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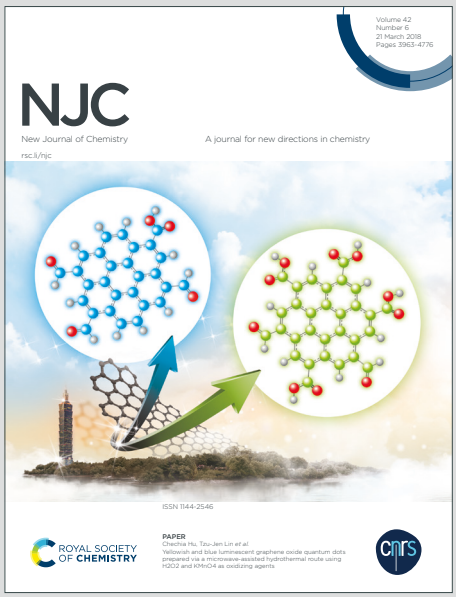

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ARTICLE

A coumarin based fluorescent chemodosimeter for phosgene gas detection instantaneously in solution and gas phase

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A coumarin based compound, 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (DCCO), has been developed as a visual fluorescent chemodosimeter for selective detection of highly toxic phosgene gas. DCCO exhibits absorption bands at 330 nm and 425 nm. In the presence of phosgene, the absorbance at 330 nm increases and the peak at 425 nm is shifted to 420 nm with decreasing absorbance accompanying a color change from yellow to colorless. Fluorescence intensity of the probe at 483 nm enhances in the presence of phosgene (λ_{ex} = 425 nm) but nerve agents and other acid chlorides including trisphosgene could not induce any significant enhancement of the fluorescence. DCCO on interaction with phosgene is converted to the corresponding nitrile derivative, 7-(diethylamino)-2-oxo-2H-chromene-3-carbonitrile (DCC). Quantum yield has been increased by 13 fold on conversion from DCCO to DCC. Fluorescence enhancement has been explained by ICT mechanism which has been supported by theoretical calculations. It exhibits rapid response for naked eye detection of phosgene. DCCO has been used for the detection of phosgene in solution and gas phase.

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Introduction

Development of chemosensors for small neutral molecules becomes important as the compounds have potential to be used in the terrorist activities. Nerve agents such as sarin, soman, cyclosarin, tabun, etc. along with phosgene are known as chemical warfare agents (CWAs).[1] These agents have intended uses as chemical weapons. Generally, nerve agents covalently bind with acetylcholinesterase to inhibit activity of the neurotransmitter acetylcholine, causing severe effects on humans and animals.[2] On the other hand, phosgene ($COCl_2$) is a colorless toxic gas due to the presence of its highly active acyl chloride group. It had been used in a chemical weapon in World War I.[3] It is responsible for 80% deaths caused by the use of chemical weapons. Exposure of phosgene can damage the respiratory track and lungs of humans, including noncardiogenic pulmonary edema and even lead to death.[4] It has been reported that lungs injury takes place severely within 2 min under exposure 20 ppm phosgene and 90 ppm exposure becomes fatal.[5] It is extensively used as an intermediate in the production of several important substances such as insecticides, plastics, pharmaceuticals, pesticides, etc. Use of nerve agents has been forbidden whereas phosgene is readily accessible.[6] Thereby, phosgene has become a serious threat to human safety and environment because of its possible use in terrorist activity and accidental exposure from industries. Thus, there is demand for the development of effective chemosensor for detection of this poisonous gas.

Presence of phosgene has been indicated by some conventional methods such as chromatographic techniques coupled with mass spectrometry,[7] electrical methods,[8] colorimetric procedures,[9] and fluorogenic methods.[10] Among all mentioned techniques, the fluorescence method is considered to be the best because of its operational simplicity, high selectivity, good sensitivity, rapidity, low cost, non-destructive methodology and direct visual perception. In addition to these, other techniques suffer several limitations e.g. on-site detection, portability issue, time consuming or complex analysis, etc.

