Supplementary Material

Detection of volatile primary aliphatic amines: highly selective and sensitive vapoluminescent sensing of *n*-butylamine

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The static liquid gas distribution method

The desired concentration of the involved VOCs was calculated by the static liquid gas distribution method with the following formula:

$$C = \left(\frac{22.414 \times \rho_a \times V_a \times T}{273.15 \times MM_a \times V_{TOT}}\right) \times 10^6 \quad \textbf{(S1)}$$

where C (ppm) is the concentration of the VOC, 22.414 (L/mol) is the molar volume at STP, ρ_a (g/mL) is the density of the pure liquid VOC, T (K) is the temperature in the exposure conditions, V_a (mL) is the volume of the pure VOC, MM_a (g/mol) is the molecular mass of the VOC, and V_{TOT} (L) is the total volume (1.15 L) of the sealed glass chamber used for the static exposure.

Since to obtain concentrations of the VOCs lower than 200 ppm it would be necessary to inject sub-microliter volumes of the pure liquids into the sealed chamber, stock solutions of the involved VOCs in *n*-pentane (b.p. 36.1 °C) with a concentration of 0.473 M were prepared. Solutions with a concentration of 0.0473 M were prepared by dilution of the stock solutions. These concentrations were chosen such that 1 µL of the 0.0473 M solution injected into the sealed chamber (T = 23 °C) is equal to a concentration of 1 ppm (useful in the range from 1 to 100 ppm); while 1 µL of the 0.473 M solution injected into the sealed chamber is equal to a concentration of 10 ppm (useful for concentrations above 100 ppm). In these cases, eq. S1 for calculating the concentration of the VOCs involved becomes:

$$C = \left(\frac{22.414 \times \mathrm{M}_a \times V_s \times T}{273.15 \times V_{TOT}}\right) \times 10^6 \quad \textbf{(S2)}$$

where C (ppm) is the concentration of the VOC, 22.414 (L/mol) is the molar volume at STP, M_a (mol/L) is the molarity of the VOC *n*-pentane solution, V_s (L) is the volume of the *n*-pentane solution, T (K) is the temperature in the exposure conditions, and V_{TOT} (L) is the total volume (1.15 L) of the sealed glass chamber used for the static exposure. Test exposure experiments at defined concentrations of BA, either as pure liquid or as *n*-pentane solution, gave the same results.

In the case of gaseous MA and EA amines and ammonia, standardized aqueous solutions were used. Solutions with concentrations of 0.16 M and 0.96 M were used for exposure experiments at 50 ppm and 300 ppm, respectively. These concentrations ensure that the volume of the aqueous solution injected in the sealed chamber, previously dried with nitrogen stream, does not produce a RH greater than 60% after its complete evaporation. In these cases, the exposure experiments were performed by introducing PBS into the chamber after complete evaporation of the solution. To assess this procedure, exposure experiments using aqueous BA solutions gave the same results as those obtained using BA solutions in *n*-pentane (paragraph 2.5.).

Calculation of the limit of detection

The limit of detection for BA vapors was calculated in the dynamic linear range (0 - 50 ppm) with the following formula:

$$LOD = K \times \frac{S_b}{S} \quad \textbf{(S3)}$$

where K is a constant, S_b is the standard deviation of the blank calculated considering the fluorescence emission of over 100 PBS films at λ_{em} = 617 nm, and S is the slope derived from the linear fit curve. The calibration curve was obtained from the plot of the fluorescence intensity at λ_{em} = 617 nm versus the concentration of the amine added. Each point is related to the mean value obtained from at least three replicate measurements. Using eq. S3, with K = 3, S_b = 18 and S = 27, a LOD value of 2.0 ppm was calculated.

Spectrophotometric and spectrofluorometric measurements

The fluorescence emission for as-cast and annealed films of **1** on glass substrates, and for as-cast or annealed films before and after exposure to saturated BA vapors, was recorded at the excitation wavelength of the isosbestic point. Analogously was done for PBS before and after exposure to saturated BA vapors. The excitation wavelength (λ_{exc}) for annealed cast films on glass substrates, upon exposure to saturated vapors of different VOCs, was chosen as λ_{exc} = 508 nm for the N-VOCs (approximately related to the longest wavelength absorption maximum for involved species) and, using the same criterion, as λ_{exc} = 459 nm, for the other investigated VOCs. The excitation wavelength for PBS in quantitative and competitive experiments involving BA was chosen as λ_{exc} = 500 nm, according with the longest wavelength absorption maximum for the **1**·BA adduct.

Fig. S1. Experimental apparatus for static exposure experiments.

