ChemistrySelect

Supporting Information

'Off-the-Shelf' Material for Ratiometric Sensing of Phosgene at Nanomolar Level Both in Solution and Gaseous Phase

Nilanjan Dey*

Experimental Section

Materials and methods: All reagents, starting materials, and silica gel for TLC and column chromatography were obtained from the best-known commercial sources and were used without further purification. FT-IR spectra were recorded on a PerkinElmer FT-IR Spectrum BX system and were reported in wave numbers (cm^{-1}). ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker Advance DRX 400 spectrometer operating at 400 and 100 MHz for ^{1}H and ^{13}C NMR spectroscopy, respectively. Chemical shifts were reported in ppm downfield from the internal standard, tetramethylsilane (TMS). Mass spectra were recorded on a Micro mass Q-TOF Micro TM spectrometer.

Spectroscopic studies: UV-vis and fluorescence spectra were recorded on a Shimadzu model 2100 UV-vis spectrometer and a Cary Eclipse spectrofluorimeter respectively. In the emission experiments, the slit widths were kept a 2.5 nm for the excitation and emission channel respectively. The excitation wavelength was chosen as 340 nm. The $CHCl_3$ solution of P_1 (0.5×10^{-5} M) was mixed with different warfare agents (Final conc.: 0.5×10^{-5} M) and incubated for 20 min before subjected to fluorometric analysis.

Preparation of P_1 coated paper strips: To prepare the coated paper strips, 20 µL of $CHCl_3$ solution of P_1 (0.02 mM) was drop-cast onto the filter paper using a micropipette to form a spherical luminescent spot of diameter ~1.0 cm. The concentration of P_1 in the solution as well as immersion time were optimized to obtain uniform film with blue fluorescence to begin with. The solution was completely absorbed in filter paper within 10 min and then were kept overnight to airdry. Finally, the air-dried paper strips were ready for sensing studies. Fluorometric analysis Phosgene was prepared according to the reported method. Different concentrations of triphosgene solutions were prepared with dichloromethane as solvent. 10 µL of the solutions were placed at the bottom of a bottle, and the test paper was hanged and fixed above the solution inside the bottle, afterwards the addition of 10 µL of dichloromethane containing 0.1% TEA into the solution was conducted; after that, the lid was closed immediately. Fluorescence changes of OPD-TPE-Py-2CN loaded test strips with exposure to different concentrations of phosgene for 10 min were recorded on a fluorimeter (excitation wavelength: 340 nm). The test strips were exposed to phosgene or other analytes in the selectivity experiments.

Fluorescence Decay Experiment. Fluorescence lifetime values were measured by using a time-correlated single photon counting fluorimeter (Horiba Jobin Yvon). The system was excited with 340 nm nano LED of Horiba - Jobin Yvon with pulse duration of 1.2 ns (slit width of 2/2, λem is 454 nm for P_1 and 387 nm for P_1O). Average fluorescence lifetimes (τav) for the exponential iterative fitting were calculated from the decay times (τi) and the relative amplitudes (ai) using the following relation,

$$\tau_{av} = (a_1\tau_1^2 + a_2\tau_2^2 + a_3\tau_3^2)/(a_1\tau_1 + a_2\tau_2 + a_3\tau_3)$$

Where a_1, a_2 and a_3 are the relative amplitudes and τ_1, τ_2, and τ_3 are the lifetime values, respectively. For data fitting, a DAS6 analysis software version 6.2 was used.

Theoretical Calculations. All calculations were performed using the Gaussian 09 and Gaussian 16 programs at the PBE0/6-31+G(d) level of theory. DFT structural optimizations and frequency calculations at PBE0/6-31+G(d) level of theory and the following single-point

TD-DFT calculations at the same level were performed both in S_0 and S_1 state. By using the minimized structures, HOMO−LUMO levels of each molecule were calculated.

