Electronic Supplementary Material (ESI) for ChemComm.

An inexpensive and sensitive turn-on luminescence protocol for sensing formaldehyde

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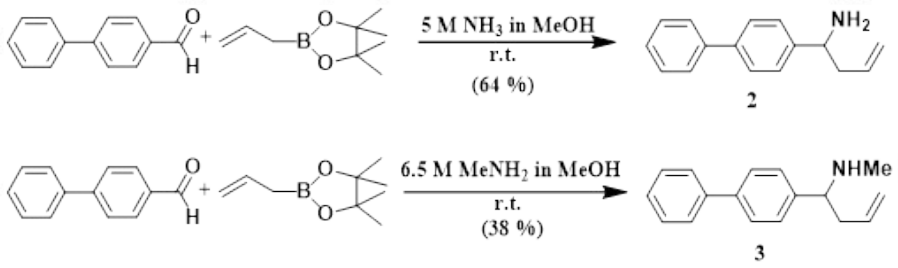
1. Materials and methods

Sodium cholate, terbium nitrate pentahydrate, biphenyl-4-carboxaldehyde (**1**), allyl pinacol boronate were purchased from Sigma-Aldrich. Western blotting paper (thickness: 0.83 mm) was locally purchased. MiliQ water (18.2 MΩ.cm at 25 ^{o}C) was used for all the experiments. An ultrasonic bath (frequency: 33 kHz) was used for the gel preparation. NMR spectra were recorded in Bruker 400 MHz spectrometer. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane (δ 0, s). Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), tdd (triplet of doublets of doublets), m (multiplet). Coupling constants are reported in Hertz (Hz) and the number of protons associated with a given resonance is indicated as nH. High resolution mass spectra (HRMS) were recorded in Xevo G2-XS QTof instrument. Absorption spectra were recorded on UV-3600 Shimadzu UV-Vis-NIR spectrometer. Time delayed emission from gel samples were recorded on Varian Cary Eclipse spectrometer in phosphorescence mode (delay time: 0.2 ms, gate time: 3.0 ms). A Varioskan® Flash Spectral Scanning Multimode Reader was used for the luminescence measurement of gel coated paper discs in TRF mode with delay time of 200 μs, integration time of 1000 μs, λ_{ex} = 300 nm, and λ_{em} = 545 nm. The error bars reflect the standard deviations of four set of measurements. HPLC analysis was performed on a Shimadzu HPLC system equipped with LC-10ATvp gradient pump and SPD-M10Avp UV-Vis detector. A reversed-phase C18 column (Phenomenex, 5 μm, 250 x 4.60 mm) was used for analysis. AFM images were recorded using JPK Nano Wizard II instrument.

2. Synthesis of *pro*-sensitizers:

Pro-sensitizers were synthesised following Scheme S1.

Scheme S1: Synthetic route of *pro*-sensitizers



2.1. Synthesis of 2:

In an oven dried vial (8 mL), equipped with a magnetic stir bar containing biphenyl-4-carboxaldehyde (25 mg, 0.14 mmol, 1 eq), NH_3 in MeOH (0.45 mL of 5 M, 2.25 mmol, 16 eq) was added and stirred at room temperature for 0.5 h. Allyl pinacol boronate (30 µL, 0.16 mmol, 1.14 eq) was added and the reaction was allowed to continue at room temperature under constant stirring for 16 h. The reaction mixture was diluted with MeOH (3 mL), transferred to a round bottomed flask and concentrated to obtained oily white mass. Oily white mass was dissolved in 5 mL of ethyl acetate, washed with saturated $NaHCO_3$ solution (2x10 mL). The washings were combined and extracted with ethyl acetate (3x5 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated to obtain crude product. The crude product was purified by column chromatography on silica gel using MeOH-$CHCl_3$ (0.5-3 %) to get compound **2** (20 mg, 64 %) as a liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.60-7.56 (m, 4H), 7.45-7.41 (m, 4H), 7.35 – 7.32 (m, 1H), 5.79-5.73 (m, 1H), 5.17-5.09 (m, 2H), 4.07-4.04 (dd, j = 7.6 Hz, j = 8 Hz, 1H), 2.56-2.49 (m,1H), 2.45-2.38 (m, 1H). (Figure S1)

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 144.39, 140.92, 140.07, 135.23, 128.79, 127.23, 127.09, 126.86, 117.96, 55.15, 43.91. (Figure S2)

HRMS: Calculated for $C_{16}H_{18}N$ [M+H] 224.1439, Observed $C_{16}H_{18}N$ [M+H] 224.1437.