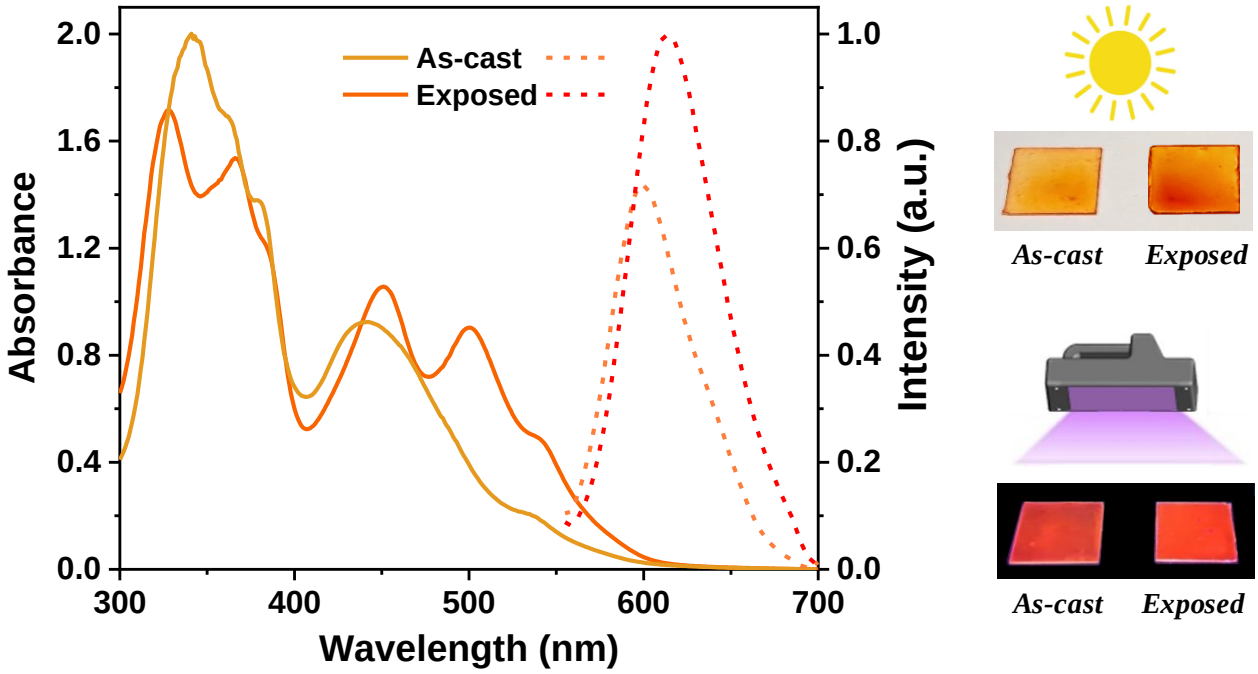

Fig. S2. UV-vis absorption (solid line) and fluorescence (dotted line; λ_{exc} = 473 nm) spectra of an as-cast film of **1** deposited onto a glass substrate and after exposure to saturated BA vapors. Photographic images of films of **1** as-cast and exposed to BA vapors under natural light (top) and 365 nm light (bottom).

