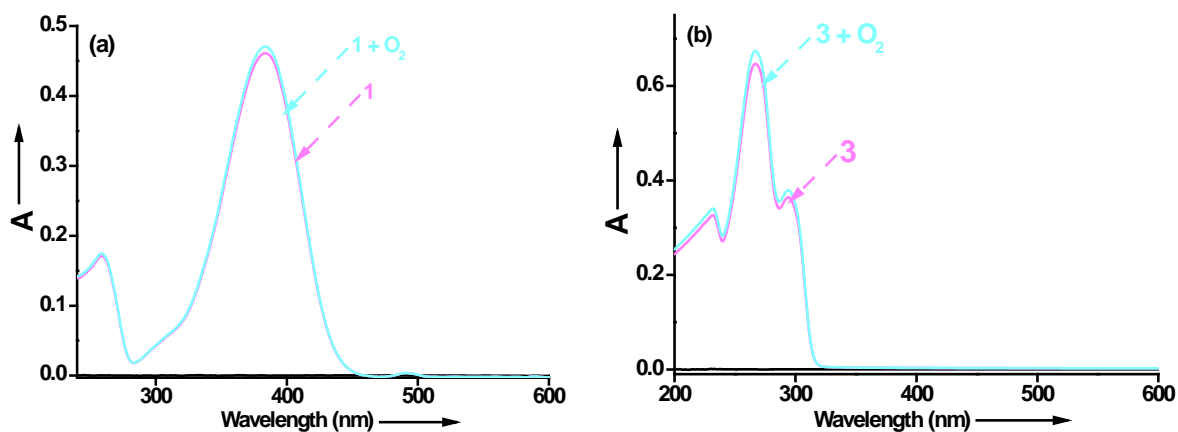


Figure S2. (a) UV-Vis spectra of **1** (pink line) and **1** + O₂ (blue line, pure O₂ for 10 min), (b) UV-Vis spectra of **3** (pink line) and **3** + O₂ (blue line, pure O₂ for 10 min).

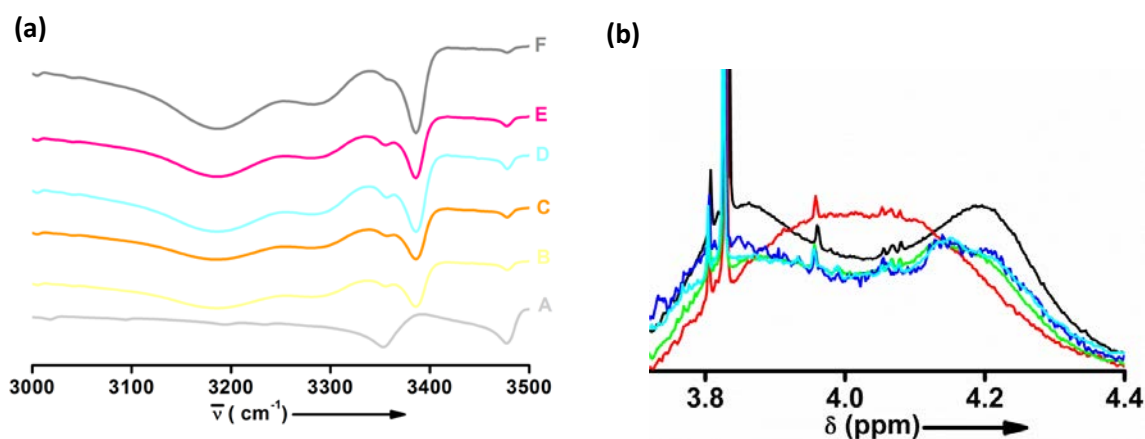


Figure S3. (a) Change in IR spectra of **2** (A, grey) after addition of various concentration of O₂ ranging from 50ppm (B, yellow), 100ppm (C, orange), 150ppm (D, blue), 200ppm (E, pink), 250ppm (F, dark grey). (b) ¹H NMR spectra of **2** after exposing with different concentration of O₂ in N₂ for 10 min. 0 ppm (black spectra), 50 ppm (blue spectra), 100 ppm (cyan spectra), 200 ppm green spectra, 300 ppm (red spectra).

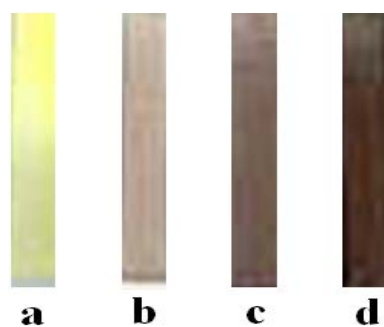


Figure S4. Change in colour of the test paper dyed with **2** after exposing with N₂ (a), 100 ppm of O₂ (b), 200 ppm of O₂ (c), 300 ppm of O₂ (d) for 10 min.

