An ICT based organic framework for fluorogenic detection of lethal pulmonary agent phosgene

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1. Determination of detection limit (LOD)

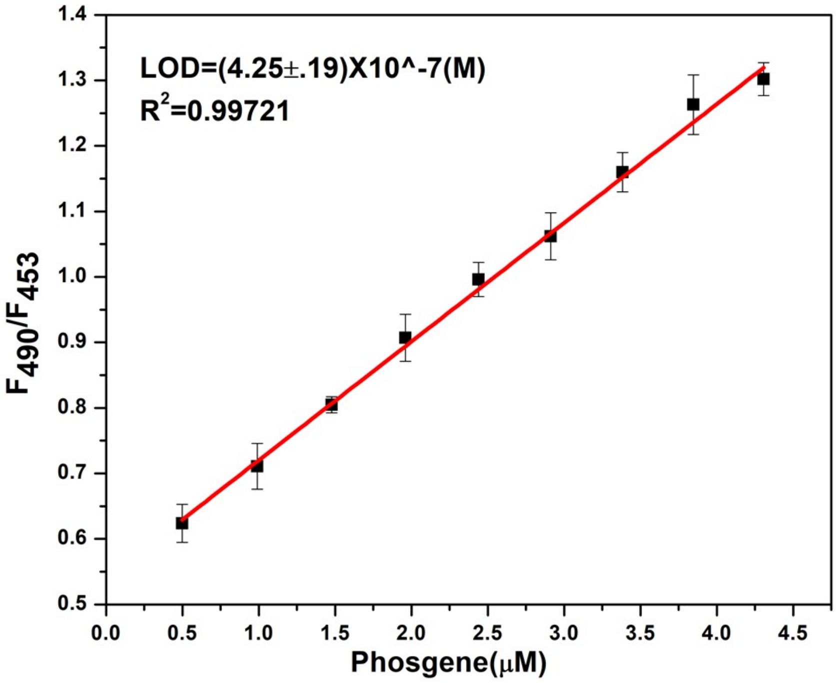


Figure S1: The linear response curve of emission intensity ratio (F_{490}/F_{453}) of BPCI as a function of phosgene concentration (λ_{ex} = 360nm).

2. UV-vis and fluorescence spectra

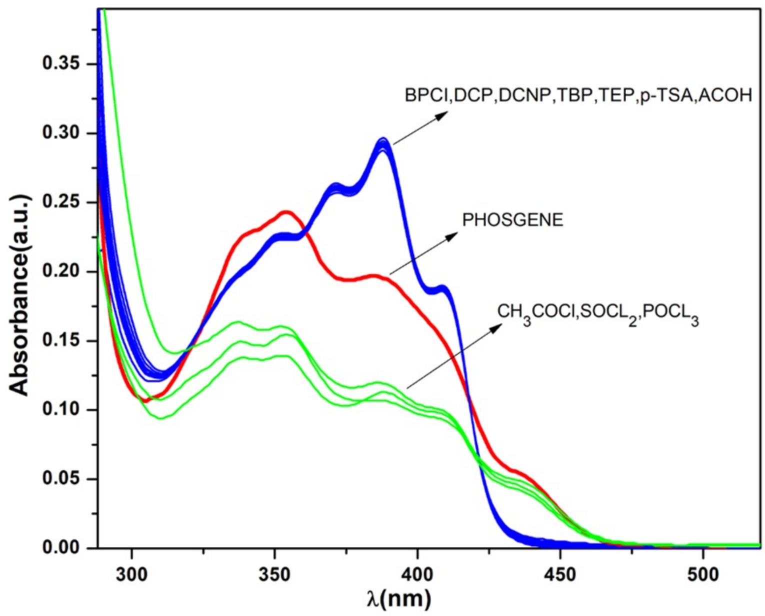


Figure S2: Change in absorption spectrum of BPCI (10 μM) upon addition of different guest analytes (20 μM) in THF solution.