Phosgene undergoes very fast acylation reactions with various nucleophilic moieties such as amino, hydroxyl and sulfhydryl groups.[11] There are various types of probe for phosgene where phosgene undergoes acylation reaction with amine-containing coumarin,[12] naphthalimide,[13] BODIPY,[14] rhodamine,[15] pyronin,[16] or benzothiadiazole.[17] Most of the above mentioned probes are developed on photoinduced electron transfer (PET)[16] or intramolecular charge transfer (ICT)[16,17] mechanism. Besides these, there are few chemodosimeters reported based on fluorescence resonance energy transfer (FRET) via phosgene-induced covalent cross-linking[10a] the ring opening of rhodamine derivatives,[10e,10h,13c] the cyclization of a flexible chromophore precursor,[18] aggregation induced emission (AIE)[19] and excited-state intramolecular proton transfer (ESIPT).[20] But most of the sensors show poor selectivity. Some of these sensors have been impeded by formaldehyde and nitric oxide.[21] Few

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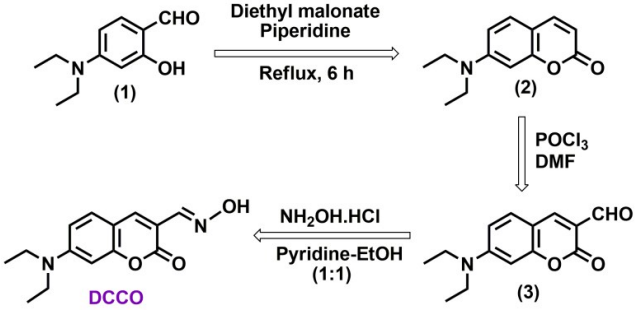
phosgene sensors could not discriminate between triphosgene and phosgene because of amine catalyzed decomposition of triphosgene to phosgene.[22] So, it is important to design probes that can easily discriminate between phosgene and triphosgene. Now-a-days, with increasing demand of phosgene as important chemical in organic synthesis and in terrorist attack, it is necessary to design and develop a very rapid, highly selective probe for the detection of phosgene.



Scheme 1 Synthesis of the chemodosimeter (DCCO) for phosgene

In this context, we report here the synthesis, characterization and phosgene sensing properties of a coumarin based compound, 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (DCCO) (Scheme 1). In this work we have chosen coumarin as fluorophore unit because the coumarin derivatives were widely used in the preparation of medicine, perfumes, biology and fluorescent dye.[23] Carbon atom of phosgene is highly electron deficient as two chlorine atoms are attached with it and this leads to easy nucleophilic substitution at carbon center. DCCO has oxygen atom (at oxime unit) which undergoes reaction with $COCl_2$. Some theoretical calculations have been carried out to support formation of DCCO and its product with phosgene.

Experimental

General Methods

All Solvents and Chemicals used in this work were purchased from commercial sources and were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded by using Brucker 300 MHz instruments. $CDCl_3$ was used as solvent for NMR spectra. UV-vis titration experiments were done by using Perkin Elmer Lambda 750 spectrophotometer. Fluorescence experiments were performed on Perkin Elmer LS 55 with a fluorescence cell of 10 mm path. Silica gel (100–200 mesh) was used to perform Column chromatography. Fluorescence lifetime experiment was performed by using TCSPC (Time-correlated single photon counting) set-up. All the measurement experiments were carried out under ambient conditions.

DFT-D3 calculation was performed using Turbomole software package (V. 7.3), OS: MACOS.[24] The structure of the DCCO and its phosgene interacted product was prepared from the reported crystal structure.[25] def2-SVP was considered for every atoms at the level of B3-LYP using COSMO for acetonitrile.[26]

Here, the quantum yield ϕ was measured by using the following equation

$$\phi_x = \phi_s (F_x / F_s)(A_s / A_x)(n_x^2 / n_s^2)$$

where, X and S indicate the unknown and standard solution respectively, ϕ = quantum yield, F = area under the emission curve, A = absorbance at the excitation wave length, n = index of refraction of the solvent. Here ϕ measurements were performed using anthracene in ethanol as standard (ϕ = 0.27).[27]

Synthesis of Probe:

Synthesis of 7-diethylamino coumarin (2):

30.0 mL of ethanol was added to a mixture of 4-diethylaminosalicylaldehyde (1.93 g, 10 mmol), diethylmalonate (3.2 g, 20 mmol), piperidine (1.0 mL). It was refluxed for 6 h. The mixture was cooled to room temperature. Solvent was evaporated under reduced pressure. Glacial acetic acid (20.0 mL) and concentrated HCl (20.0 mL) were added to the reaction mixture for hydrolyze and the mixture was stirred for 6 h. The solution was cooled to room temperature and poured onto 100 mL of ice water. NaOH solution (40%) was added dropwise to adjust pH (to approx. 5) and a pale yellow precipitate was formed immediately. After stirring for 30 min, the mixture was filtered, washed with water, dried, and recrystallized from toluene to afford 7-diethylaminocoumarin (1.65 g, 8.0 mmol) in 76% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.54 (d, 1H, 9.3 Hz), 7.27 (t, 2H, 5.4 Hz), 6.57 (q, 1H, 6.3 Hz), 6.50 (d, 1H, 2.4 Hz), 6.04 (d, 1H, 9.3 Hz), 3.42 (q, 4H, 7.2 Hz), 1.26 (m, 6H).

