Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

SUPPORTING INFORMATION

Detection of exposed phosgene in household bleach: Development of a selective and cost-effective sensing tool

Shrabani Saha and Prithidipa Sahoo*

Department of Chemistry, Visva-Bharati University, Santiniketan, 731235, India.

E-mail: prithidipa@hotmail.com.

.

1. NMR Studies:

^{1}H NMR of ANO in DMSO-d_6:

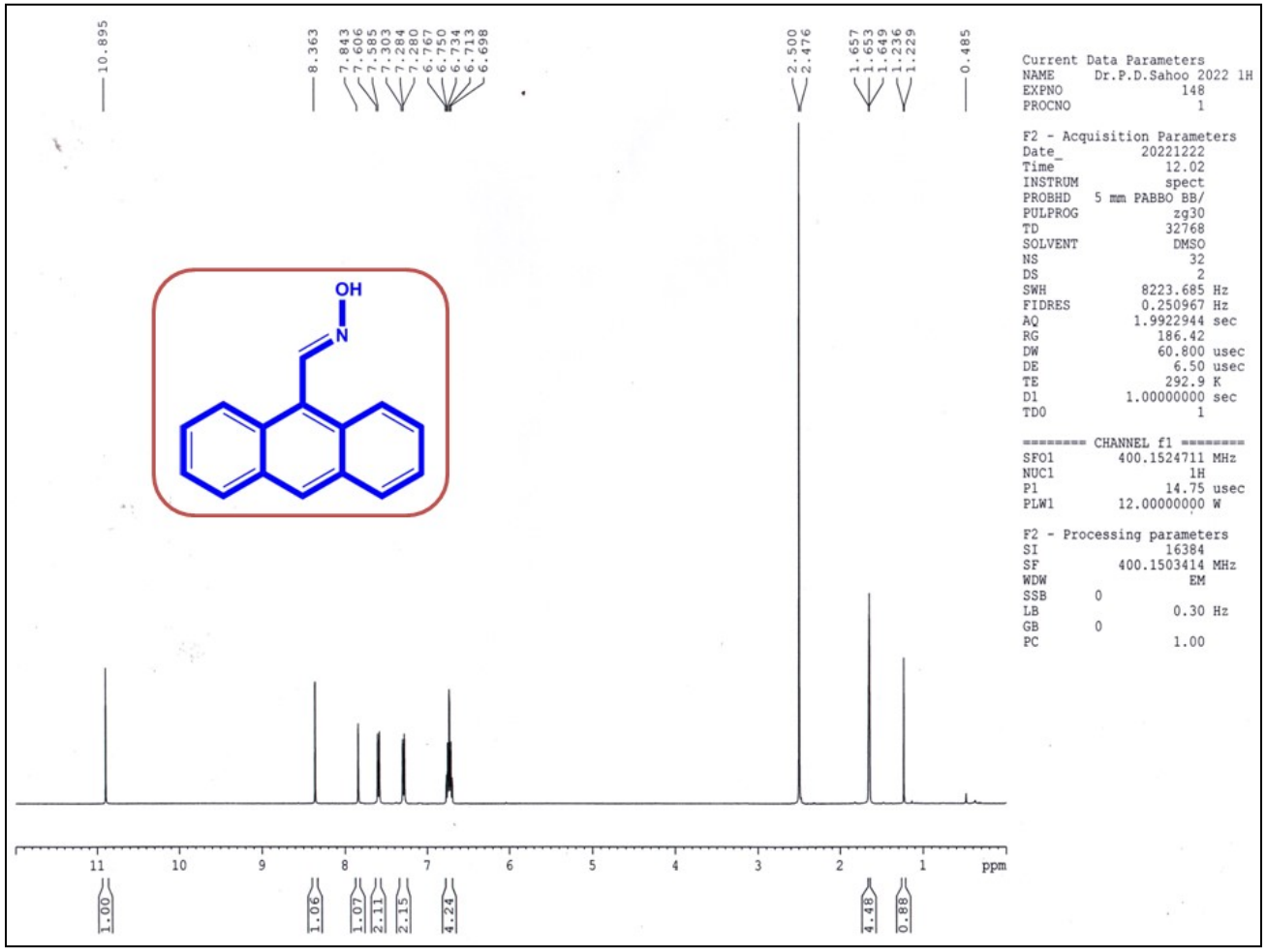

Fig.S1 ^{1}H NMR of **ANO** in DMSO-d_6 (400 MHz).