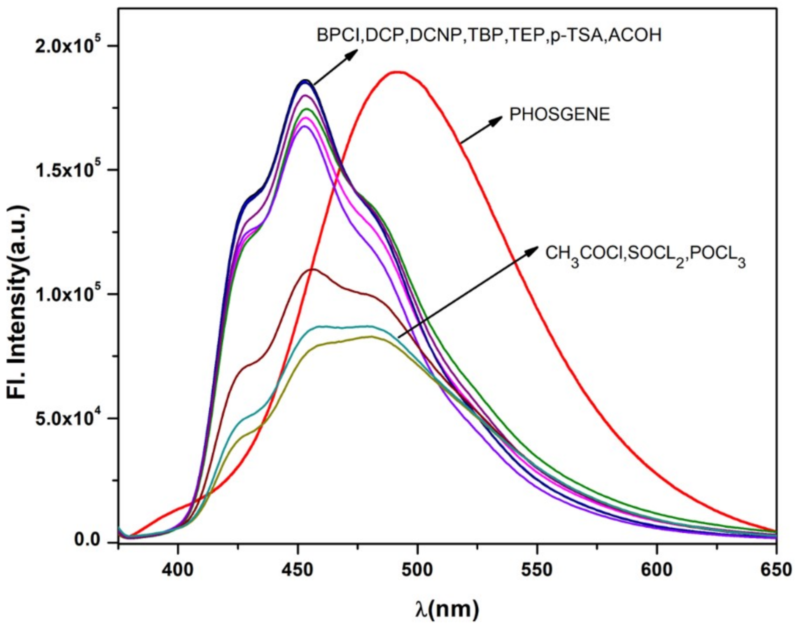


Figure S3: Change in emission spectra of BPCI (10 μM) in presence of different guest analytes (20 μM) in THF solution.

3. Competition study

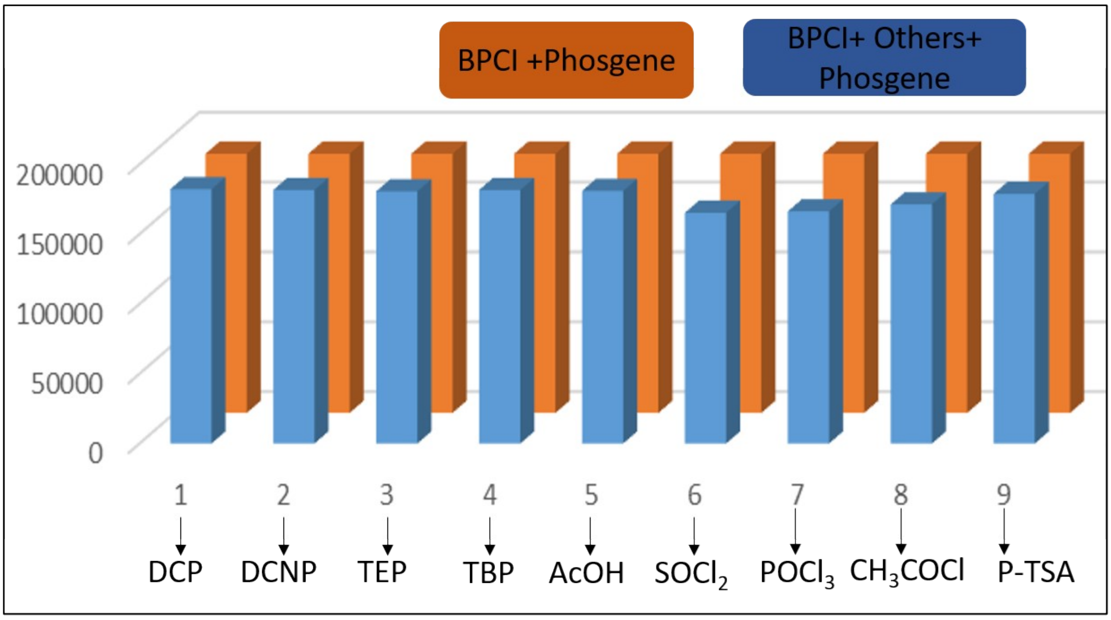


Figure S4: A comparative study of emission intensity (at 490 nm) after the addition of different analytes in the solution of BPCI in the presence of phosgene.

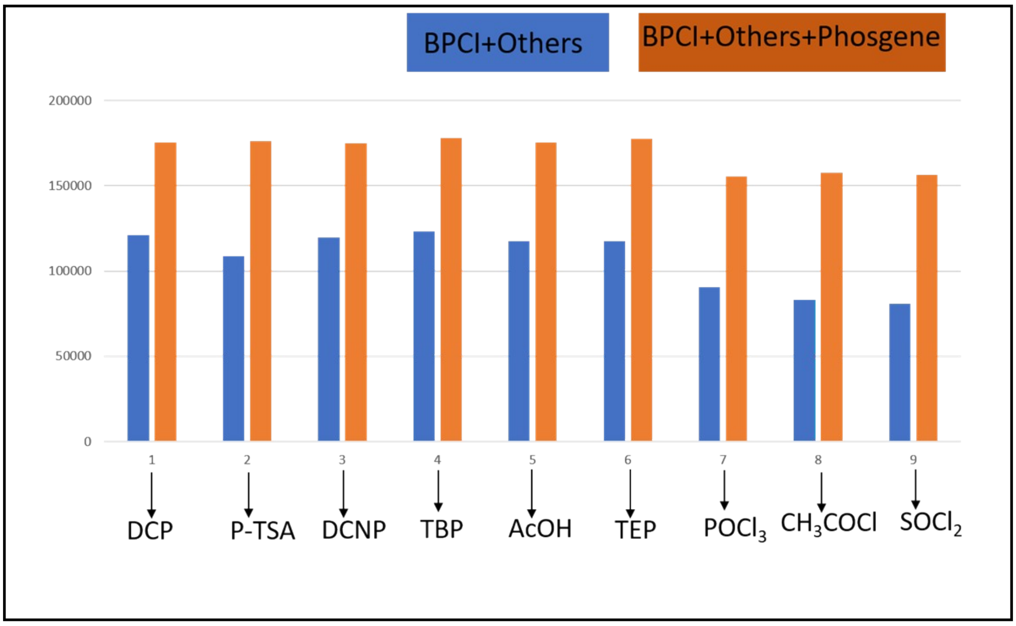


Figure S5: A comparative study of emission intensity (at 490 nm) after the addition of phosgene in the solution of BPCI in the presence of different analytes.