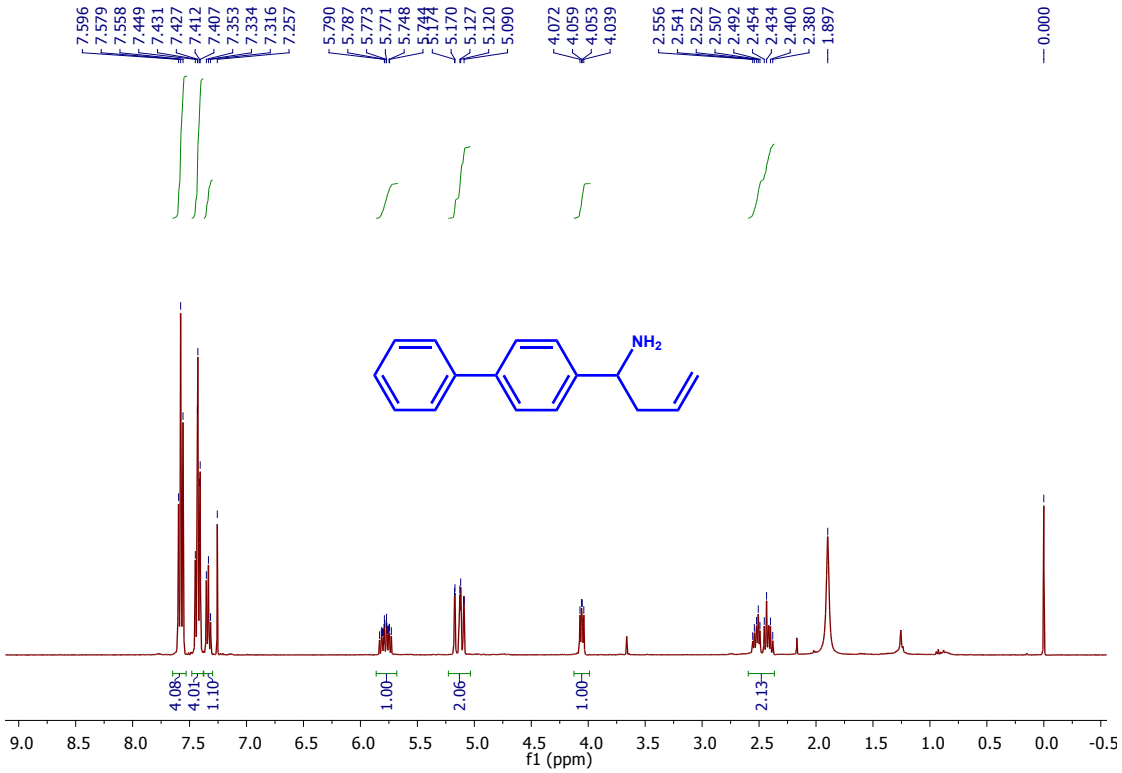


Figure S1: ^{1}H NMR spectrum of **2** ($CDCl_3$, 400 MHz).

