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Fabrication of a new fluorogenic probe for detection of phosgene in solution and vapor phase

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ABSTRACT

A new fluorogenic probe, COUBM (where, COUBM = 3-(1H-benzoimidazol-2-yl)-8-benzothiazol-2-yl-chromen-2-ylideneamine) is designed and synthesized for selective and rapid detection of phosgene both in solution and gas phase. COUBM reacts with phosgene to form a cyclic carbamylated product (COUBM-PHOS) and consequently a sharp increase in fluorescence intensity is observed. The probe is efficiently used to detect phosgene in vapor phase using the COUBM loaded filter paper kit. Theoretical calculation by DFT/B3LYP/6−31+G(d) method is performed to interpret the electronic structure and the probable sensing mechanism of the probe for the detection of phosgene.

1. Introduction

Phosgene is one of the worst fatal chemical warfare gas (CWA) used in World War I [1–4]. CWAs are classified in various types such as nerve agent, pulmonary agent, asphyxiant and blister agents [5]. Phosgene is a toxic pulmonary agent. Initially, it causes eye, nose, throat and respiratory irritation. Exposure of 90 ppm of phosgene for 30 min is lethal, can cause noncardiogenic pulmonary edema, pulmonary emphysema and finally leads to death [6–12]. All the CWAs like Sarin, Soman, Tabun are strictly prohibited, unlike phosgene, due to its versatile use in industrial purposes. It is an important precursor for the production of pesticides, insecticides, pharmaceuticals, isocyanate based polymer, and aniline dyes, etc [13,14]. Due to its ready availability, it is a potential threat of terrorist attack to all mankind. Devastating annihilation can also occur from industrial leakage of phosgene. Therefore, it is very important to develop a kit for urgent alert of this threat.

Gas chromatography can be used for accurate detection of phosgene, but due to its very bad portability, a low cost, portable, highly selective and highly sensitive detection engine must be needed. There are very few publications worked on the detection of phosgene till now. Usually, these are based on nucleophilic substitution of phosgene by an amine and hydroxyl group-containing molecular probe [15–20]. Reacting with phosgene, generally, they form a cyclic compound inhibiting the photoinduced electron transfer of fluorescence quenching, to induce the emission property. Some of the groups also reported their chemosensors based on fluorescence resonance transfer [21], opening of the amino-containing spiro (deoxy) lactum [22], conversion of cinnamic acid to coumarins [23] processes.

In the present work, we have designed and synthesized a highly selective, sensitive fluorogenic chemosensor, based on nucleophilic substitution of the probe to the electrophilic phosgene to form a carbamide molecule. The probe is named as COUBM after its precursor coumarin and benzimidazole derivative. It is very selective for phosgene over various acyl chlorides and nerve agent mimics. Vapor phase detection of phosgene is also tested by test kit made of filter paper immersed with COUBM solution. All of these tests permit the probe for onsite detection of phosgene.

2. Experimental

2.1. Material and methods

All the essential chemicals are bought from Sigma Aldrich and utilized for synthesis of the probe without purifications. Elemental analysis of the probe was carried out by a 2400 Series-II CHN analyzer, Perkin Elmer, USA. Waters (Xevo G2 Q-TOF) mass spectrometer was used for the spectrometric studies of the probe and its adduct. An infrared spectrum of the probe was recorded from RX-1 Perkin Elmer spectrophotometer by preparing KBr pellet of the sample. UV–vis absorption studies were carried out on a PerkinElmer Lambda 750 spectrophotometer. Luminescence properties were observed by Shimadzu RF-6000 fluorescence spectrophotometer at room temperature (298 K). ^{1}H and

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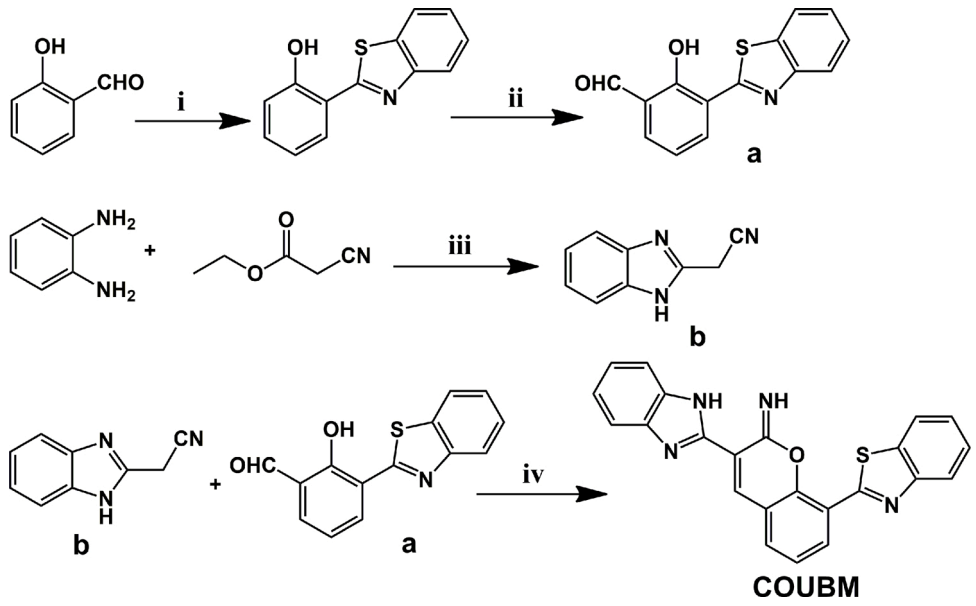