4. Determination of Quantum yield of BPCI

For measurement of the quantum yields of BPCI and its reaction product with Phosgene (BPCI-PHOS), we recorded the absorbance of the compounds in THF solution. The emission spectra were recorded using the maximal excitation wavelengths and the integrated areas of the emission-corrected spectra were measured. The quantum yields were then calculated by comparison with coumarin 153 (φ_s = 0.544) as reference using the following equation:

$$\Phi_x = \Phi_s \times \left(\frac{Ix}{Is}\right) \times \left(\frac{As}{Ax}\right) \times \left(\frac{nx}{ns}\right)^2$$

Where, x & s indicate the unknown and standard solution respectively, Φ is the quantum yield, I is the integrated area under the fluorescence spectra, A is the absorbance and n is the refractive index of the solvent. We calculated the quantum yields of BPCI and BPCI-PHOS using the above equation and the values are 0.182 and 0.291 respectively.

Table S1: Fluorescence lifetime data

THF (solvent)	Quantum yield (ϕ)	τ (ns)	k_r (10^8×s-1)	k_{nr} (10^8×s-1)
BPCI	0.182	0.946	1.92	8.58
BPCI-PHOS	0.291	1.445	2.01	4.91

5. ^{1}H NMR spectrum of BPCI

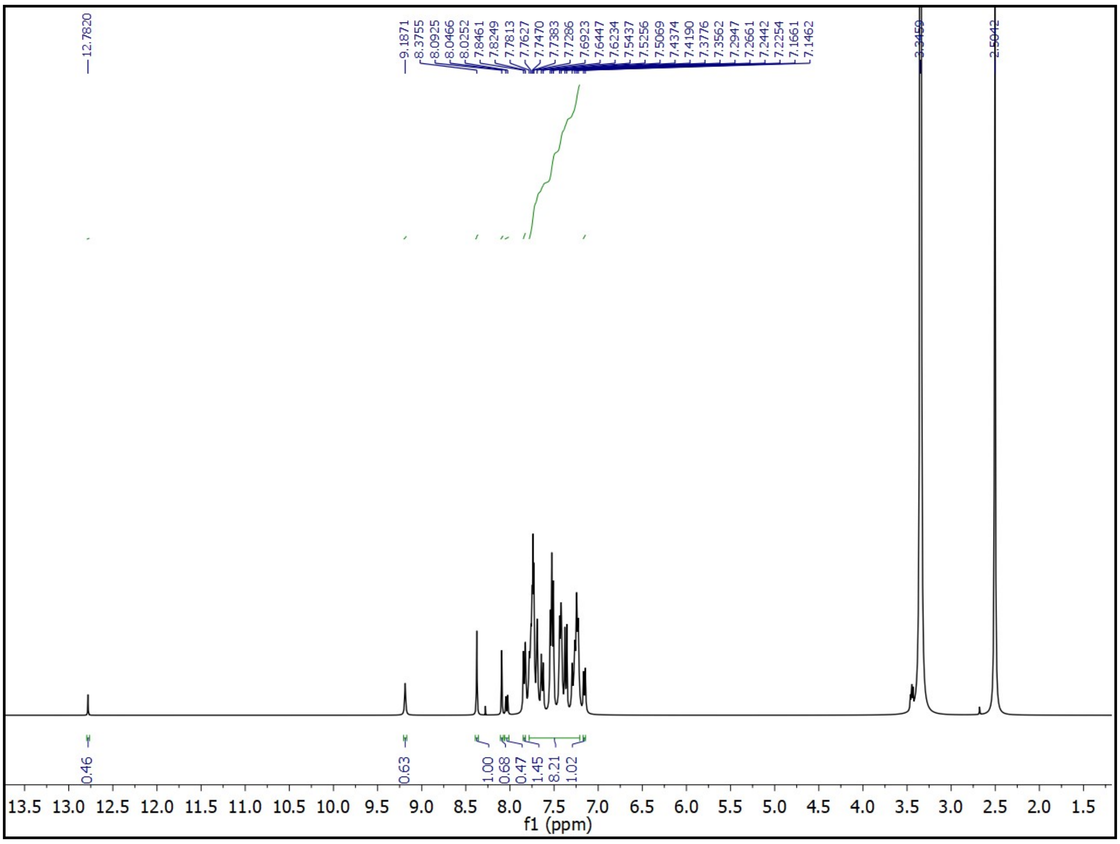


Figure S6: ^{1}H NMR (400 MHz) spectrum of the probe (BPCI) in DMSO-d_6.