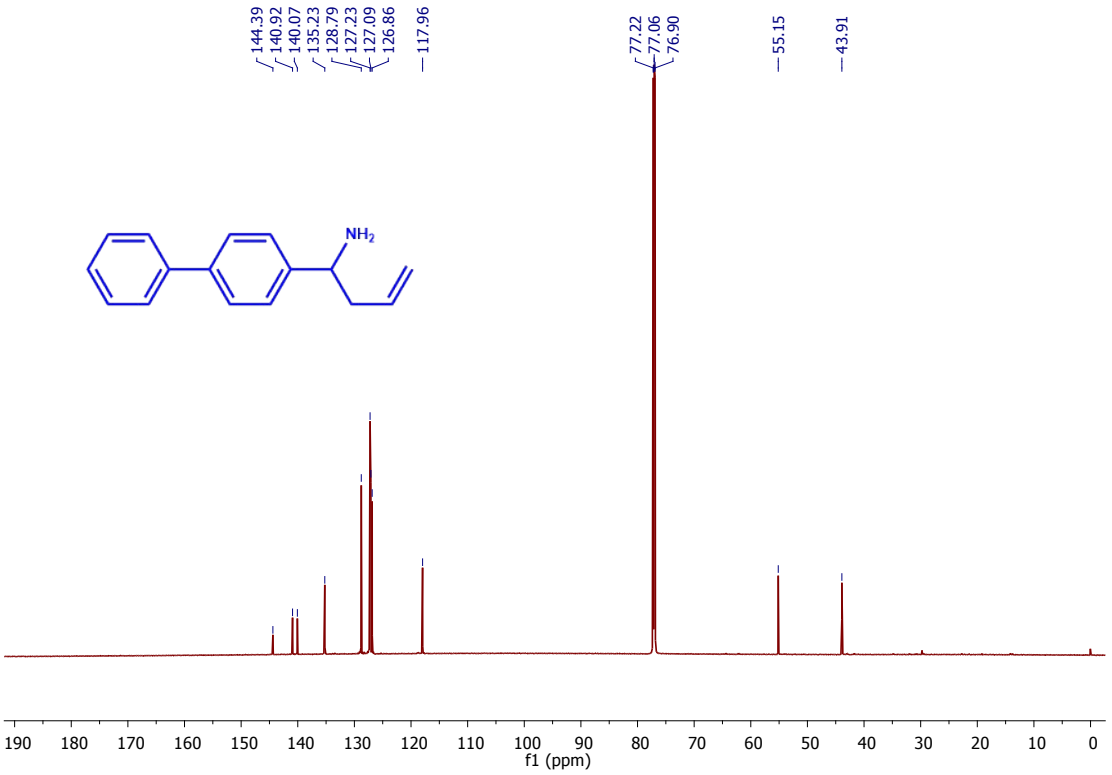


Figure S2: ^{13}C NMR spectrum of **2** ($CDCl_3$, 100 MHz).

2.2. Synthesis of 3:

Biphenyl-4-carboxaldehyde (26 mg, 0.14 mmol, 1 eq) was taken in an oven dried vial (8 mL) equipped with a magnetic stir bar. To it $MeNH_2$ in MeOH (0.45 mL of 6.5 M, 2.9 mmol, 21 eq) was added and stirred at room temperature for 1 h. Allyl pinacol boronate (28 µL, 0.15 mmol, 1.07 eq) was added and the reaction was allowed to continue at room temperature for 16 h under constant stirring. The reaction mixture was diluted with MeOH (5 mL), transferred to a round bottomed flask and concentrated to obtained oily yellowish mass. Oily yellowish mass was dissolved in chloroform (5 mL), washed with saturated $NaHCO_3$ solution (2x10 mL). The washings were combined and extracted with chloroform (3x5 mL). The combined chloroform layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure to obtain crude product. The crude product was purified by column chromatography on silica gel using MeOH-$CHCl_3$ (0.5-3 %) to obtain compound **3** (12.7 mg 38 %) as a liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.61-7.57 (m, 4H), 7.46-7.32 (m, 5H), 5.80-5.69 (tdd, j = 7.2 Hz, j = 10 Hz, j = 17.2 Hz,1H), 5.154-5.06 (m, 2H), 3.64-3.61 (t, j= 6.8 Hz, 1H), 2.53-2.50 (dd, j = 6.8 Hz, j = 7.2 Hz, 2H), 2.33 (s, 3H). (Figure S3)

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 141.96, 141.10, 140.34, 135.29, 135.27, 128.95, 127.94, 127.38, 127.25, 118.06, 64.49, 42.61, 34.47. (Figure S4)

HRMS: Calculated for $C_{17}H_{19}NH$ [M+H] 238.1596, Observed $C_{17}H_{19}NH$ [M+H] 238.1594.