Scheme 1. Reagents and conditions: (i) 2- aminothiophenol, EtOH, reflux for 6 h; (ii) TFA, hexamine, reflux for 4 h; (iii) I_2, 180–200 °C, 2 h; (iv) piperidine, EtOH, reflux.

^{13}C NMR spectra were recorded using a Bruker (AC) 300 MHz and 400 MHz FT-NMR spectrometer of ~0.05 M solutions of the compounds in $CDCl_3$ using TMS as an internal standard. In every step of the reaction, products are monitored by a thin-layer chromatographic technique using an aluminum TLC plate of silica gel 60 F254. Purifications of reaction products were done by column chromatographic technique using silica gel of mess 200–300, petroleum benzene and ethyl acetate solvents. All spectrometric measurements are performed in HPLC grade solvents.

2.2. Synthesis

2.2.1. Synthesis of 2-benzothiazol-2-yl-phenol

2-Benzothiazol-2-yl-phenol was prepared following a published work [24]. A mixture of 2- aminothiophenol (250 mg, 2 mmol) and benzaldehyde (212 mg, 2 mmol) was stirred in 15 mL methanol at room temperature for three hours in presence of 0.5 mg I_2 until a greenish-yellow precipitate appears. The precipitate was collected by filtration, dried for the use in next step synthesis of 3-benzothiazole-2-yl-2-hydroxy-benzaldehyde (a). Yield: (0.25 g) 55 %.

2.2.2. Synthesis of 3-benzothiazole-2-yl-2-hydroxy-benzaldehyde (a)

It was also synthesized following our previously reported procedure [25]. 2-Benzothiazole-2-yl-phenol (0.22 g, 1 mmol) and hexamethylenetetraamine (0.14 g, 1 mmol) were dissolved in 10 mL of trifluoroacetic acid and refluxed at 90 °C -100 °C for 6 h. Then the reaction mixture was allowed to cool at room temperature followed by stirring in 30 mL 6 N HCl solution for 30 min. Product was extracted from the solution with dry DCM. Finally, column chromatography was performed for further purification of the compound. Yield: (0.13 g) 50 %.

^{1}H NMR (300 MHz, $CDCl_3$): ^{TM}(ppm): 7.08 (t, 1 H), 7.45–7.54 (m, 3H, Ar), 7.90–8.04 (m, 3H, Ar), 9.99 (s, 1 H), 10.54 (s, 1 H). HRMS: MS-ES+ (*m/z*): $[M+H]^+$: Calculated: 256.0427; Found: 256.0421 (Figs. S5-S6).

2.2.3. Synthesis of 2-cyanomethylbenzimidazole (b)

A mixture of o-phenylenediamine (0.430 g, 4 mmol) and ethyl cyanoacetate (0.9 g, 8 mmol) was heated in an oil bath for 2 h at 175 °C. Then the reaction mixture was cooled to approximately 100 °C and

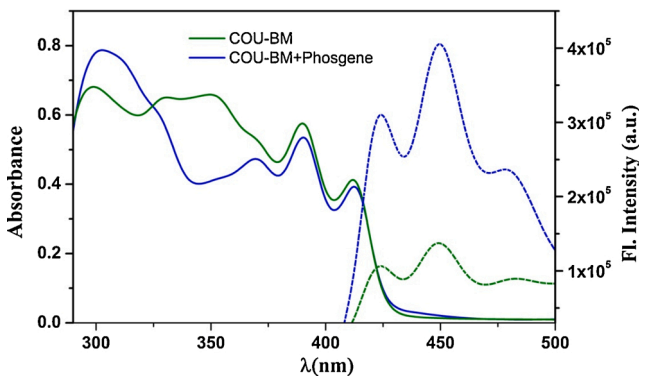


Fig. 1. Absorption and emission spectra of the probe (COUBM) (10 μM) before and after addition of phosgene in $CHCl_3$.

