

Rapid ‘Naked eye’ response of DCP, a nerve agent simulant: from molecules to low cost devices for both liquid and vapour phase detection

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CONTENTS

1. General	2
2. General methods of UV-vis and fluorescence titration experiments	2
3. Theoretical and computational methods	2
4. Experimental Procedure	2-3
5. Calculation of the detection limit.....	3
6. Detection of Quantum yield.....	3-4
7. ¹H NMR, ¹³C NMR and MS spectra.....	4-7
8. Details of computational study.....	7
9. References.....	7

1. General:

Unless otherwise mentioned, chemicals and solvents were purchased from Sigma-Aldrich Chemicals Private Limited and were used without further purification. ^1H -NMR and ^{13}C -NMR are recorded on Bruker 400 MHz instruments. For ^1H -NMR and ^{13}C -NMR spectra, CDCl_3 are used as solvents respectively, TMS is used as an internal standard. Chemical shifts are expressed in δ units and ^1H - ^1H coupling constants in Hz. UV-vis titration experiments were performed on a JASCO UV-V530 spectrophotometer and fluorescence experiment was done using PTI fluorescence spectrophotometer using a fluorescence cell of 10 mm path.

2. General method of UV-vis and fluorescence titration:

For UV-vis and fluorescence titrations, stock solution of the sensor was prepared ($c = 1 \times 10^{-5} \text{ ML}^{-1}$) in DCM (in presence of 3% Et_3N , 25°C). The solution of the guest species using in the order of $2 \times 10^{-4} \text{ ML}^{-1}$ was prepared in CH_3CN solvent. Solutions of various concentrations containing sensor and increasing concentrations of guest were prepared separately. The spectra of these solutions were recorded by means of UV-vis and fluorescence methods.

3. Methods for the preparation of the receptor i.e. RHM:

Rhodamine B (500mg, 0.95mmol) in 1,2-DCE (10ml) was taken in a 100ml round bottom flask fitted with dropping funnel. Then POCl_3 (0.6ml) was added drop wise into this solution. Next, the whole solution is refluxed for 4 hours in nitrogen atmosphere. After that the reaction mixture was cooled and evaporated in vacuum to give Rhodamine B acid chloride as a violet red oil which was dissolved in THF and mixed with Et_3N (0.1ml) and diaminomaleonitrile (250mg, 2.31mmol) stirring for 4 hours. Finally, the solvent was evaporated and purified by column chromatography (60-120mesh silica, eluted by DCM) to get the desired product (150mg, yield 20%).

^1H NMR (CDCl_3 , 400 MHz): δ (ppm): 8.18 (d, 2H, $J = 10.8$ Hz), 7.56 (m, 3H) 7.38 (m, 2H), 6.72 (s, 2H), 6.29 (s, 2H), 3.79 (q, 2H, $J = 9.4$ Hz), 3.50 (s, 2H), 3.19 (q, 2H, $J = 9.2$ Hz), 1.27 (t, 3H, $J = 9.4$ Hz), 0.99 (t, 3H, $J = 9.6$ Hz)

¹³C NMR (CDCl₃, 150 MHz): δ_c (ppm): 162.2, 158.2, 137.4, 134.6, 131.2, 128.3, 126.3, 125.2, 122.8, 114.8, 113.8, 55.5, 47.0, 45.0, 14.5, 12.1.

MS (ESI MS): (m/z, %): 532.2576 [(M+H)⁺, 100 %].

4. Determination of Detection Limit:

The detection limit DL of RHM for DCP was determined from the following equation [S1]. $DL = K * Sb1/S$

Where K = 2 or 3 (we take 3 in this case); Sb1 is the standard deviation; S is the slope of the calibration curve.

Thus using the formula we get the Detection Limit = 0.20 μM i.e. RHM can detect DCP in this minimum concentration.

