Supplementary Information (SI) for Materials Advances.
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Supporting information

Comparative Analysis of Monomeric vs. Dimeric Salen Fluorescent Probes: Transition from Turn-On to Ratiometric Response Towards Nerve Gas Agents in Organic to Aqueous Media

Sourav Mondal, and Nilanjan Dey*

Department of Chemistry, Birla Institute of Technology and Science Pilani, Hyderabad

Secunderabad, Telangana 500078

E-mail: nilanjandey.iisc@gmail.com, nilanjan@hyderabad.bits-pilani.ac.in

EXPERIMENTAL SECTION

Materials and Instrumentations All reagents and starting materials were obtained from the best-known commercial sources and were used without further purification. Solvents were distilled and dried before use. FTIR spectra were recorded on a Perkin-Elmer FT-IR Spectrum BX system and were reported in wave numbers (cm^{-1}). ^1H NMR and ^{31}P NMR spectra were recorded on a Bruker Advance DRX 400 spectrometer operating at 400 and 100 MHz for ^1H and ^{31}P NMR spectroscopy, respectively.

UV−Vis and Fluorescence Spectroscopy The UV−vis and fluorescence spectroscopy were recorded on a Shimadzu model 2100 spectrometer and Cary Eclipse spectrofluorometer respectively. The slit widths were kept at 5 nm (excitation) and 5 nm (emission).

Dynamic Light Scattering Studies (DLS) DLS measurements were done using a Malvern Zetasizer Nano ZS particle sizer (Malvern Instruments Inc., MA) instrument. Samples were prepared and examined under dust-free conditions. The mean hydrodynamic diameters reported were obtained from Gaussian analysis of the intensity-weighted particle size distributions.

Detection limit determination. The method used for the calculation of the detection limit is known as the blank variation method. In this method, the calibration curve was prepared by fluorescence titration of **P-1** (10 μM) with DClP in an aqueous medium. The fluorescence signal of the compound without the added analytes was considered a blank reading. The standard deviation value was calculated from the blank readings and fluorescence titration data. Using this standard deviation value, we calculated the limit of decision by the following equation.

$$L_C=t_C \times s \times (1 + 1/N)^{1/2} \quad (1)$$

where, N = the number of blank replicates taken; the value of tc for 10 blank readings is 1.833; and s = the standard deviation value. The detection limit (L_D) was calculated as the double of the decision limit obtained,

$$L_D=2L_c \quad (2)$$

^{1}H NMR Titration Studies. ^1H NMR titration studies with probes **P-1** were performed (5 mM) in $CDCl_3$ medium. To that, DClP was added (1:20) and the spectra were recorded using identical parameters. The chemical shifts have been represented as ‘δ ppm’.

Scanning Electron Microscopy: Solution of **P-1** (concentration 10 μM) in water with and without DClP was drop cast over double-sided tapes attached to the brass stubs and air-dried for 48 h. The samples were then coated with gold vapor and analyzed on a Quanta 200 SEM operated at 15 kV.

Synthesis of compound P-1

The compound **P-1** was synthesized following the previous literature.[1] Briefly, 3,3'-diaminobenzidine (1.0 mmol) and salicylaldehyde (4.2 mmol) were mixed in ethanol (50 mL) and stirred for 20 min at room temperature. After refluxing at 80°C for about 8 hours, a thick orange suspension was formed. The orange phase was filtered and washed with cold methanol to afford the desired product. The orange solid was mixed in 50 mL DMF, and heated at 100˚C for 30 min. The mixture was filtered and evaporated naturally. Yield: 80%

Synthesis of compound P-2

The compound P-2 was synthesized following the previous literature[2]. Briefly, o-Phenylenediamine (1.0 mmol) dissolved in methanol was added to salicylaldehyde (2.1 mmol) dissolved in methanol. The solution was stirred at reflux for 3h. The solution was then cooled to give an orange precipitate, which was collected by vacuum filtration and dried. Yield: 82%