6.^{13}C NMR spectrum of BPCI

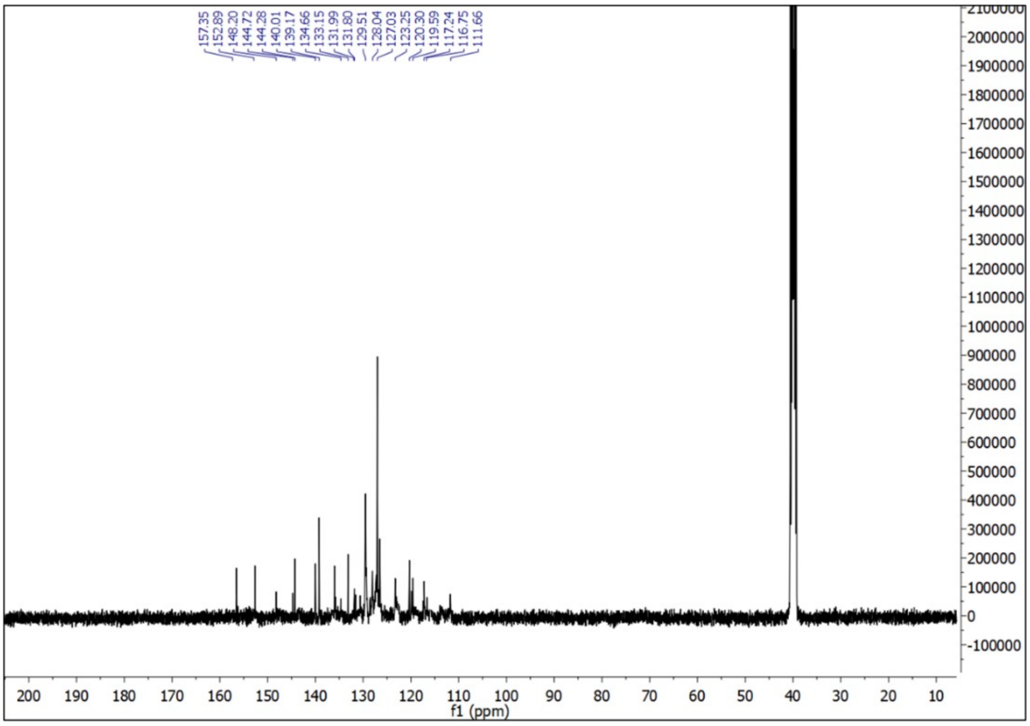


Figure S7: ^{13}C NMR (100 MHz) spectrum of the probe (BPCI) in DMSO-d_6

7. Mass spectrum (HRMS) of BPCI

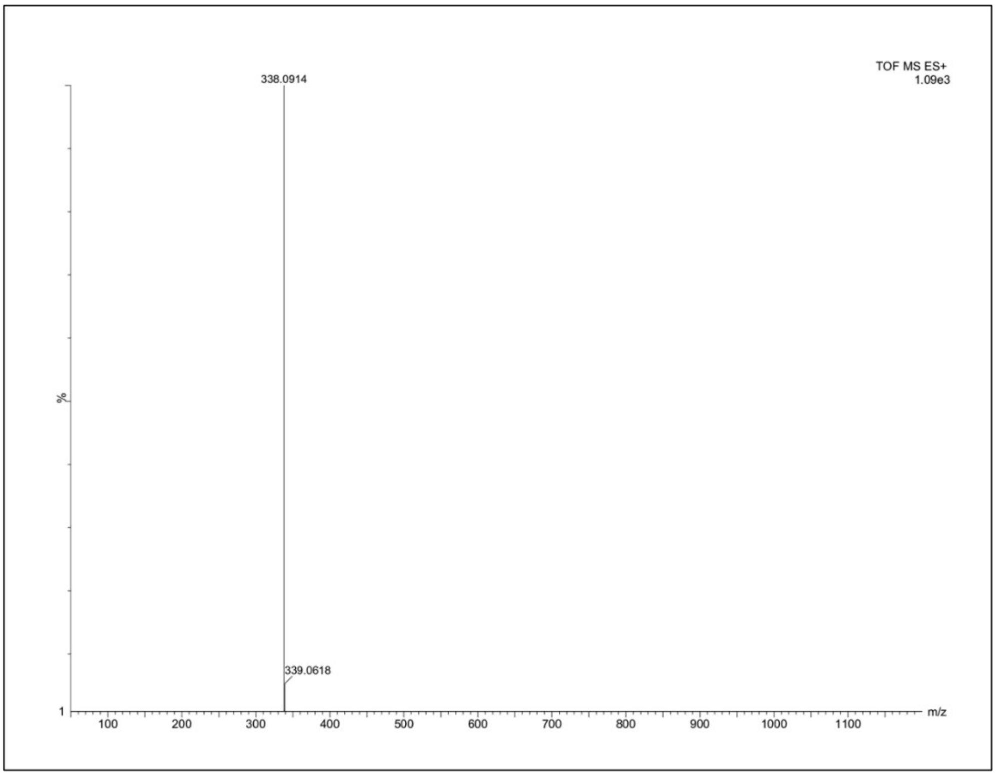


Figure S8: HRMS of the probe (BPCI).

