

Supporting Information for:

A boron dipyrromethene (BODIPY) based probe for selective passive sampling of atmospheric nitrous acid (HONO) indoors

Danial Nodeh-Farahani,^a Jordan N. Bentley^a, Leigh R. Crilley^a, Christopher B. Caputo^a, and Trevor C. VandenBoer*^a

Department of Chemistry, York University, Toronto, Ontario M3J 1P3, Canada

*Corresponding author: Trevor VandenBoer (tvandenb@yorku.ca)

Section S1: Synthesis

General Considerations and Procedures

All manipulations were performed using Schlenk line under N₂ atmosphere and all glassware was oven-dried at 110 °C before use. Solvents were prepared from an MBraun MB-SPS 800 solvent drying system under N₂ atmosphere. Commercially available reagents were purchased from either Sigma-Aldrich, TCI Chemicals, or Oakwood Chemicals and employed without further purification; unless otherwise stated. Chloroform-*d* and benzene-*d*₆ were transferred to Strauss flasks and dried over activated molecular sieves, then degassed using freeze-pump-thaw technique. Experiments monitored by NMR spectrum were conducted in NMR spectrum tubes (8" x 5 mm) sealed with standard plastic caps and wrapped with Parafilm or J-young screw cap. ¹H, ¹¹B, ¹³C{¹H}, and ¹⁹F{¹H} NMR spectrum spectra were acquired at 25 °C on either a Bruker 700 MHz, Bruker DRX 600 MHz, Bruker ARX 400 MHz, or Bruker ARX 300 MHz Spectrometers. Chemical shifts are reported relative to SiMe₄ and referenced to the residual solvent signal (¹H, ¹³C{¹H}) of CDCl₃ (δ 7.26, 77.16 ppm) or C₆D₆ (δ 7.16, 128.06 ppm). ¹¹B and ¹⁹F{¹H} NMR spectrum spectra were referenced relative to 15% BF₃-Et₂O. NMR spectrum spectra were analyzed using either TopSpin 4.0.1 or MestReNova 12.0.3-21384 software. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. The conventional abbreviations were used as follows: s (singlet), d (doublet), dt (doublet of triplets), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), br (broad). Absorption measurements were recorded with a Cary 5000 UV-Vis-NIR Spectrophotometer from Agilent Technologies. Recordings were obtained at 25 °C and taken with the instrument operating in single beam mode and referenced to the respective solvent.

NMR Spectra of Synthesized Compounds

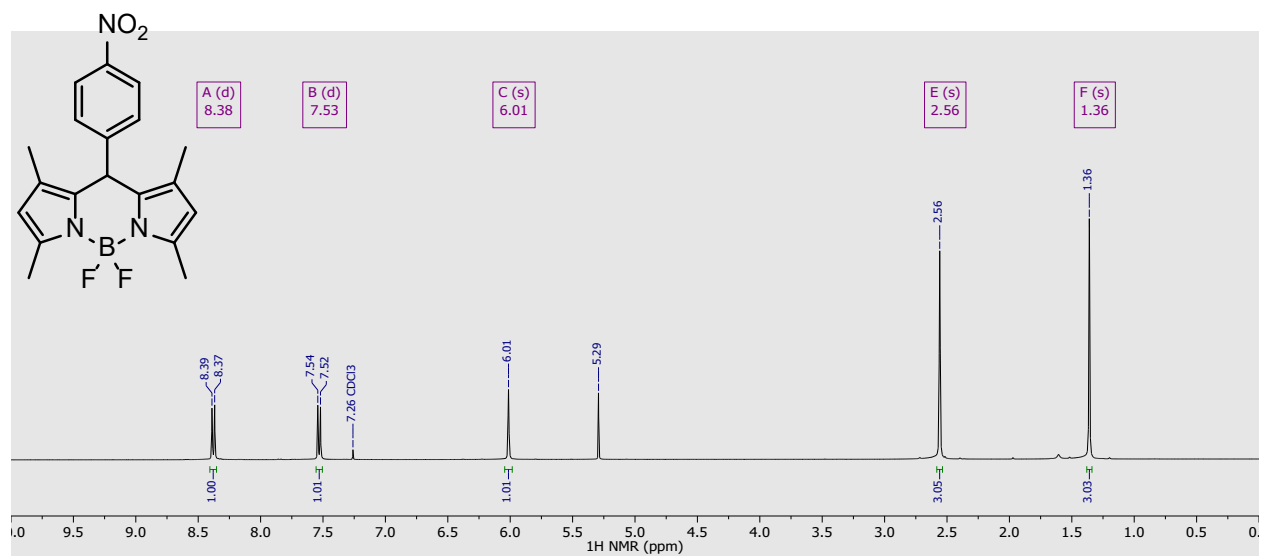


Figure S1. ¹H NMR spectrum of *m*-(4-nitrophenyl)-tetramethyl-BODIPY in CDCl₃.

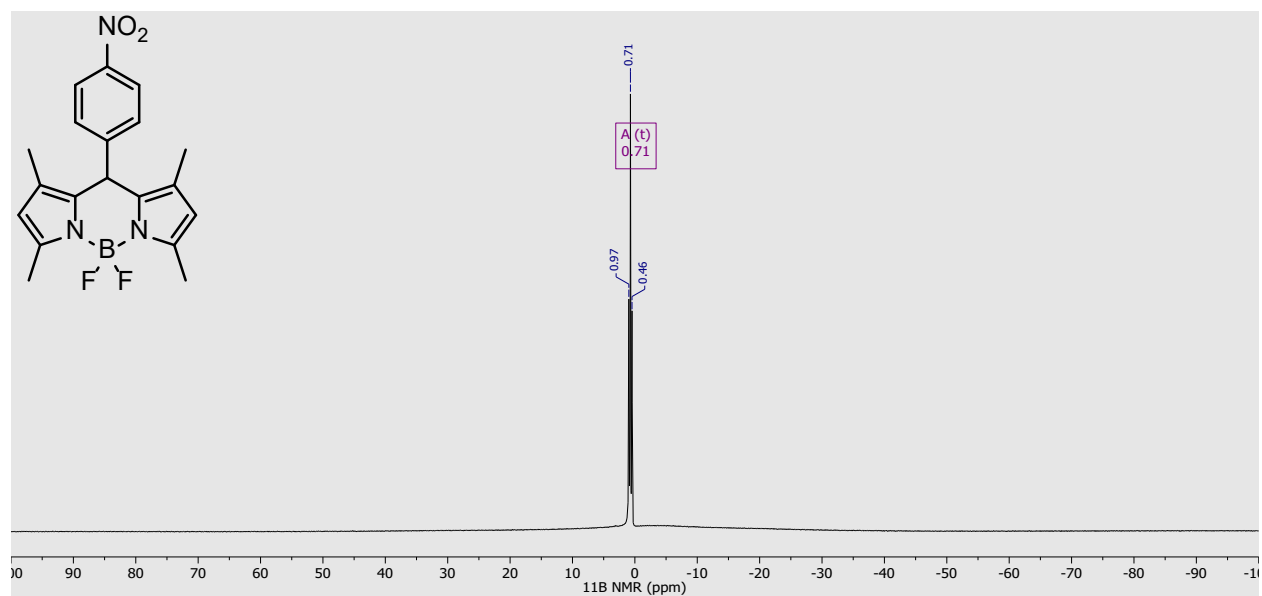


Figure S2. ¹¹B NMR spectrum of *m*-(4-nitrophenyl)-tetramethyl-BODIPY in CDCl₃.