Synthesis of 7-diethylamino coumarin-3-aldehyde (3):

2.0 mL of dry DMF was added drop by drop to $POCl_3$ at 0 ºC under N_2 atmosphere and stirred for 1 h to obtain a red solution. This solution was combined with 7-diethylaminocoumarin (1.52 g, 7.0 mmol, dissolved in 10 mL DMF). The mixture was then stirred at 60 °C for overnight and then poured into 100 mL of ice water. NaOH solution (20%) was added until precipitation occurred. Then the precipitate was filtered, washed with water, dried and recrystallized in absolute ethanol to get 7-diethylaminocoumarin-3-aldehyde (1.23 g, 5.0 mmol) in 71% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 10.14 (1H, S), 8.27 (1H, S), 7.42 (1H, d, 9 Hz), 6.65 (1H, q, 6.6 Hz), 6.50 (1H, d, 2.4 Hz), 3.49 (4H, q, 7.2 Hz), 1.28 (6H, q, 7.2 Hz).

Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (DCCO):

Compound **3** (0.5 g, 2.03 mmol) was dissolved in dry ethanol (15 mL). Triethylamine (0.36 mL, 2.8 mmol) and hydroxylamine hydrochloride (0.12 g, 1.72 mmol) were added to it. The resulting reaction mixture was heated to reflux for overnight and a yellow precipitate was formed. The precipitate was washed properly with water. The crude product was recrystallized in $CHCl_3$–CH_3OH (1: 1) to yield a yellow solid; yield: 73% (0.19 g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 10.69 (1H, s), 9.07 (1H, s), 8.17 (1H, s), 8.04 (1H, s), 7.42 (1H, d, 1.2 Hz), 7.28 (1H, d, 8.7 Hz), 3.41 (4H, q, 6.9 Hz), 1.21 (6H, q, 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): 160.63, 155.58, 151.02, 150.66,

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137.94, 130.17, 129.29, 109.67, 108.91, 107.96, 44.40, 11.98; HRMS (ESI TOF): (*m/z*, %): 261.1300 [(DCCO + H^+), 100 %].

Synthesis of 7-(diethylamino)-2-oxo-2H-chromene-3-carbonitrile (DCC):

DCCO (0.050 g, 0.19 mmol) was dissolved in dry acetonitrile (4.0 mL). Triethylamine (0.1 mL, 0.7 mmol) and triphosgene (0.070 g, 0.23 mmol) was added to it. The reaction mixture was allowed to stir at room temperature for 5 min. The solvent was evaporated to dryness and the residue was purified by silica-gel column chromatography and reddish yellow product was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.98 (1H, s), 6.62 (2H, d, 9 Hz), 6.48 (1H, s), 3.43 (4H, t, 5.4 Hz), 1.23 (6H, d, 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): 160.00, 155.56, 150.09, 128.94, 127.97, 127.19, 124.28, 107.46, 96.02, 95.89, 43.90, 11.43 ; HRMS (ESI TOF): (*m/z*, %): 243.1126 [(DCC + H^+)].

General method of UV-vis and fluorescence titrations by UV-vis and fluorescence:

Stock solution of chemodosimeter (DCCO) was prepared (c = 2 × 10^{-5} ML^{-1}) in acetonitrile: water (1:1, v/v). The solution of the guest ions and amine containing compounds were prepared (2 × 10^{-4} ML^{-1}) in acetonitrile: water (1:1, v/v) immediately before performing the experiment. The solution of probe and other analytes were prepared in doubly distilled deionized water by using appropriate dilution technique. Absorption and fluorescence spectra were recorded by transferring appropriate amount of stock solution to deionized water. After well mixing, the solutions were allowed to stand at room temperature for 1 min. Then, absorption and fluorescence spectra were recorded.

Detection of phosgene using TLC plate sticks:

TLC plate sticks were prepared by immersing TLC plates into the solution of DCCO (2 × 10^{-4} M) in CH_3CN and exposing it to air to evaporate the solvent. The detection of phosgene was carried out by inserting the TLC plate to the solution of phosgene (1 mM) and evaporating solvent to dryness.