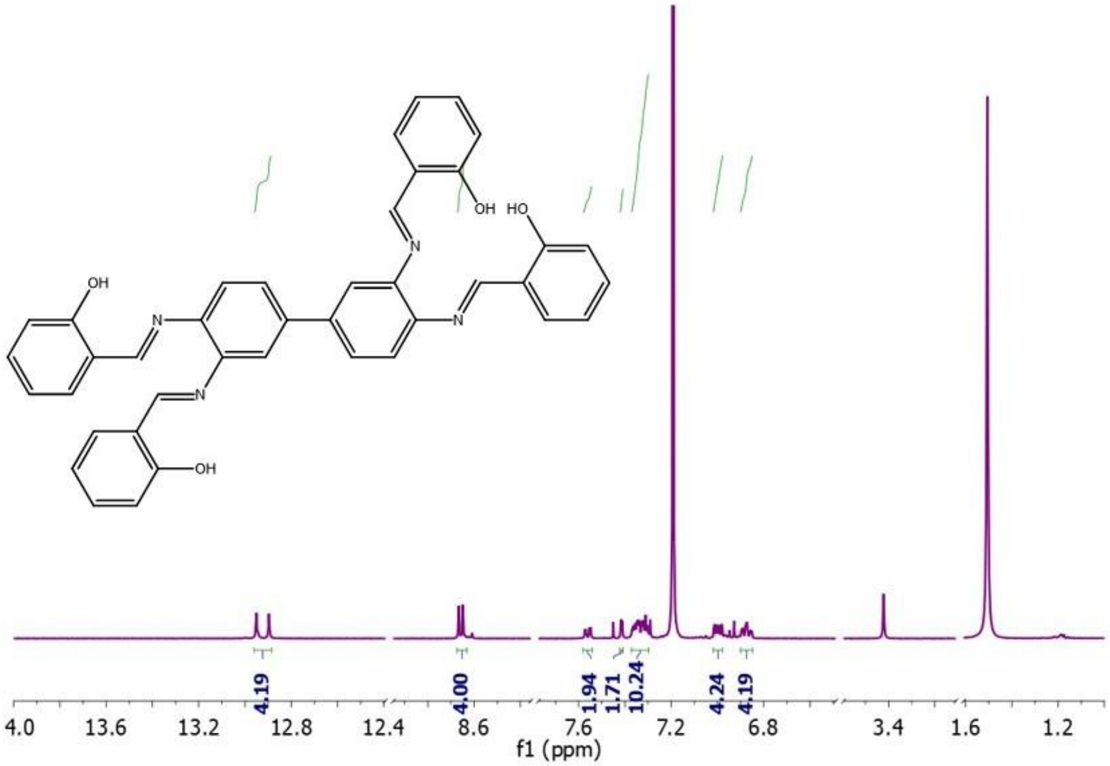


Figure S1. ^{1}H-NMR spectra of **P-1** in $CDCl_3$ medium.

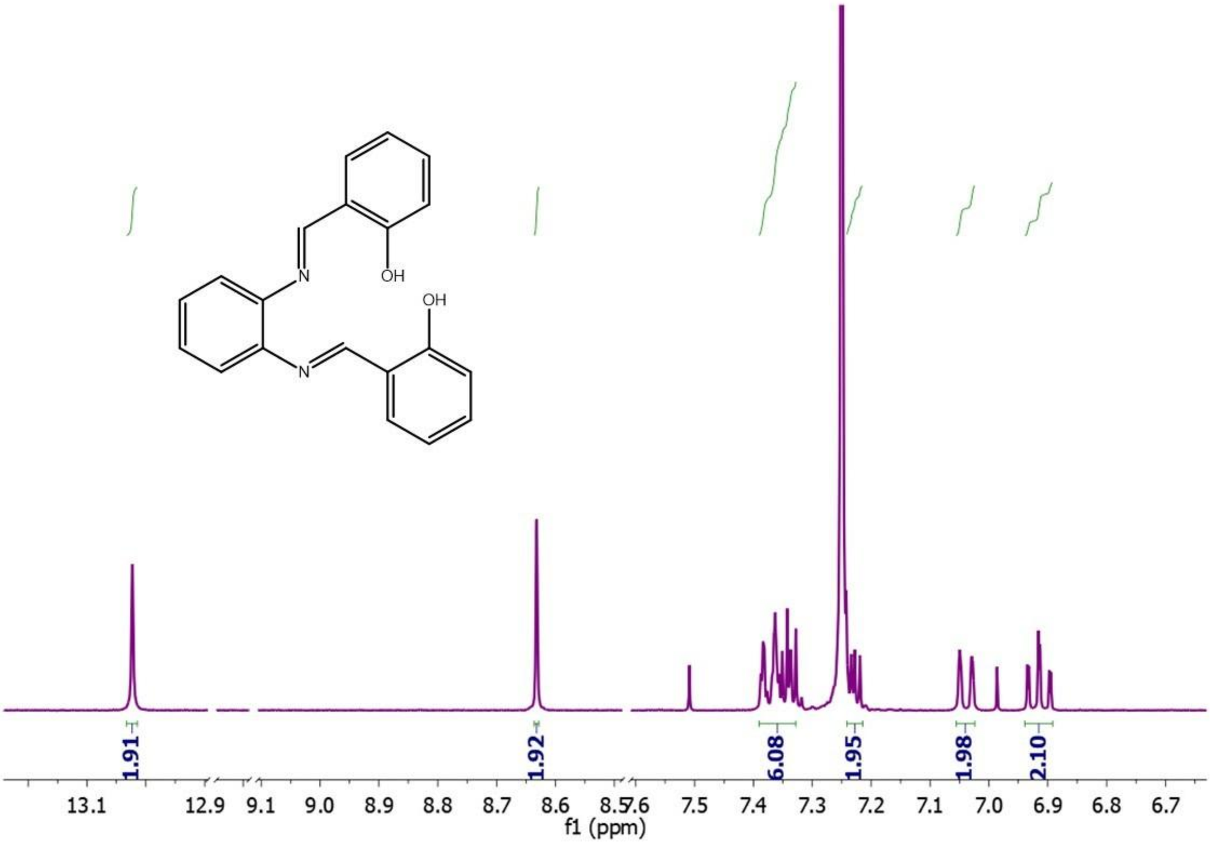


Figure S2. ^{1}H-NMR spectra of **P-2** in $CDCl_3$ medium.

