

“On-off” fluorescence detection of exposed phosgene via pyrazine ring formation on triphenyl amine backbone supplemented with theoretical approach and practical environmental applications

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1. Preparation of phosgene gas

As phosgene is toxic, volatile and difficult in handling hence, during the experiments we use less toxic, nonvolatile triphosgene ($\text{CCl}_3\text{OC}(\text{O})\text{OCCL}_3$) as the precursor of phosgene gas. It generates phosgene gas in presence of triethylamine (TEA). In all the experiments acetonitrile was used as solvent.

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

By UV-vis method:

For UV-vis titrations, stock solution of the sensor was prepared ($c = 2 \times 10^{-5} \text{ M}$) in CH_3CN . Triphosgene solution of concentration $c = 2 \times 10^{-4} \text{ M}$ was prepared in CH_3CN and Triethylamine was added to the solution (1:5 molar ratio). The solution of the guest interfering analytes like CH_3COOH , $\text{C}_4\text{H}_9\text{Cl}$, $\text{C}_4\text{H}_9\text{Br}$, $\text{C}_4\text{H}_9\text{I}$, CH_3COCl , $\text{C}_6\text{H}_5\text{COCl}$, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, SOCl_2 were also prepared in the order of ($c = 2 \times 10^{-4} \text{ M}$). Initially sensor **ADM** solution was prepared by dissolving the sensor in 2 ml acetonitrile followed by the gradual addition of corresponding guest analytes with the particular concentration. Solutions of various concentrations containing sensor and increasing concentrations of analytes were prepared separately. The spectra of these solutions were recorded by means of UV-vis methods.

By fluorescence method:

For fluorescence titrations, stock solution of the sensor ($c = 2 \times 10^{-5} \text{ M}$) was prepared for the titration of analytes in CH_3CN . Initially sensor **ADM** solution was prepared by dissolving the sensor in 2 ml acetonitrile followed by the gradual addition of corresponding guest analytes with the particular concentration. The solution of the guest analytes in the order of $2 \times 10^{-4} \text{ M}$ were also prepared. Solutions of various concentrations containing sensor and increasing concentrations of analytes were prepared separately. The spectra of these solutions were recorded by means of fluorescence methods.

3. Determination of fluorescence quantum yield:

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

$$\phi_x = \phi_s \left(\frac{F_x}{F_s} \right) \left(\frac{A_s}{A_x} \right) \left(\frac{n_x^2}{n_s^2} \right)$$

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 $\sim 10\%$)

4. Calculation of the detection limit:

The detection limit (DL) of **ADM** for phosgene was determined from the following equation:

$$DL = K * Sb_1/S$$

Where $K = 2$ or 3 (we take 3 in this case); Sb_1 is the standard deviation of the blank solution; S is the slope of the calibration curve.

From the graph Fig.S1, we get slope = 4.8394 , and Sb_1 value is 6.8183

Thus, using the formula, we get the Detection Limit for phosgene = $4.23 \mu\text{M}$.

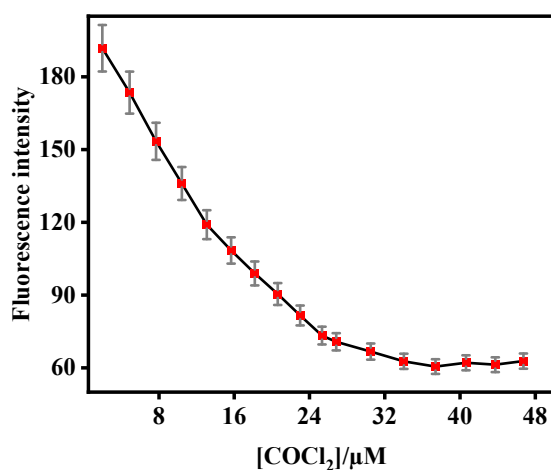


Fig. S1: Changes of fluorescence intensity of **ADM** as a function of $[\text{COCl}_2]$.

5. Stern–Volmer (SV) plot:

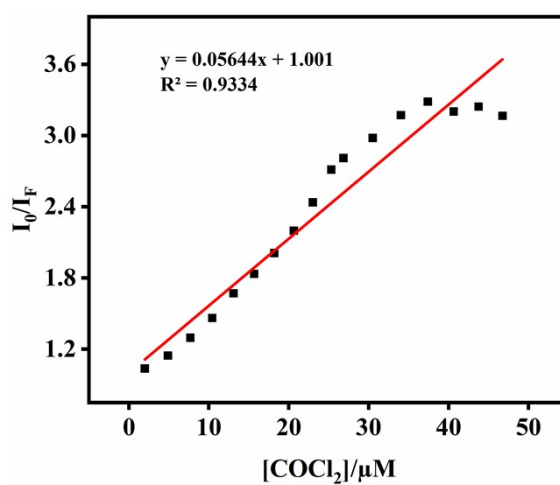


Fig. S2: Stern-Volmer plot of **ADM** towards COCl_2 .

