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

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Supporting information

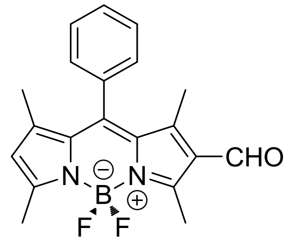
Experimental Section

General remarks

CH_2Cl_2 and CH_3CN were distilled from P_2O_5 under Ar prior to use. Silica gel 60 F254 (Merk) plates were used for TLC. Colum chromatography was performed on silica gel (60, 40-63 micras). ^1H NMR, ^{13}C NMR (300 MHz) spectra were determined on a Bruker AV 300 spectrometrer. 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 and a Varian Cary Eclipse spectrofluorimeter. 8-phenyl-1,3,5,7-tetrametilboron dipyirromethene (Ph-BDP) was prepared following the procedure described in reference 15.

Synthesis and characterization of BODIPY derivatives

Synthesis of 2-formyl-8-phenyl-1,3,5,7-tetramethylboron-dipyrromethene (1)



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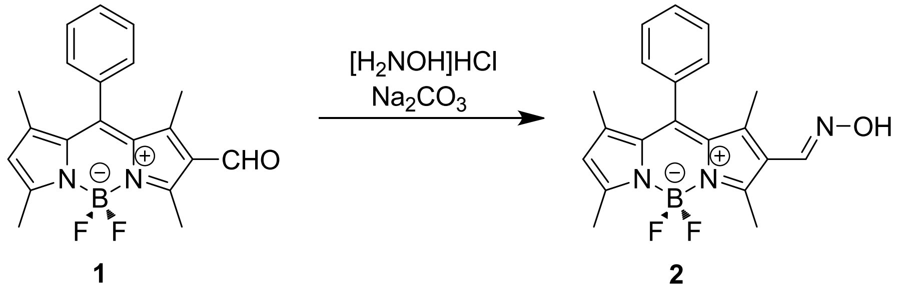
12 mL of a (1:1) mixture of DMF and $POCl_3$ were placed in a round botton flask. A solution of 200 mg of Ph-BDP (0.62 mmol) in 60 mL of 1,2-dichloroetane was added to the flask under argon atmosphere. The mixture was stirred and heated at 60º C for 2 h. The reaction was cooled at room temperature and then, 15-20 mL of an aqueous solution of $NaHCO_3$ 1M at 0º were added. The mixture was stirred for 30 minutes and

then the organic phase was separated, washed with water, dried with $MgSO_4$ and evaporated. The product was purified by column chromatography (hexane-ethyl acetate) to give a solid (0.05 g, 20%). m.p.= 208-210ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.57 – 7.49 (m, 3H), 7.32 – 7.26 (m, 2H), 6.15 (s, 1H), 2.82 (s, 3H), 2.62 (s, 3H), 1.64 (s, 3H), 1.43 (s, 3H);^{13}C NMR (75 MHz, $CDCl_3$) ^{13}C NMR (126 MHz, CDC13) δ 158.08, 154.10, 145.04, 144.83, 142.42, 139.99, 134.72, 132.51, 130.54, 129.27, 127.94, 122.46, 121.44, 14.80, 14.59, 13.96, 12.34.; HRMS (EI): m/z (%) calc for $C_{20}H_{19}BF_2N_2O$: 352.1559 $[M+1]^+$ found: 353.16. UV-Vis (CH_3CN λ_{max}/nm) 491; emission (CH_3CN λ_{max}/nm, λ_{exc} 485) 512.

Synthesis of probe 2.