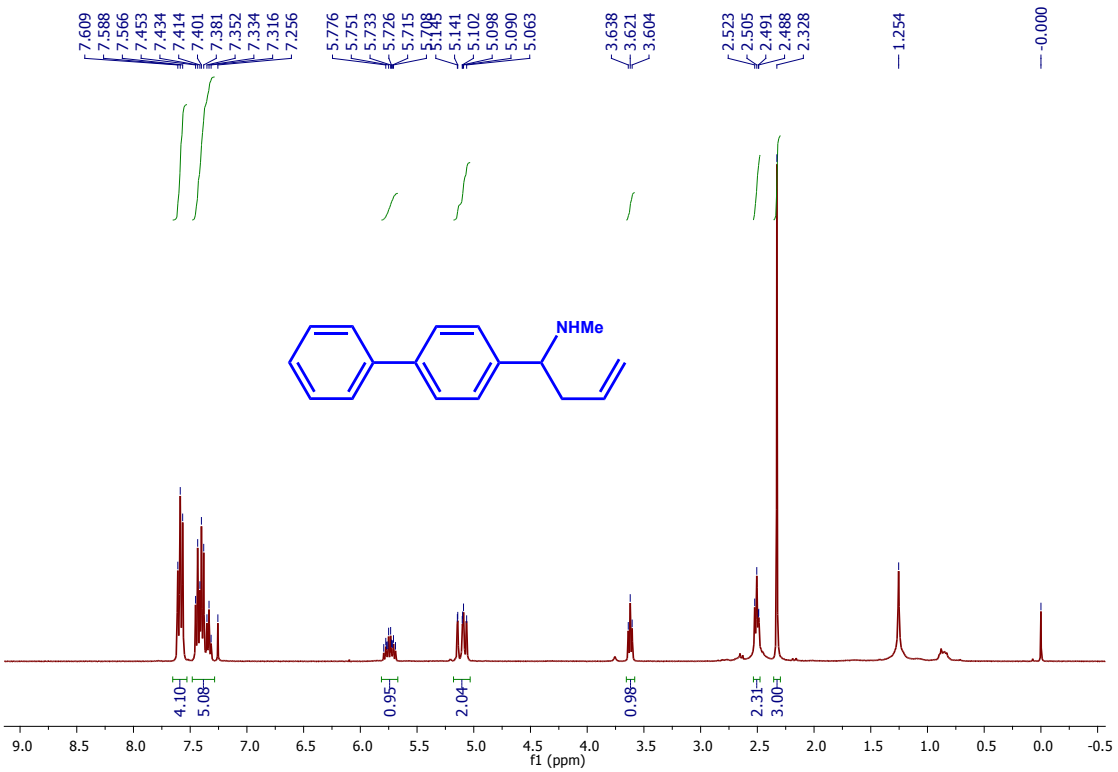


Figure S3: ^{1}H NMR spectrum of **3** ($CDCl_3$, 400 MHz).