The quenching efficiency and sensitivity were evaluated by calculating the Stern–Volmer quenching constant (K_{SV}), calculated by the Stern–Volmer (SV) equation: $I_0/I = 1 + K_{SV}[\text{COCl}_2]$, where K_{SV} is the quenching constant (M^{-1}), I_0 and I are the fluorescence intensities of complexes before and after the addition of phosgene, and $[\text{COCl}_2]$ is the molar concentration of phosgene.

The changes of emission curve of ADM ($c = 2 \times 10^{-5} \text{M}$) at different time interval by addition of phosgene ($c = 2 \times 10^{-4}$) and calculation of first order rate constant:

Fig.S2 represents the changes of emission intensity at different time interval by addition of triphosgene/TEA. From the time vs. fluorescent intensity plot at fixed wavelength at 554 nm by using first order rate equation we get the rate constant $K = \text{slope} \times 2.303 = 1.6593 \times 2.303 = 3.821 \text{ Sec}^{-1}$.

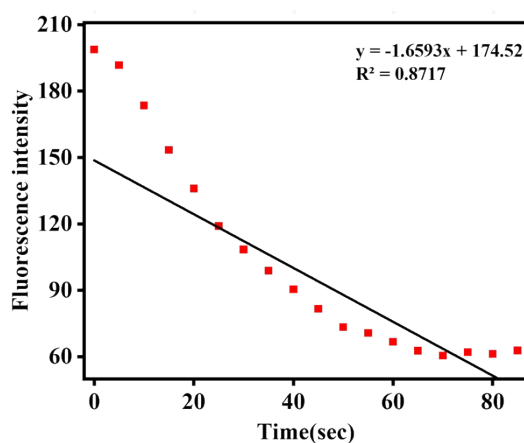


Fig. S3. The first order rate equation by using Time vs. fluorescent intensity plot at 554 nm.