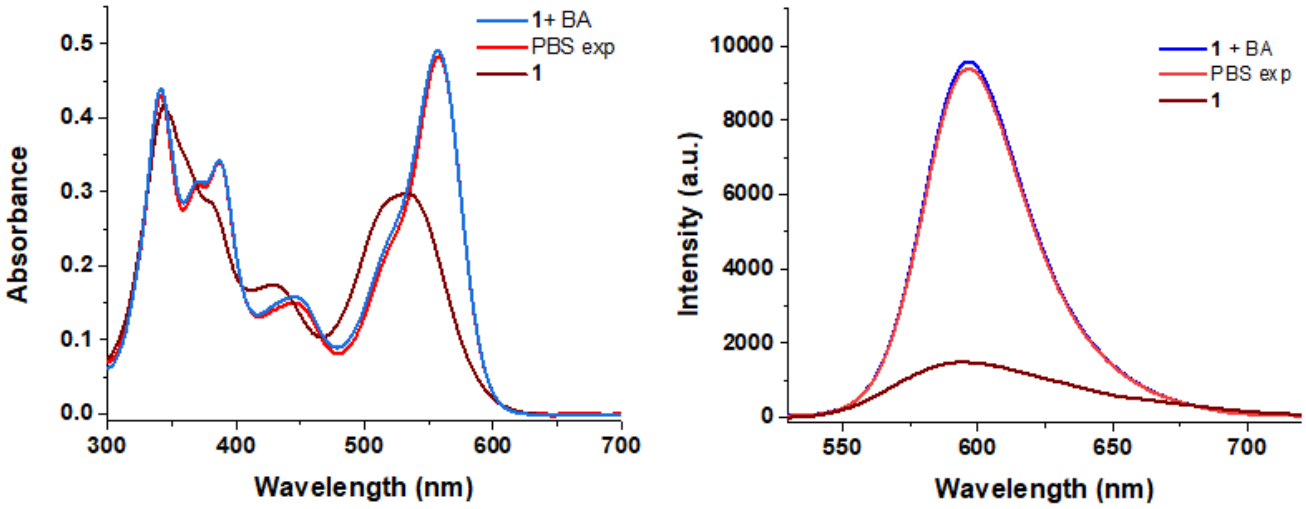

Fig. S3. UV-vis absorption (left) and fluorescence (right; λ_{exc} = 467 nm) spectra of the **1**·BA adduct (10 μM solution in DCM) obtained from a PBS film after exposure to saturated vapors of BA and dissolved in DCM (red line). The optical absorption and fluorescence spectra of **1** (10 μM solution in DCM), before (red-brown line) and after (blue line) the addition of BA (12 μM) are reported for comparison.