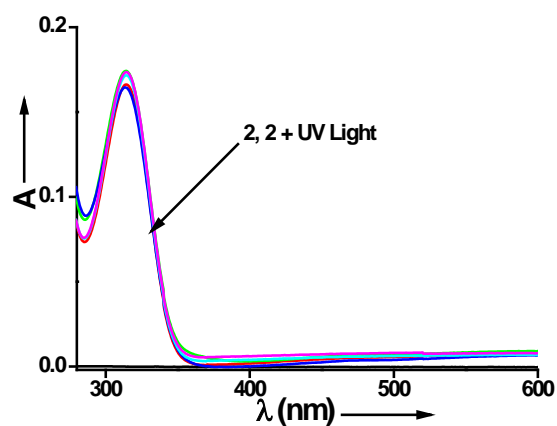


Figure S5. Representative UV-Vis spectra of **2** (0.5×10^{-5} M in acetonitrile, blue line) and spectra after irradiating the **2** with UVlight for 5 min (red line), 10 min (green line), 20 min (cyan line), 30 min (magenta line).

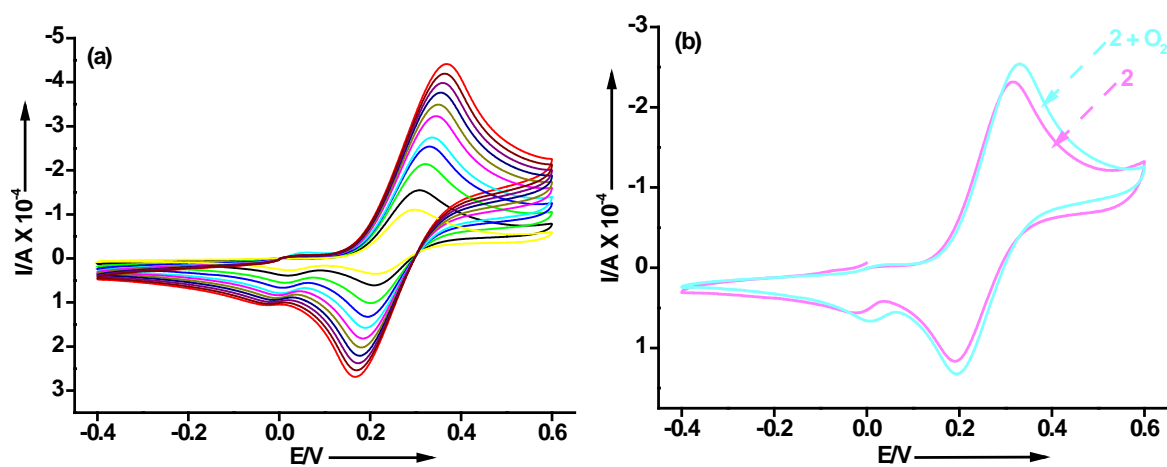


Figure S6. (a) Cyclic voltammograms of **2** (10^{-2} M) in acetonitrile containing 1.0 M Bu_4NClO_4 at scan rate from 100 to 1000 mV. The glassy carbon was used as working electrode, platinum wire was used as counter electrode, and Ag/AgCl in 1.0 M KCl aqueous solution was used as reference electrode (b) Comparative spectra of **2** and **2** after passing pure O_2 . Scan rate = 300 mVs^{-1} .

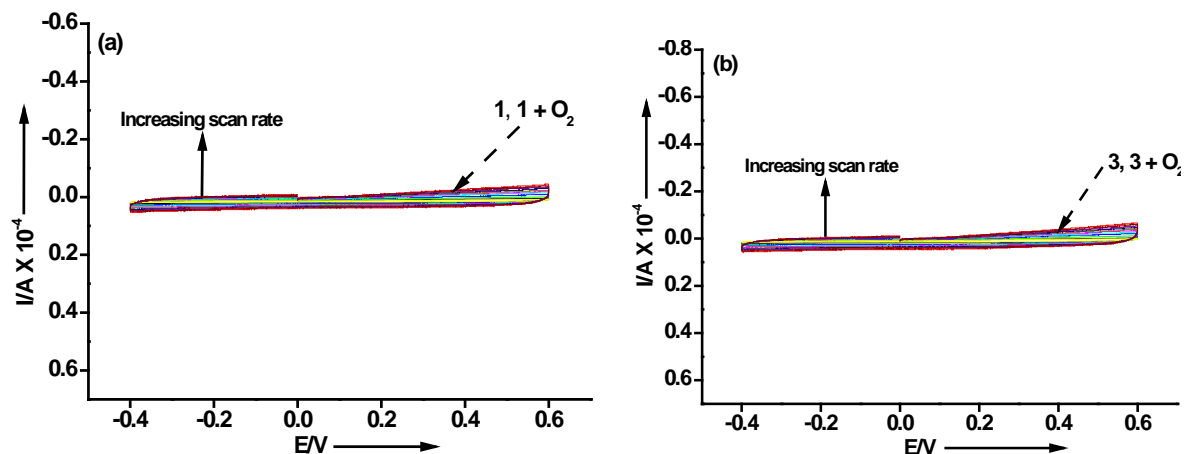


Figure S7. (a) Cyclic voltammograms of **1** and **3** (10^{-2} M in acetonitrile) after passing pure O_2 for 10 min. Scan rate = 100-1000 mV.

Reference

S1. L. F. Tietze, J. Looft and T. Feuerstein, *Eur. J. Org. Chem.* 2003, 2749.

S2. M. I. J. Polson, S. L. Howell, A. H. Flood, A. K. Burrell, A. G. Blackman and K. C. Gordan, *Polyhedron* 2004, **23**, 1427.