Results and discussion

Absorption spectral studies

Phosgene is a volatile and highly toxic compound, while its precursor triphosgene is a nonvolatile, easily controllable and less toxic solid material. In the presence of triethylamine, triphosgene is converted into phosgene.[28] So, we have used triphosgene in the presence of triethylamine instead of phosgene. We have first investigated the absorption spectra of the probe (DCCO) in acetonitrile containing triethylamine (100 μM) immediately after the addition of different amounts of triphosgene (0–50 μM). Initially, DCCO shows two major absorption bands at 330 nm and 425 nm. But when we have gradually added triphosgene to the probe solution the absorbance at 330 nm increases and the peak at 425 nm has slightly shifted to 420 nm with gradually decreasing absorbance. A clear isosbestic point has been noticed at 358 nm (Fig. 1). Thus, a blue shift phenomenon has been observed in this case due to the formation of CN group in the product (DCC). These spectral changes are in accordance with the naked eye observation. The yellow color solution of DCCO becomes colorless as soon as triphosgene and triethylamine are added to the solution which indicates formation of new product (Fig. 1, inset). The ratiometric value (A_{425}/A_{330}) changes from 0.36 to 22.65 (63 fold enhancement) in the presence of 1 equivalent phosgene (Fig. S1).

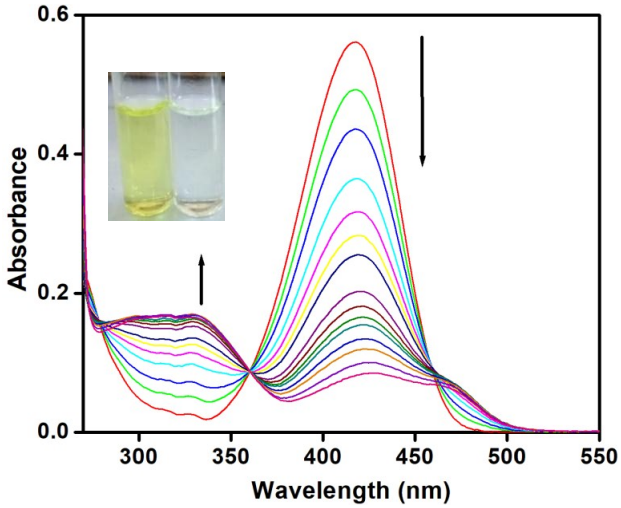

Fig. 1 Absorption titration spectra of DCCO (10 μM) in acetonitrile : water (1:1) with triethylamine (100 μM) immediately after the addition of different amounts of triphosgene (0–50 μM) at 25 °C and the visual color change of DCCO with addition of 1 eqv. of phosgene under UV light (inset).

The response of the probe towards various competing acid chlorides has been studied in acetonitrile in the presence of triethylamine by recording absorption spectra of DCCO with different acid chlorides. A plot of (A_{425}/A_{330}) in the presence of phosgene, diethyl cyanophosphate (DCNP), diethyl chlorophosphate (DCP), trifluoroacetic acid (TFA), HCl, p-toluenesulfonyl chloride (p-TsCl), thionyl chloride ($SOCl_2$), phosphorus oxychloride ($POCl_3$), oxalyl chloride $(COCl)_2$, acetyl chloride (CH_3COCl) is shown in Fig. S2. As shown in the figure, it is clear that the probe displays a high selectivity towards phosgene among all other acid chlorides. Thus, the probe exhibits high selectivity towards phosgene.

Fluorescence studies

Fluorescence spectra of DCCO (10 μM) have been obtained in acetonitrile containing triethylamine (100 μM) immediately after the addition of different amounts of triphosgene (0–50 μM) at 25 °C (λ_{ex}: 425 nm) (Fig. 2). From the figure it is evident that the probe shows low intensity fluorescence peak at 488 nm in absence of phosgene with quantum yield (ϕ) of 0.004. Upon gradual addition of phosgene to the probe, the intensity at 483 nm gradually increases. From this spectral behavior, it is clear that chemosensing reaction between the probe and phosgene is very effective. The fluorescence intensity gradually increases with the increase in the concentration of phosgene. Quantum yield has been increased to 0.52. Thus, a 13 fold increment of fluorescence quantum yield has been observed in this case. A change in color of probe has been occurred from blue to green in the presence of $COCl_2$ (Fig. 2, inset).

Sensitivity of the probe has been determined following 3σ method.[29] The determination of detection limit has been carried out based on the formula K × Sb1/S, where Sb1 is the standard

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deviation of blank measurements and S is the slope of the calibration curve (See Supplementary Information). A plot of the fluorescence intensity of DCCO vs. concentration of triphosgene in the presence of triethylamine ranging from 0 to 2.0 μM shows linear fit (R^2 = 0.997) (Fig. S3). From this linear fit data we have calculated the detection limit of the probe for phosgene to be 0.12 μM.