Additional Spectral Data

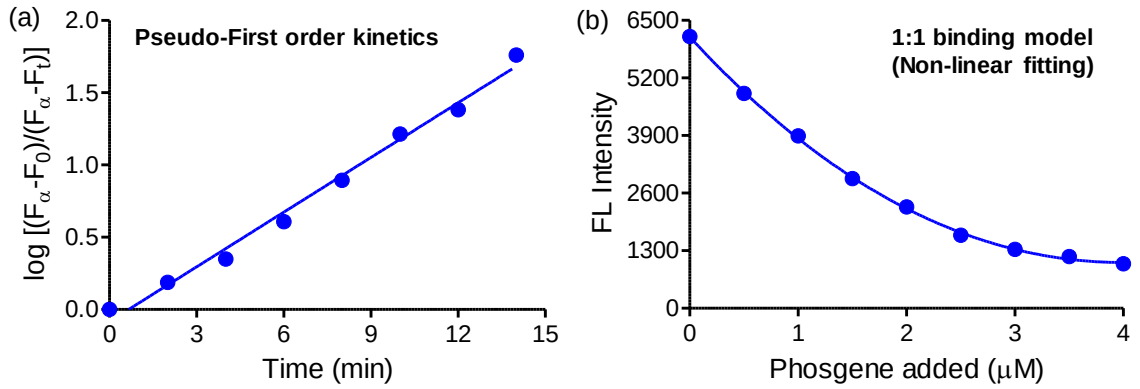


Figure S1. (a) Time-course of **P_1** (5 μM) and phosgene (15 μM) interaction fitted by Pseudo-first order rate kinetics in CHCl3 medium at 298 K. (b) Determination of binding constant of **P_1** with phosgene by non-linear fitting, considering one-site specific model.

Detail procedure for calculating detection limit

A solution of **P_1** (containing 0.1 vol % TEA) was treated with different amounts of triphosgene and fluorescence spectra were recorded after ~30 min of mixing. The changes in fluorescence intensity was considered at ~454 nm (λex = 340 nm). Overall, 7 measures and 10 blank replicates were used for calibration.

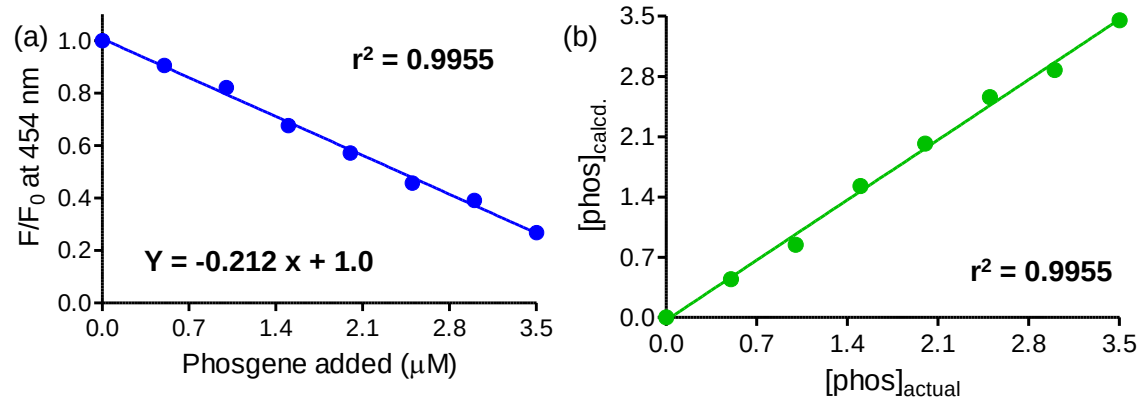


Figure S2. (a) Change in fluorescence intensity of **P_1** (5 μM) with phosgene (0 – 3.5 μM) at 454 nm in CHCl3 medium at 298 K. (b) Calibration plot shows [phos]calcd. Vs. [phos]actual.