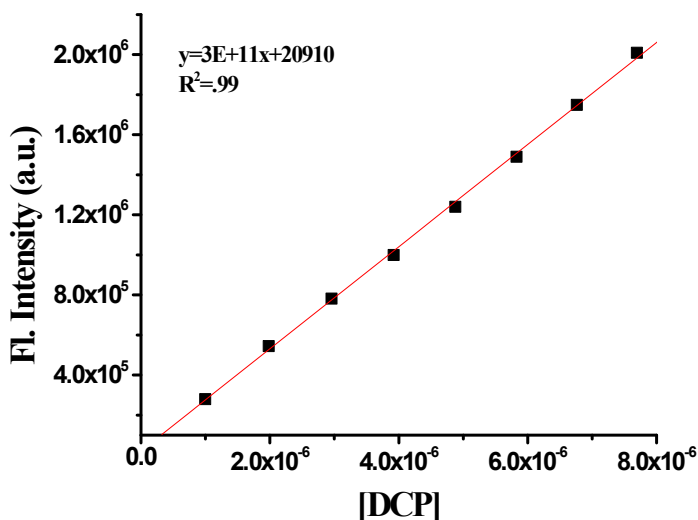


Figure S1: Intensity spectra of RHM @ 582nm vs. con. of DCP. From the curve Sb1= 20614.51749 and slope= 3E+11.

5. Determination of fluorescence quantum yield:

Here, the quantum yield φ was measured by using the following equation,

$$\phi_x = \phi_s (F_x / F_s)(A_s / A_x)(n_x^2 / n_s^2)$$

Where,

X & S indicate the unknown and standard solution respectively, φ = quantum yield,

F = area under the emission curve, A = absorbance at the excitation wave length,

n = index of refraction of the solvent. Here ϕ measurements were performed using anthracene in ethanol as standard [$\phi = 0.27$] (error $\sim 10\%$).

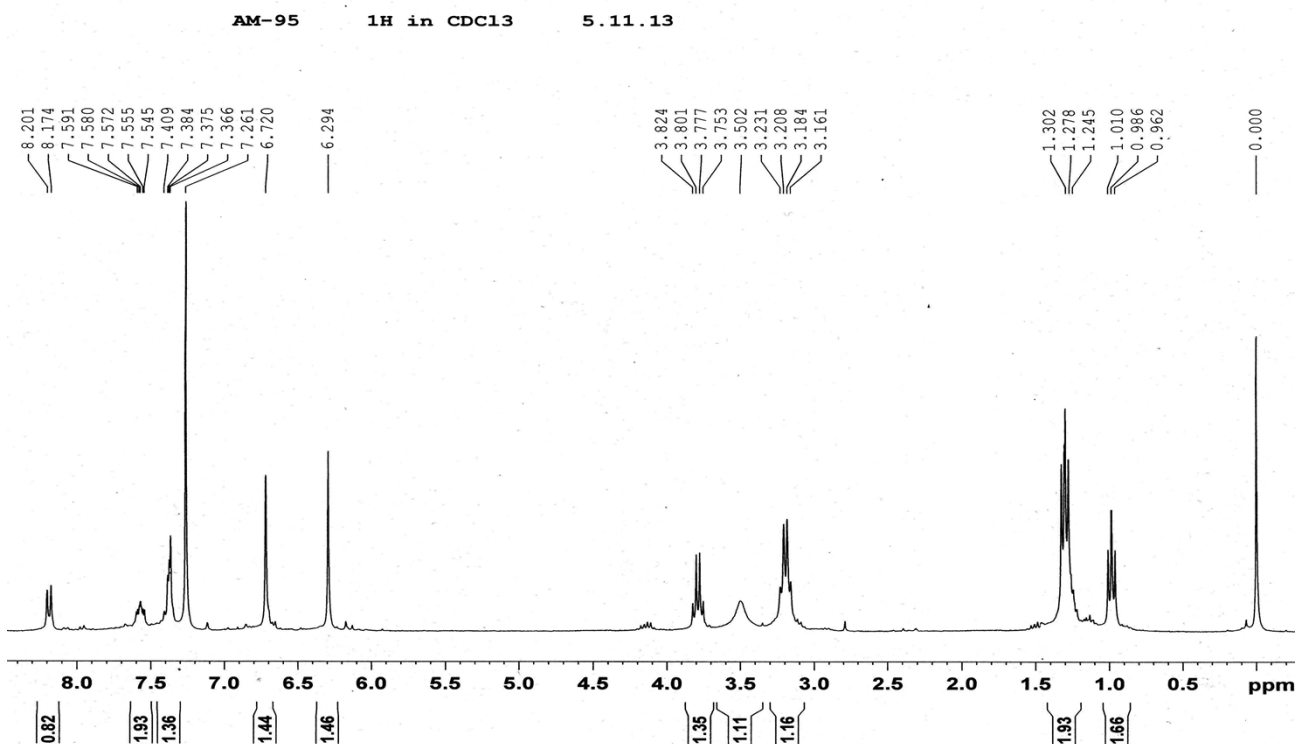
The quantum yield of RHM itself is 0.004 is remarkably change into 0.398 after addition of DCP.