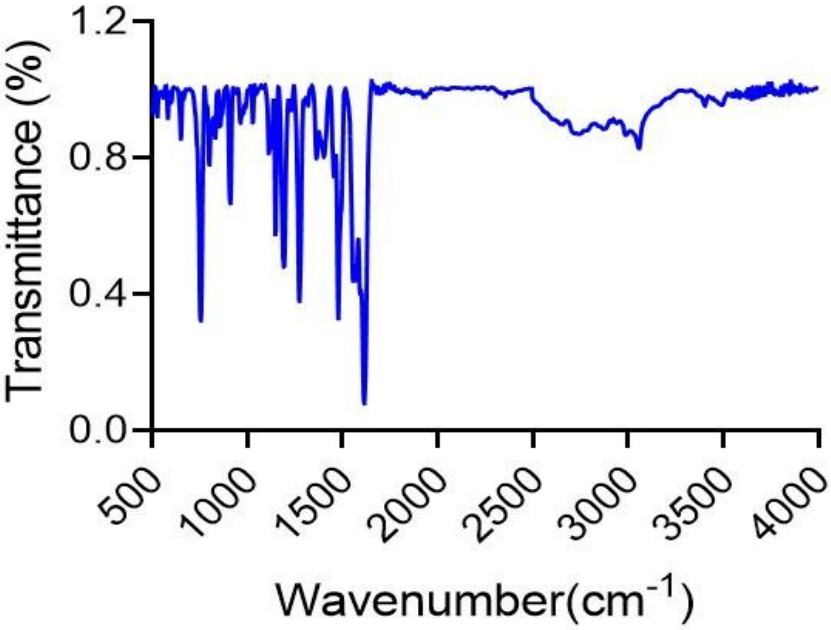


Figure S3. FTIR spectra of **P-1** compound.

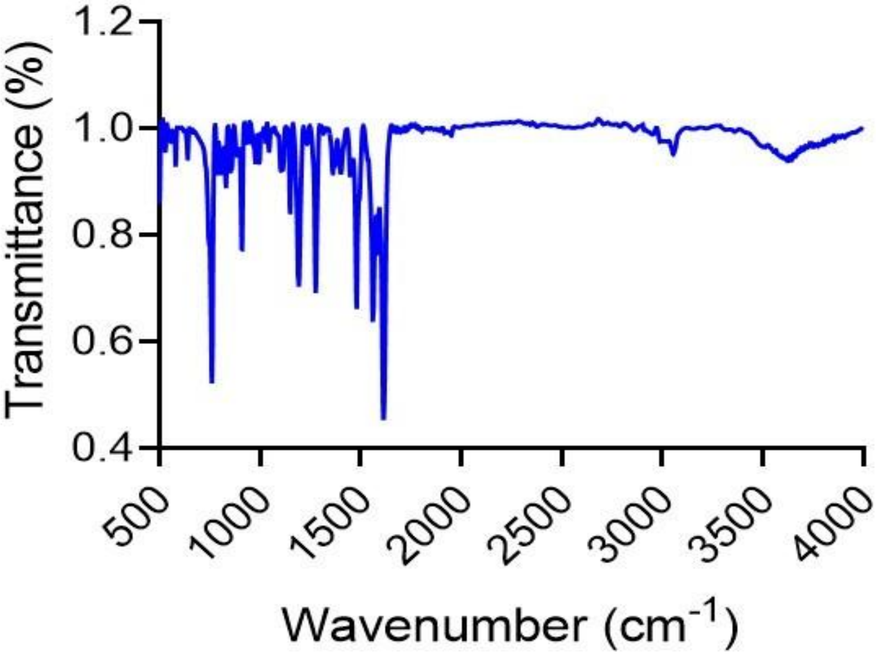


Figure S4. FTIR spectra of **P-2** compound.

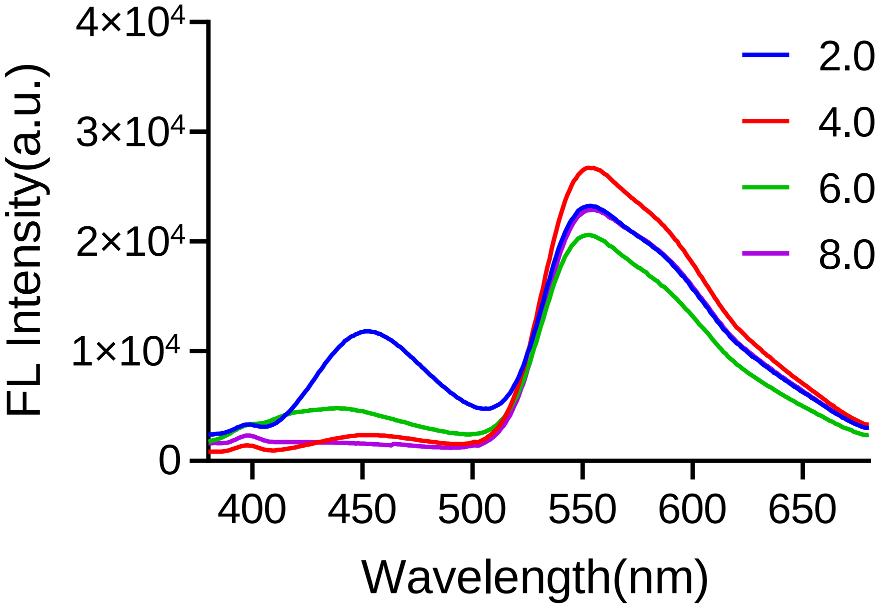


Figure S5. Emission spectra of the **P-1** compound (10 μM) in different pH (λ_{ex}=350 nm).