Form titration studies, the calibration curve was obtained,

$Y = 1 - 0.212 x$ ($r^2 = 0.995$)……1

phosgene concentrations were calculated from the calibration plot (equation 1). These were calculated values of [phosgene], represented as [phos]calcd. were plotted against actually added phosgene concentrations, represented as [phos]actual. Slope (b) of this plot (fig. 2) was further used for calculating the detection limit in terms of concentration.

Thereafter, from the measured blank emission values of **P_1** (10 μM, λex = 340 nm), the concentrations of phosgene were calculated using the equation [1].

The mean (x) and the standard deviation (s) from the phosgene concentrations as calculated from the blank replicates are, $(x \pm s) = (0.159 \pm 0.00385) \times 10^{-6}$

The decision limit (L_c) was calculated using equation [2].

$L_c = t_c \times s \times (1 + 1/N)^{1/2}$ .....[2]

For the probability level of 5%, tc will be 1.833 for 9 degrees of freedom (GL = N-1 = 10-1 = 9) and N denotes the number of blank replicates.

So, in the present case, considering N = 10, we obtain,

$L_c = 1.833 \times (0.00385 \times 10^{-6}) \times (1 + 1/10)^{1/2} = 0.0074 \times 10^{-6}$

The detection limit (LD) is considered as the double of the decision limit,

$L_D = 2 \times L_c = 0.0148 \times 10^{-6}$

The detection limit (x_D) in concentration term will be

$x_D = 2x_c = 2\, L_c/b = (0.0148 \times 10^{-6})/0.995 = 0.0148 \times 10^{-6}$ M

Thus, the detection limit for phosgene is obtained as 14.8 nM

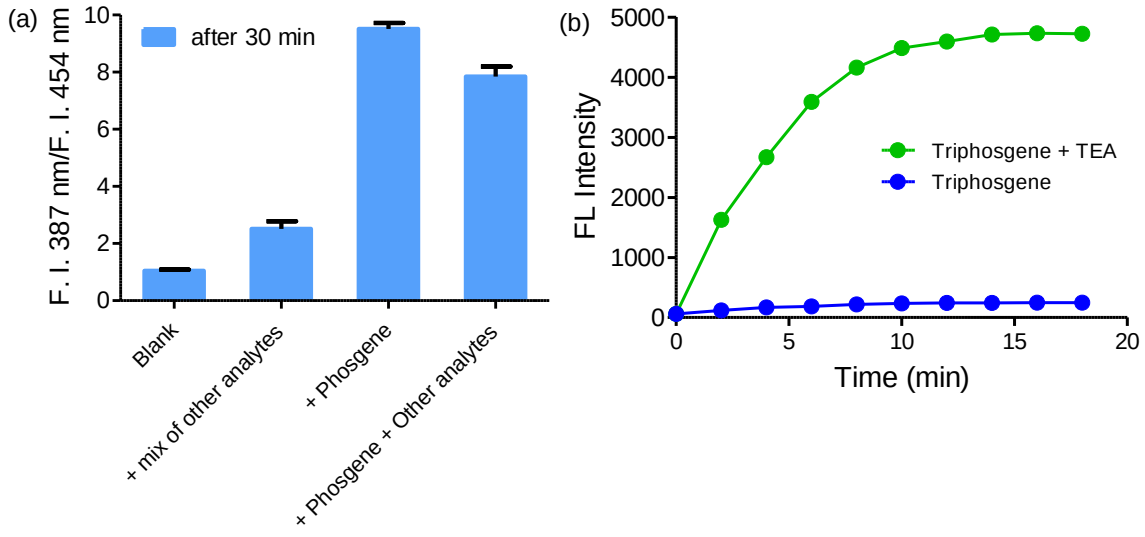


Figure S3. (a) Interaction of **P_1** (5 μM) with phosgene (5 μM) in presence of other analytes in $CHCl_3$ medium at 298 K. (b) Compare the interaction of **P_1** with phosgene (triphosgene with 0.1 vol% of TEA) and triphosgene in $CHCl_3$ medium at 298 K.