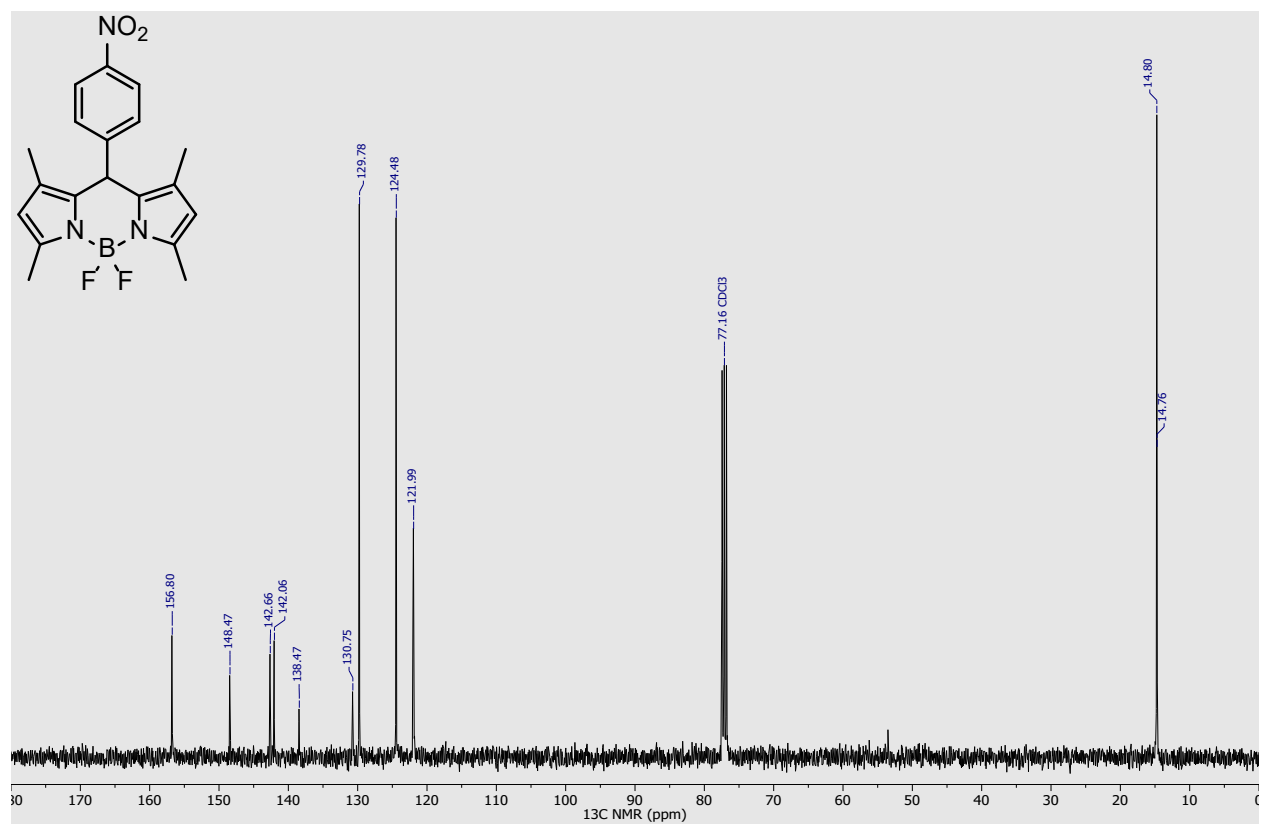


Figure S3. ¹³C NMR spectrum of *m*-(4-nitrophenyl)-tetramethyl-BODIPY in CDCl₃.

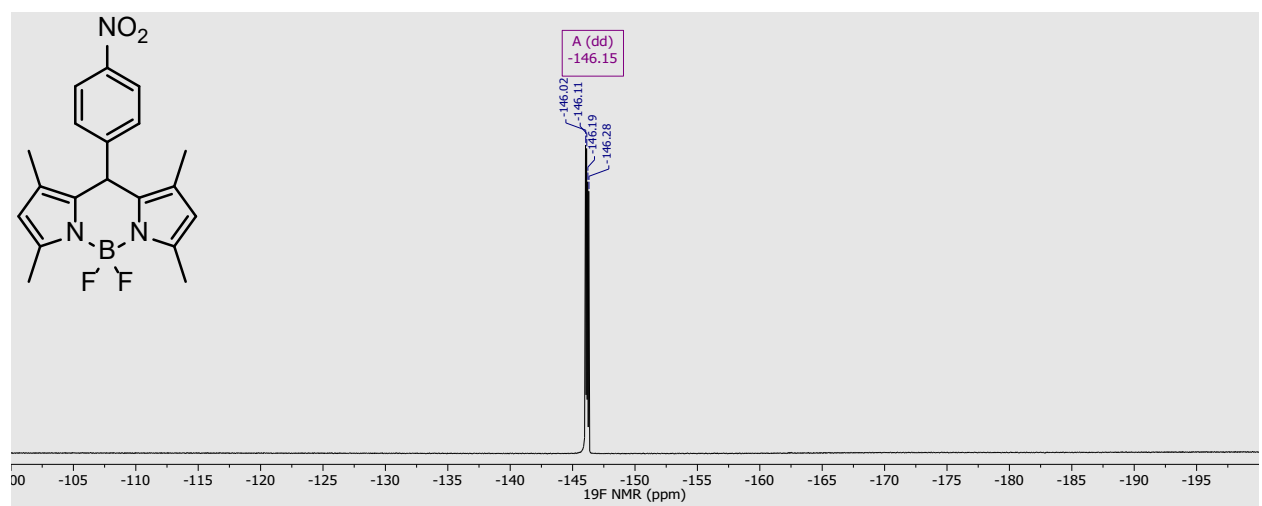


Figure S4. ¹⁹F NMR spectrum of *m*-(4-nitrophenyl)-tetramethyl-BODIPY in CDCl₃.

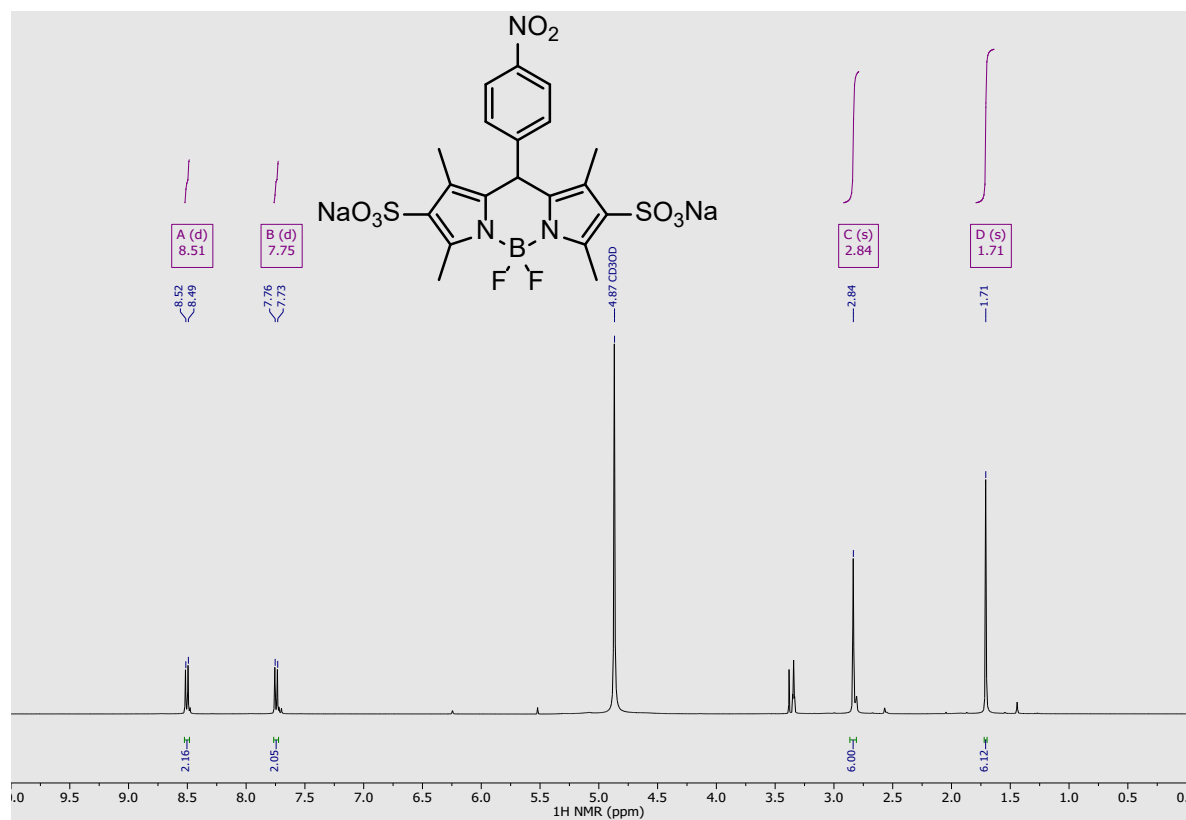


Figure S5. ^1H NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-nitrophenyl)-tetramethyl-BODIPY in CD_3OD .

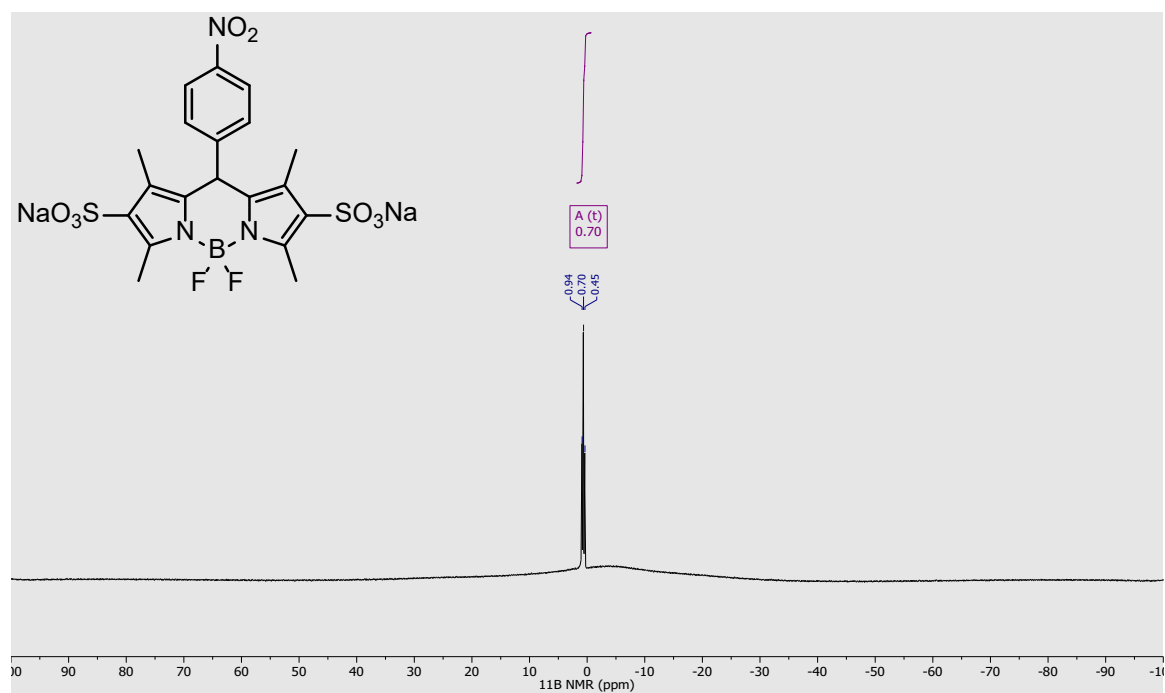


Figure S6. ^{11}B NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-nitrophenyl)-tetramethyl-BODIPY in CD_3OD .