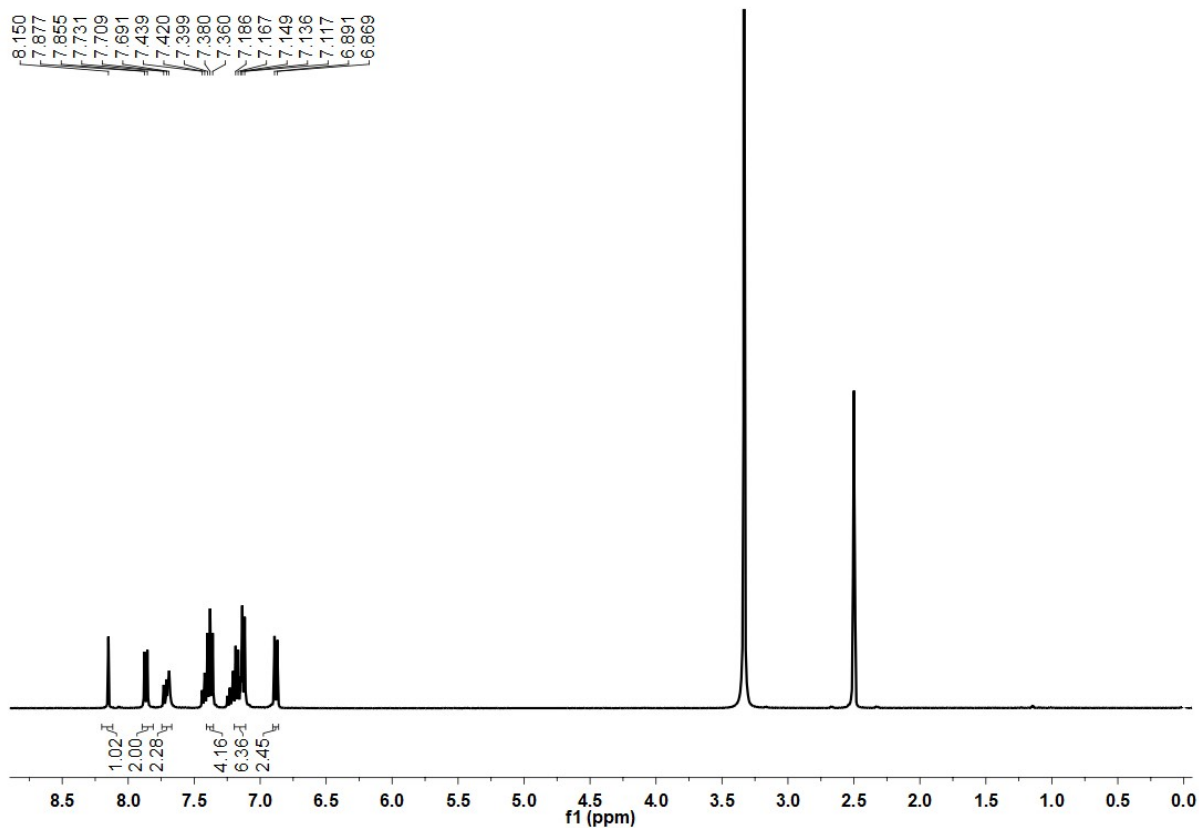


Fig.S4. ¹H NMR spectrum of ADM

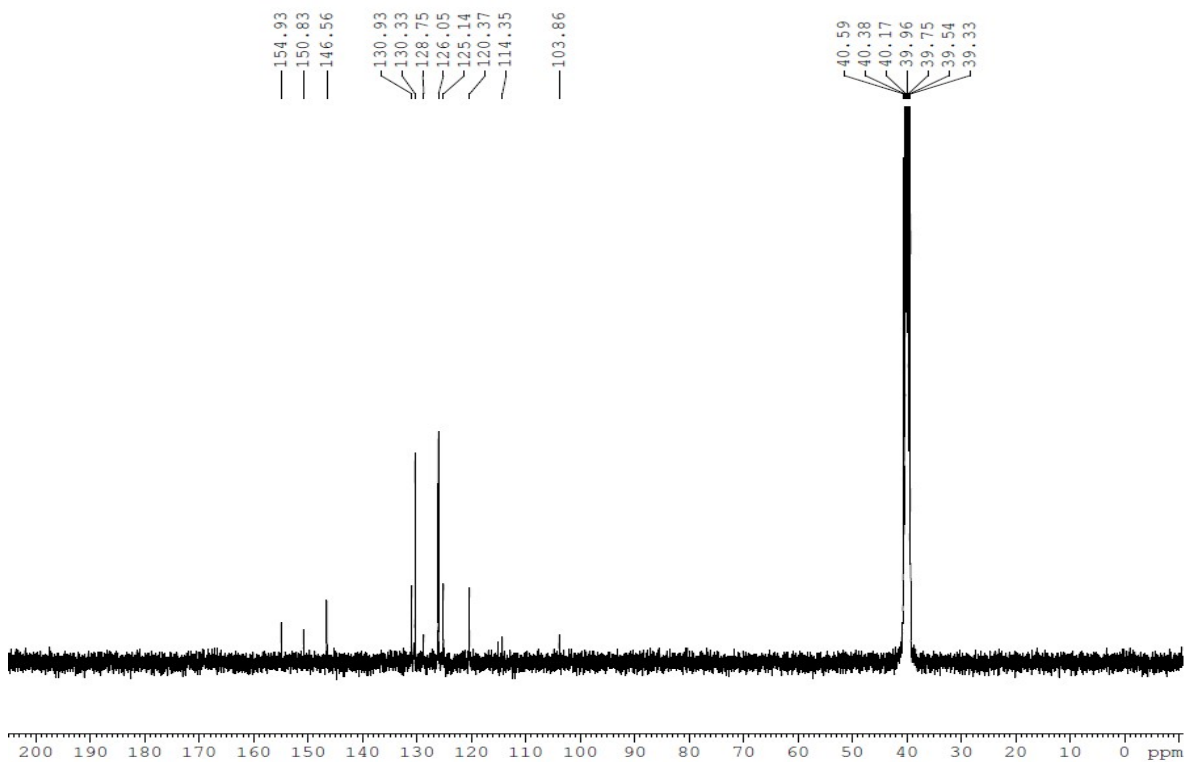


Fig.S5. ¹³C NMR spectrum of ADM