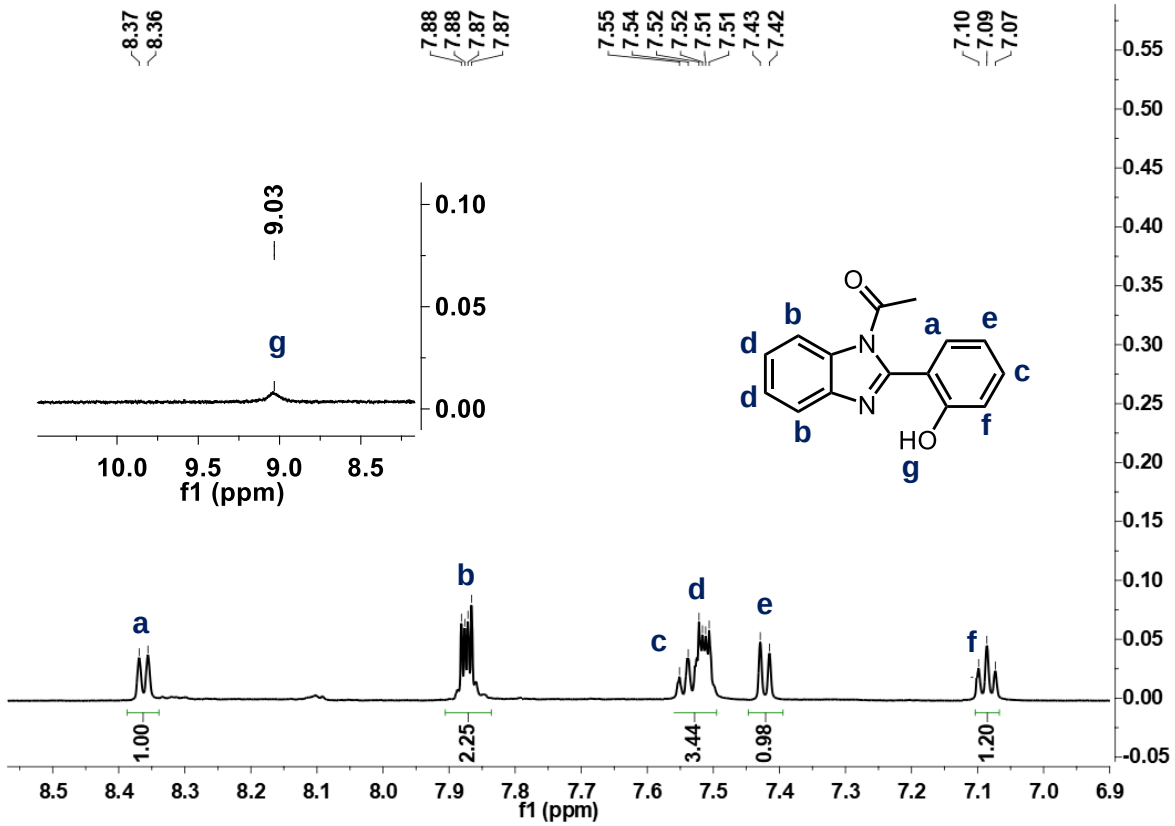


Figure S4. 1H-NMR spectrum of **P_1** with acetyl chloride in DMSO-d_6 medium.