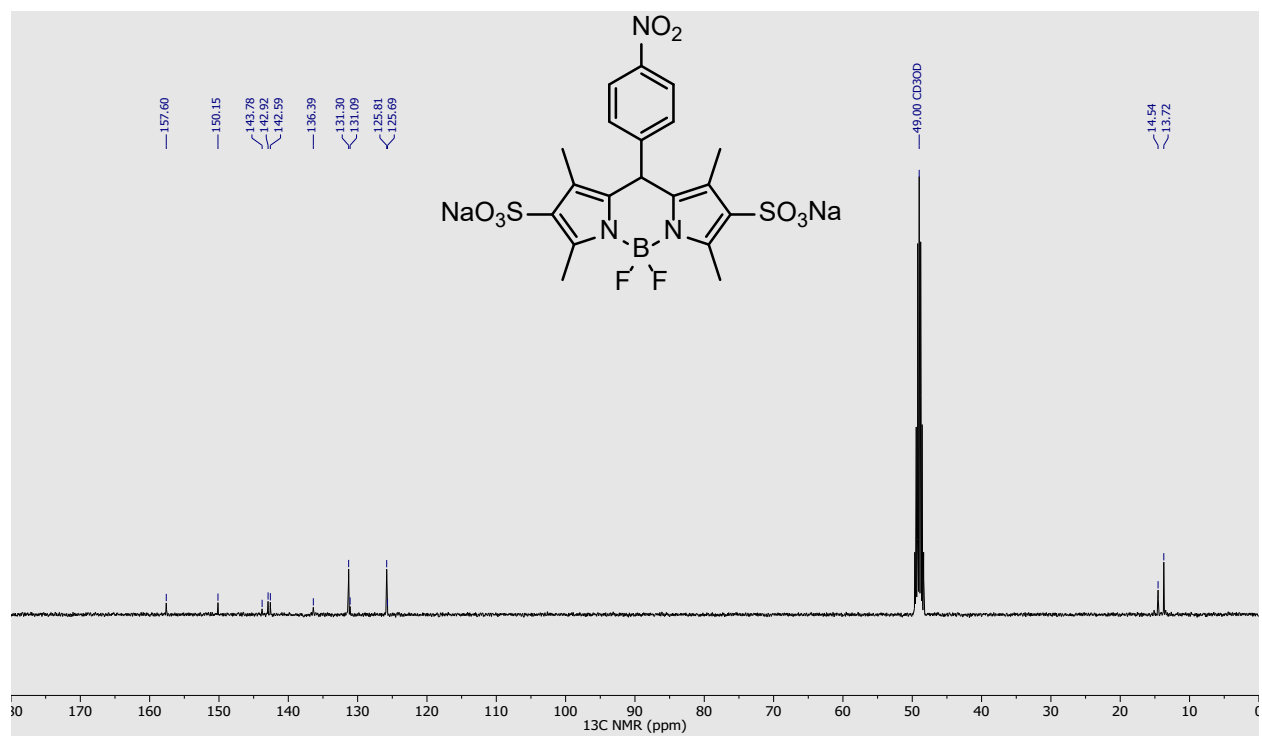


Figure S7. ¹³C NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-nitrophenyl)-tetramethyl-BODIPY in CD₃OD.

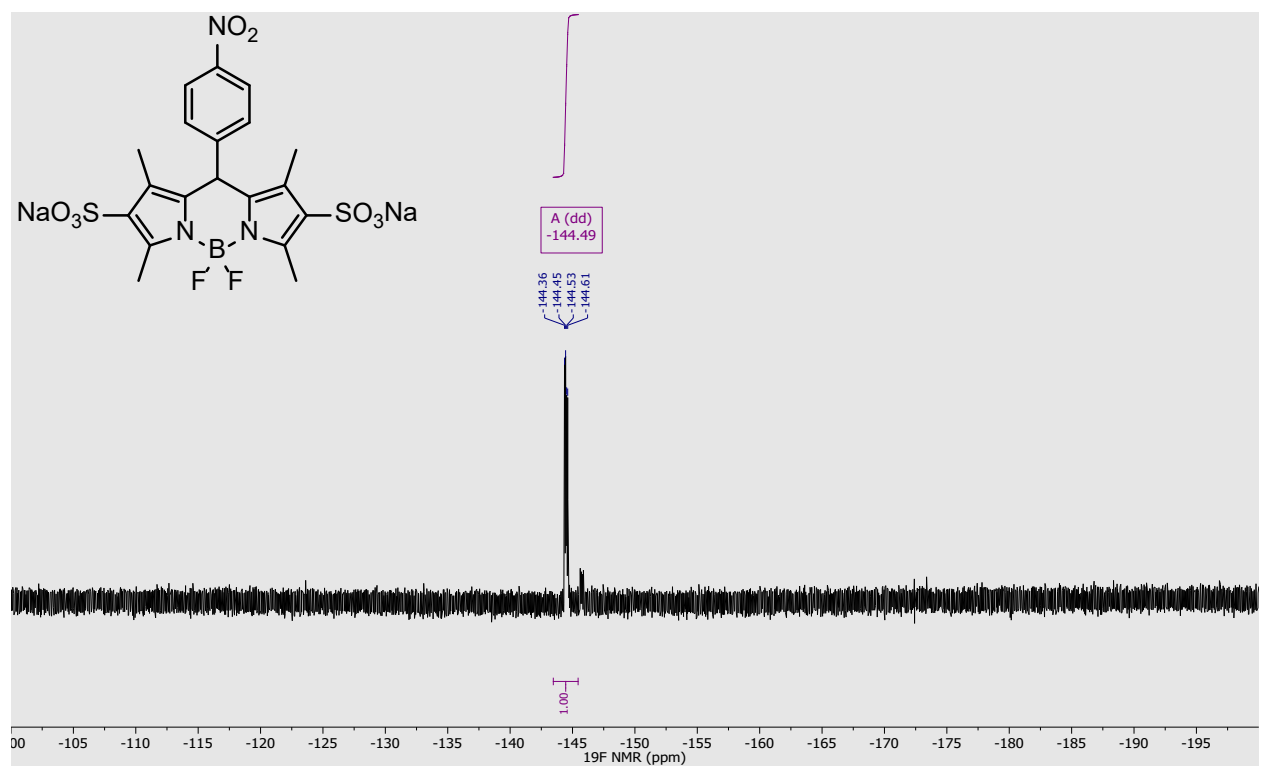


Figure S8. ¹⁹F NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-nitrophenyl)-tetramethyl-BODIPY in CD₃OD.

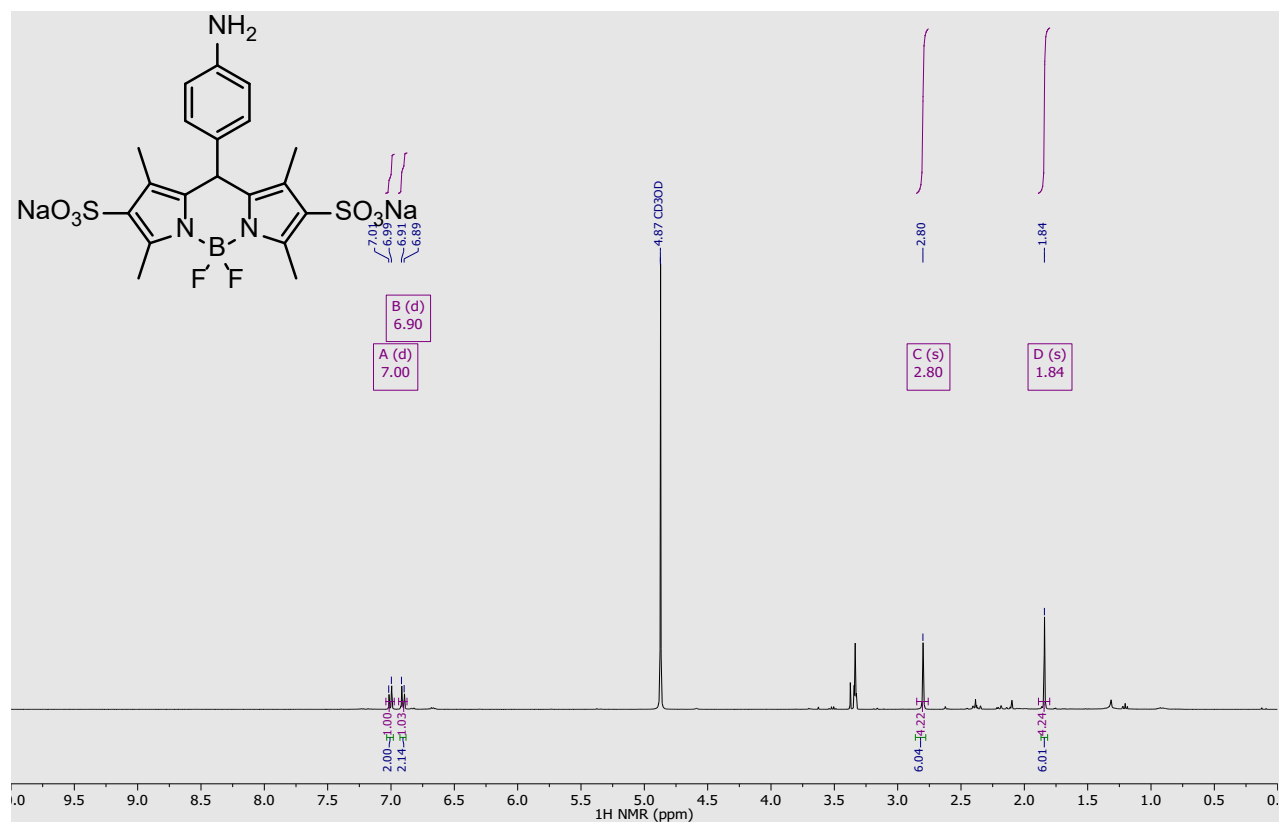


Figure S9. ¹H NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-aminophenyl)-tetramethyl-BODIPY in CD₃OD.