8. IR spectra of probe BPCI

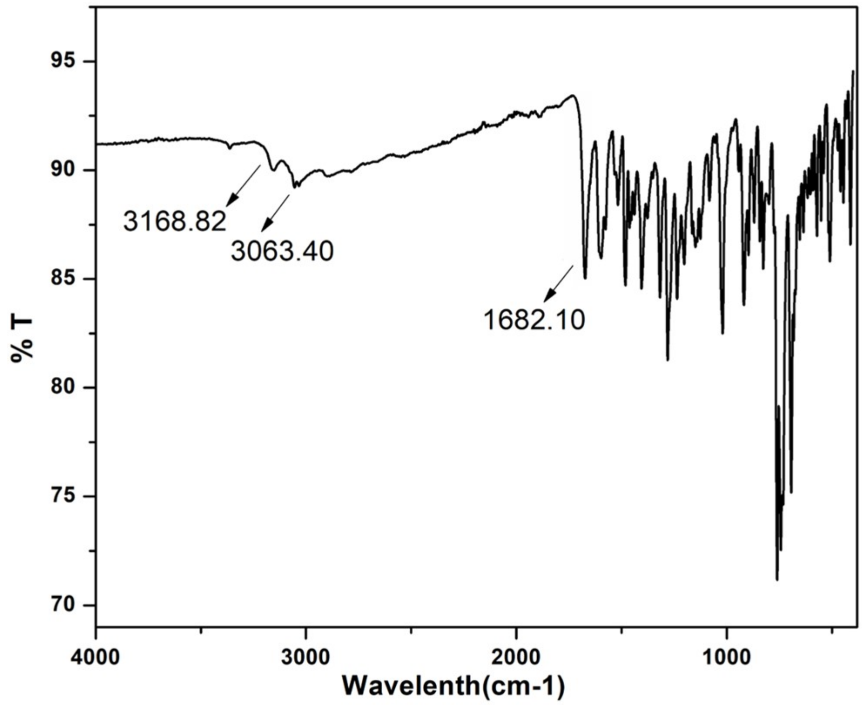


Figure S9: IR spectra of the probe BPCI (KBr disk).