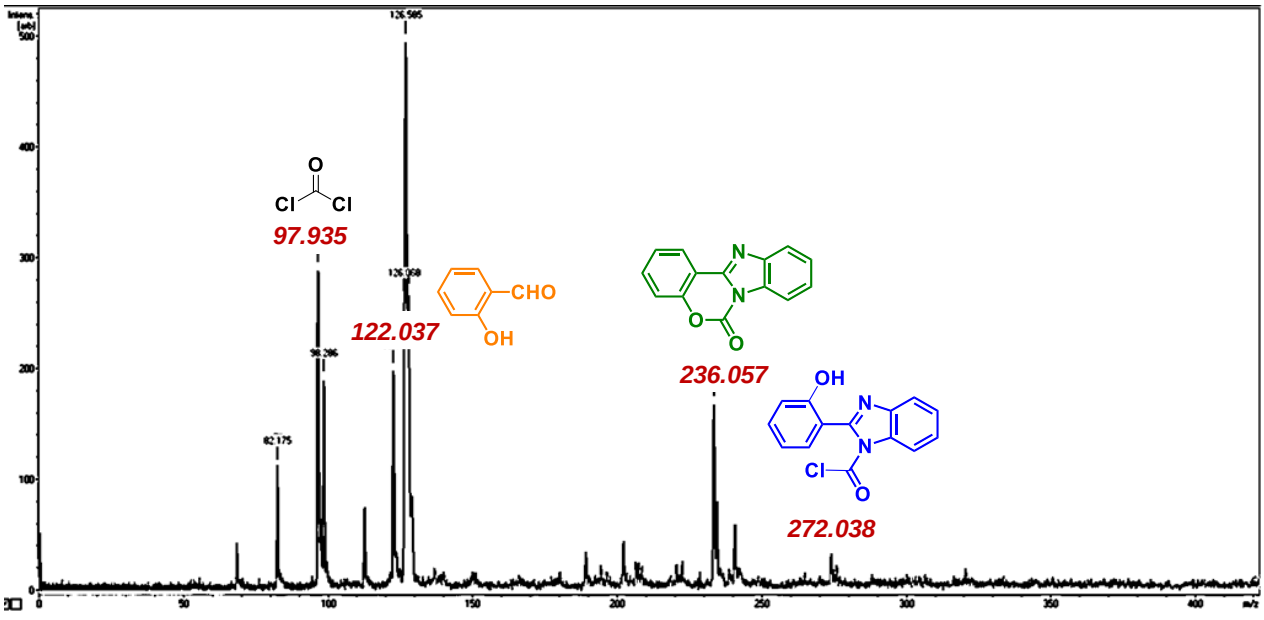


Figure S5. MADLDI-TOF mass spectral analysis of **P_1** + phosgene mixture.

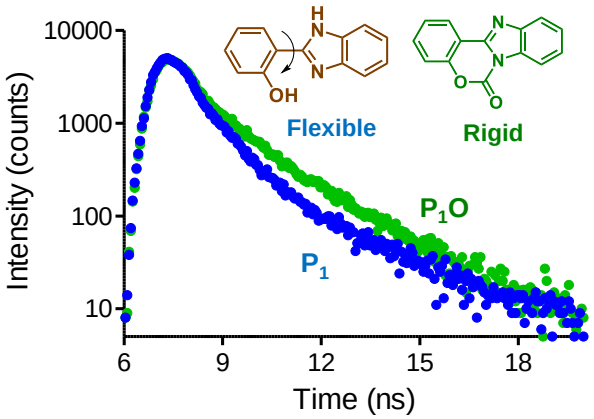


Figure S6. Fluorescence decay spectra of **P_1** (5 µM, λex = 340 nm) with phosgene (5 µM) at 454 and 387 nm respectively in $CHCl_3$ medium at 298 K.