0.7116 g (2 mmol) of 2-formyl-8-phenyl-1,3,5,7-tetramethylboron dipyrromethene (**1**) and 0.161 g (2,2 mmol) of hydroxylamine hydrochloride were dissolved in 45 mL of ethanol. 0.84 g of sodium carbonate dissolved in 40 mL of ethanol:water (5:1) were added to the previously prepared solution. The reaction was stirred for 3 h and followed by TLC (dichloromethane:ethyl acetate (10:2)). The ethanol was evaporated and the residue was dissolved in diethyl ether (4x40mL). The organic phase was washed with 30 mL of brine and 30 mL of water and dried with $MgSO_4$. The evaporation of the solvend gave the wanted product that was purified by columm chromatography (dichoromethane:ethyl acetate (9:1) to give a final solid (0,052 g, 7%); m. p. = 236-238 ºC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.57 – 7.47 (m, 3H), 7.41 – 7.27 (m, 2H), 6.04 (s, 1H), 5.30 (s, 1H), 2.71 (s, 3H), 2.60 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 13C NMR (101 MHz, $CDCl_3$) δ 185.65, 170.90, 161.49, 156.46, 147.12, 143.52, 142.84, 134.11, 129.42, 127.67, 126.29, 123.87, 14.77, 13.99, 12.85, 11.33.; HRMS (EI): m/z (%) calc for $C_{20}H_{20}BF_2N_3O$: 367.1667 $[M+1]^+$ found: 368.17. UV-Vis (CH_3CN λ_{max}/nm) 512; emission (CH_3CN λ_{max}/nm, λ_{exc} 500) 560.

Spectroscopic studies: All the solvents were purchased at spectroscopic grade from Aldrich Chemicals Co., used as received, and were found to be free of fluorescent impurities. Absorption and fluorescence spectra were recorded using a Shimadzu UV-2600 spectrophotometer and a Varian Cary Eclipse spectrofluorimeter, respectively. Fluorescence quantum yields were measured at room temperature in the N_2-purgued solution in relation to rhodamine B at 500 nm for **2** and in relation to fluorescein at pH= 8.06 at 490 nm for **1.** The fluorescence quantum yields were calculated from Eq. (1).

Here F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium.

$$\Phi_{exp} = \Phi_{ref}\frac{F\{1 - exp(-A_{ref} ln10)\}n^2}{F_{ref}\{1 - exp(-A\, ln10)\}n_{ref}^2}$$

General Procedure for limit of detection (LOD) determinations

Increasing amounts of the corresponding gas) were added to probe **2** in acetonitrile (10^{-5} M. The UV-vis and fluorescence spectra were recorded in 1-cm path length cells at 25 ºC (termostatted). Representation of absorbance/fluorescence at the appropriate wavelength vs. concentration of NO_2 allowed the limit of detection to be calculated.

$$LOD = \frac{3S_b}{m}$$

Membrane Preparation

Polyethylene oxide (2 g, Mw 400,000 Dalton) was slowly added to a solution of **2** (10^{-3} M solution) in dichloromethane (40 mL). The mixture was stirred until a highly viscous mixture was formed. This mixture was poured into a glass plate (40 cm^2) and kept in a dry atmosphere for 24 h.