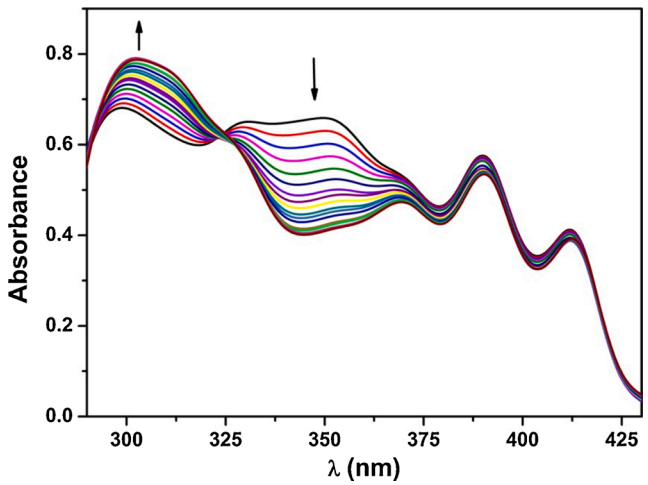


Fig. 2. Change in absorption spectra of COUBM (10 μM) upon the gradual addition of phosgene (0-40 μM) in $CHCl_3$.

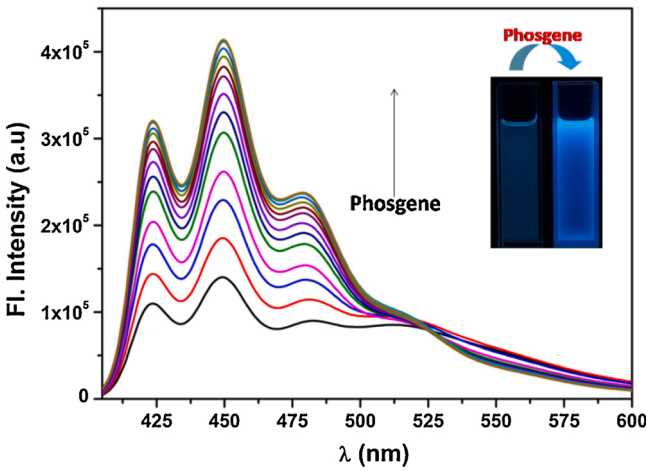


Fig. 3. Change in emission spectra of COUBM (10 μM) upon gradual addition of phosgene (0-40 μM) in $CHCl_3$ (λ_{ex} =390 nm). Inset shows the visual change of COUBM in presence of phosgene under UV light.

dioxane was added. The whole mixture was then cooled to room temperature and the precipitate was filtered out, washed with ethanol and dried [26]. Yield: (0.36 g) 60 %.

^{1}H NMR (300 MHz, DMSO-d6): ^{TM}(ppm): 4.37 (s, 2 H), 7.17 (s, 2 H), 7.53 (s, 2 H), 12.59 (s, 1 H), HRMS: MS-ES+ (*m/z*): $[M+H]^+$: Calculated: 158.0713; Found: 158.0717 (Figs. S7-S8).

2.2.4. Synthesis of the probe 3-(1H-benzoimidazol-2-yl)-8-benzothiazole-2-yl-chromen-2-ylideneamine (COUBM)

In a clean and dry round bottom flux, 3-benzothiazole-2-yl-2-hydroxy-benzaldehyde (a) (0.13 g, 0.5 mmol) was dissolved in 15 mL of ethanol. Then, 2-cyanomethylbenzimidazole (b) (0.08 g, 0.5 mmol) was added to the solution. The whole mixture was stirred and the catalytic amount of piperidine was added. Then it was refluxed for 5 h. A light yellow colored product was precipitated which was then filtered and dried. Finally, it was purified by column chromatography. Yield: (0.15 g) 76 %;

Elemental analysis: Anal. Calcd for $C_{23}H_{14}N_4OS$: C, 70.03 %; H, 3.58 %; N, 14.20 %; Found C, 70.08 %; H, 3.53 %; N, 14.17 %. IR (cm^{-1}, KBr): 1680 υ(-C = N).

^{1}H NMR (400 MHz, $CDCl_3$): ^{TM}(ppm):7.02 (t, *J* =8.6 Hz, 1 H), 7.17 (d, *J* =8.8 Hz, 2 H), 7.35 (m, 4 H), 7.50 (m, 2 H), 7.90 (s, 1 H) 7.97 (d, *J* =9.04 Hz, 1 H), 8.07 (d, *J* =8.76 Hz, 1 H), 9.32 (s, 1 H), 12.48 (s, 1 H). ^{13}C NMR (300 MHz, $CDCl_3$): ^{TM}(ppm): 163.4, 159.6, 152.2, 152.1, 151.9, 139.3, 136.2, 131.1, 130.8, 125.8, 124.4, 123.7, 123.0, 122.5, 121.4, 119.7, 118.2, 113.9, 111.2, 110.8. HRMS: MS-ES+ (*m/z*): [M+H]+: Calculated: 395.0967; Found: 395.0894.