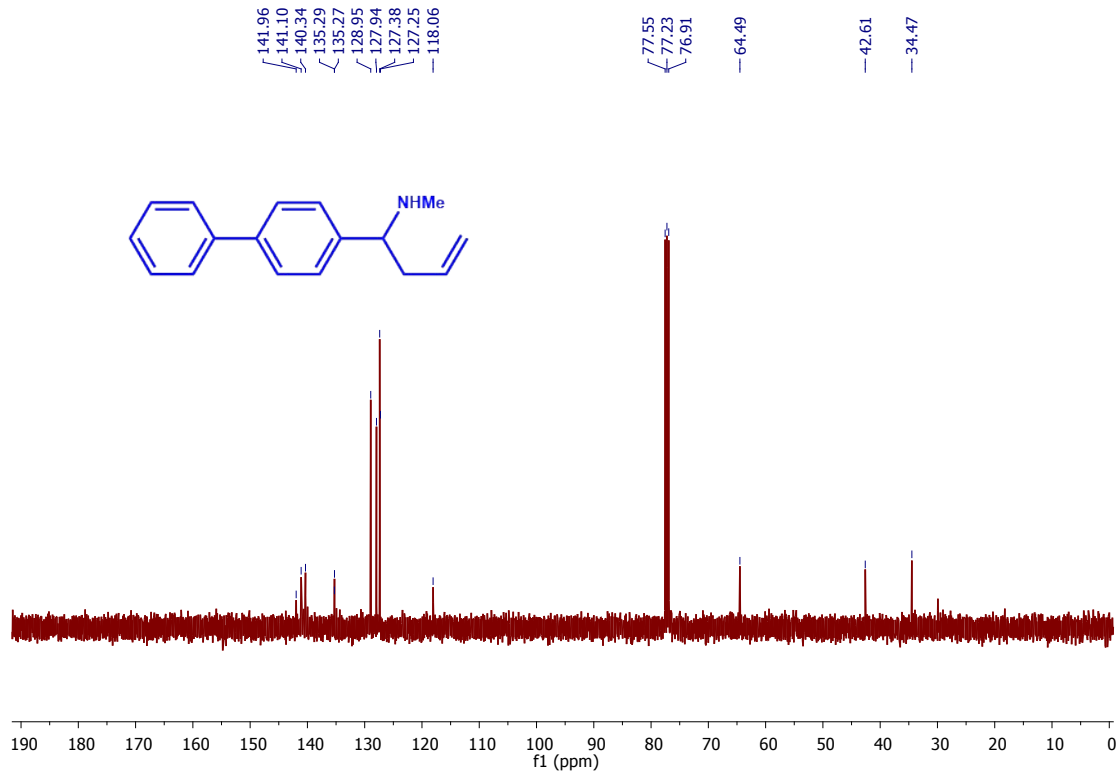


Figure S4: ^{13}C NMR spectrum of **3** ($CDCl_3$, 100 MHz).

3. Absorption spectra of 1, 2 and 3, and emission spectrum of 1:

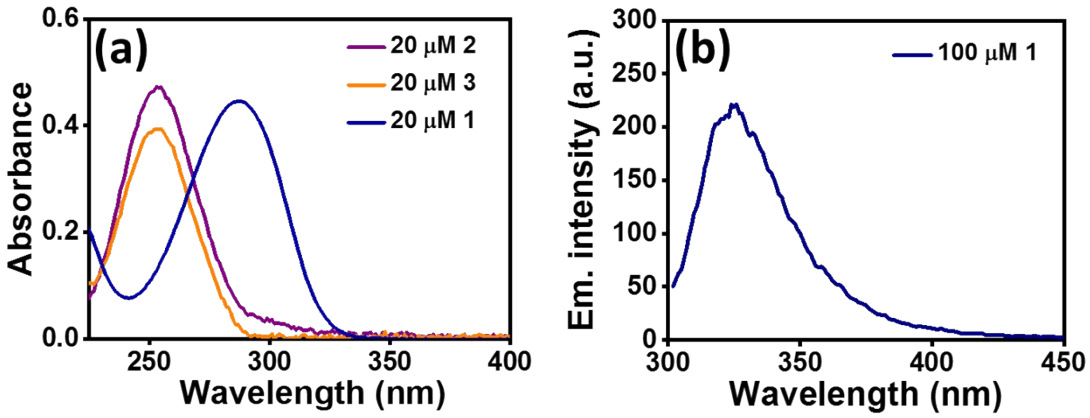


Figure S5: (a) Absorption spectra of **1**, **2** and **3** in methanol. (b) Emission spectrum of **1** in MeOH, λ_{ex} = 288 nm.