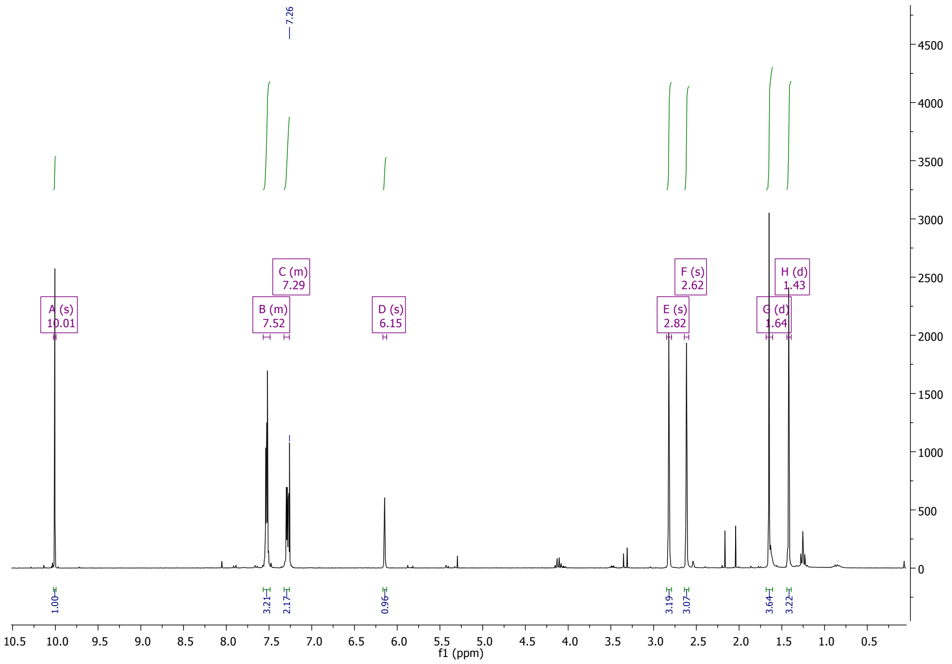


Figure S.1. ^{1}H NMR sepectrum of **1** in $CDCl_3$.

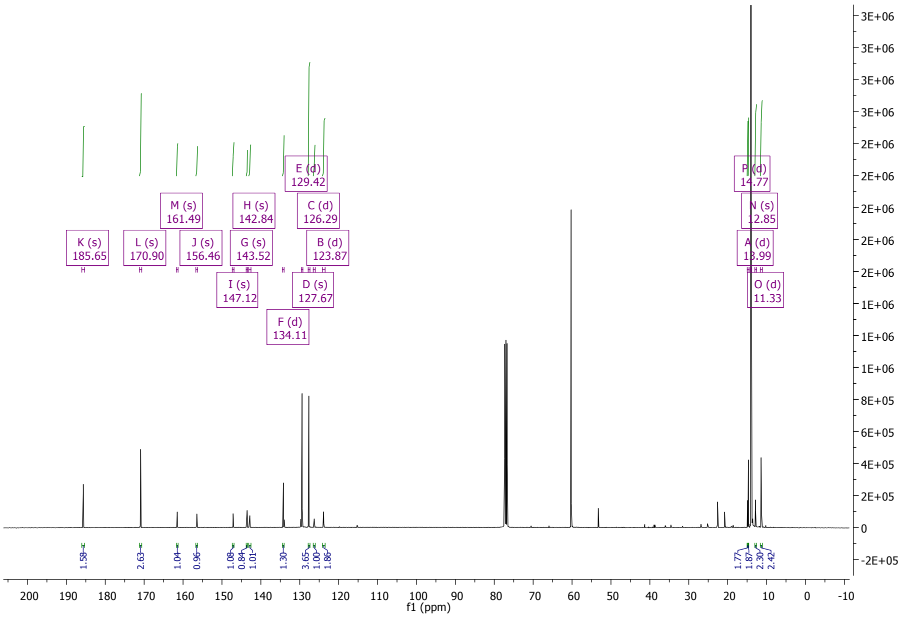


Figure S.2. ^{13}C NMR sepectrum of **1** in $CDCl_3$.

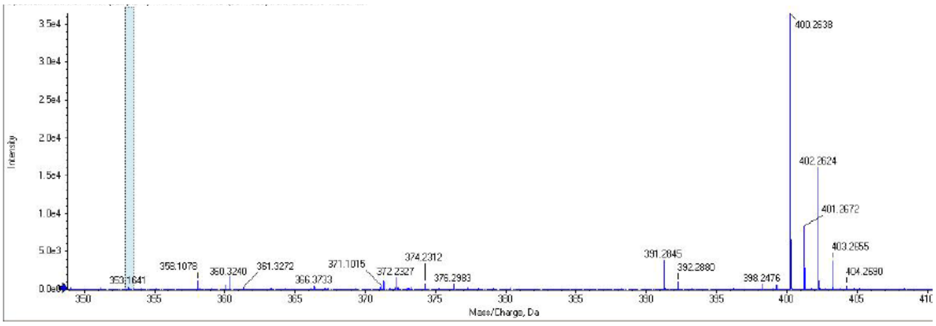


Figure S.3 HRMS of **1**.