^{13}C NMR of ANO in DMSO-d_6:

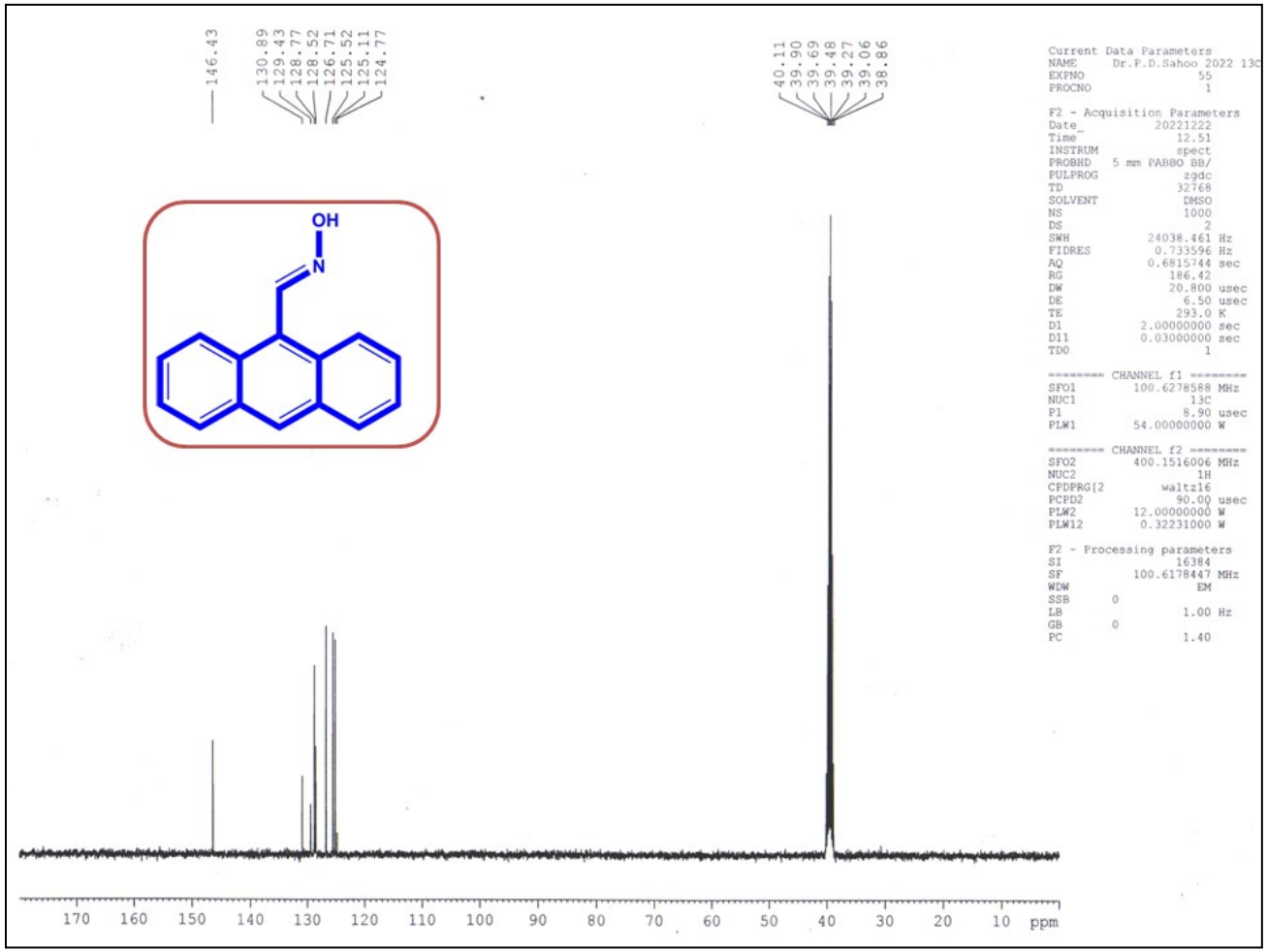

Fig.S2 ^{13}C NMR of ANO in DMSO-d_6 (100 MHz).