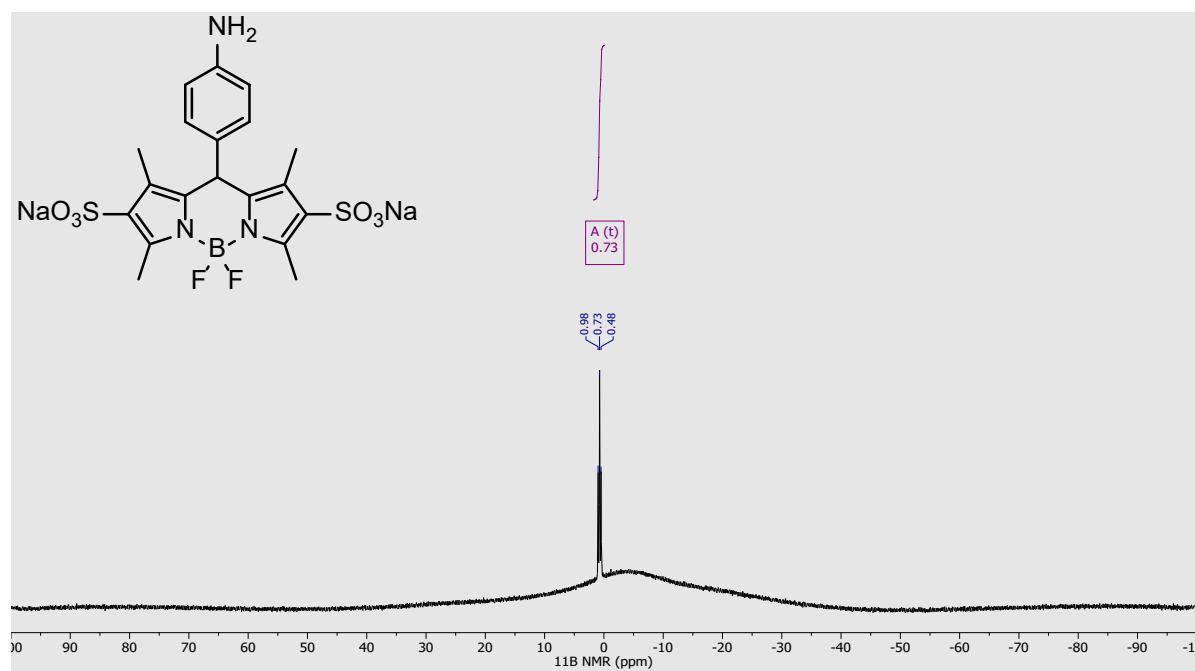


Figure S10. ¹¹B NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-aminophenyl)-tetramethyl-BODIPY in CD₃OD.

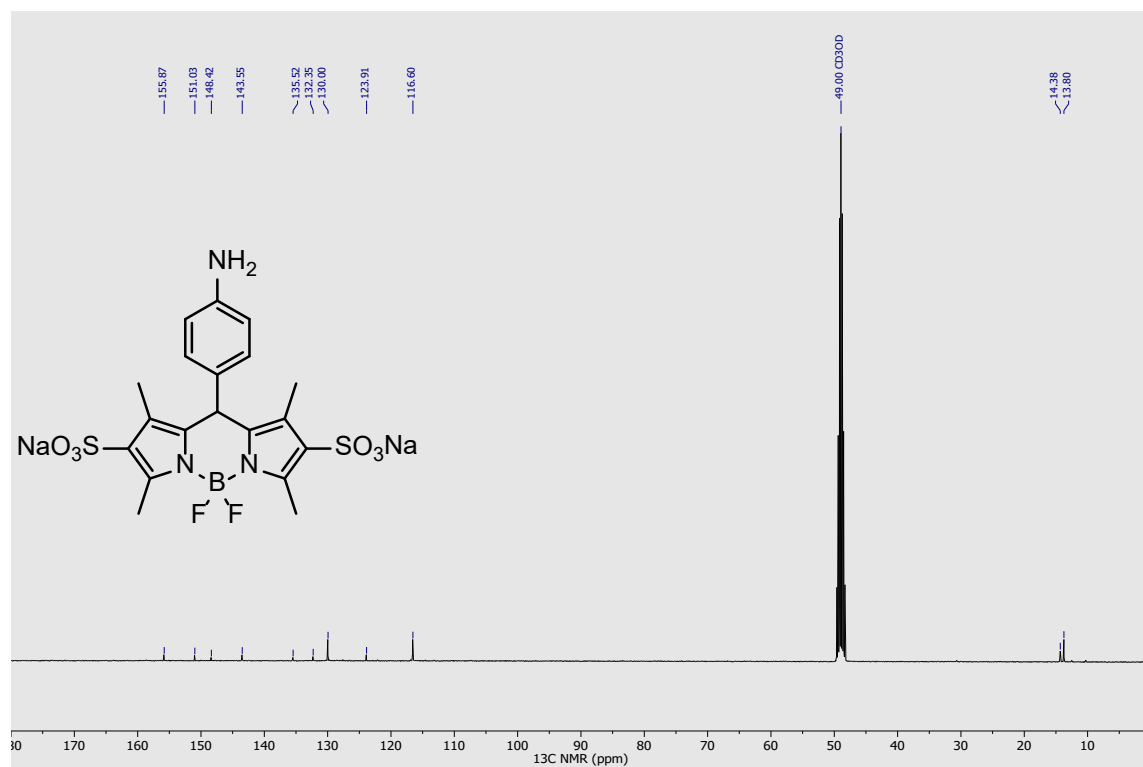


Figure S11. ^{13}C NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-aminophenyl)-tetramethyl-BODIPY in CD₃OD.

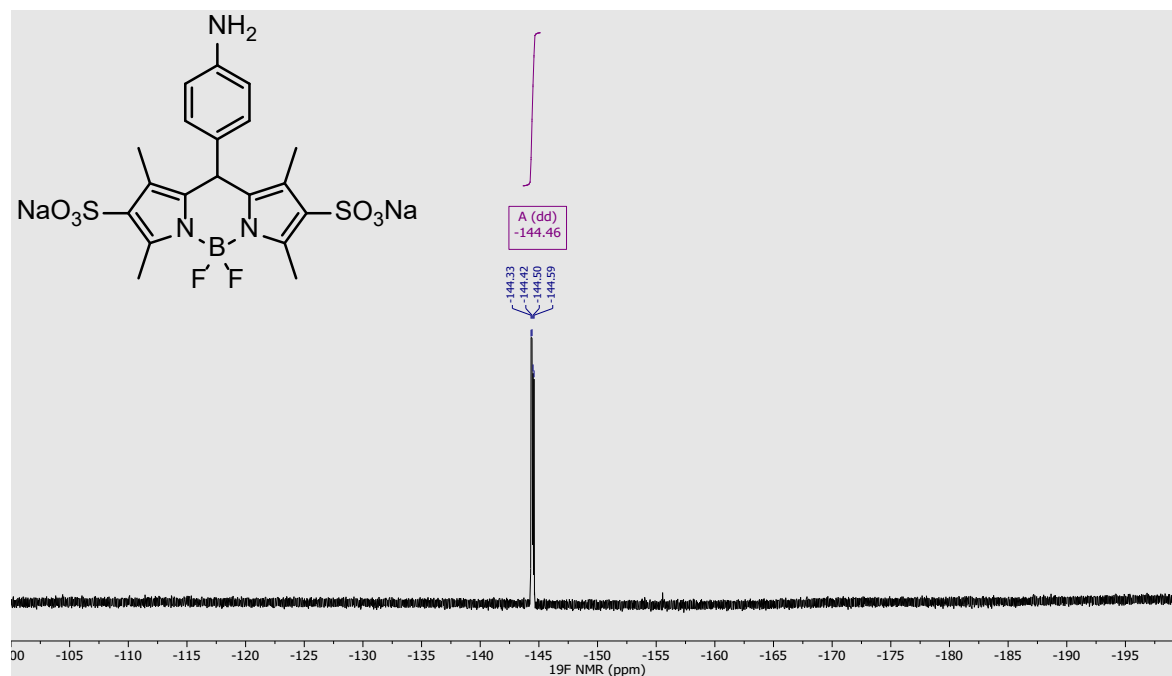


Figure S12. ^{19}F NMR spectrum of sodium 2,6-disulfonyl-*m*-(4-aminophenyl)-tetramethyl-BODIPY in CD₃OD.