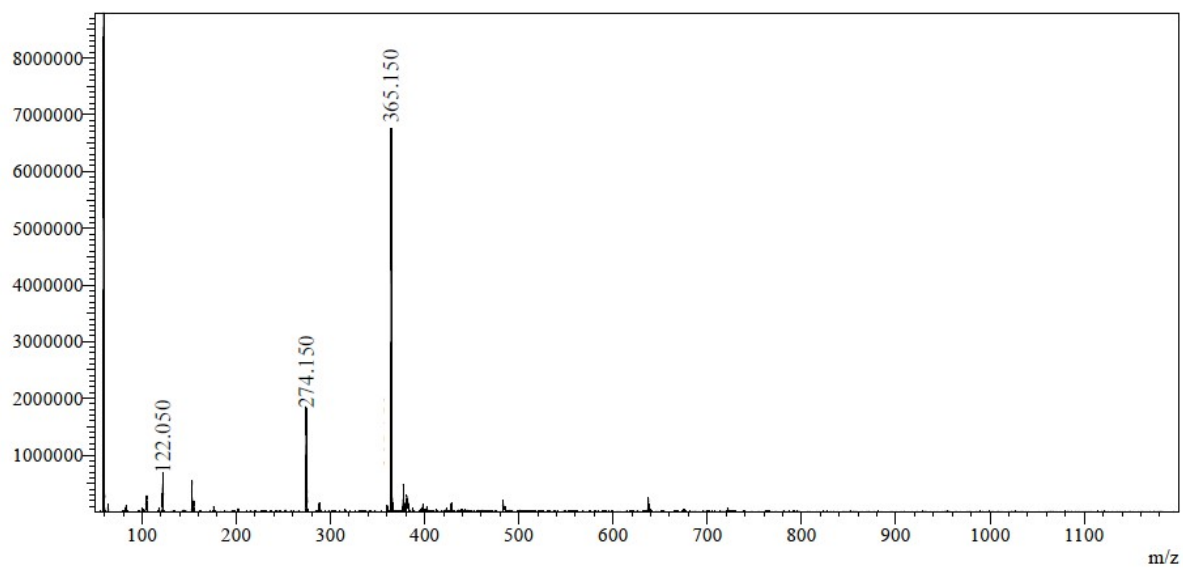


Fig.S6. Mass spectrum of ADM

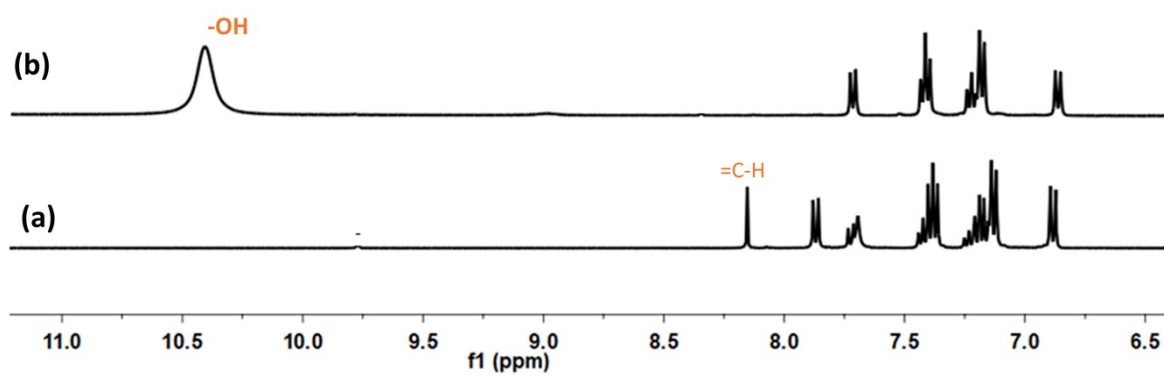


Fig.S7. ¹H-NMR spectra of (a) ADM and (b) ADM + phosgene