2. Materials and Instruments

9-anthracenecarboxaldehyde, Hydroxylamine hydrochloride, Ethanol, Triethylamine, Ethyl acetate and all other chemicals were purchased from Sigma-Aldrich Pvt. Ltd. Unless otherwise mentioned, materials were obtained from commercial suppliers and were used without further purification. Solvents were dried according to the standard procedures. Elix Millipore water was used throughout all the experiments. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. For NMR spectra and NMR titration, DMSO-d_6 was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ ppm units and ^{1}H–^{1}H and ^{1}H–C coupling constants in Hz. The following abbreviations are used to describe spin multiplicities in ^{1}H NMR spectra: s = singlet; d = doublet; t = triplet; m = multiplet. The mass spectrum (HRMS) was carried out using a micromass Q-TOF Micro™ instrument by using DMSO as a solvent. Fluorescence spectra were recorded on a Fluorescence spectrophotometer Hitachi 7100. UV spectra were recorded on a Hitachi U-2910 spectrophotometer.

3. Preparation of phosgene gas. As phosgene is toxic, volatile and difficult in handling hence, during the experiments we use nontoxic, nonvolatile triphosgene ($CCl_3OC(O)OCCl_3$) as the precursor of phosgene gas. It generates phosgene gas in presence of triethylamine (TEA). In all our experiments we use acetonitrile as solvent.

4. The general method for UV-vis and fluorescence spectral studies. A stock solution of **ANO** (1 μM) was prepared in CH_3CN. Triphosgene solution of concentration 10 μM was prepared in CH_3CN and Triethylamine was added to the solution (1:5 molar ratio). During the titration, each time a 1 μM solution of **ANO** was filled in a quartz optical cell of 1 cm optical path length and Triphosgene/TEA stock solution was added into the quartz optical cell gradually by using a micropipette. Spectral data were recorded at 1 min after the addition of Triphosgene/TEA**.** For all fluorescence measurements, excitations were provided at 250 nm, and emissions were collected from 370 to 600 nm.

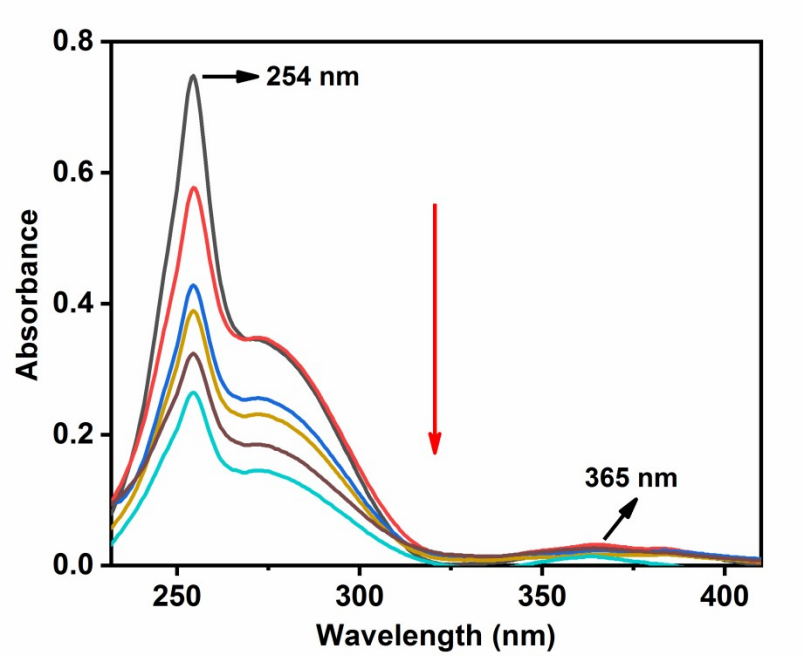

Fig.S3 UV−Vis absorption spectra of **ANO** (1 μM) upon gradual addition of Triphosgene/TEA (1:5 molar ratio) up to 0.6 μM in CH_3CN.