Section S2: Mass Balance calculations for the gaseous HONO sampling

Note all measurements reported in this work have been background corrected by the measurement of ultra pure zero air. All possible fates have been considered to evaluate the experimental system by mass balance. Since the fate of gaseous HONO from the calibration source in the gas handling lines is different from its fate in the aqueous sampling solution, we measure and include the transformations from each part of the experimental system separately. Nitrogen monoxide (NO) is measured by the NO channel of the NO_x analyzer, while HONO and NO₂ are measured as a sum on the NO₂ channel of the NO_x analyzer. So with potential losses or transformations in the three components of our experiment: calibration source, aqueous phase and, output; we break the NO_x analyzer measurements into corresponding terms. Since it is not possible to directly measure HONO uptake into the bubbler solution, we needed to define the HONO that is exiting the bubbler and subtract that from the HONO supplied to calculate the loss. Fig S13, which follows the mass balance, shows the schematic of the sampling setup components and gas handling.

S2.1: HONO calibration source responsible for HONO input to bubbler system

S2.1.1: NO₂ channel of the NO_x analyzer

The NO₂ channel quantitatively detects HONO, so the reading of the HONO calibration source is equal to its output. Therefore, this measurement enables quantitation of the HONO input to the bubbler.

Based on this the HONO input (HONO_{in}) could be calculated as in equation 1 (ES1).

$$\text{HONO}_{\text{in}} = \text{HONO}_{\text{cs}} \quad \text{ES1}$$

Thus, the value of HONO_{cs} is measured using the NO₂ channel of the instrument.

S2.1.2: NO channel of the NO_x analyzer

Based on previous studies HONO calibration sources can have up to 10% NO impurities.¹ This is what is observed in the output of the HONO calibration source used in this work, with NO mixing ratios (NO_{cs}) quantified at 4.1 ppb when generating HONO at approximately 60 ppb. The NO_{cs} is measured on the NO channel of the instrument and the impurity coming from the calibration source (NO_{impurity}) is equal to this (ES2).

$$\text{NO}_{\text{cs}} = \text{NO}_{\text{impurity}} \quad \text{ES2}$$

S2.2: Fate of HONO in bulk aqueous solution (aq)

When HONO goes through acidic solution there are two possible outcomes. Either it will be taken up by reaction with the BODIPY-NH₂ (HONO_{uptake}), or it will not react (HONO_{unreact}). The HONO that does not react with BODIPY-NH₂ will either end up decomposing through Reaction S1 or leave the solution as HONO_(g). According to our measurements 96-100% of HONO input to the solution was observed to react with the BODIPY-NH₂ probe. This suggests that the dominant and preferred fate for HONO is reaction with the BODIPY-NH₂ probe when it is available. However, all the possible outcomes should be considered in the mass balance to understand observations made in the absence of BODIPY-NH₂ (ES3).



$$\text{HONO}_{\text{unreact}} = \text{HONO}_{\text{aq}} + \text{HONO}_{\text{aq_Decomp}} \quad \text{ES3}$$

Where the HONO_{aq} is the moles of HONO that come out of the solution in the form of HONO and the HONO_{aq_Decomp} is the amount of HONO decomposed in the solution

S2.3: Impinger output measurements

S2.3.1: NO channel

The main assumption here is that any NO will not be lost at pH 0. This means that any NO impurity from the calibration source (NO_{impurity}) would pass through the bubbler unaltered and be measured in the NO_{output}. In addition, any HONO that decomposed through R1 in the solution would also be measured in the NO_{output}. According to RS1, the amount of NO₂ produced from the HONO decomposition is equal to the amount of NO produced. The sum of NO and NO₂ produced from decomposition would represent the amount of HONO that is decomposed (HONO_{aq, Decomp}) according to Equation S4.

$$\text{NO}_{\text{Output}} = (\text{NO}_{\text{impurity}}) + (\text{HONO}_{\text{aq_Decomp}}/2) \quad \text{ES4}$$

S2.3.3: NO₂ channel

The NO₂ channel on the NO_x analyser would measure any HONO that came out of the solution and also any NO₂ due to the decomposition of HONO in aqueous phase (Equation S5). Thus, the measured NO₂ in the impinger output (defined as NO_{2 output}) would represent the sum of HONO and NO₂ as per Eqn S5.

$$\text{NO}_{2 \text{ output}} = \text{HONO}_{\text{aq}} + (\text{HONO}_{\text{aq_Decomp}}/2) \quad \text{ES5}$$

Taking the sum of ES4 and ES5 we arrive at Equation S6:

$$\text{NO}_{\text{Output}} + \text{NO}_{2 \text{ output}} = \text{HONO}_{\text{aq}} + \text{HONO}_{\text{aq_Decomp}} + \text{NO}_{\text{impurity}} \quad \text{ES6}$$

Then, drawing from ES3:

$$\text{NO}_{\text{Output}} + \text{NO}_{2 \text{ output}} = \text{HONO}_{\text{unreact}} + \text{NO}_{\text{impurity}}$$

Next, incorporating a rearrangement for $\text{NO}_{\text{impurity}}$ from ES2 into this, the unreacted HONO is quantified according to Equation S7.

$$\text{HONO}_{\text{unreact}} = (\text{NO}_{\text{Output}} + \text{NO}_{2 \text{ output}}) - (\text{NO}_{\text{cs}}) \quad \text{ES7}$$

This then allows the calculation of the desired $\text{HONO}_{\text{uptake}}$ quantity according to Equation S8.

$$\text{HONO}_{\text{uptake}} = \text{HONO}_{\text{in}} - \text{HONO}_{\text{unreact}} \quad \text{ES8}$$

By replacing HONO_{in} from ES1 and $\text{HONO}_{\text{unreact}}$ from ES3 $\text{HONO}_{\text{uptake}}$ can be calculated from the measurements made by the NO_x analyzer using Equation S9.

$$\text{HONO}_{\text{uptake}} = \text{HONO}_{\text{cs}} - [\text{NO}_{\text{Output}} + \text{NO}_{2 \text{ Output}} - (\text{NO}_{\text{cs}})] \quad \text{ES9}$$

To test if there was disproportionation of HONO in the absence of reaction with BODIPY-NH₃⁺ or aniline via RS1, gaseous HONO (17 ± 0.2 ppbv) was bubbled through 1 M HCl, and the impinger output was measured with a NO_x analyzer (Fig S13). From Fig S13, the NO_x level at the output of the impinger increased over time and reached a steady state (700 min), replicating the observations of the corresponding control experiment (Fig 7). While the NO_x level exiting the impinger output reached this steady state, it was then scrubbed using an annular denuder (URG, NC, USA) coated with Na₂CO₃ to remove any HONO (Fig S13, 1000 min). Thus, the difference in the NO₂ channel measurement before and after the insertion of the denuder into the gas flow would be equal to the HONO mixing ratio. The observed decrease in measured NO₂ (Fig S13, 12.5 ppbv), demonstrates that most of the HONO going into the impinger also exited it as molecular HONO (76%), and the remaining difference is explained by known chemistry where the HONO is decomposing in solution (e.g., RS1).

We observed a slightly higher NO mixing ratio than NO₂ mixing ratio when the impinger output was passing through the denuder (Fig S13). This observation suggests that the RS1 is not the sole mechanism controlling HONO decomposition, but the difference is less than 5% of total HONO going into the solution, suggesting an NO-producing mechanism of minor importance. We do not expect this minor pathway to add significant error in our analysis for to three reasons. The HONO calibration source mixing ratio has a precision ranging from 10-25%, with <10% NO impurity¹. Thus we expect that the variability in HONO mixing ratio delivered to the experimental impinger would have the most contribution to the uncertainty in the mass balance via NO. Second, we expect this increase in NO production to only happen without the presence of BODIPY-NH₃⁺ or aniline since initially NO and NO₂ mixing ratios are equal (e.g. see Fig S13, 100 min). Since the mass balance calculation is performed when the impinger NO_x output increases, this should not have any influence. Third, the NO output of impinger ($\text{NO}_{\text{Output}}$) is taken into account in the mass

balance (see ES9), as long as the unknown HONO to NO conversion [i.e. not RS1] follows a 1:1 mole ratio, and will again have no effect.