9.[1]H NMR spectrum of BPCI-PHOS

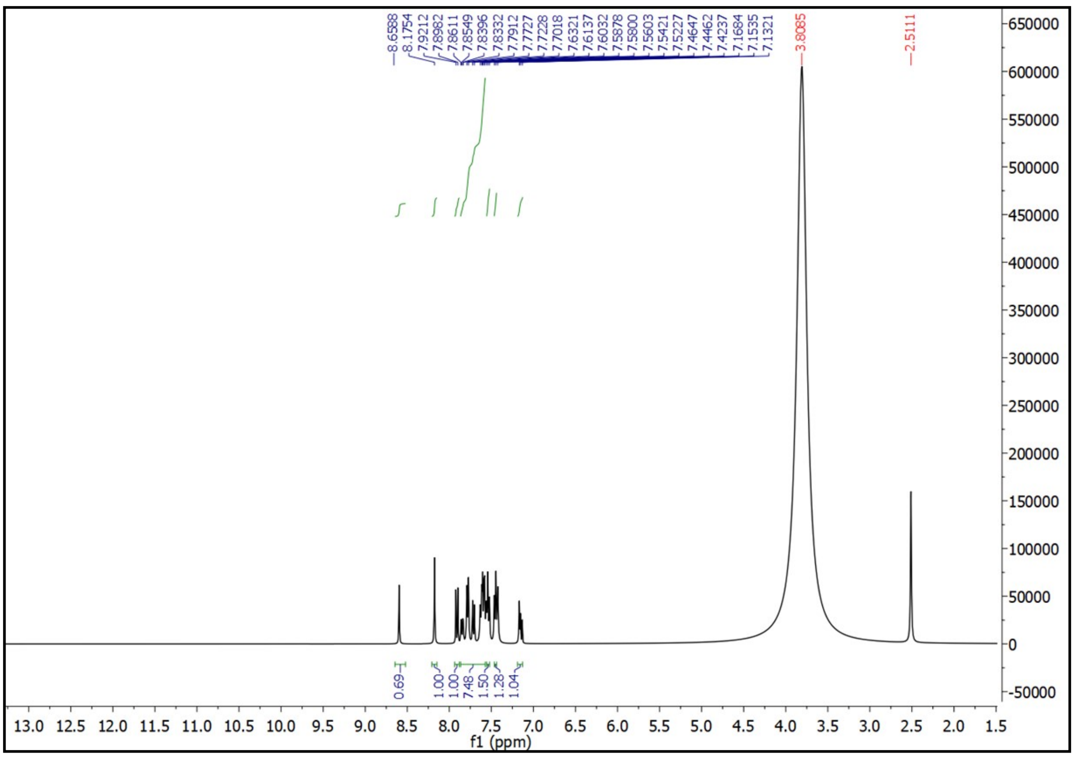


Figure S10: ^{1}H NMR (400 MHz) spectrum of the BPCI-PHOS in DMSO-d_6

10. ^{13}C NMR spectrum of BPCI-PHOS

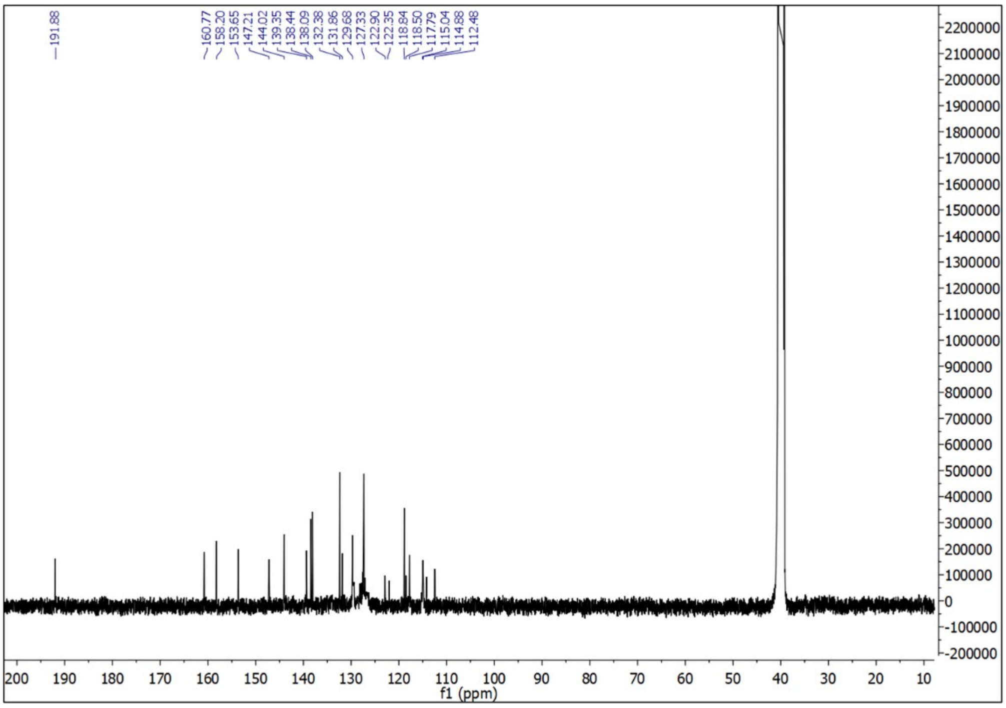


Figure S11: ^{13}C NMR (100 MHz) spectrum of the BPCI-PHOS in DMSO-d_6

11. Mass spectrum (HRMS) of BPCI-PHOS

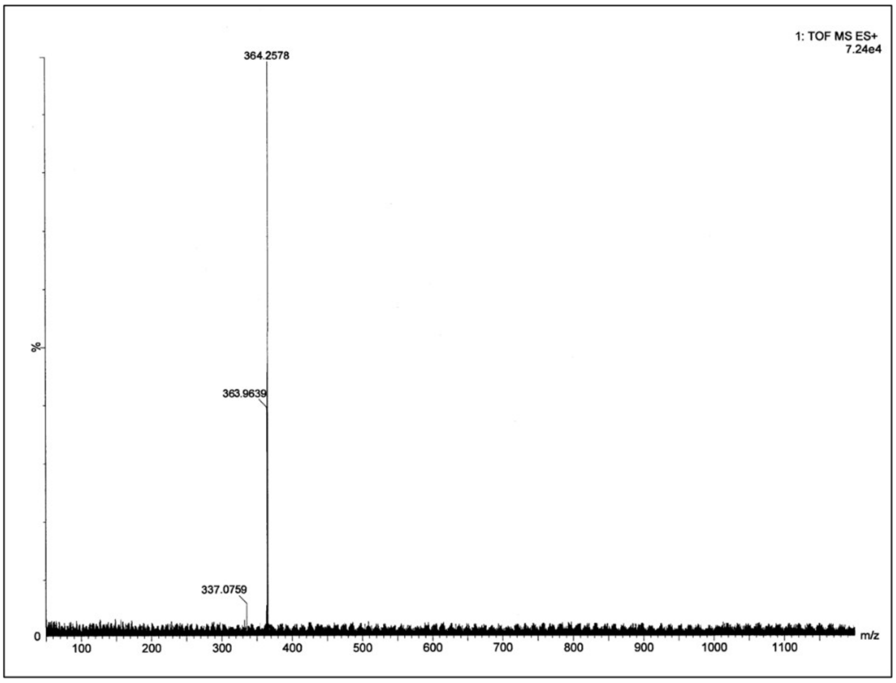
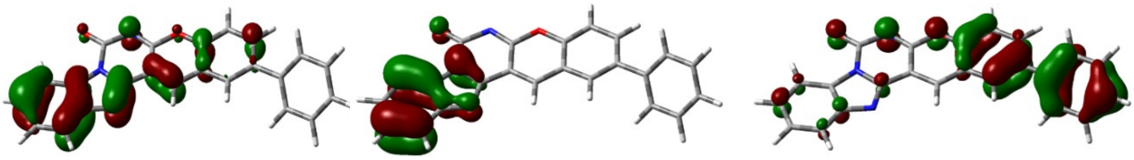