5. Calculation of Standard Deviation (SD) and limit of detection (LOD) of ANO with phosgene:

Table S1

Blank Reading (ANO)	**Fluorescence Intensities at 429 nm (X)**	**Mean (x)**	**Standard Deviation** $(\sigma) = \sqrt{\frac{\sum\|X-x\|^2}{N}}$
Reading 1	**1240.00**	**1240.248**	**0.6829**
Reading 2	**1239.42**		
Reading 3	**1240.85**		
Reading 4	**1241.23**		
Reading 5	**1239.74**		

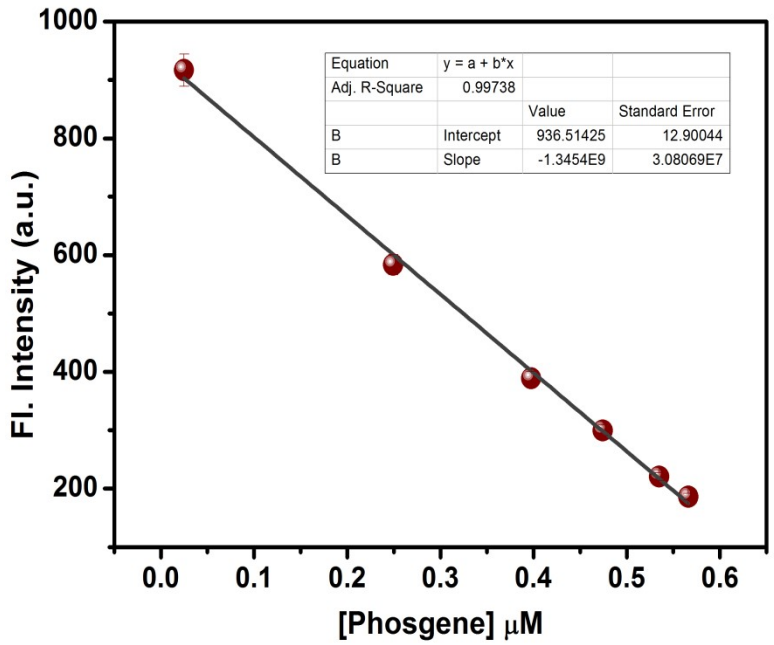

Fig. S4 Linear fit curve of **ANO** at 429 nm with respect to phosgene concentration. Standard deviations are given by error bars where, n=3.

From the linear fit graph we get slope = -1.3454×10^{9}, and SD value is 0.6829

Thus using the above formula we get the Limit of Detection = 1.52×10^{-9} M, = 1.52 nM. Therefore **ANO** can detect phosgene up to this very lower concentration by fluorescence technique.