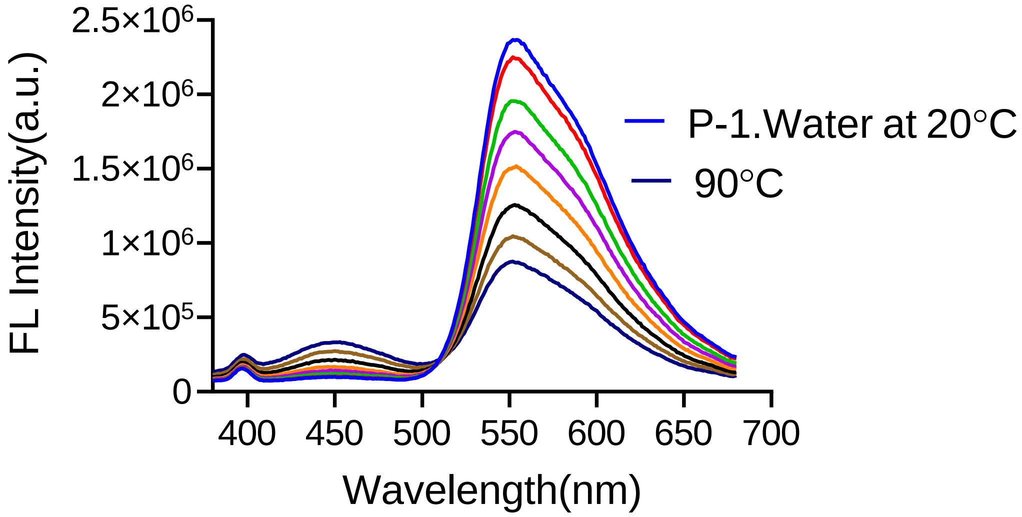


Figure S6. Emission spectra of the **P-1** compound (10 µM) in aqueous medium (20˚C-90˚C) (λ_{ex}=350 nm).

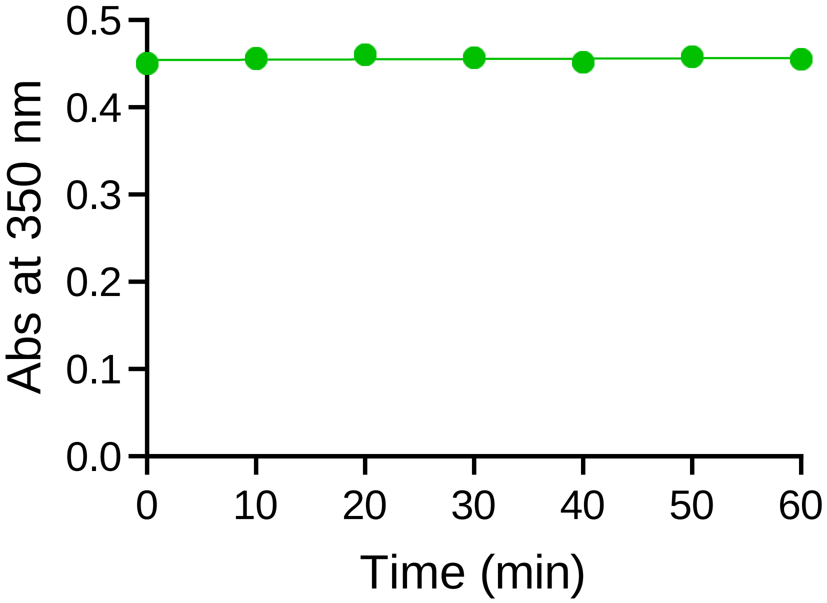


Figure S7. Change in absorbance of the **P-1** compound (10 µM) in aqueous medium in different time interval.

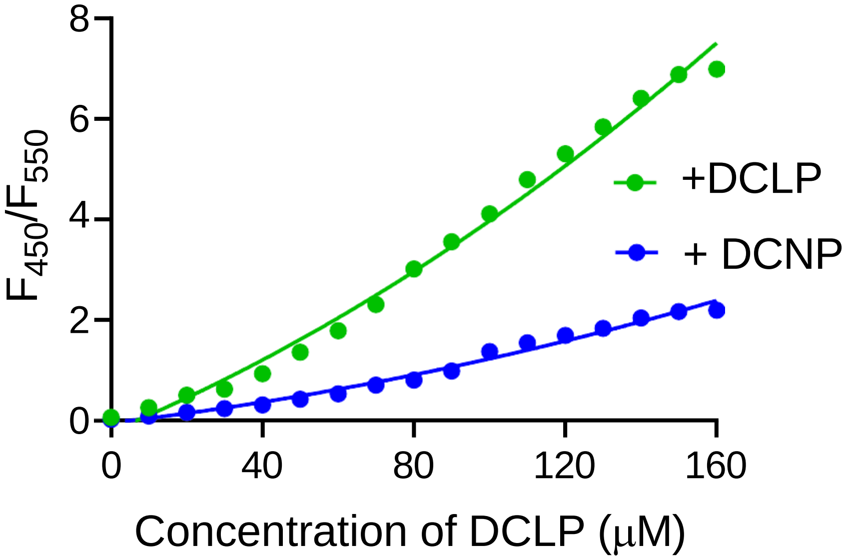


Figure S8. Change in fluorescence intensity of **P-1** (10μM) upon addition of equivalent amount(160μM) of DClP and DCNP in aqueous medium. (λex=350 nm) after incubation for 30 minutes.