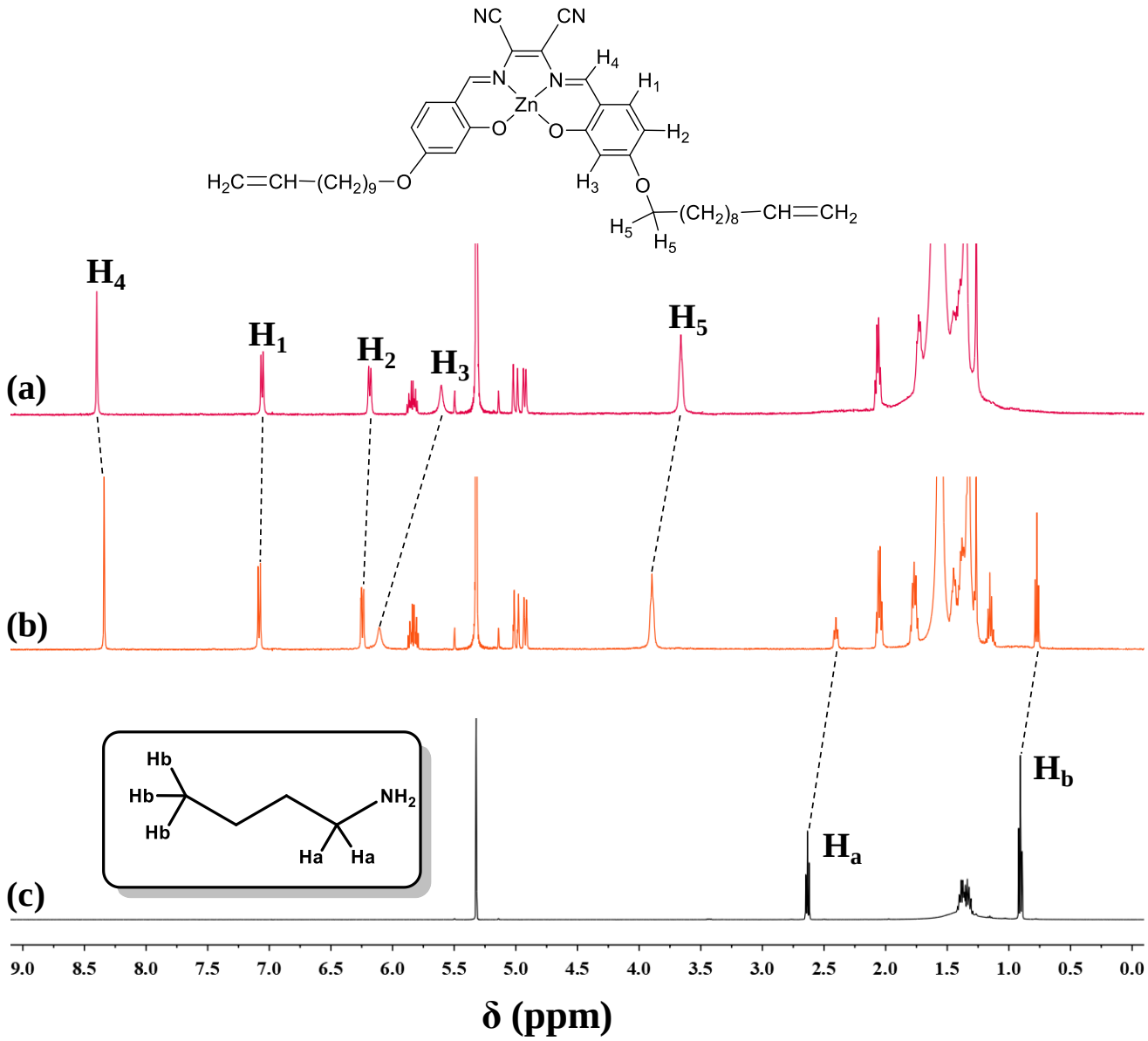

Fig. S4. ^{1}H NMR spectra of **1** in CD_2Cl_2 **(a)** and **1**·BA adduct **(b)** obtained from a PBS film after exposure to saturated vapors of BA and dissolved in CD_2Cl_2. The ^{1}H NMR spectrum of BA in CD_2Cl_2 **(c)** is reported for comparison. The downfield shift of the aromatic H_3 and OCH_2- signals relative to those of **1** clearly indicates deaggregation of **1** with formation of the **1**·BA adduct [65].

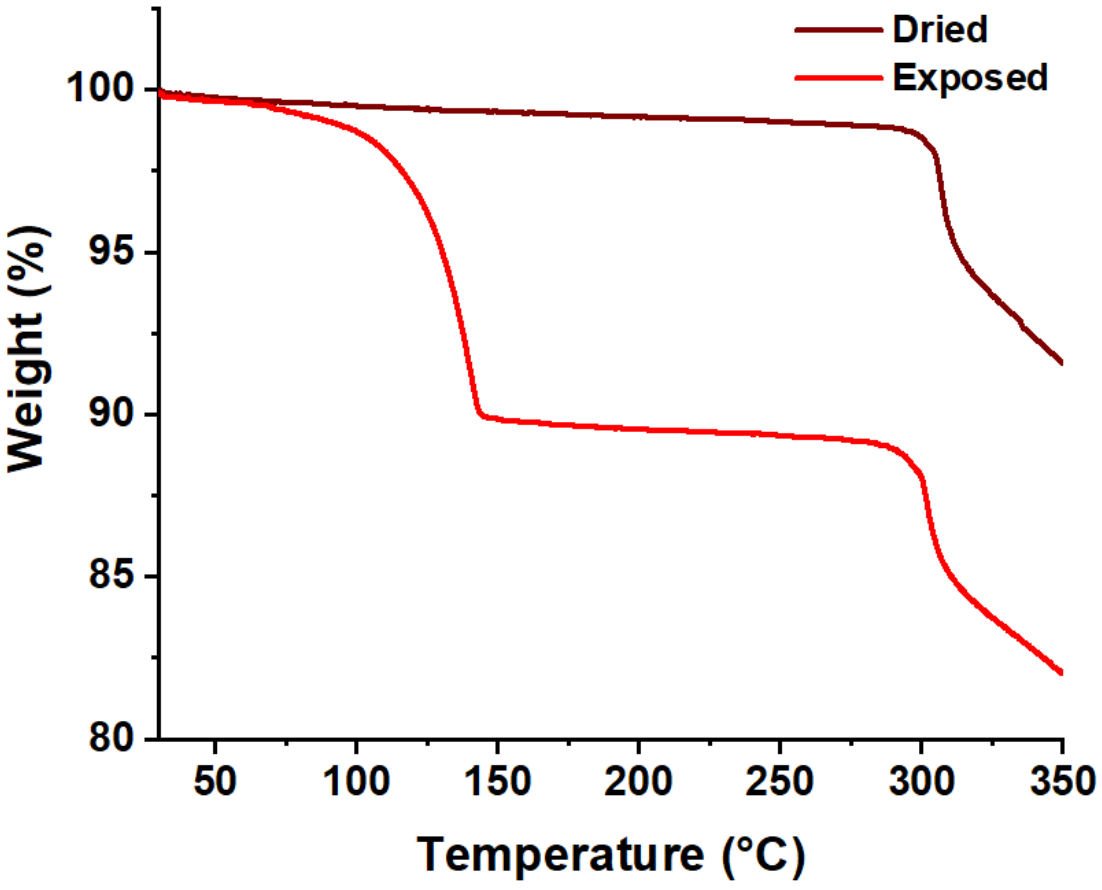

Fig. S5. Thermogravimetric analysis of the dried solid **1** after exposure to BA vapors. Thermogram of the dried solid **1** is reported for comparison.