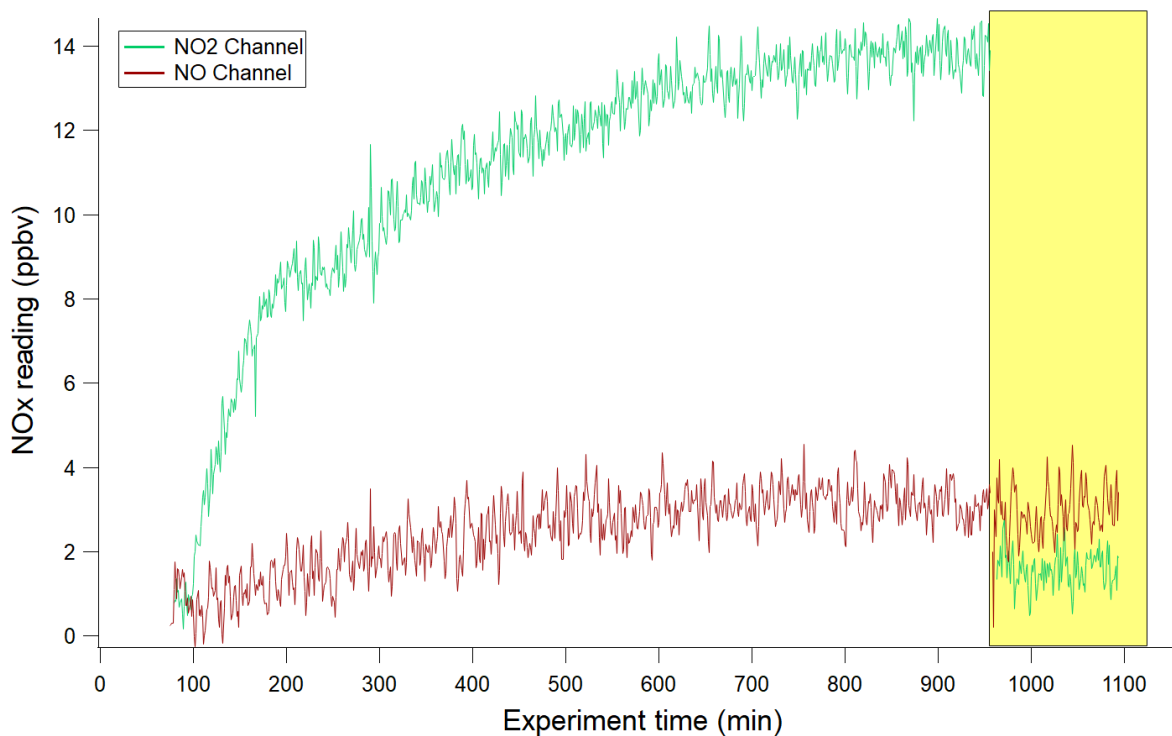


Fig S13. Measurement of the impinger output containing 1 M HCl when bubbled with 17 ± 0.2 ppbv of HONO. The yellow box indicates when the impinger output going through denuder coated with Na_2CO_3 .

Section S3: Supporting Figures

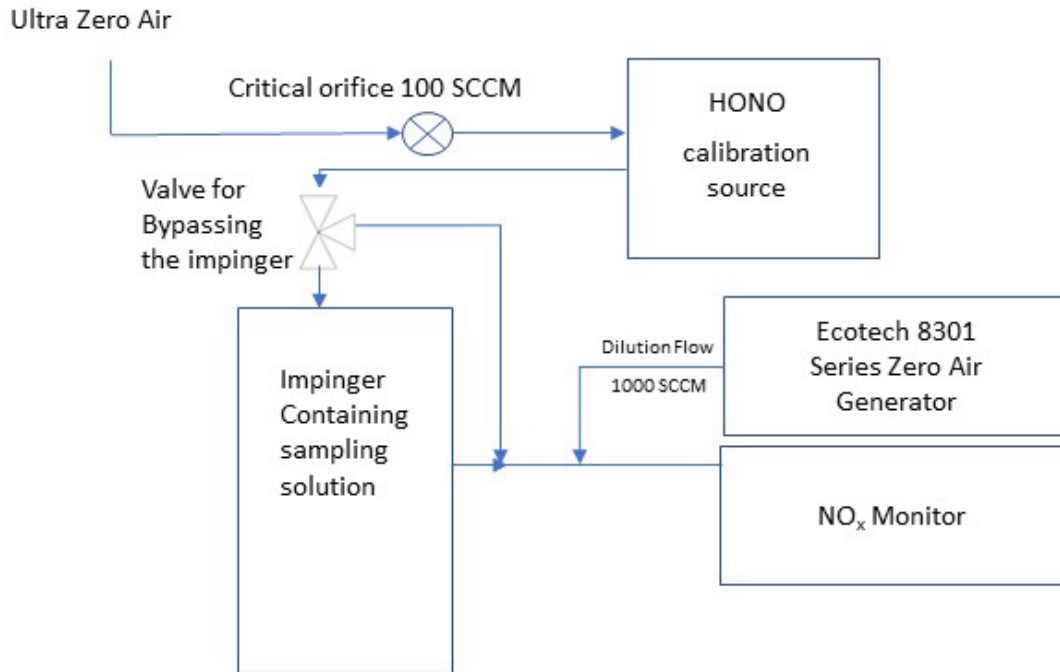


Fig S14. The gas flow and instrumental components of the HONO sampling experiments.

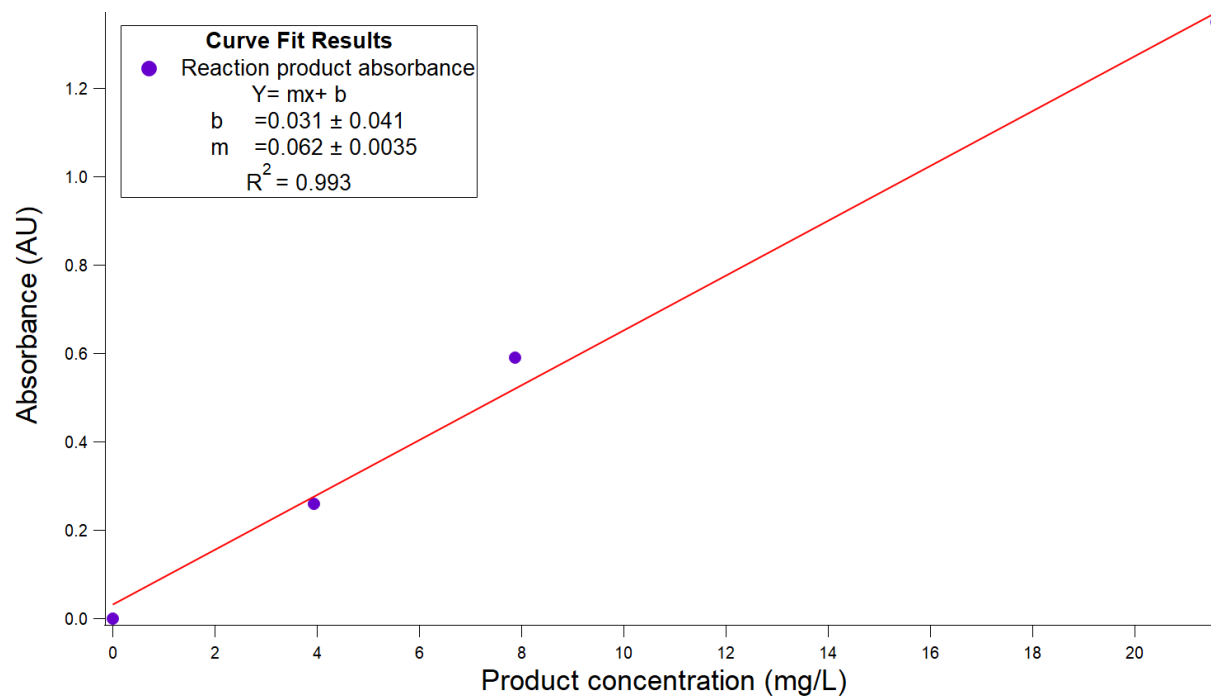


Fig S15. Calibration curve for the absorbance of reaction products of BODIPY-NH₃⁺ with 10 times excess nitrite on a molar basis (n=4, including blank)

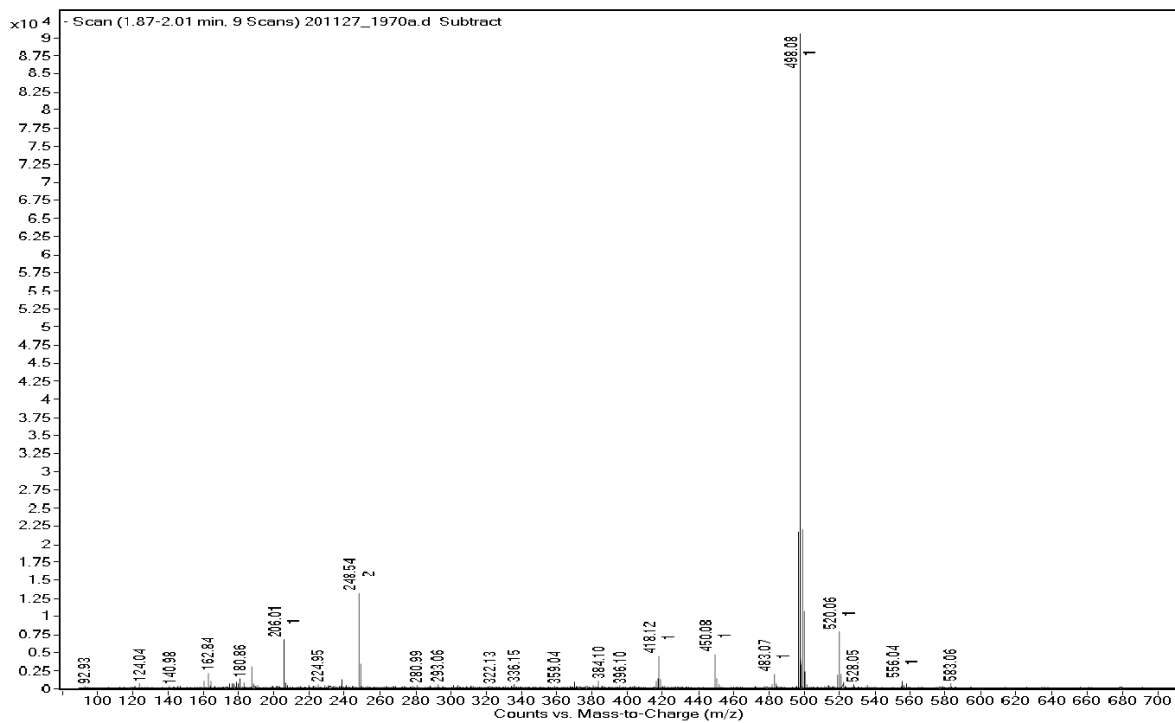


Fig S16. Mass spectra of 314 $\mu\text{g/mL}$ BODIPY-NH₂ acidified with eight drops of concentrated HCl as an unreacted sample