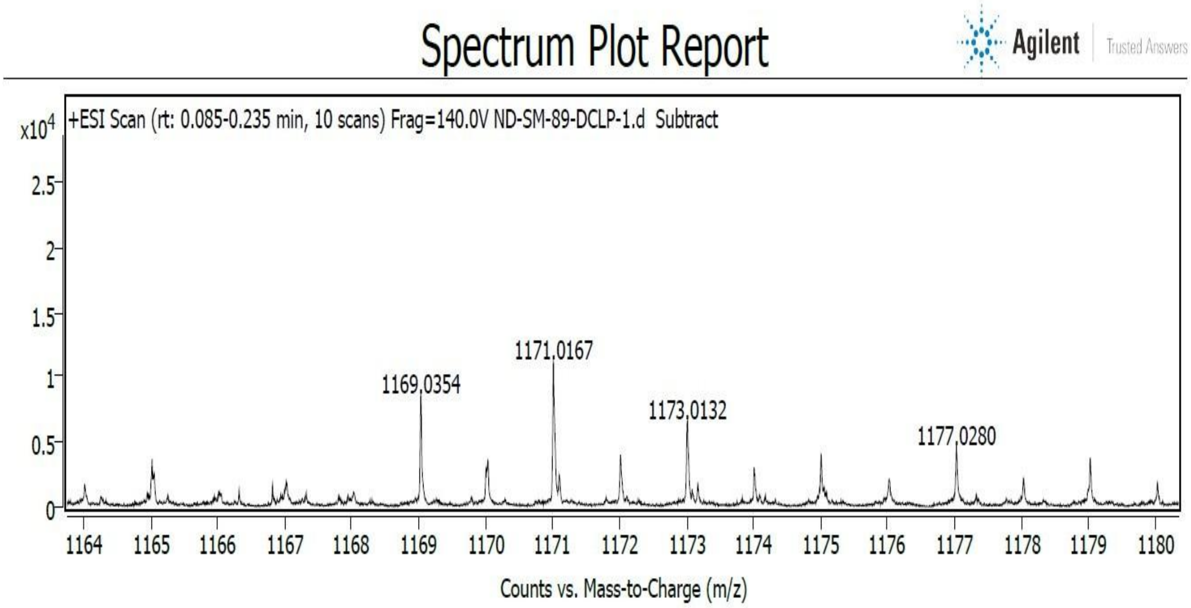


Figure S9. HRMS spectra of **P-1**(10μM) compound upon addition of DClP and incubated for 30 minutes.

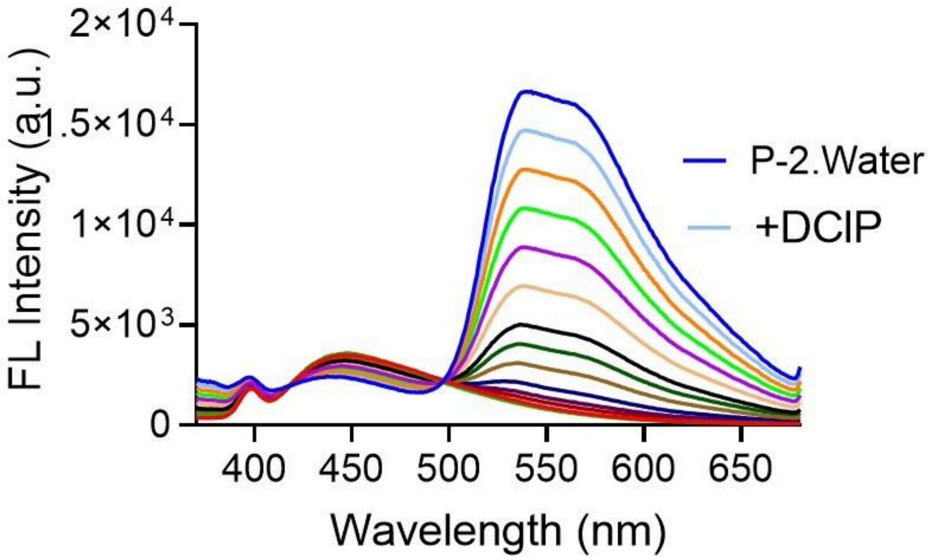


Figure S10. Fluorescence titration of the compound **P-2**(10μM) upon addition of DClP(160μM) after incubation for 30 minutes.

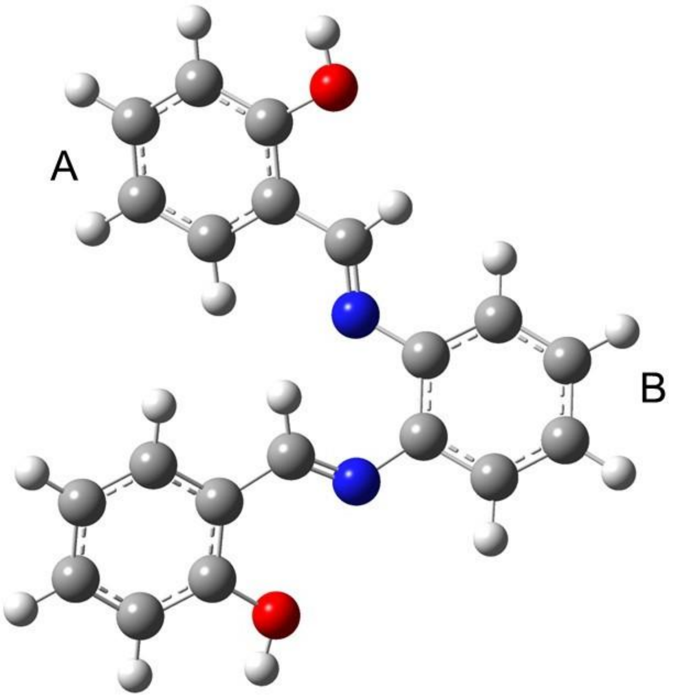


Figure S11. Optimized structure of the **P-2** compounds.