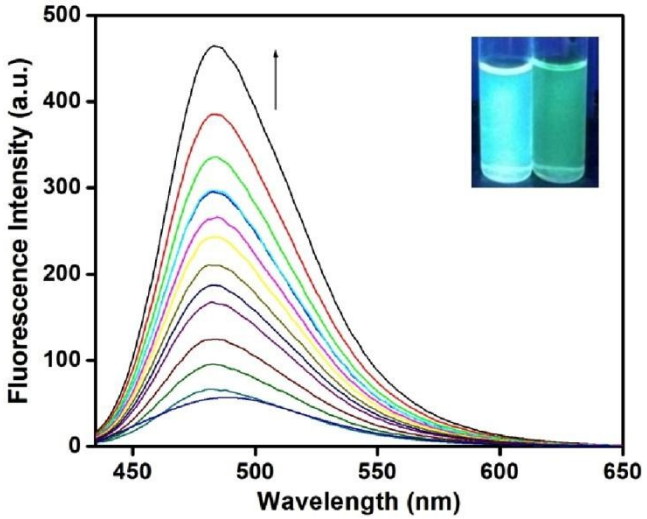

Fig. 2 Fluorescence spectra of DCCO (10 μM) in MeCN containing triethylamine (100 μM) after the addition of different amounts of triphosgene (0–50 μM) at 25 °C; (λ_{ex}: 425 nm). Inset: fluorescence color change of DCCO in the presence of phosgene.

The time dependent of fluorescence intensity of DCCO has been measured in the presence of phosgene (Fig. S4A). From the spectra it is evident that the fluorescence intensity of tested solution increases rapidly and reaches the saturated level within 1 min, with a pseudo first order rate constant of 16 × 10^{-2} s^{-1} (Fig. S5). This result strongly supports high reactivity of the probe towards phosgene. Moreover, the probe and probe-phosgene product (DCC) in acetonitrile show very good photostability under irradiation at a wavelength 485 nm for 1 h (Fig. S4B).

Selectivity and specificity test is a very important parameter for a smart probe for the detection of an analyte. Next, we have studied selectivity of DCCO towards phosgene. The probe has been treated with various competing acid chloride such as phosgene, diethyl cyanophosphate (DCNP), diethyl chlorophosphate (DCP), trifluoroacetic acid (TFA), HCl, p-toluenesulfonyl chloride (p-TsCl), thionyl chloride ($SOCl_2$), phosphorus oxychloride ($POCl_3$), oxalyl chloride $(COCl)_2$, acetyl chloride (CH_3COCl) and fluorescence intensity has been measured (Fig. 3). From the figure, it is clear that only phosgene shows remarkable fluorescence enhancement. From Fig. 3A it is evident that only triphosgene cannot induce any increment in fluorescence intensity of the probe while from Figure 3B it can be observed that fluorescence intensity of DCCO and phosgene does not change in the presence of triphosgene. It indicates clearly that DCCO is a highly selective chemodosimeter for phosgene and triphosgene cannot interfere the detection procedure of phosgene. These results are in accordance with that obtained in absorption spectral studies. It is important to investigate the sensing ability of the probe towards formaldehyde and nitric oxide as some previously reported chemosensors for phosgene[21] experienced interference from these species (Fig. S6). We can see that formaldehyde and nitric oxide do not have any significant effect on fluorescence intensity of DCCO.

Excited state behaviors of DCCO and DCC are examined by nano-second time resolved fluorescence technique (Fig. S7). The fluorescence decay curves of the compounds are obtained by using the mono exponential functions. Life times (τ) of DCCO and DOCC are found to be 0.667 ns and 3.22 ns, respectively. Using the equations $\tau^{-1} = k_r + k_{nr}$ and $k_r = \Phi_f / \tau$ (Supplementary Information)[30] we have calculated the radiative rate constant (k_r) and total non radiative rate constant (k_{nr}) (Table S1). It has been observed that radiative rate constant increases by 27 times whereas non-radiative rate constant value decreases by 10 fold on the conversion of DCCO to DCC. This event leads to the significant enhancement of fluorescence.