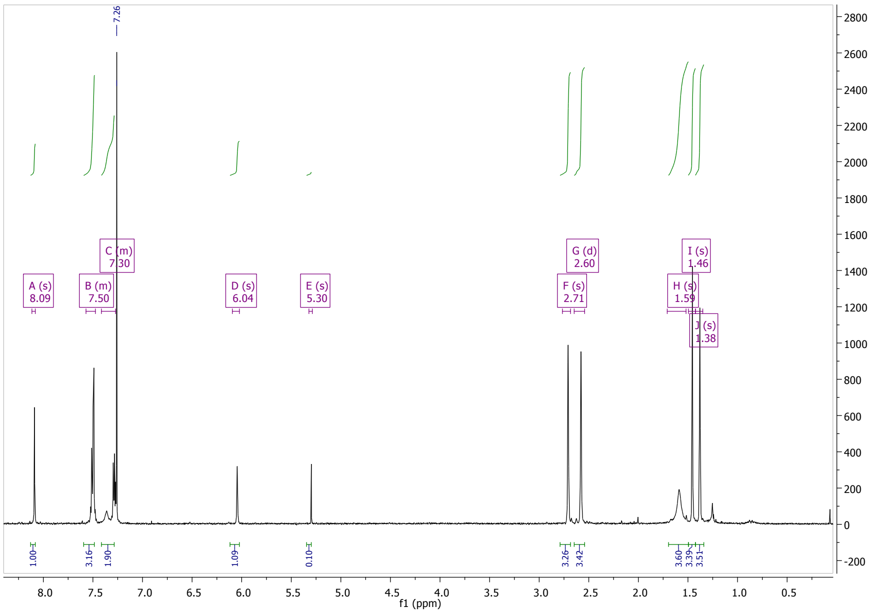


Figure S.4. ^{1}H NMR sepectrum of probe **2** in $CDCl_3$.

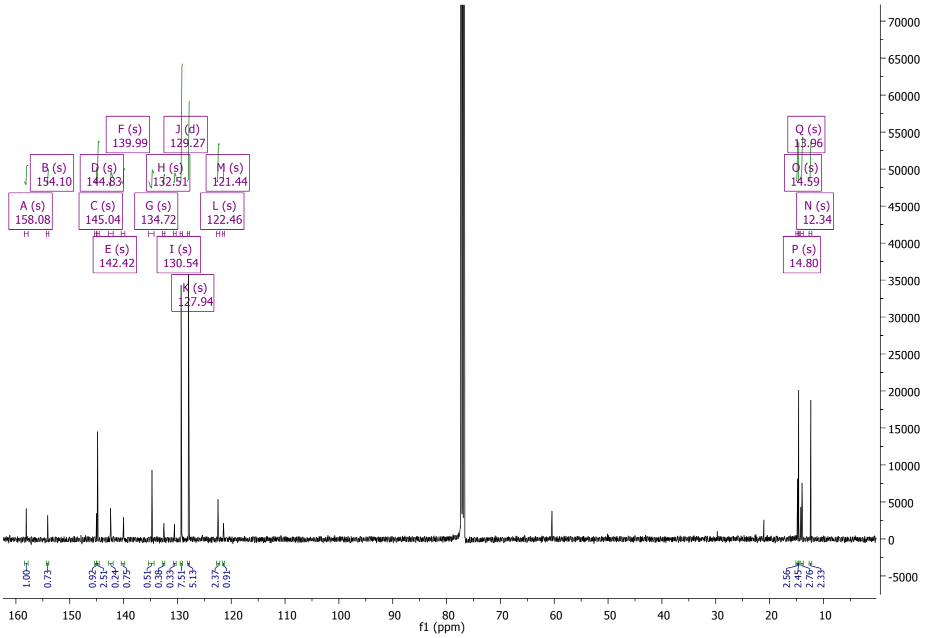


Figure S.5. ^{13}C NMR sepectrum of probe **2** in $CDCl_3$.