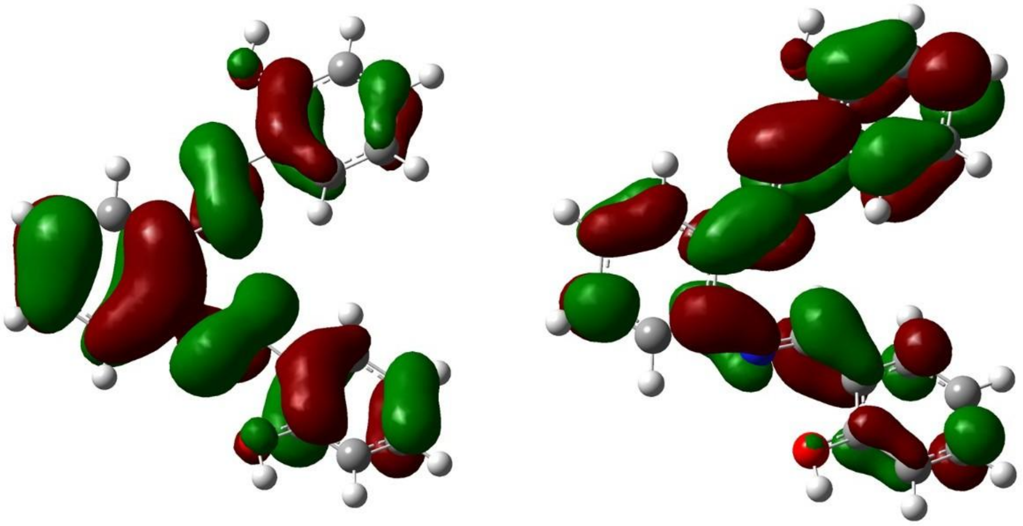


Figure S12. HOMO and LUMO orbital of **P-2** compound.

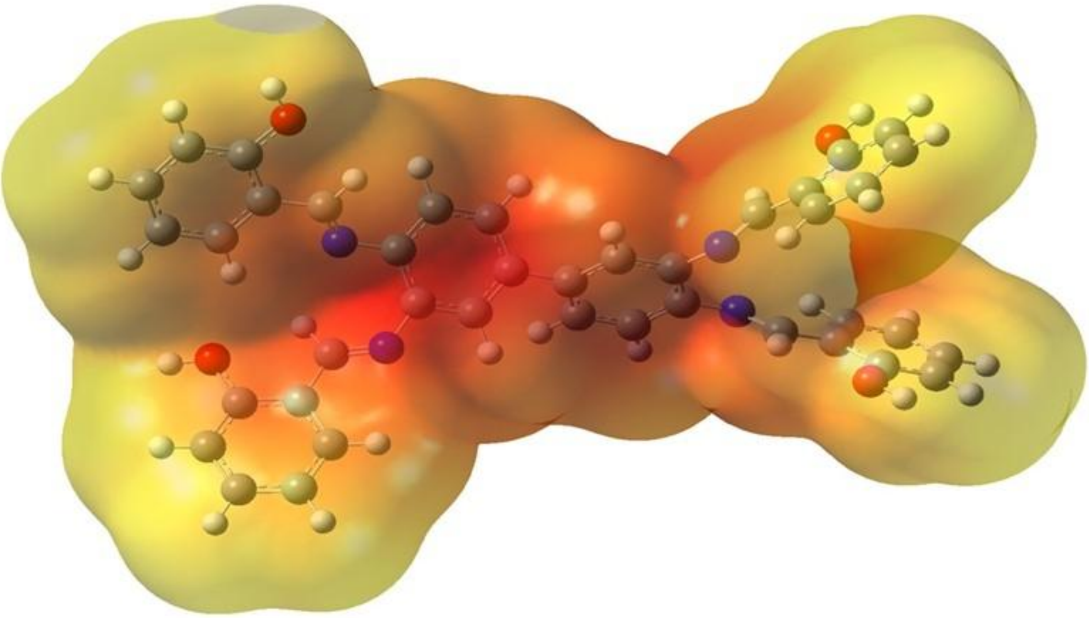


Figure S13. Electrostatic potential map of **P-1** compound.

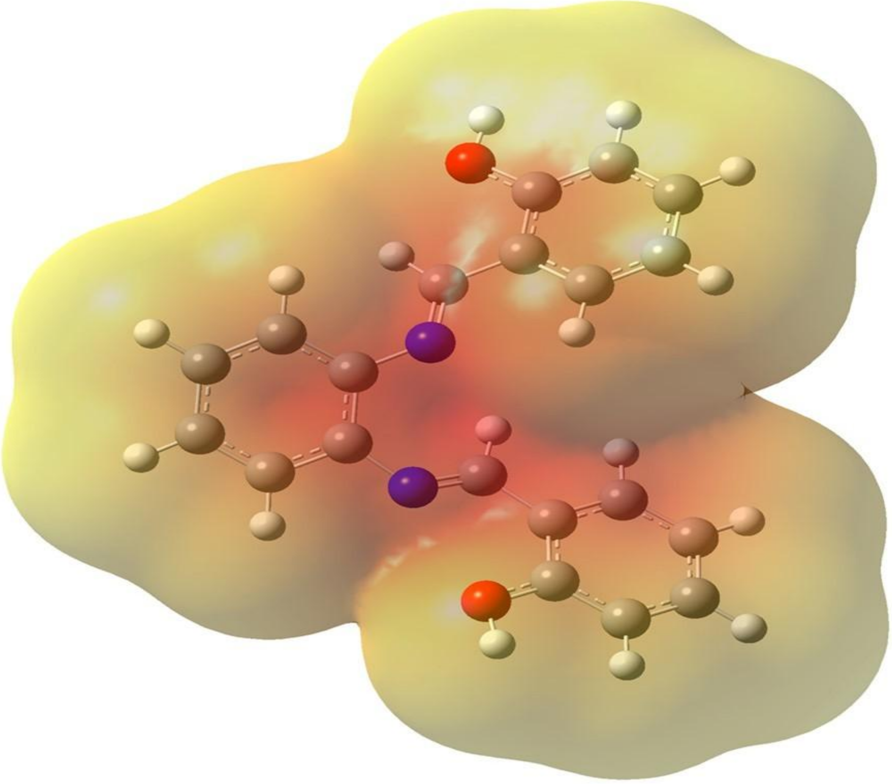


Figure S14. Electrostatic potential map of **P-2** compounds.