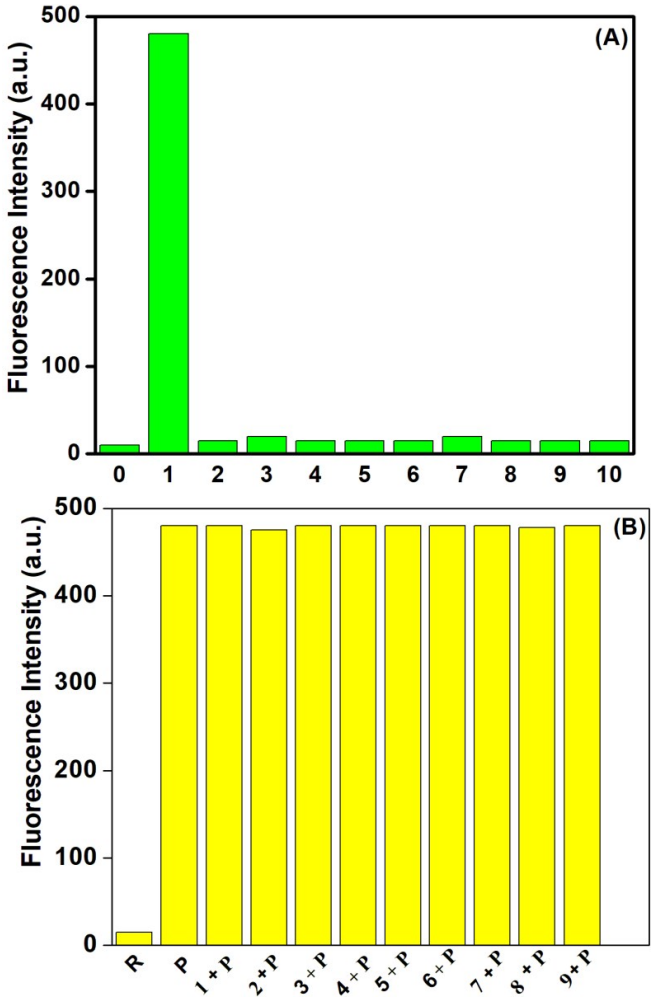

Fig. 3 (A) Fluorescence increment of DCCO in the presence of (1) phosgene (triphosgene/triethylamine), (2) DCNP (3) DCP (4) triphosgene (5) TFA (6) p-TsCl (7) $SOCl_2$ (8) $POCl_3$ (9) $(COCl)_2$ and (10) CH_3COCl. (b) Fluorescence intensity of DCCO (2.0 × 10^{-5} M) toward phosgene (1.0 equiv) containing 10 equiv of (1) DCNP (2) DCP (3) triphosgene (4) TFA (5) p-TsCl (6) $SOCl_2$ (7) $POCl_3$ (8) $(COCl)_2$ and (9) CH_3COCl. Here, R is DCCO and P denotes phosgene.

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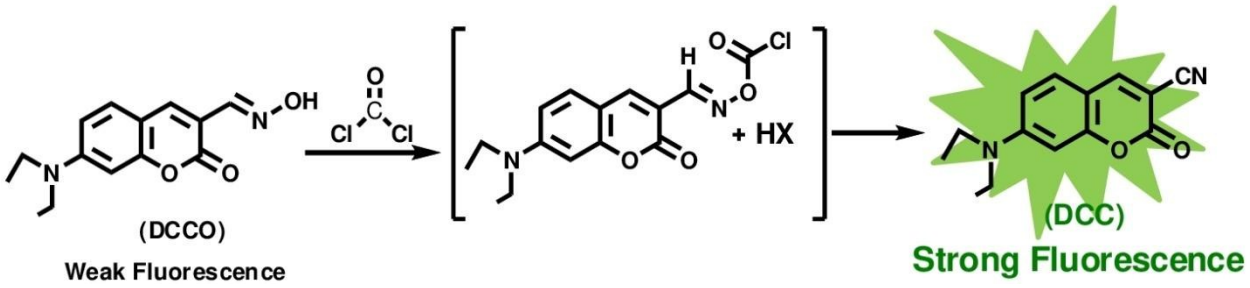

Scheme 2. Fluorescence enhancement on conversion of DCCO to DCC.

Sensing mechanism:

Strong fluorescence has been observed when DCCO reacts with phosgene to yield DCC (Scheme 2). We propose that the sensing of phosgene of DCCO starts with nucleophilic substitution by oxime hydroxyl group with the removal of Cl^- from phosgene and formation of oxime-N-O-oxychloride intermediate (Scheme 2). Final product has been obtained after the elimination of C (=O)(Cl)(OH) group and cyanide group has been generated in place of oxime hydroxyl group. In order to support the sensing mechanism, ^{1}H NMR (Fig. S8-S11), ^{13}C NMR (Fig. S12, S13) and mass spectra (Fig. S14, S15) have been recorded. NMR and mass spectra of DCCO are in accordance with its formation. ^{1}H NMR spectrum of DCCO shows the hydroxyl proton signal at 10.69 ppm and the formyl proton signal at 9.07 ppm. These peaks disappear when triphosgene-triethylamine have been added to it indicating the conversion of the probe (DCCO) to probe-phosgene product (DCC).