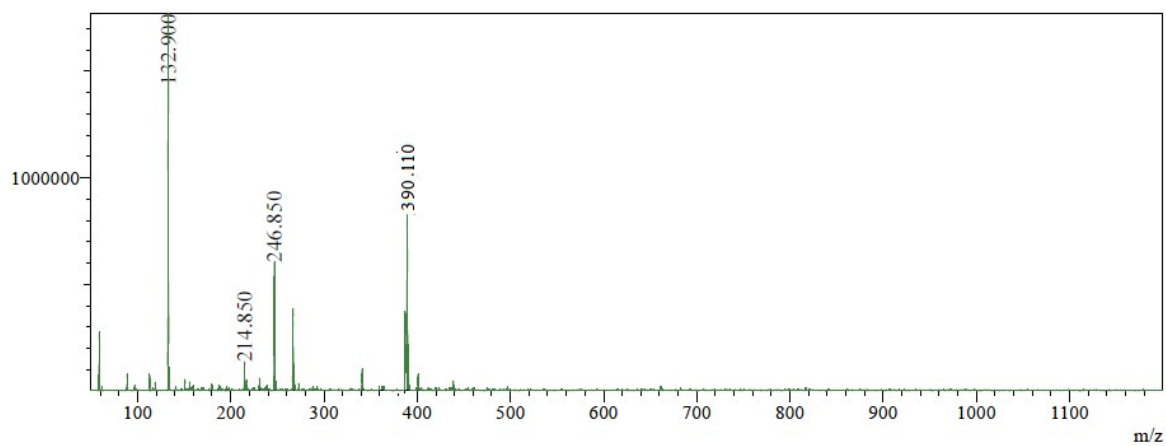


Fig.S8. Mass spectrum of ADM + phosgene

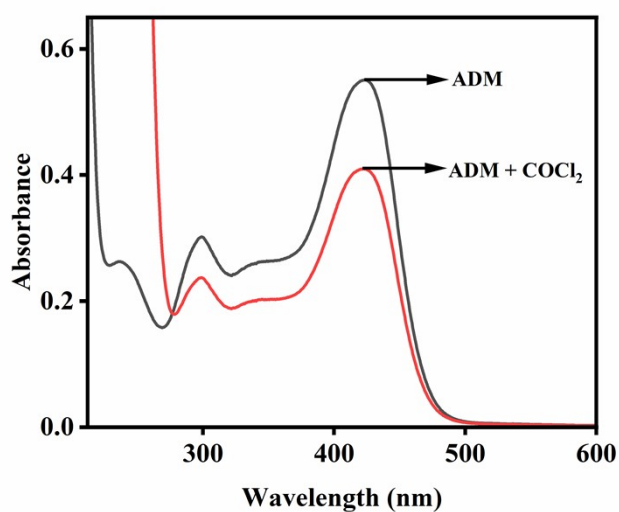


Fig.S9. Absorbance spectra of ADM and ADM + COCl₂.