2.2.5. Synthesis of the probe and phosgene adduct (COUBM-PHOS)

A solution of the probe (0.1 mg, 0.25 mmol) in THF was taken in a round bottom flask and stirred with an equimolar amount of triphosgene at room temperature for half an hour. The precipitate was collected through filtration, washed with dry THF and dried. The product was characterized by spectroscopic techniques.

^{1}H NMR (400 MHz, DMSO-d6): ^{TM}(ppm): 7.51 (m, 4 H), 7.65 (t, *J* =7.78 Hz, 1 H), 7.87 (d, *J* =9.36 Hz, 1 H), 8.09 (m, 2 H), 8.15 (d, *J* =8.56 Hz, 1H), 8.24 (d, *J* =7.36 Hz, 1 H), 8.35 (d, *J* =7.8 Hz, 1 H), 8.72 (d, *J* =9.44 Hz, 1 H). ^{13}C NMR (300 MHz, DMSO-d6): ^{TM}(ppm): 192.3, 165.8, 160.4, 159.8, 157.8, 152.5, 151.6, 151.4, 144.9, 135.6, 134.9, 134.0, 133.4, 127.5, 127.3, 126.4, 126.3, 126.1, 125.6, 123.5, 122.8, 120.8, 155.4, 114.3. HRMS: MS-ES+ (*m/z*): [M+H]+: Calculated: 421.0754; Found: 421.0763.

2.3. Spectral study

A stock solution of COUBM (1 mM) was prepared in chloroform solvent of HPLC grade. Various analytes like DCP, DCNP, AcOH, $SOCl_2$, TEP, TBP, $POCl_3$, CH_3COCl, and PTSA solutions were prepared in chloroform of 1 mM concentration. Due to the high toxicity of phosgene, it was not used directly. One of its precursors, triphosgene was used for in situ preparation of phosgene in the experimental solution for various studies. Triphosgene solution (1 mM) was prepared in chloroform. Sensing of the probe has been investigated through the studies of UV–vis absorptions and fluorescence emissions for different solutions of various concentrations of the receptor (M) with increasing concentration of analytes (M). For emission spectral studies, excitation wavelength was 390 nm (excitation slit = 5.0 and emission slit = 5.0). All the spectra were taken at room temperature (25 °C) and plotted by origin pro 8.5.

2.4. Computational method

Gaussian 09 (G09) program [27] was used for theoretical calculations. Full geometry optimizations of COUBM and COUBM-PHOS were carried out by DFT/B3LYP/6−31+G(d) method [28,29]. The vibrational frequency calculations on the optimized geometries were performed to ensure that the optimized geometries represent the local minima and there were only positive Eigen values.

3. Results and discussion

3.1. Synthesis of the probe COUBM

The probe COUBM was synthesized using very low-cost chemical precursor, o-phenylenediamine, benzaldehyde, and ethyl cyanoacetate. Synthetic root is shown in scheme 1 . Compound 'a' and 'b' were synthesized following the published procedures [24–26]. Finally, COUBM was obtained by coupling of compounds 'a' and 'b' in the presence of piperidine in ethanol medium. The probe was thoroughly characterized by elemental analysis, NMR, IR and mass spectrometric measurement which are given to the electronic supplementary information (ESI) (Figs. S9-S12, supporting information).

3.2. Sensing property of the probe COUBM in solution

The sensing property of the probe COUBM in solution phase was investigated in chloroform. The absorption and fluorescence spectra of COUBM were taken in presence of diethyl chlorophosphate (DCP), diethyl cyanophosphate (DCNP), triethyl phosphate (TEP), tributyl

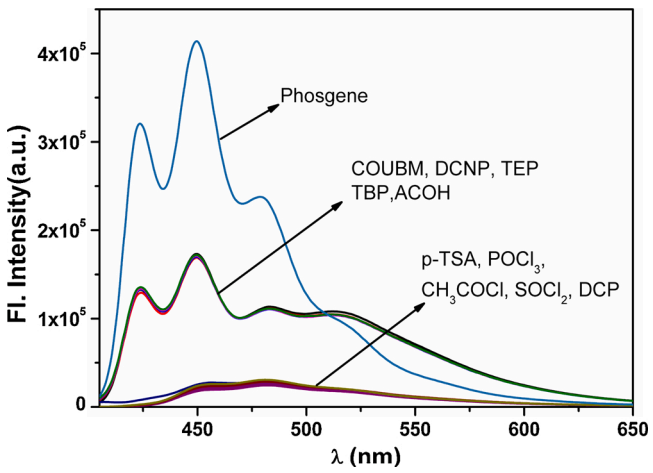
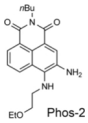
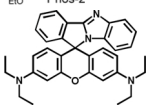
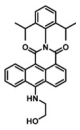
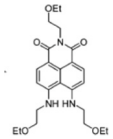
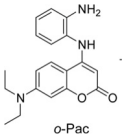
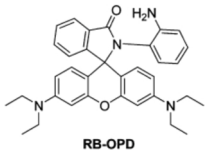
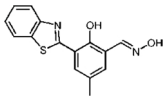


Fig. 4. Change in emission spectra of COUBM (10 μM) in presence of different guest analytes (40 μM) in $CHCl_3$ solution.