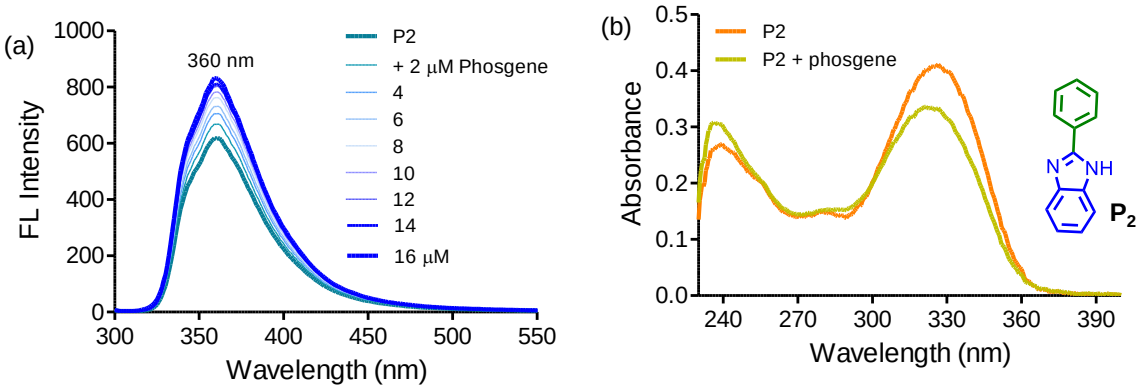
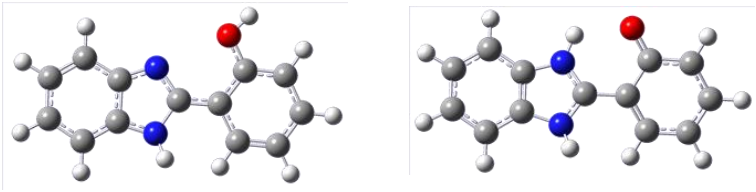


Figure S7. (a) Fluorescence titration of **P_2** (5 µM, λex = 340 nm) with phosgene (0 - 16 µM) in $CHCl_3$ medium at 298 K. (b) UV-visible spectrum of **P_2** with phosgene (20 µM) in $CHCl_3$ medium at 298 K.

(a)



P_1 (keto form)

(b)

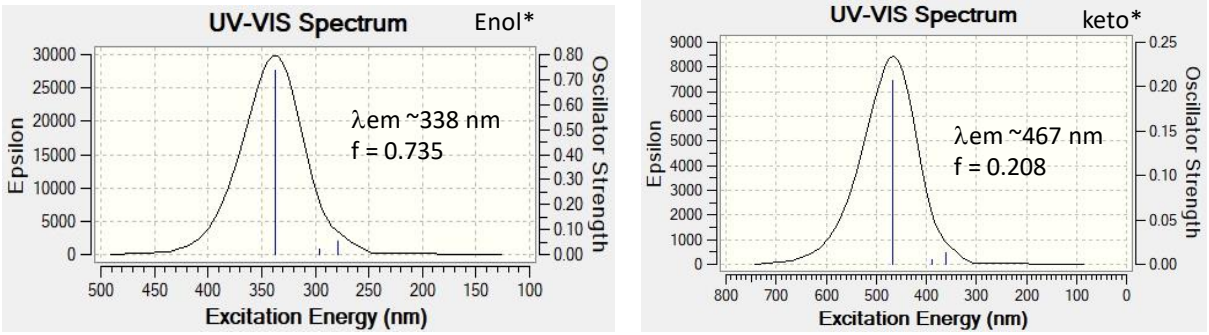
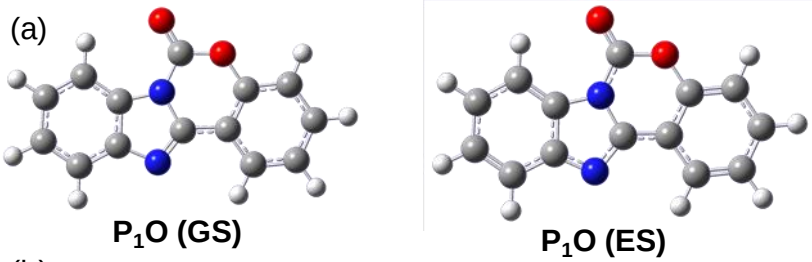


Figure S8. (a) Energy minimized structures of **P_1** (keto and enol form) at lowest energy excited state using PBE0/6-31+G(d) level of theory. (b) Calculated fluorescence spectrum of **P_1** in keto and enol form.