4. Extent of Tb^{3+} luminescence sensitization by 1, 2 and 3:

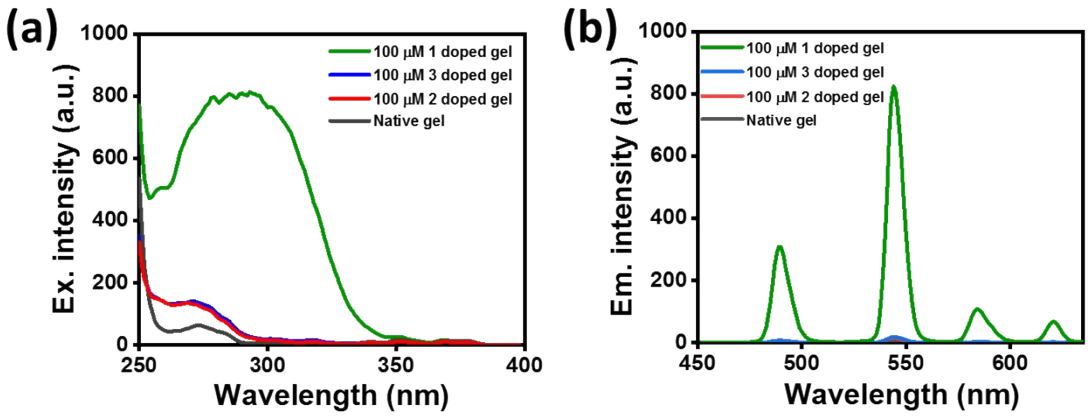


Figure S6: Time-delayed (a) excitation spectra (λ_{em} = 545 nm) and (b) emission spectra (λ_{ex} = 300 nm), of sensitizer and *pro*-sensitizer doped TbCh gels.

5. HPLC chromatogram:

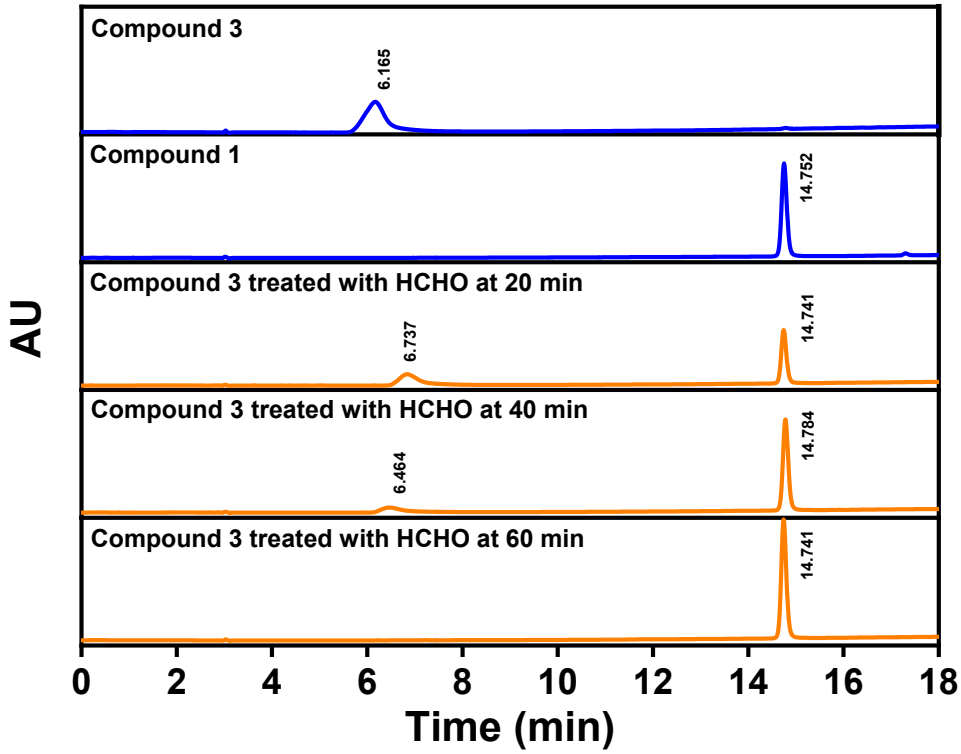


Figure S7: HPLC chromatogram (monitored at 270 nm) of formaldehyde (0.3 mM) treated solution of compound **3** (0.1 mM) heated at 100 ^{o}C (mobile phase: 50 % MeOH/H_2O to 90 % MeOH/H_2O).