6. Job's plot for determining the stoichiometry of binding by fluorescence method:

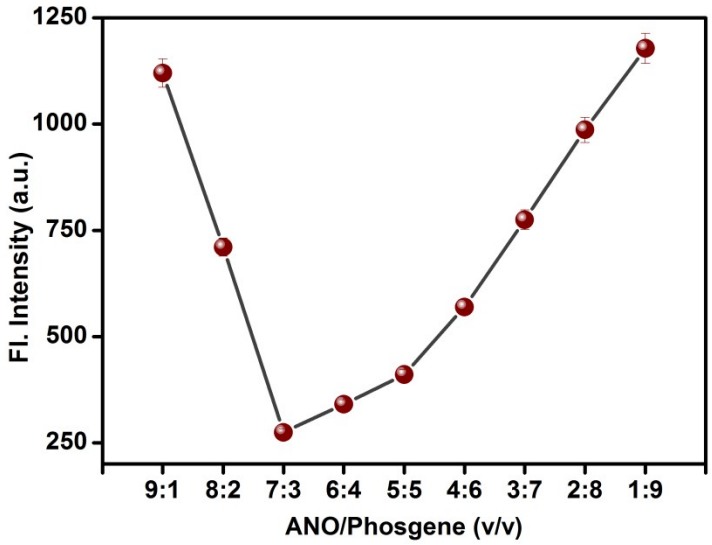

Fig. S5 Job's plot of **ANO** (1 μM) with Triphosgene (1 μM) /TEA (1:5 molar ratio) in CH_3CN by fluorescence method, indicates 2:1 stoichiometry for **ANO** with phosgene**.** Standard deviations are given by error bars where, n=3.

7. Dependence of the fluorescence intensity of ANO with phosgene as a function of time:

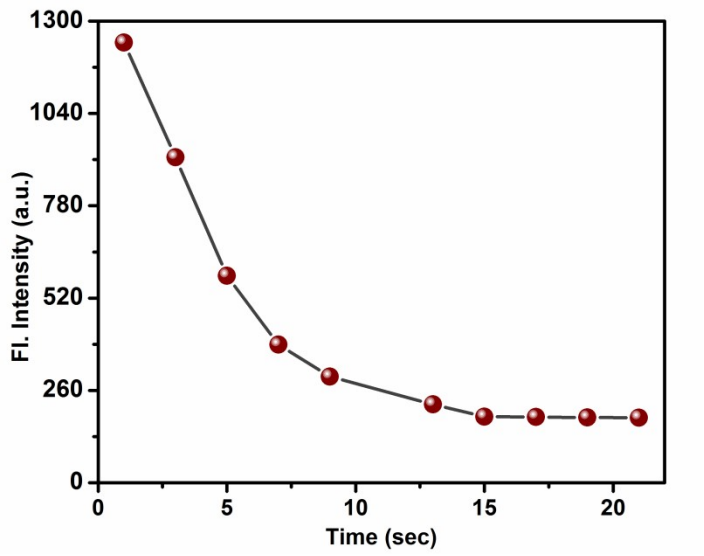

Fig. S6 Fluorescence intensity of **ANO** decreases at 429 nm upon gradual addition of phosgene (triphosgene/TEA) with time in acetonitrile (λ_{ex}= 250 nm).

8. Competitive selectivity in presence of other analytes

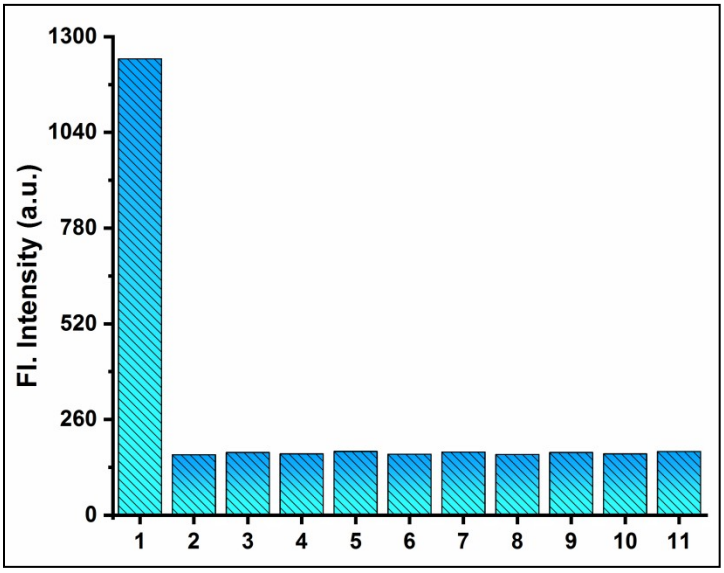

Fig. S7 Histogram representing competitive fluorescence spectra of **ANO+Triphosgene/TEA** in presence of different analytes at 429 nm (λ_{ex}= 250 nm) in CH_3CN [1) Blank, 2) Triphosgene/TEA, 3) Triphosgene/TEA+CH_3COCl, 4) Triphosgene/TEA+$POCl_3$, 5) Triphosgene/TEA+$SOCl_2$, 6) Triphosgene/TEA+p-TsCl, 7) Triphosgene/TEA+$(COCl)_2$, 8) Triphosgene/TEA+HCl, 9) Triphosgene/TEA+DCP, 10) Triphosgene/TEA+DCNP, 11) Triphosgene/TEA+TFA]