ESI-mass spectra have also been recorded to verify the formation of DCCO and DCC. Mass spectrum of DCCO exhibits an *m/z* peak at 261.1300 which may be attributed to the presence of (Probe + H^+) species. Mass spectrum of phosegene mediated product through the reaction of an equimolar mixture of probe and triphosgene has been recorded. The mixture shows a major peak at *m/z* 243.1126 [(DCC + H^+)] which corroborates the formation of DCC.

Depending on functional moieties such as amino, hydroxyl, sulfhydryl groups, etc. on the probe, phosgene produces different end products after the reaction with the probes. When ethylenediamine derivatives are allowed to react with $COCl_2$, cyclic products such as imidazole, benzimidazole, oxazole derivatives, etc. have been obtained with usually an extended delocalization feature leading to high fluorescence increase.[10h,10j,12b,14a,32] Carboxylate and hydroxyl groups at suitable disposition can react with phosgene to form coumarin derivative with the generation of strong fluorescence.[18] With oxime functionality, the probe reacts with phosgene to give an amide derivative as the end product.[13a] There is another report with that hydroxylamine functionality, in where phosgene converts it into nitrile group.[28] As DCCO has similar oxime functional group, it is reasonable to expect that the end product could have been corresponding nitrile compound and we get the result as expected. Very rare examples are known for phosgene sensors where end product is not formed because of cyclisation. Our present study is one of the chemosensors for phosgene in this category.

DFT-D3 analysis of DCCO and its phosgene interacted product (DCC):

Geometry optimized structures of DCCO and its phosgene interacted product (DCC) have been obtained from density functional theory (DFT) calculations (See Supplementary Information). Considering the dispersion correction, DFT-D3 has been employed during the calculation. Vibrational stretching frequency of both DCCO and DCC has also been measured which shows no negative vibration (See Supplementary Information). Distribution of HOMO-LUMO oribitals for both of the compounds are shown in Fig. 4.

ΔHOMO-LUMO for the DCCO and DCC is 3.438 eV and 3.448 eV, respectively, which is almost similar. However, the NBO popluation analysis of DCCO and DCC reveals that imine carbon and nitrogen (C13-N3 in DCCO) has 0.03972 and -0.17827 charge which has increased drastically to 0.34387 and -0.40999 (C31-N32 in DCC) after interaction with phosgene due to changing the hybridisation (See Supplementary Information). Significant increment of charge distribution has resulted in enhanced charge transfer within the molecule, in turn helps in fluorescence enhancement.

Detection of Phosgene Gas with the Test Paper:

To test practical applicability of the probe towards phosgene, dip stick method has been followed. For this purpose TLC plates are dipped in the solution of DCCO. The test paper stripes have been placed into centrifuge tube with 20 ppm concentration of phosgene. Upon exposure of phosgene for 1 min, the color of test paper stripes changes from yellow to colorless under normal light and from blue to green under UV light (Fig. 5). Thus, the presence of phosgene can be detected by test paper strips implying that the probe detects the phosgene at very low concentration.

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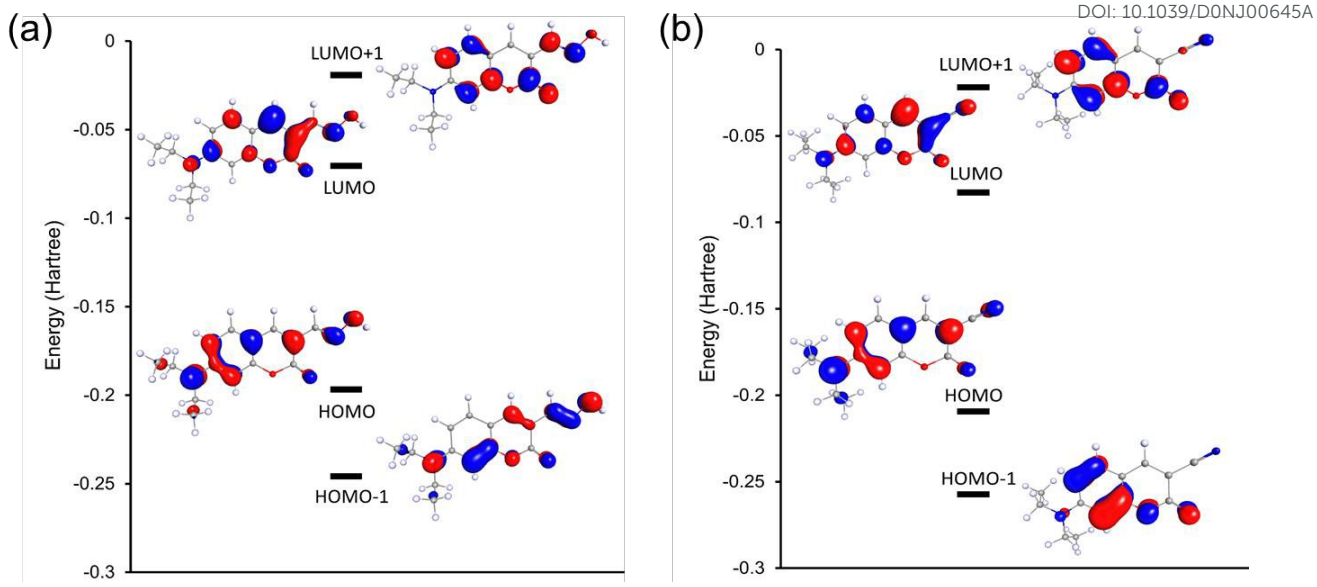