Table 1
Comparison of the present probe (COUBM) with the previously reported literature for the selective detection of phosgene.

Receptor	Solvent system	Detection limit	Time course of sensing	Reference
	DCE	0.2–0.7 nM	–	Chem. Eur. J. 24 (2018) 5652 [15]
Phos-2 	$CHCl_3$	3.2 ppb	2 min.	Anal. Chem. 90 (2018) 3382 [13]
	$CHCl_3$	2.3 nM	5 min.	Anal. Chem. 90 (2018) 8686 [17]
	DCE	1.3 nM	20 min.	Chem. Commun. 53 (2017) 1530 [30]
	$CHCl_3$	3 nM	0.5 min.	ACS Sens. 2 (2017) 178 [18]
o-Pac  RB-OPD	$CHCl_3$-CH_3OH (95/5, v/v)	2.8 ppb	3 min.	ACS Appl. Mater. Interfaces 8 (2016) 22,246 [16]
	CH_3CN	0.48 nM	20 min.	Dyes Pigm. 163 (2019) 483 [31]
This work	$CHCl_3$	1.65 nM	3 min.	

phosphate (TBP), $POCl_3$, $SOCl_2$, CH_3COCl, p-toluenesulfonic acid (PTSA), AcOH and phosgene. Changes in absorption and fluorescence intensity of COUBM in presence of phosgene are shown in Fig. 1.

The probe exhibits absorption bands at 350 nm, 390 nm and 412 nm in chloroform. In presence of AcOH, DCNP, TEP and TBP, no significant alteration in absorption spectra is noticed. Upon treatment with DCP, $POCl_3$, CH_3COCl, $SOCl_2$ and phosgene, significant changes in absorption spectra are observed. For DCP, $POCl_3$, CH_3COCl and $SOCl_2$ a new band at 435 nm is generated, while for phosgene the band at 350 nm for free probe disappeared and a new band is developed at 303 nm. For better understanding, COUBM solution was titrated with phosgene solution. Upon gradual addition of phosgene, absorption of the probe at 350 nm decreases sharply along with the increase in absorption at 303 nm (Fig. 2). The change in absorption spectra may be because of the nucleophilic substitution of COUBM to give a carbamylated compound, COUBM-PHOS which is further characterized by various spectroscopic studies. For DCP, $POCl_3$, CH_3COCl and $SOCl_2$ the changes in absorption spectra are probably due to the protonation at the electron-donating nitrogen atom.

The fluorescence response of the probe towards phosgene was monitored with the increasing concentration of phosgene in COUBM solution (Fig. 3). Upon excitation at 390 nm, free probe exhibits multiple emission bands at 442 nm, 483 nm and 517 nm along with emission λ_{max} at 449 nm. The emission quantum yield of the free probe is found to be 0.164. Upon gradual addition of phosgene (0–40 μM) to the 10 μM solution of COUBM a sharp increase in fluorescence intensity at 449 nm is observed along with the increase in emission quantum yield to 0.372. The enhancement of fluorescence intensity is due to the carbamylation of COUBM with phosgene and inhibition of photoinduced electron transfer process (PET). To understand the selectivity of the probe towards phosgene, fluorescence responses of COUBM were also measured with AcOH, DCNP, TEP, TBP DCP, $POCl_3$ CH_3COCl, $SOCl_2$ and PTSA. For DCNP, TEP, TBP and ACOH no significant change in fluorescence intensity is observed, while for DCP, $POCl_3$ CH_3COCl, $SOCl_2$ and PTSA quenching in emission intensity is observed (Fig. 4). Therefore, phosgene interacts in a different way to give a significantly different fluorescence response towards the probe compare to the other analytes. Moreover, to understand the sensitivity of the probe, fluorescence intensity of COUBM-PHOS solution was measured in presence of AcOH, DCNP, TEP, TBP DCP, $POCl_3$ CH_3COCl, $SOCl_2$, and PTSA (Fig. S2). The result shows that the probe can detect phosgene in the presence of these analytes.

For the investigation of quantitative measurement of phosgene, change in fluorescence intensity at 449 nm with the increasing concentration of phosgene is plotted (Fig. S4). It shows that with the increase of phosgene concentration (0–40 μM), emission intensity of the receptor at 449 nm increases almost linearly. Moreover, one of the most important feature for a potent chemosensor is that the limit of detection towards the target analyte should be very low. Detection limit of the present probe (COUBM) towards phosgene is calculated with the help of the equation LOD = K × SD/S where SD and S stand for standard deviation and slope of linear response curve respectively. The curve is obtained from the data of fluorescence titration. Calculated LOD of the receptor is found to be 1.65×10^{-9} M which is very low. So the receptor can be considered to be used for onsite detection of phosgene (Fig. S4). The limit of detection, time course of sensing and solvent systems of some reported phosgene sensors are compared with the present probe (COUBM) (Table 1).