9. Plausible Mechanism

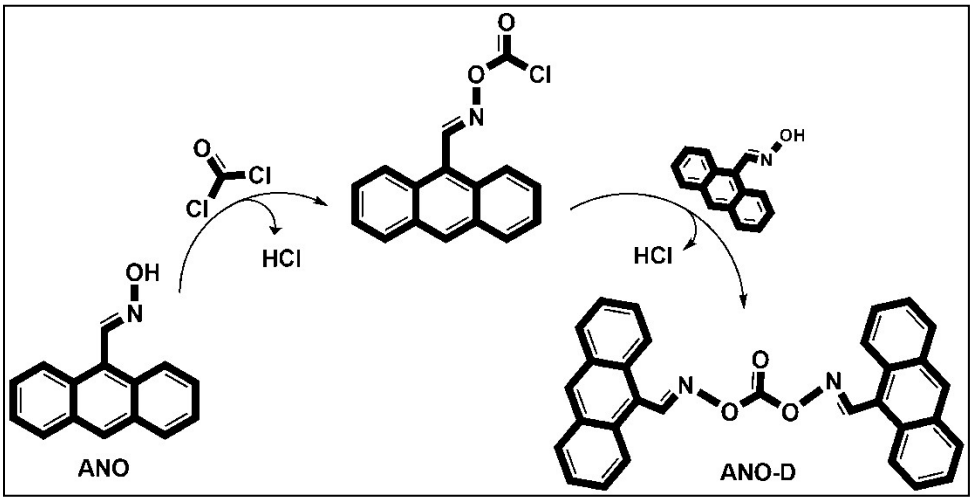

Fig. S8 A plausible mechanism of interaction of **ANO** with phosgene

10. Mass spectrometry of ANO-D

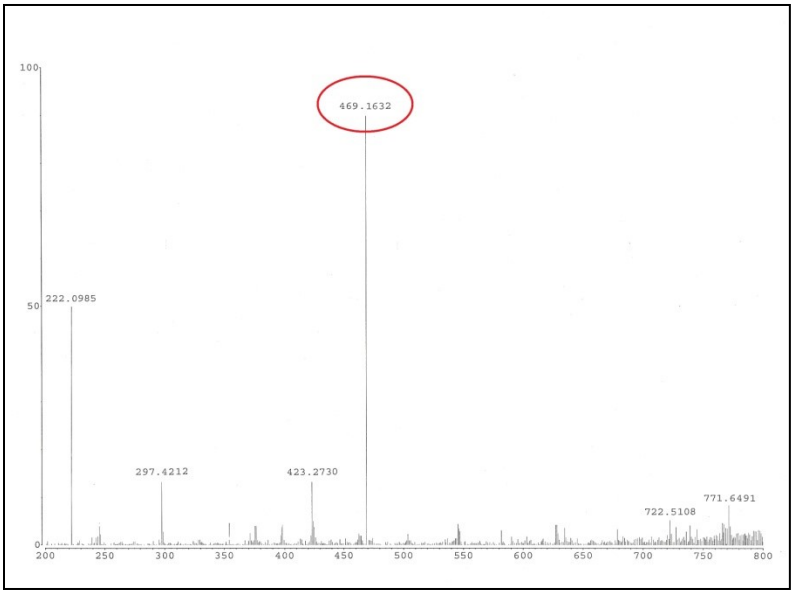

Fig. S9 HRMS of **ANO-D**

11. Density Functional Theory Calculations

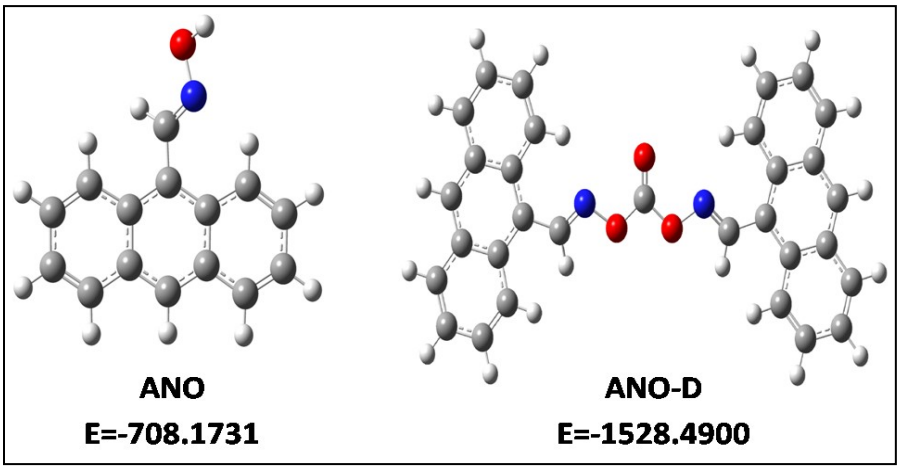

Fig. S10 Energy minimized structures of **ANO** and **ANO-D** from B3LYP level.

12.Table S2 Details of the geometry optimization in Gaussian 09 program.

Details	ANO	ANO-D
Calculation method	B3LYP	B3LYP
Basis set	6-31G(d, p)	6-31G (d, p)