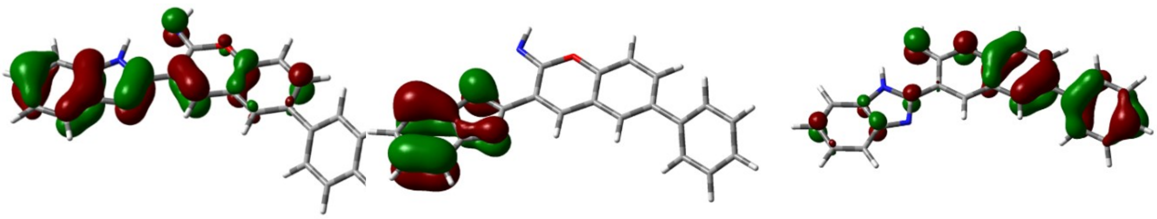
Figure S12: HRMS of BPCI-PHOS.

12. Computational Study

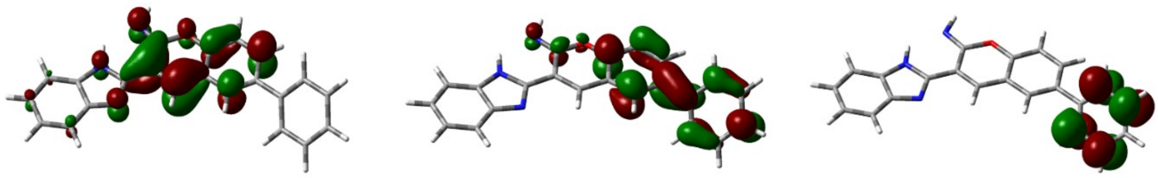
Figure S13: Contour plots of some selected molecular orbitals of BPCI



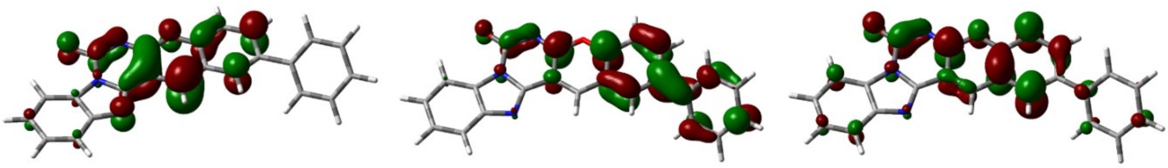
HOMO (E = -6.29 eV) | HOMO-1 (E = -6.7eV) | HOMO-2 (E = -6.86 eV)



HOMO (E = -5.81 eV) | HOMO-1 (E = -6.23 eV) | HOMO-2 (E = -6.5 eV)



LUMO (E = -2.42 eV) | LUMO+1 (E = -1.34 eV) | LUMO+2 (E = 0.69 eV)



LUMO (E = -3.2 eV) | LUMO+1 (E = -1.79 eV) | LUMO+2 (E = -1.25 eV)

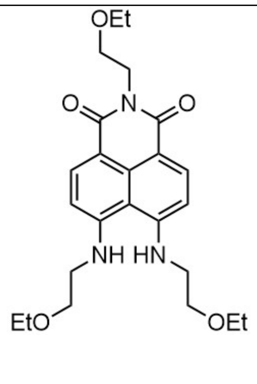
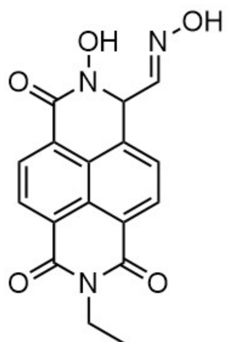
Figure S14: Contour plots of some selected molecular orbitals of BPCI-PHOS