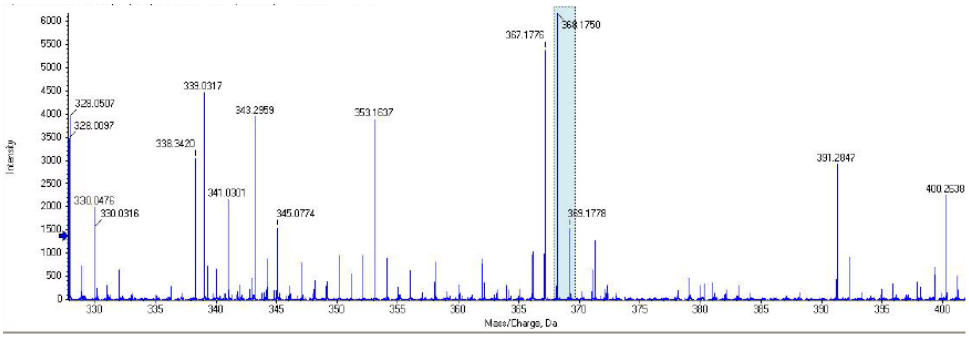


Figure S.6 HRMS of probe **2**.

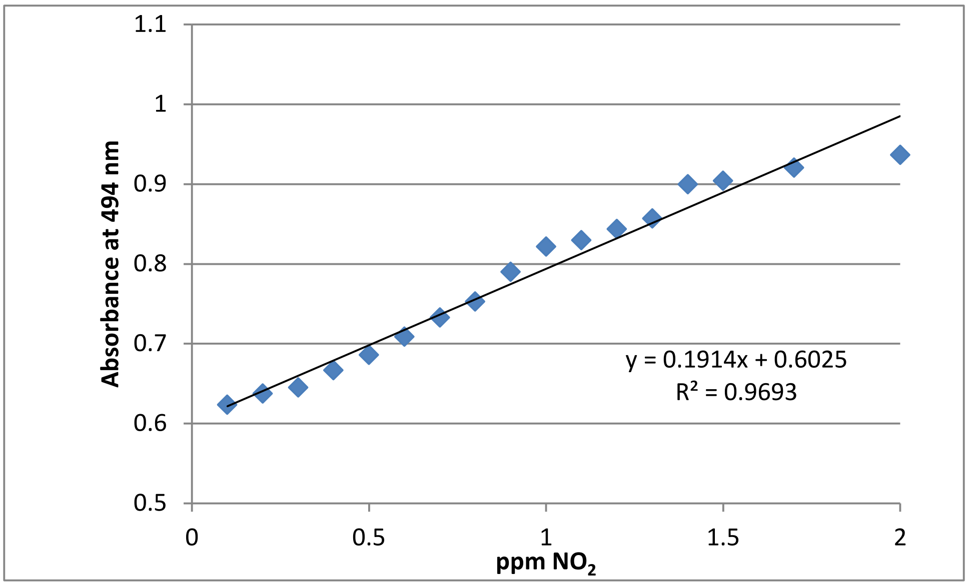


Figure S-7. Absorbance at 494 mn of **2+NO_2** (1.0 x 10^{-5}M in acetonitrile) *versus* increasing amounts of NO_2 at room temperature.