E(CAM-B3LYP) (a.u.)	-708.1731	-1528.4900
Charge, Multiplicity	0, 1	0, 1
Solvent (CPCM)	Acetonitrile	Acetonitrile

13. TDDFT Calulation

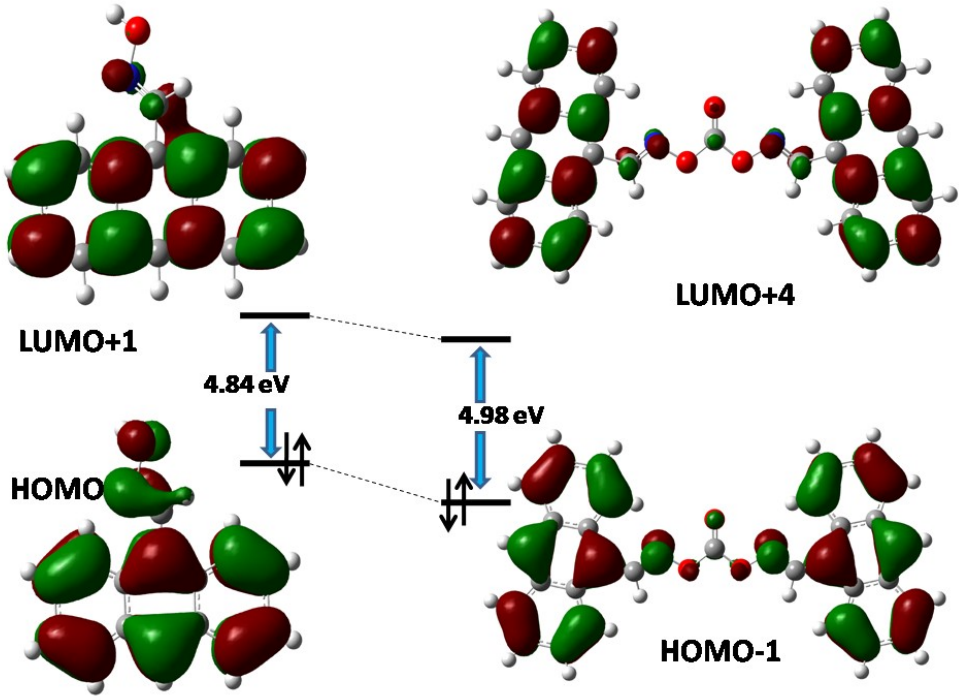

Fig. S11 DFT optimized charge densities and the HOMO-LUMO energy gap of **ANO** and **ANO-D**

14. Table S3. Selected electronic excitation energies (eV), oscillator strengths (f), main configurations of the low-lying excited states of all the molecules and complexes. The data were calculated by TDDFT//B3LYP/6-31G(d,p) based on the optimized ground state geometries.