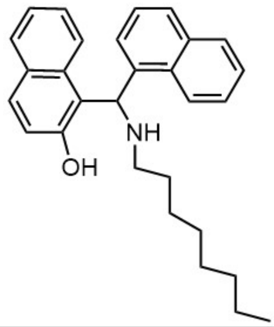
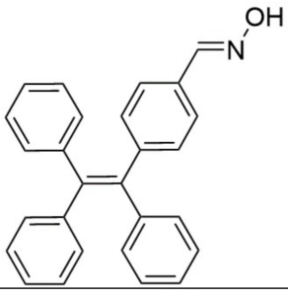
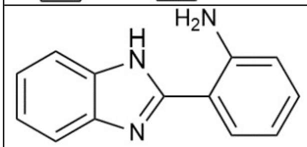
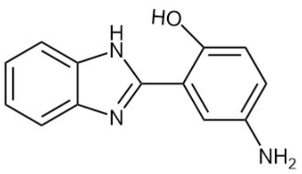
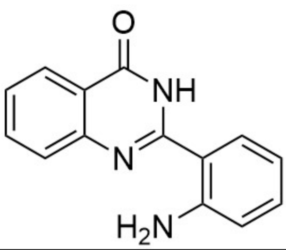
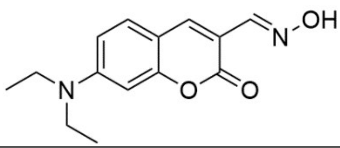
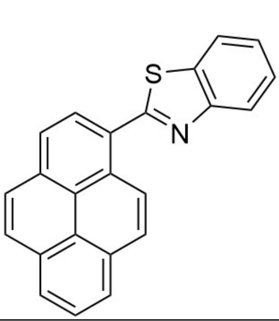
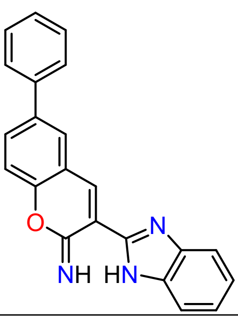
Table S2: Vertical electronic transition of BPCI and BPCI-PHOS calculated by TDDFT/CPCM method

Compd.	Wavelength (nm)	Energy (eV)	Osc. Strength (f)	Key transitions	Character
	399.7	3.1014	0.7762	(98%) HOMO→LUMO	$\pi\rightarrow\pi^*$
BPCI	351.7	3.5249	0.1367	(61%) HOMO-1→LUMO	$\pi\rightarrow\pi^*$
	354..3	3.4990	0.0102	(59%) HOMO-2→LUMO	$\pi\rightarrow\pi^*$
	296.4	4.6850	0.0274	(58%) HOMO→LUMO+1	$\pi\rightarrow\pi^*$
	439.9	2.8179	0.6757	(98%) HOMO→LUMO	$\pi\rightarrow\pi^*$
BPCI-PHOS	406.2	3.0521	0.0135	(94%) HOMO-1→LUMO	$\pi\rightarrow\pi^*$
	388.9	3.1879	0.0431	(94%) HOMO-2→LUMO	$\pi\rightarrow\pi^*$
	296.5	3.1813	0.1388	(75%) HOMO→LUMO+1	$\pi\rightarrow\pi^*$

13. Comparison table:

Table S3: The comparison of the present probe (BPCI) with some previous probes for detection of phosgene

Receptor	**Type of response**	**Test kit**	**Detection limit**	**Detection in gaseous phase**	**Reference**
	Fluorometric (ratiometric)	Yes (Test-strip method)	1.3 nM	Yes	*Chem. Commun.*, 2017, **53**(9), 1530-1533
	Colorimetric, fluorometric (ratiometric)	Yes (Test-strip method)	0.09 nM	Yes	*J. Mater. Chem. A.*, 2019, **7**(4),

					1756-1767
	Fluorometric (turn-on)	Yes (Dip-stick method)	0.40 µM	No	*New J. Chem.*, 2019, **43**, 11743
	Fluorometric (Turn-on)	Yes (Test strip method)	9.3 nM	No	*Chem. Commun.*, 2022, **58**, 5296
	Fluorometric (ratiometric)	Yes (Dip-stick method)	1.27nM	Yes	*Talanta*, 2021, **221**, 121477
	Fluorogenic (ratiometric)	Yes (Test-strip method)	5.3 nM	Yes	*RSC Adv.*, 2021, **11**, 10836
	Fluorometric (Turn-on)	Yes (Test-strip method)	0.16 ppm	Yes	*New J. Chem.*, 2021, **45**, 5631
	Colorimetric, fluorometric (ratiometric)	Yes (Dip-stick method)	0.12 µM	Yes	*New J. Chem.*, 2020, **44**, 5784
	Colorimetric, fluorometric (ratiometric)	Yes (Dip-stick method)	1.54 nM	Yes	*New J. Chem.*, 2019, **43**, 14991
	Fluorometric (ratiometric)	Yes (Dip-stick method,	$(4.25\pm0.19)\times10^{-7}$ (M)	Yes	Present Work

		Test-strip method)			