(a)



P_1O (GS) **P_1O (ES)**

(b)

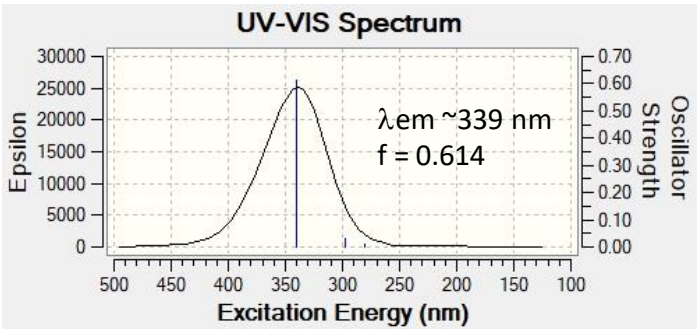


Figure S9. (a) Energy minimized structures of **P_1O** both at S_0 and S_1 states using PBE0/6-31+G(d) level of theory. (b) Calculated fluorescence spectrum of **P_1O**.

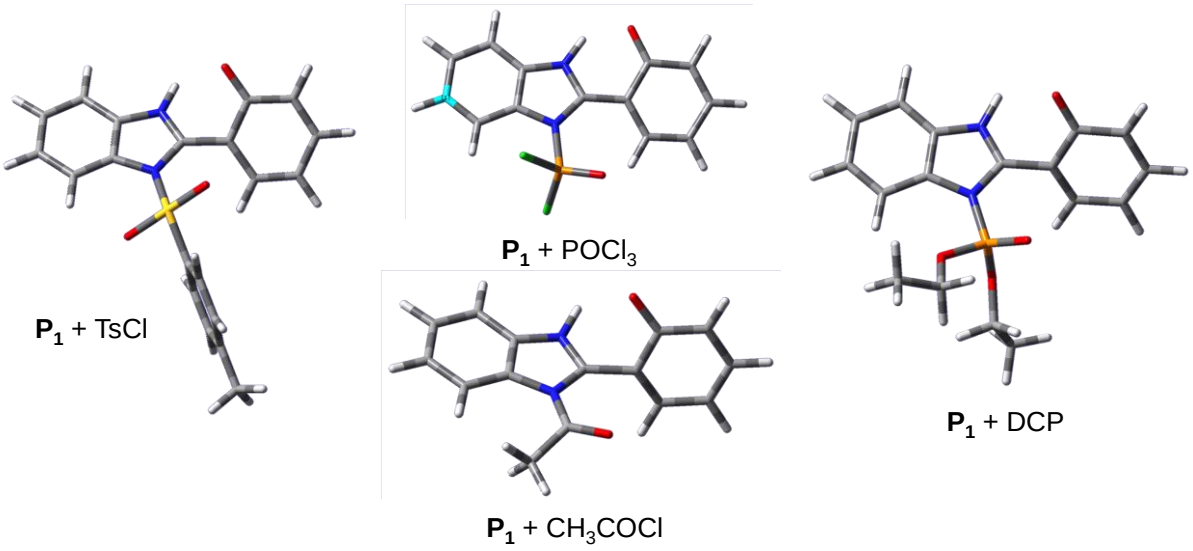


Figure S10. Energy minimized structures of **P_1O** with different competitive analytes in S_1 state (K* form).