Molecules	Electronic Transition	Excitation Energy[a]	f[b]	Composition[c](%)
ANO	$S_0 \rightarrow S_8$	4.8569eV255.27 nm	0.8262	H → L+1 (35%)
ANO-D	$S_0 \rightarrow S_{20}$	4.7326eV 261.98 nm	0.4691	H-1 → L+4 (46%)

[a]Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength.[b]Oscillator strength. [c]H stands for HOMO and L stands for LUMO.

15. Table S4. Energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

Species	**E_{HOMO} (a.u)**	**E_{LUMO} (a.u)**	**ΔE(a.u)**	**ΔE(eV)**	**ΔE(kcal/mol)**
ANO	-0.19793	-0.02005	0.17788	4.84	111.61
ANO-D	-0.20555	-0.02254	0.18301	4.98	114.84

16. Gaseous phosgene sensing by paper strip method

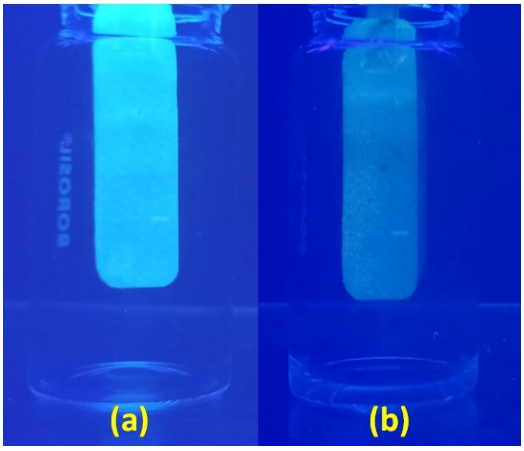

Fig. S12 Filter paper strips loaded with **ANO** (1 mM) exposed to UV lamp (365 nm) to visualize fluorescence changes after 1 min (a) **ANO** alone (b) **ANO** + phosgene gas (50 ppm)

17. Paper strip-based performance of ANO in presence of phosgene with other analytes in the solution phase

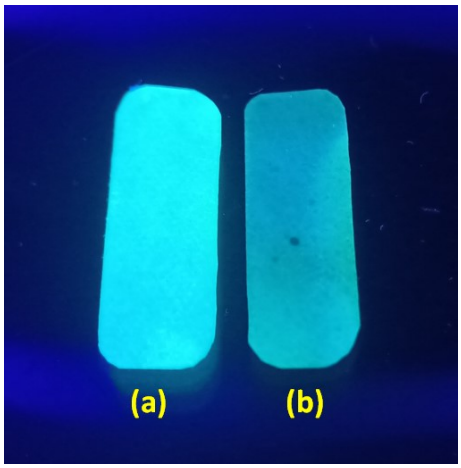

Fig. S13 (a) Only ANO (b) ANO in presence of phosgene and other analytes in solution

18. Determination of conc. of phosgene in different environmental samples using fluorescence emission and the HPLC method

Table S5:

Sample	Conc. of phosgene added (μM)	Conc. of phosgene found (μM)	Recovery %	HPLC Method (μM)
Tap Water	3	2.89	96.33	2.96
	5	4.91	98.20	4.95
	7	6.86	98.00	6.80
Pond Water	2	1.93	96.50	1.97
	4	3.88	97.00	3.95
	6	5.85	97.50	5.79
Soil	1	0.96	96.00	0.98
	3	2.91	97.00	2.89
	5	4.86	97.20	4.95