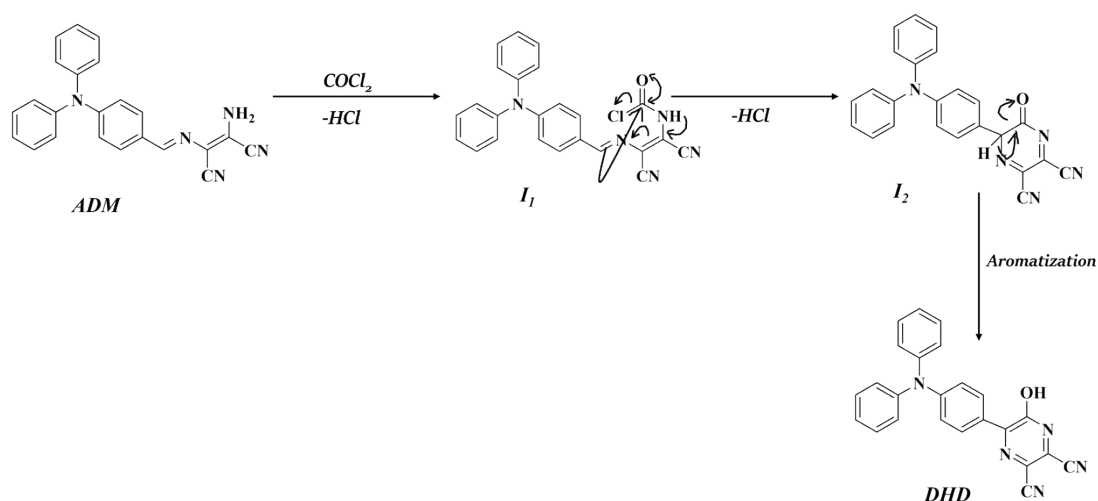


Fig S10. A plausible mechanism of interaction of ADM with phosgene

6. Soil Analysis

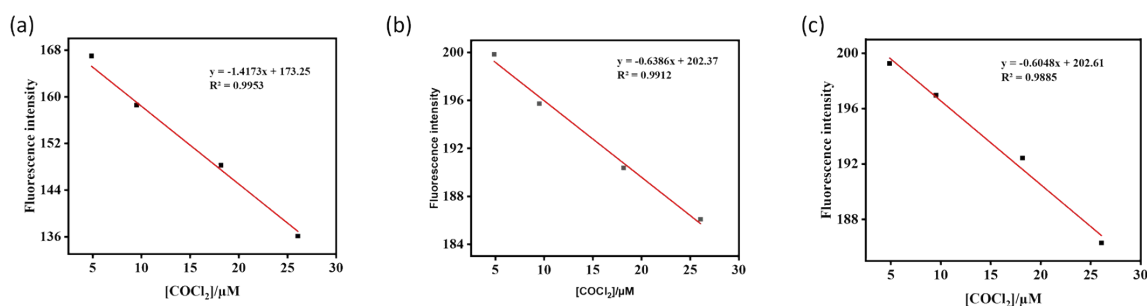
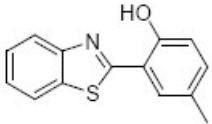
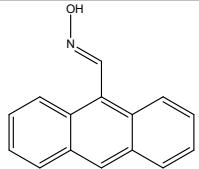
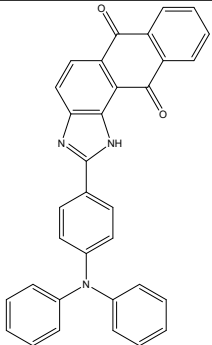
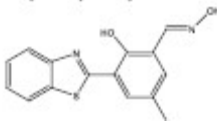
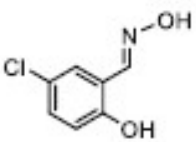
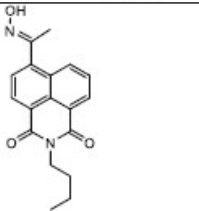
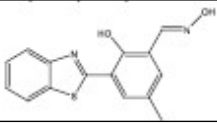


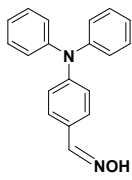
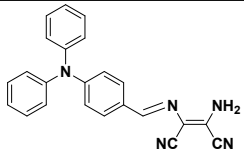
Fig. S11. The changes of emission intensity for probe ADM at 565 nm with different concentration of phosgene in (a) sand soil, (b) clay soil (c) field soil.

7. Computational details

Density Functional Theory (DFT)¹ calculations were conducted using the Gaussian 09 (Revision A.02) package, with "Gauss View" utilized for visualizing molecular orbitals. Becke's three-parameter hybrid-exchange functional, the Lee-Yang-Parr expression for nonlocal correlation, and the Vosko-Wilk-Nuair 1980 local correlation functional (B3LYP) were employed in the calculation.² Optimization of **ADM** and **DHD** in the gas phase were performed using the 6-31+(g) basis set. The absorbance spectral properties of **ADM** and **DHD** were calculated by time-dependent density functional theory (TDDFT)³ associated with the conductor-like polarizable continuum model and we computed the lowest 40 singlet – singlet transition. For H, C, N, O, atoms we used 6-31+(g) basis set for all the calculations. The calculated electron-density plots for frontier molecular orbitals were prepared by using Gauss View 5.1 software. All the calculations were performed with the Gaussian 09W software package.⁴

Table S1: Comparison table of ADM with the reported similar type of chemosensors

Ligands	Analytes	Solvent used	Probe type	Detection limit	Applications	References
	Phosgene	CH ₃ CN	Turn on	0.48 nM	Dipstick method	[5]
	Phosgene	CH ₃ CN	Turn off	1.52 nM	Detection of phosgene in household bleach	[6]
	Phosgene	1,4-dioxane solvent	Turn on	22.8nM	Soil analysis	[7]
	Phosgene	CH ₃ CN	Turn on	0.48 nM	The TLC plate	[8]
	Phosgene	CH ₂ Cl ₂	Turn on	4 nM	The test paper	[9]
	Phosgene	CH ₃ CN	Turn on	6.3 nM	Test strip	[10]
	Phosgene	CH ₃ CN	Ratiometric	0.09 nM	PCL nanofibre	[11]
Harrison's reagent supported into a porous nanocrystalline TiO ₂ matrix film	Phosgene	EtOH	Turn on	26 ppb	-	[12]

	Phosgene	CH ₃ CN	Turn off	21.53 μM	Detection of phosgene in household bleach, dipstick, soil analysis	[13]
	Phosgene	CH ₃ CN	Turn off	4.23 μM	Detection of phosgene source from chlorinated hydrocarbons, dipstick, Soil analysis	This work

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