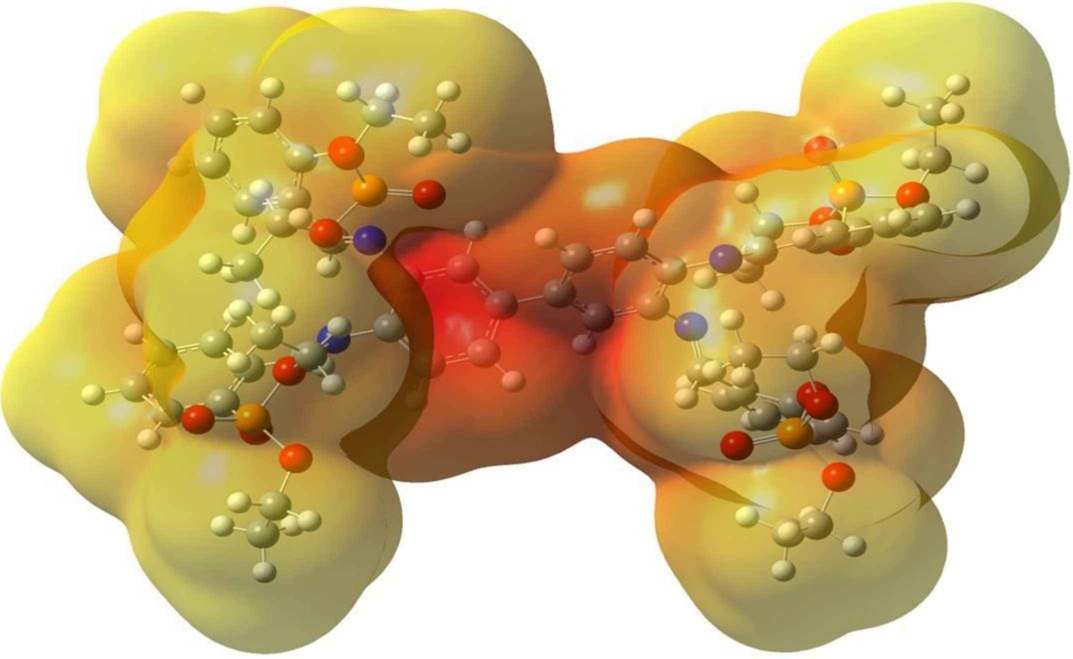


Figure S15. Electrostatic potential map of the phosphorylated adduct of the compound of **P-1.**

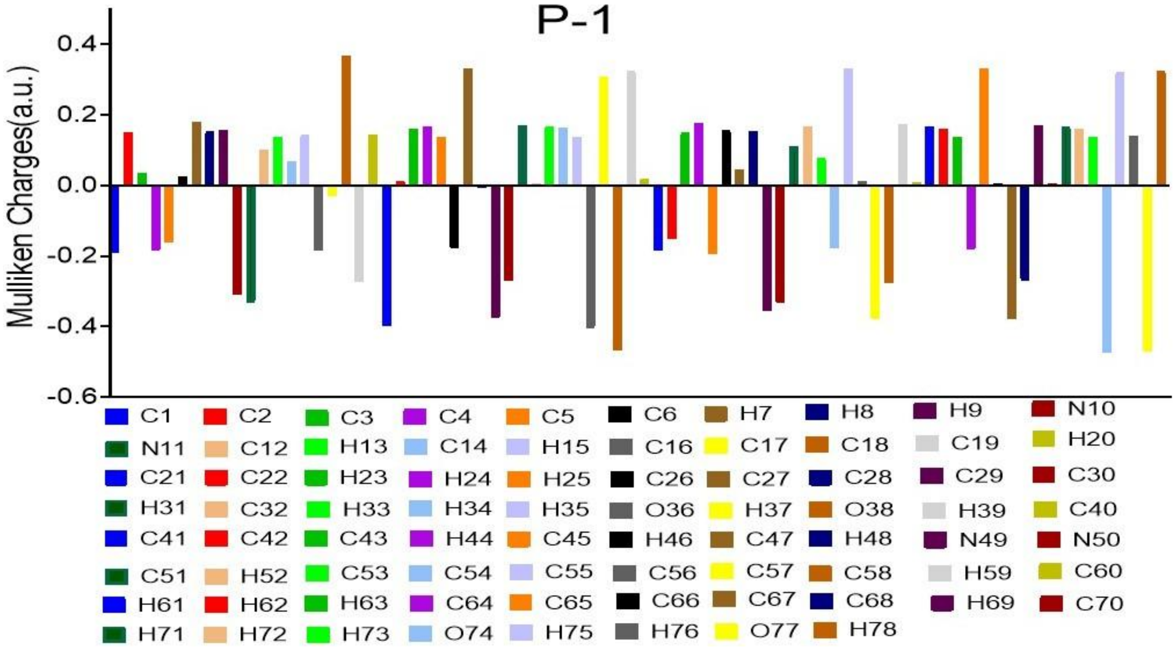


Figure S16. Mulliken charge distribution plot of **P-1** compound.