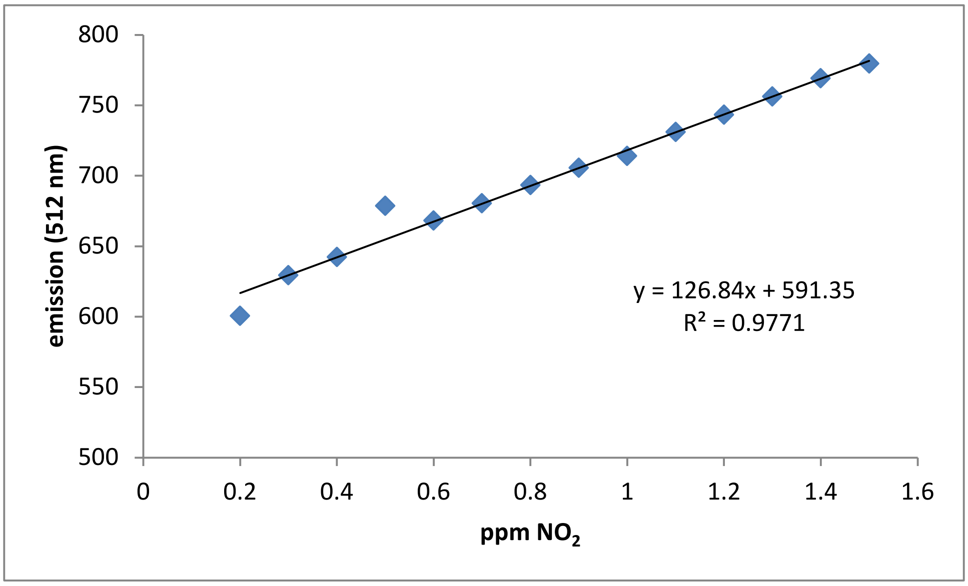


Figure S-8. Emission at 512 mn of **2+NO_2** (1.0 x 10^{-5}M in acetonitrile) *versus* increasing amounts of NO_2 at room temperature.

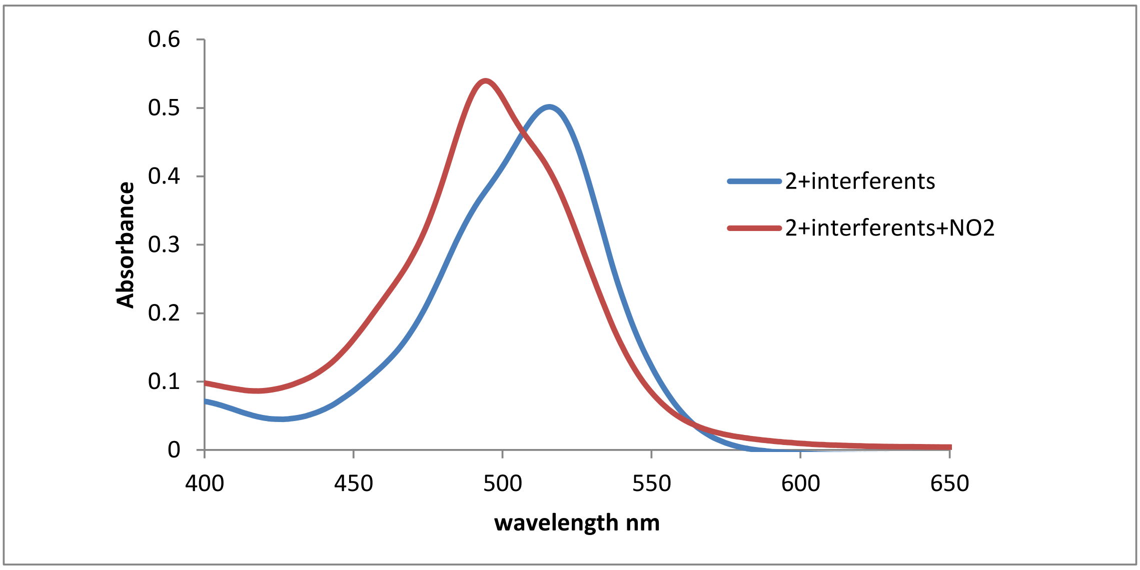


Figure S-9. UV spectra of probe **2**+interferents (CO_2+NO+H_2S+SO_2) and probe **2** in the presence of interferents plus NO_2.