The excited state property of the probe (COUBM) and its adduct with phosgene (COUBM-PHOS) was studied by nanosecond time-correlated single-photon counting (TCSPC) method. The probe has a lifetime of 0.91 ns in chloroform at room temperature. After reaction with phosgene, the lifetime value of the probe increases noticeably to 1.73 ns. Fluorescence decay profile diagram of COUBM and COUBM-PHOS is shown in Fig. 5.

Again, a sensor is considered to be very efficient when it has the ability to identify the guest analyte rapidly and selectively in very minuscule level, in the presence of other interfering species for the best use of real-time detection. COUBM can detect phosgene within 3 min

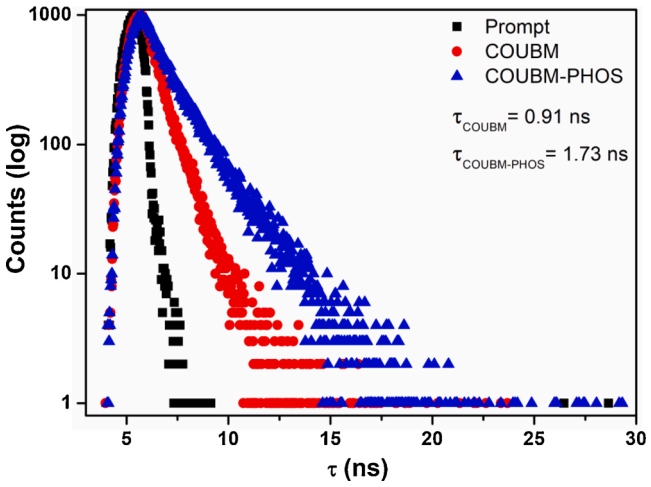


Fig. 5. Time-resolved fluorescence decay of COUBM (●●●), COUBM-PHOS adduct (▲▲▲) and prompt (■■■) in $CHCl_3$ (λ_{ex} =370 nm).

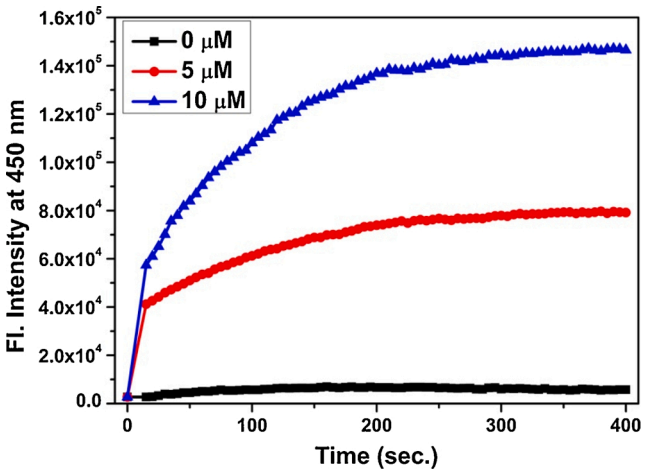


Fig. 6. Fluorescence response of COUBM (10 μM) in presence of phosgene (5 μM and 10 μM) at diff ;erent time interval in $CHCl_3$.

upto 1.65 nM concentration in the solution phase. Sensing time was investigated by measuring the fluorescence intensity of COUBM (10 μM) at different time intervals in presence of phosgene (5 and 10 μM) (Fig. 6). Within 20 s of addition of phosgene, almost 40 % of the reaction is completed and there is no significant change in fluorescence intensity is observed after 200 s. So, the sensing time of the present probe towards phosgene is comparable or even lower than other reported probes (Table 1).

3.3. Gas-phase detection

The rapid and prominent reaction towards phosgene in vapor phase allows the probe for making a suitable kit for onsite detection of phosgene. As phosgene is gaseous toxic chemical warfare agent, it is necessary to develop a kit for detection of it in the gaseous state. Our synthesized probe can be used for the preparation of suitable kit for the use in real-time gaseous state phosgene detection. The test has been done in the laboratory preparing some test strips layered with the probe. Using the dip-stick method, we have investigated sensing in the presence of phosgene and other interfering chemicals.

For the free probe test strip exhibits a light yellow color under UV light. When it comes into contact with phosgene vapor, emission changes to green color (Fig. 8). Test strip takes almost five minutes for fully responding the phosgene gas. For other chemicals vapor, emissions of the test strips do not change noticeably. All of these experiments imply that probe COUBM is applicable for real-time gas phase detection of phosgene.