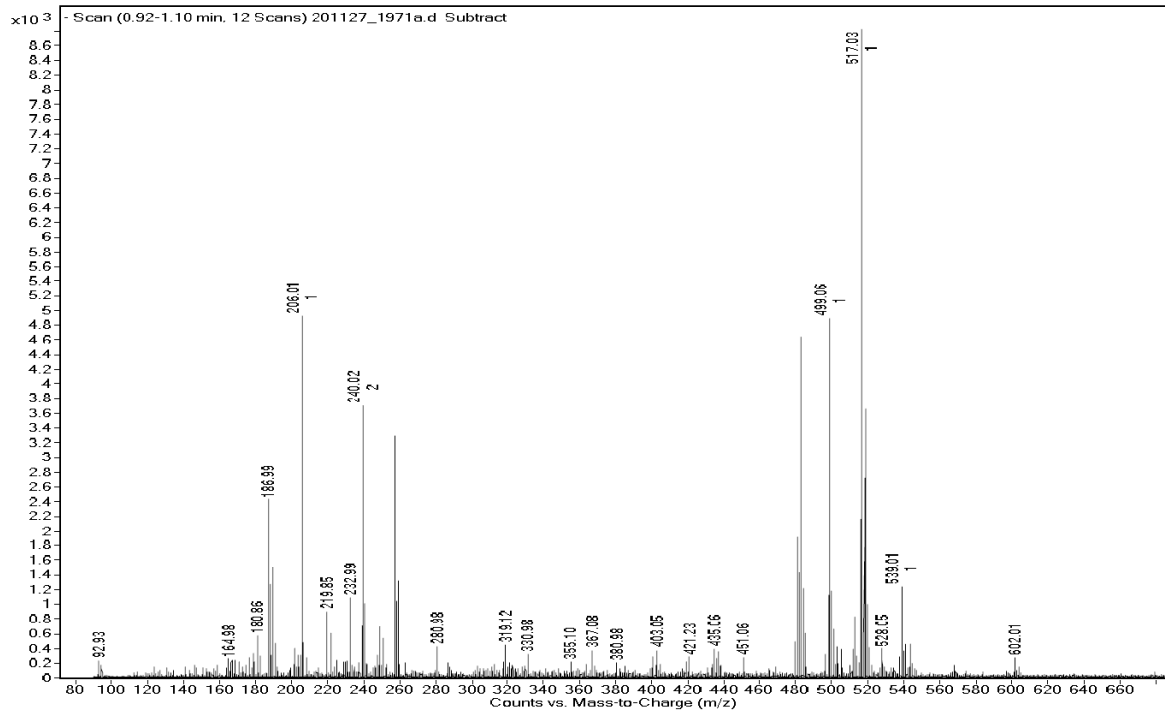


Fig S17. Mass spectra of 2.5 mL 314 $\mu\text{g}/\text{mL}$ BODIPY-NH₂ acidified with eight drops of concentrated HCl and reacted with 0.5 mL of 2360 $\mu\text{g}/\text{mL}$ NaNO₂

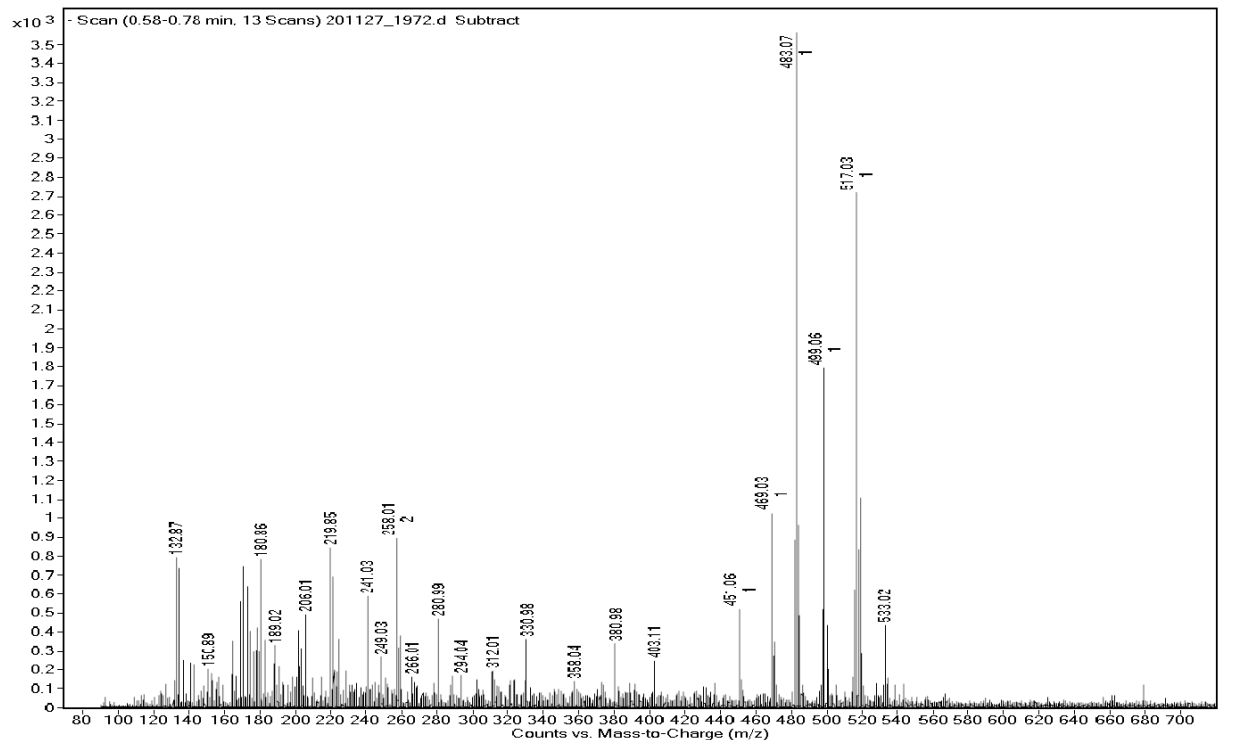


Fig S18. Mass spectra of absorbance of BODIPY-NH₂ in 1 M HCl after bubbled with 25±14 ppbv of HONO for three days

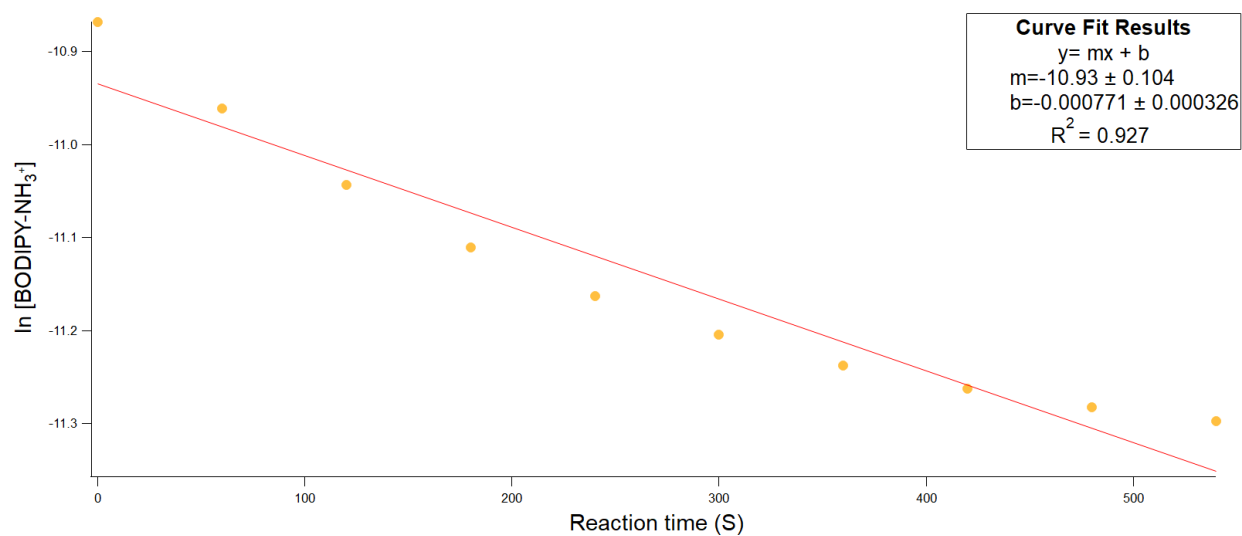


Fig S19. Changes in natural logarithm of BODIPY-NH₃⁺ concentration vs time. The absolute value of the slope shows the pseudo-first order reaction rates