6. Limit of detection (LOD) determination:

A calibration curve was constructed from the plot of time delayed emission (λ_{em} = 545 nm, λ_{ex} = 300 nm) intensity, from gel coated paper discs, versus concentration of FA (Figure S8). The LOD was calculated using the following equation,

LOD = 3*S.D./m

Where S.D. is the standard deviation for the time delayed fluorescent intensity of gel coated paper discs without FA, and m is the slope of the curve. The equation of linear fit is,

y = 4677.19x + 34097.63 (R^2 = 0.9959)

So,

LOD = 3*153/4677.19 = 98 nM

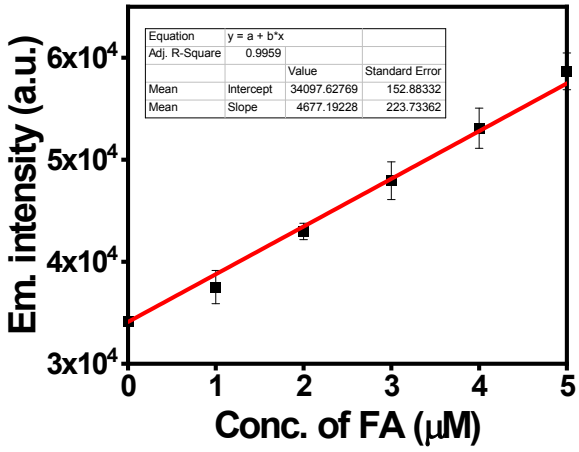


Figure S8: LOD determination plot.

7. Design and dimension of paper strip:

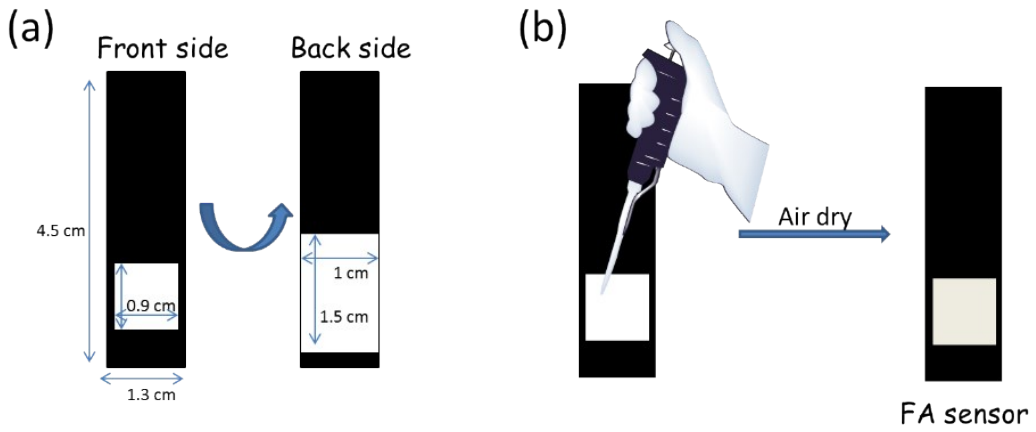


Figure S9: (a) Design and dimension of the paper strip. (b) Fabrication of the paper strip.

8. Calculation of vapour concentration:

Calculation is based on the assumption that FA present in solution vaporizes completely into gaseous state during incubation.

$$\text{Vapour conc.} = \frac{30.03 * x * y}{1000 * v} \text{ mg/m}^3 = \left(\frac{30.03 * x * y}{1000 * v}\right) * 0.814 \text{ ppm}$$

(At 25 ^{o}C, 1 mg/m^3 = 0.814 ppm)

Where x and y denote the volume (in mL) and concentration (in mM) of incubated FA solution, respectively; v ($3.5x10^{-6}$ m^3) is the volume of cuvette containing the paper strip.