Fig. 4. HOMO-1, HOMO, LUMO and LUMO+1 charge distribution for (a) DCCO and (b) DCC.

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Detection of phosgene in the gas phase:

We have been interested to study this sensing in gas phase. For this purpose probe (DCCO) coated TLC plate has been exposed in the vapor of phosgene. From the Figure 9 we can see that probe coated TLC plate turns to colorless from yellow after exposure with phosgene vapor within 10 s. From this experiment it is clear that DCCO is a very good probe towards phosgene and it also detects phosgene in solution as well as in gas phase. From Matheson gas data book, it is evident that 20 ppm phosgene can cause lung diseases within 2 min, 90 ppm is rapidly fatal for exposures of 30 min or less.[31] TLC plates coated with the probe can detect phosgene only within 1 min. From this result it is clear that DCCO is very much effective and fast to detect phosgene below concentration levels related to a health risk.

Comparison of recognition mechanisms for detecting phosgene:

We compare some important parameters of previously reported phosgene probe with our probe in supporting information. Our probe shows some advantages over other reported probe while few parameters of other probes are better in comparison to our work. Excitation and emission wavelength in visible region is always better for a probe. Our probe shows excitation and emission wavelength in visible region whereas most of the reported probes are not. This is of course a advantage property of our probe. Most of the probes including our probe detect phosgene in few seconds, while few probes detect phosgene slowly (within few mins). Some probes have LOD values in the range of nM and ppb. Our probe has LOD value of µM range. Our probe shows very good selectivity towards various acid chlorides and important analytes.

Conclusions

We have synthesized a new coumarin based chemodosimeter, 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime (DCCO), which can selectively detect phosgene over various nerve gas, triphosgene and acid chlorides. The sensing reaction between DCCO and phosgene is very fast and sensitive, and reaction almost is completed within 1 min. This is the first sensor which can detect phosgene in gas phase. The detection limit of the probe for determination of phosgene is quite low as compared to the safety level of phosgene recommended for humans. DCCO also shows very good performance in dip stick method. Thus, it is an effective practically portable probe not only for gas phase but also solid phase detection of phosgene.

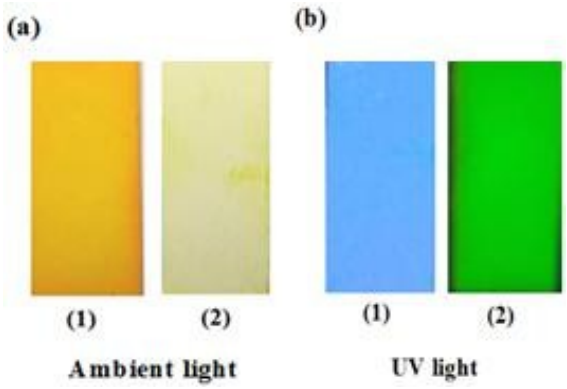

Fig. 5 Color changes on the TLC plates under (i) ambient and (ii) UV light in the presence of (a) DCCO (b) DCCO with phosgene.

Conflicts of interest

There are no conflicts to declare.

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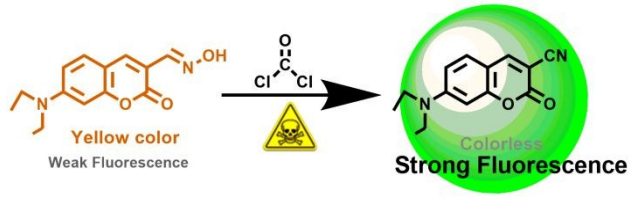

A coumarin based compound, 7-(diethylamino)-2-oxo-2H-chromene-3-carbaldehyde oxime, acts as a selective fluorescent chemodosimeter for phosgene gas in solution and as well as in gas phase.

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