6. Procedure for liquid and vapor phase detection with using TLC plate sticks:

It was easily prepared by immersing a TLC plate into the solution of RHM (2×10^{-3} M) in DCM and then exposing it to air to evaporate the solvent. The detection of DCP in vapor phase was carried out by hanging the TLC plate into the conical containing the solution of DCP. For liquid phase detection, TLC plate was contaminated with DCP solution and evaporating solvent to dryness. Finally, under the sun light and UV light the fluorescence was checked.

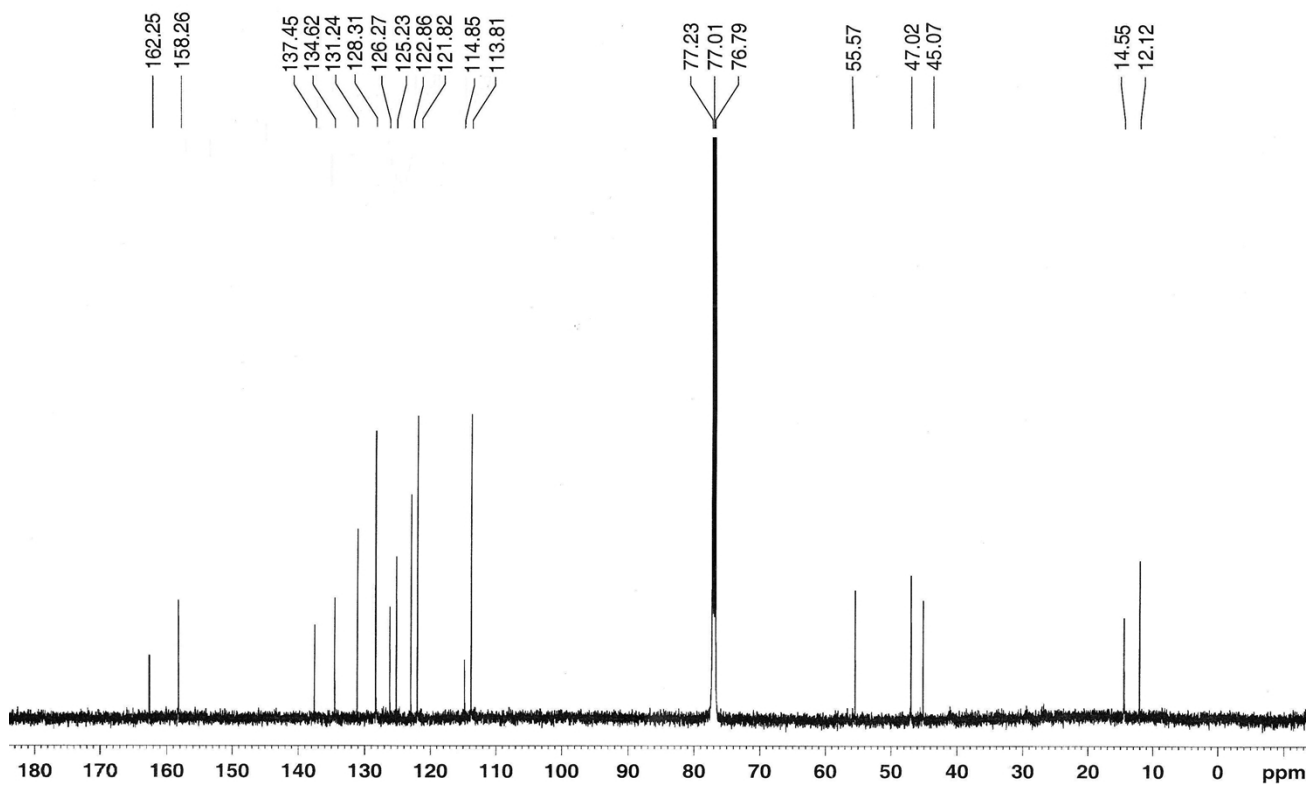
7. ^1H NMR, ^{13}C NMR and MS spectra:

^1H -NMR OF RHM:



^{13}C of RHM:

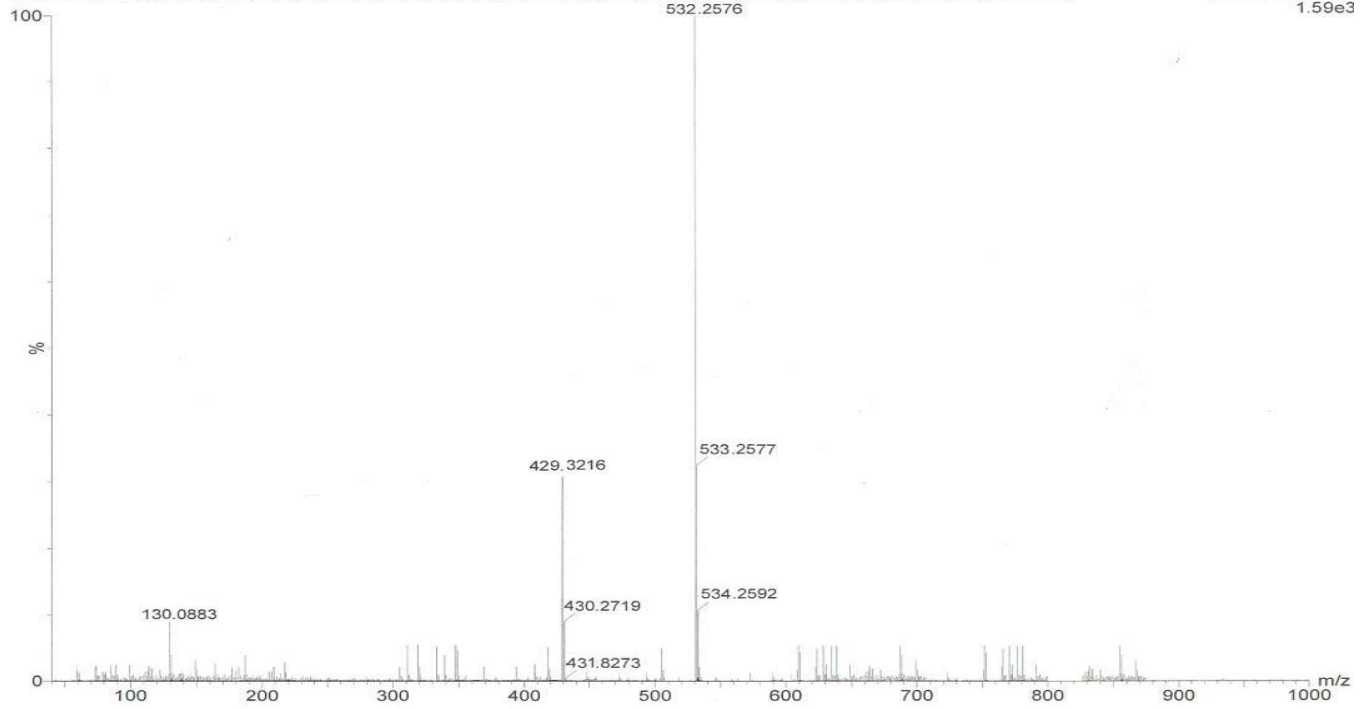
AM-95 ^{13}C in CDCl_3 5.11.13



Mass of RHM:

SPG-AM-42 33 (0.701) AM (Cen,4, 92.00, Ar,8500.0,556.28,5.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (33:40-2:7)

1: TOF MS ES+
1.59e3



Mass of RHM with DCP:

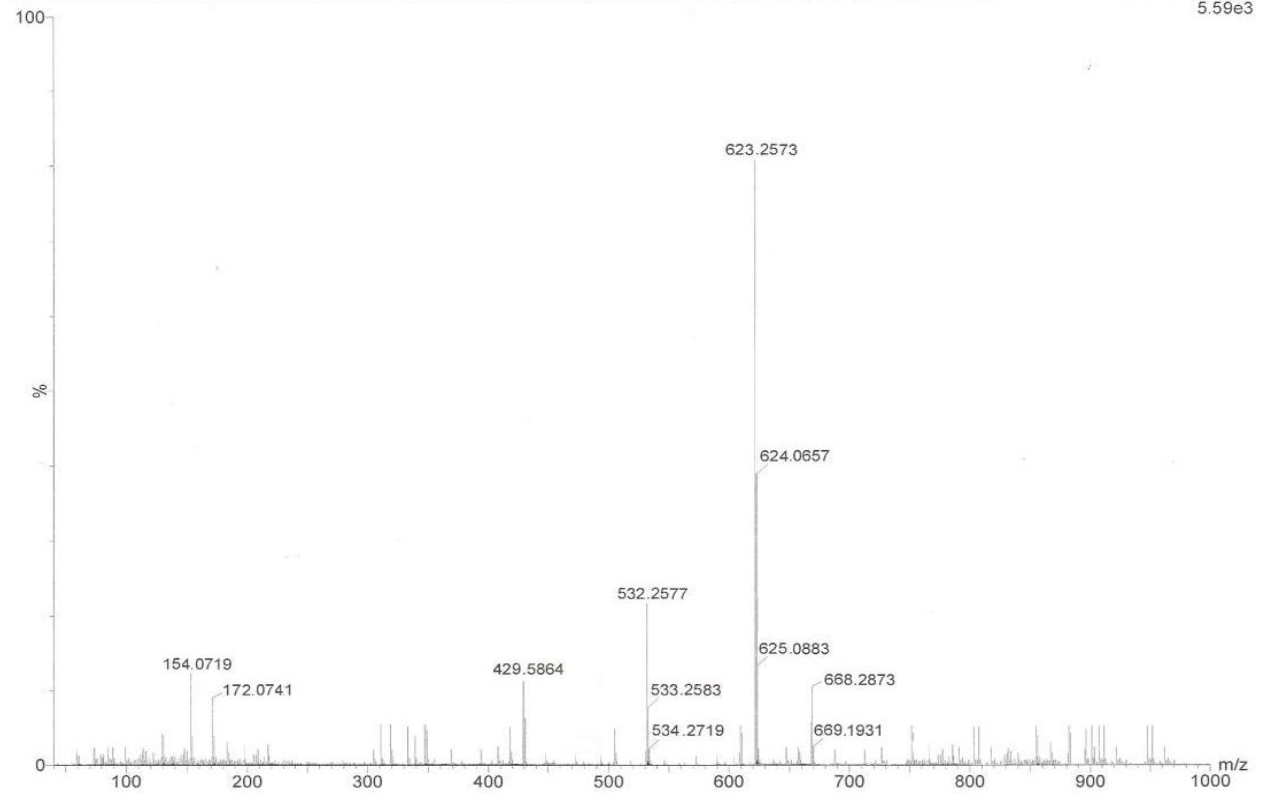
Electrospray ionisation-MS

WATERS-Q-ToF Premier-HAB213

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SPG-AM-43 33 (0.701) AM (Cen,4, 92.00, Ar,8500.0,556.28,5.00,LS 10); Sm (SG, 2x5.00); Sb (10,1.00); Cm (33:40-2:7)

1: TOF MS ES+
5.59e3



8. Details of computational study:

The ground state geometry of RHM and its adduct with DCP has been fully optimized by using the DFT functionals B3LYP (a hybrid exchange-correlation functional (Becke + Slater + HF exchange and LYP + VWN5 correlations)) [S2-S4] for the 6-311+G** basis set. The Hessian analysis showed energy minimum structures on the potential-energy hyper surface as confirmed by real frequencies obtained for all normal modes of vibration. All calculations have been carried out using the GAUSSIAN 09 package [S5].

9. References:

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