3.4. Probable sensing mechanism

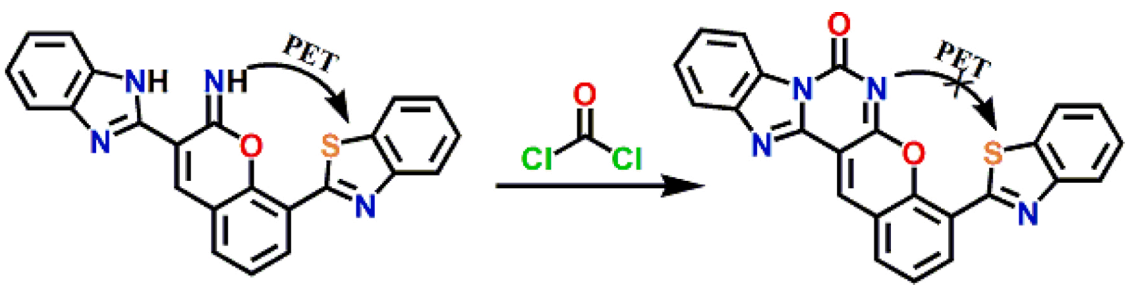
Sensing mechanism of COUBM is depicted by pictorial representation in Scheme 2. The probe itself has an electron-rich as well as electron deficient moiety. Imine nitrogen and benzimidazole moiety are electron rich and benzothiazole is electron deficient. When irradiated with UV light an effective electron transfer from benzimidazole to benzothiazole moiety can be occur by PET process. Due to this photo-induced electron transfer (PET), emission of the free probe quenched noticeably. But because of the formation of COUBM-PHOS adduct in presence of phosgene, the electron-rich centers are no longer available for effective PET process. So an immediate fluorescence enhanced is observed in presence of phosgene due to the inhibition of PET process. Further, the mechanism of PET process is perceived through the DFT calculation. A schematic diagram of molecular orbitals for feasible electron transfer process is shown in Fig. 7. For the free probe (COUBM) when irradiated with UV light, an electronic transition from the HOMO to the LUMO + 1 is observed followed by stabilization of the excited electron through the PET process, and return to the ground state (HOMO) by the way of LUMO. But when COUBM-PHOS is excited by the UV light, no such PET process is observed, electron is excited from HOMO to LUMO and subsequently stabilized through the fluorescence emission. In addition, the emission of the probe in presence of phosgene is compared with the emission of synthesized COUBM-PHOS adduct in Fig. S3. It is well supported the formation of reaction of the probe with phosgene. The formation of COUBM-PHOS adduct is also confirmed by spectroscopic analysis (Figs. S13-S15). The singlet peaks in ^{1}H NMR spectrum of free probe at 12.48 ppm and 9.32 ppm correspond to imidazole and imine protons are missing in the ^{1}H NMR spectrum of COUBM-PHOS, while in ^{13}C NMR spectrum of COUBM-PHOS a singlet peak at 192 ppm corresponds to the carbonyl carbon is observed.

3.5. DFT studies

The full geometry optimizations of the probe (COUBM) and the adduct, COUBM-PHOS were carried out by DFT/B3LYP/6−31+G(d) method. The probe has planer geometry which remains unchanged after reaction with phosgene. Optimized structures are given in Fig. 9 and the contour plots of some selected molecular orbitals of COUBM and COUBM-PHOS are presented in Figs. S16-S17. The HOMO-LUMO energy gap for COUBM is calculated to be 3.32 eV, while it is decreased for COUBM-PHOS and is found to be 3.08 eV.

4. Conclusion

Herein, we have designed and fabricated a new fluorogenic sensor by cost-effective synthetic route for fast and selective detection of phosgene in both the solution and gas phase. The selectivity test of the probe towards phosgene is performed in presence of some nerve agent stimulants and different acyl chlorides. Most importantly, the present probe is very sensitive towards phosgene and the reaction is completed within three minutes. The sensing of phosgene is interpreted based on the inhibition of PET process in the free probe. Moreover, COUBM is very efficient to detect phosgene in gas phase by test strip method. Density function theory (DFT) calculations are performed to illustrate the electronic structure and sensing mechanism of the probe.



Scheme 2. The plausible sensing mechanism of the probe COUBM with phosgene.