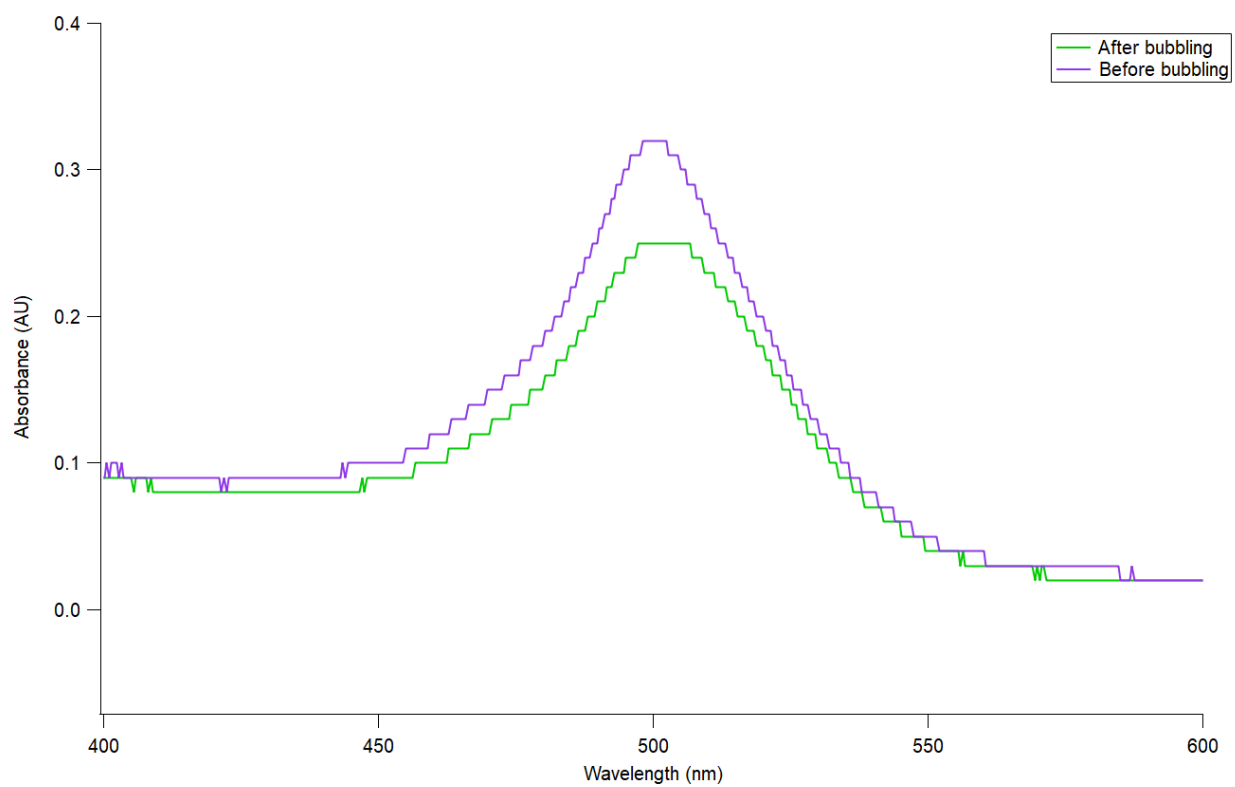


Fig S20. The loss of the reaction product exclusively by the bubbling with N_2 using the fritted impinger.

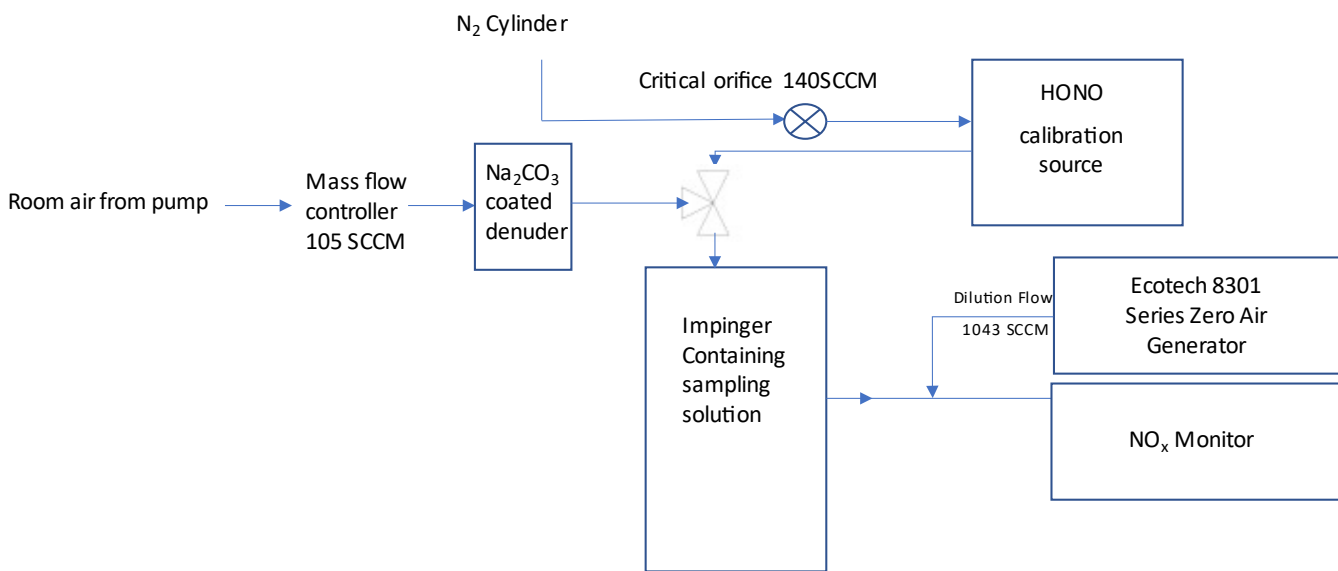


Fig S21. Schematic of the experimental set up for the HONO sampling experiment in the indoor air.

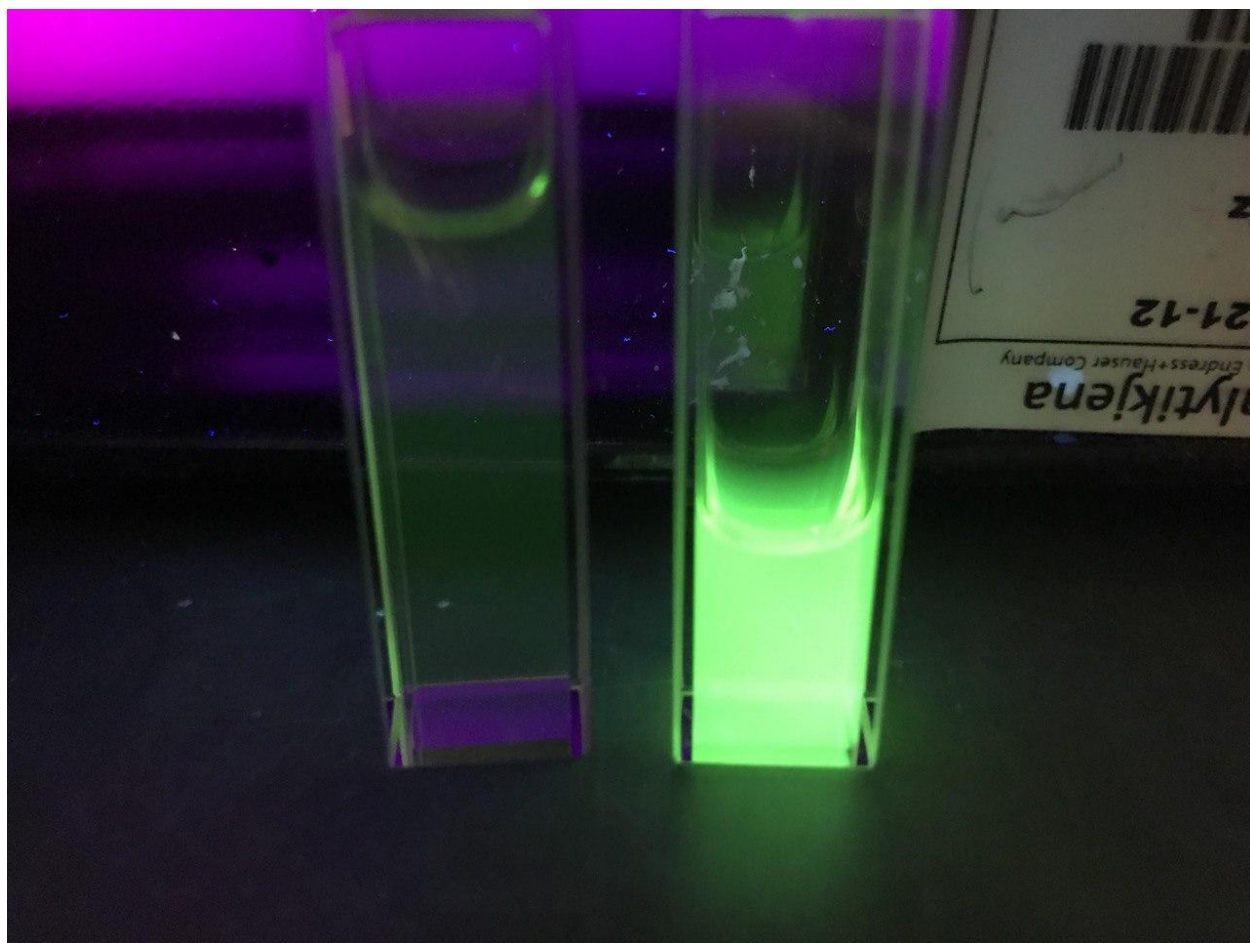


Fig S21. Emission of BODIPY-NH₃⁺ (on the right) compared with the product (on the left)

References

- 1 M. Lao, L. R. Crilley, L. Salehpoor, T. C. Furlani, I. Bourgeois, J. Andrew Neuman, A. W. Rollins, P. R. Veres, R. A. Washenfelder, C. C. Womack, C. J. Young and T. C. Vandenboer, *Atmos. Meas. Tech.*, 2020, **13**, 5873–5890.