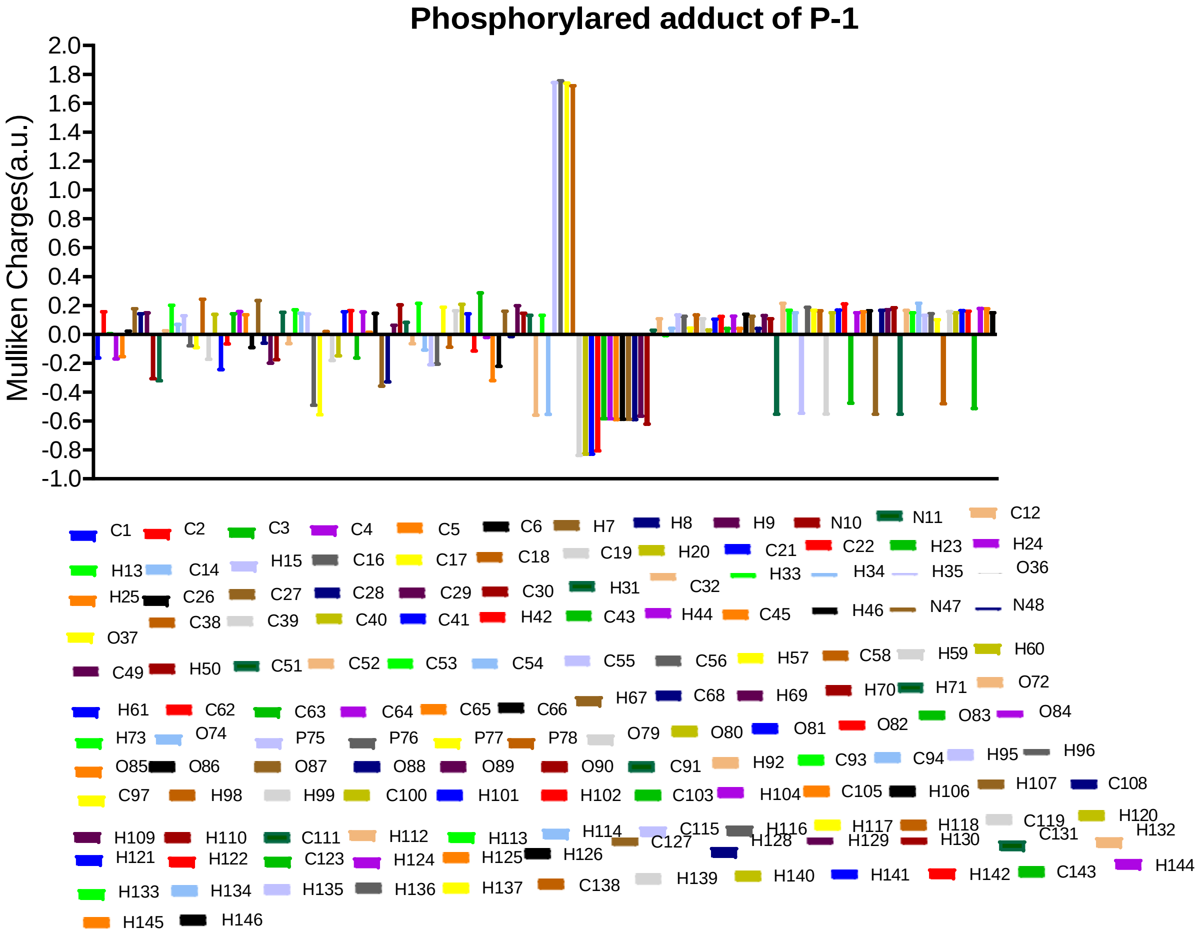
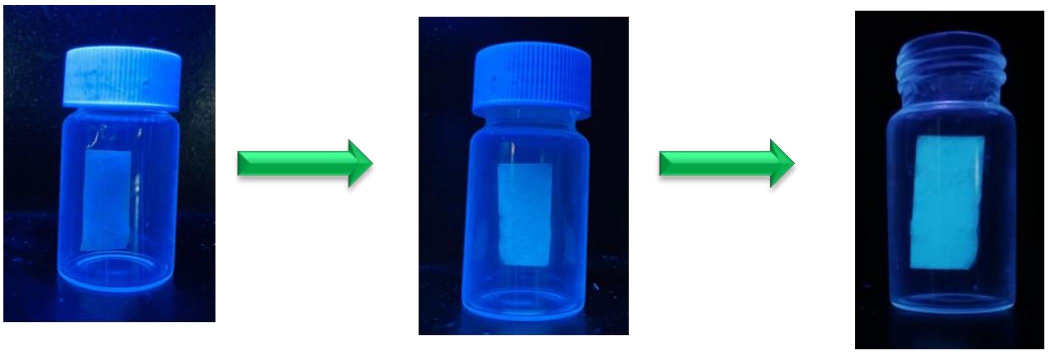


Figure S17. Mulliken charge distribution plot of phosphorylated adduct of **P-1** compound.



Sample coated
Paper strip

Exposure of DCIP
vapour instant

Exposure of DCIP
vapour after 10 min

Figure S18. Dip-Stick method for the detection of DClP in the vapor phase.

References:

1. He, X., Wu, C., Qian, Y., Li, Y., Ding, F., Zhou, Z., & Shen, J. (2019). An asymmetrical bis-salophen probe serves as a selectively and sensitively fluorescent switch of gallium ions in living cells and zebrafish. Talanta, 205, 120118.
2. Tzubery, A., & Tshuva, E. Y. (2011). Trans titanium (IV) complexes of salen ligands exhibit high antitumor activity. Inorganic Chemistry, 50(17), 7946-7948.