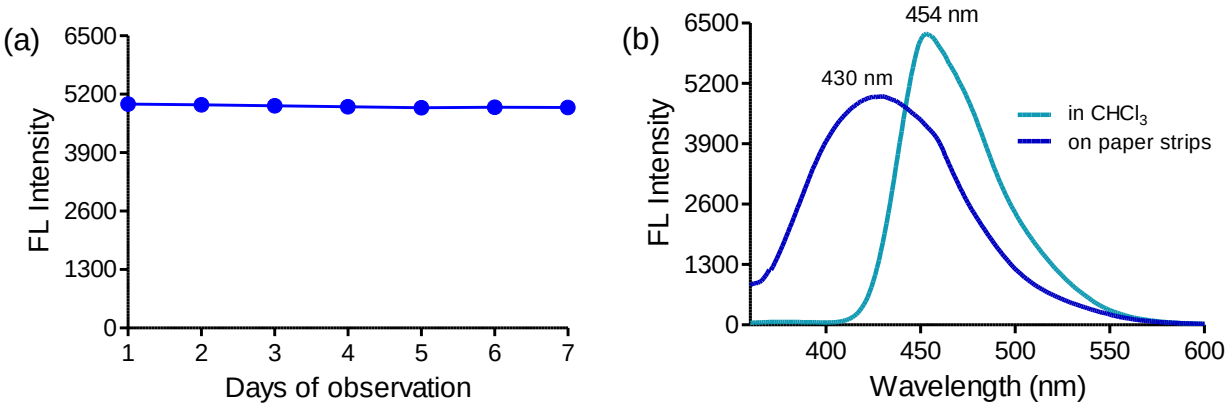


Figure S11. (a) Time-dependent change in fluorescence intensity of **P_1**-coated filter paper strips (0-7 days). (b) Compare fluorescence spectra of **P_1** in solution state ($CHCl_3$) and on solid surface (coated on paper strips) [λex = 340 nm].

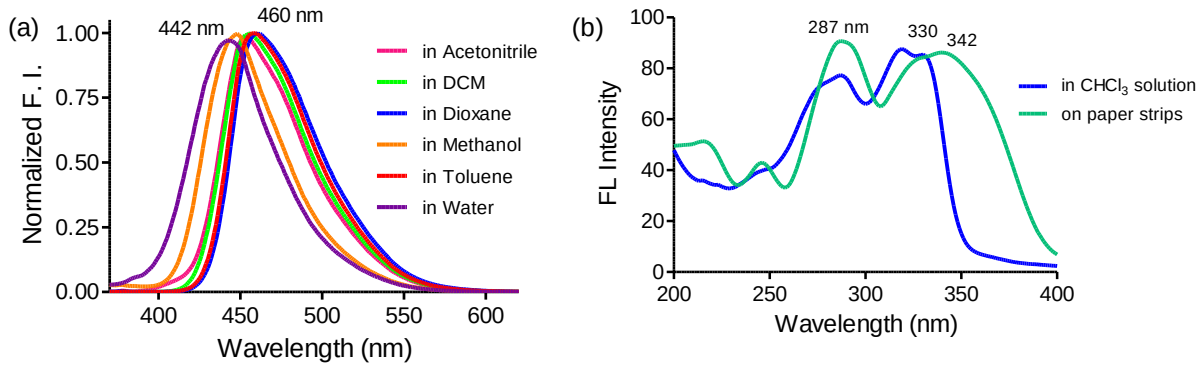


Figure S12. (a) Fluorescence spectra of **P_1** (5 µM, λex = 340 nm) in different organic solvents at 298 K. (b) Compare fluorescence excitation spectra of **P_1** in solution state ($CHCl_3$, at 454 nm) and on solid surface (coated on paper strips, 387 nm) [λex = 340 nm].

	Energy	Dihedral angle	Charge on oxygen	Charge on nitrogen	Dipole
E	-685.3872 a. u.	36.7	-0.094	-0.24	3.81
E*	-685.3713 a. u.	10.9	-0.072	-0.35	3.62
K	-685.3825 a. u.	2.12	-0.67	0.048	8.07
K*	-685.3687 a. u.	23.1	-0.53	-0.032	7.52

Table S1. Changes in structural parameters of **P_1** (both in E and K form) at S_0 and S_1 states using PBE0/6-31+G(d) level of theory.