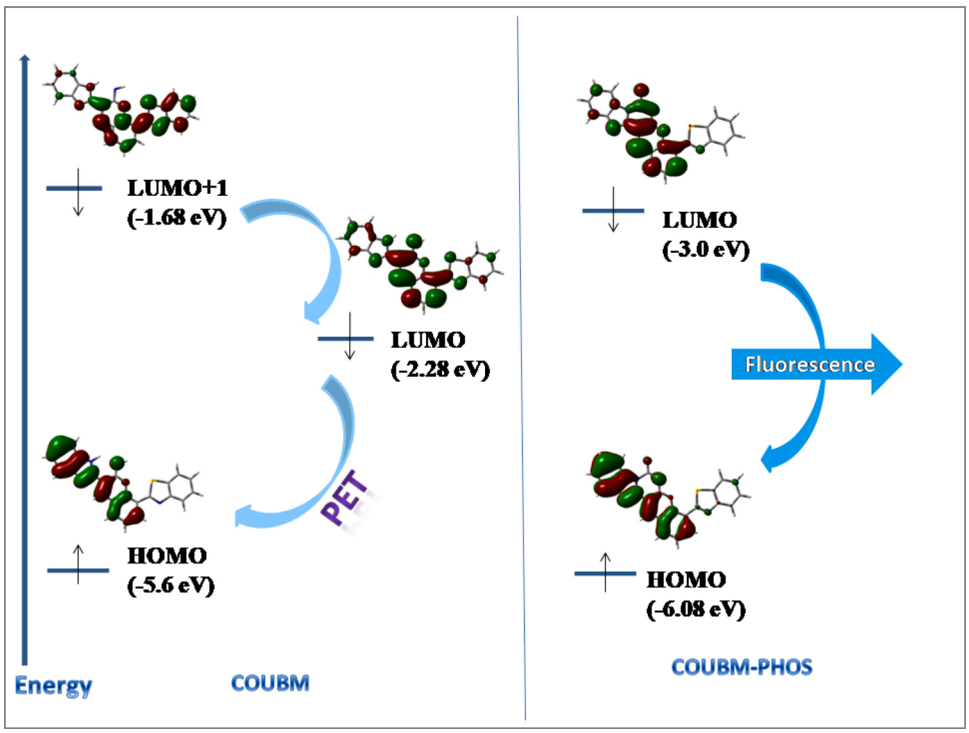


Fig. 7. Molecular orbitals of COUBM and COUBM-PHOS involved in the emission process.

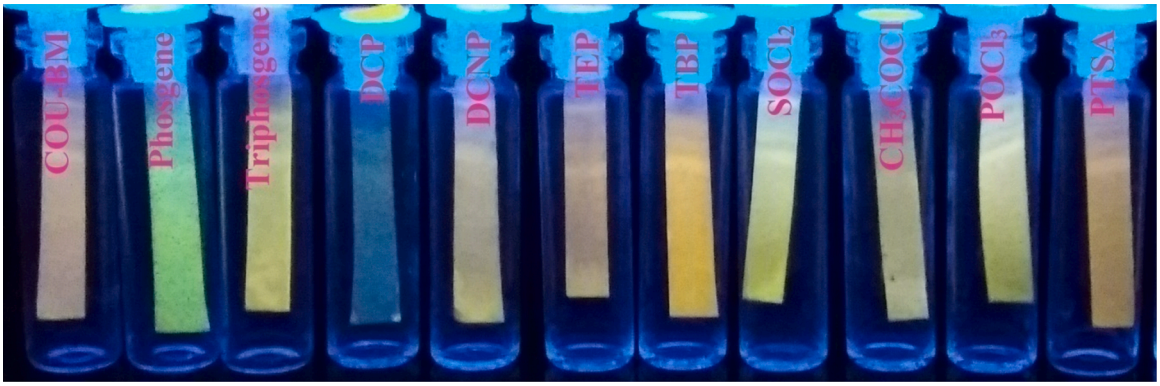


Fig. 8. Visible color change of the probe COUBM upon exposure to the vapors of different analytes under handheld UV light.

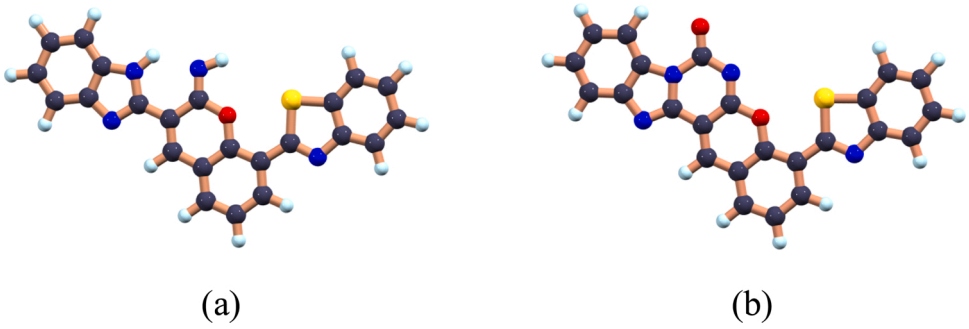


Fig. 9. Optimized structures of (a) COUBM and (b) COUBM-PHOS adduct calculated by DFT/B3LYP/6-31+G(d) method.

CRediT authorship contribution statement

Lakshman Patra: Investigation, Methodology, Writing - original draft. **Krishnendu Aich:** Investigation. **Saswati Gharami:** Investigation. **Tapan Kumar Mondal:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.snb.2020.128837.

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