

A Rapid, Highly Sensitive and Selective Phosgene Sensor Based on 5,6-Pinenepyridine

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Abstract: The toxicity of phosgene (COCl₂) combined with its extensive use as a reactant and building block in the chemical industry make its fast and accurate detection a prerequisite. We have developed a carboxylic derivative of 5,6-pinenepyridine which is able to act as colorimetric and fluorimetric sensor for phosgene in air and solution. For the first time, the formation of a pyrido-[2,1-*a*]isoindolone was used for this

purpose. In solution, the sensing reaction is extremely fast (under 5 s), selective and highly sensitive, with a limit of detection (LOD) of 9.7 nM/0.8 ppb. When fixed on a solid support, the sensor is able to detect the presence of gaseous phosgene down to concentrations of 0.1 ppm, one of the lowest values reported to date.

Introduction

Phosgene is a highly toxic and reactive gas that was broadly used in World War I as a chemical weapon. Its toxicity is due to the disruption of the air-blood barrier in the pulmonary alveoli, which leads to pulmonary oedema and eventually death.^[1–3] Due to these serious health effects, the time average occupational exposure limit (TWA) over 10 h is only 0.1 ppm, while already a 30 minute exposure to 0.6 ppm phosgene leads to severe injury and irreversible health effects (AELG-2 30 min).^[4,5] The odour threshold is between 0.5 and 1.5 ppm, but at these concentrations irreversible health damages can already occur.^[6] Regardless of its toxicity, phosgene is a useful building block and reagent for the production of dyes, polymers, pesticides and pharmaceuticals.^[7] Hence, its fast and precise detection is of high importance not only for the protection of the operators involved in the industrial processes, but also for the general safety in case of terrorist attacks or accidents. The detection of

phosgene can be done by chromatography-mass spectrometry techniques^[8,9] or electrochemical assays.^[10,11] However, for the rapid, facile, sensitive and selective detection of phosgene, colorimetric and fluorescent sensors are attractive candidates from a practical standpoint, especially when immobilized on a solid substrate. The main colorimetric and fluorescent sensing reactions for phosgene detection are using 1,2-diamine type compounds in which the acylation of one amino group by phosgene and subsequent intramolecular nucleophilic attack of the second amino group lead to the formation of cyclic urea-derivatives, resulting in an off-on response (Scheme 1).^[12–20] The fluorophores are usually BODIPY,^[20–24] coumarins,^[25,26] 1,8-naphthalimide,^[17,27,28] anthracene carboxyimide,^[29–31] 2-(2'-hydroxyphenyl)benzothiazole (HBT)^[32] or rhodamine.^[12] The response rates and sensitivity of these sensors are very diverse and can be significantly slowed down due to the inactivation of the second amino group once the first one undergoes electro-

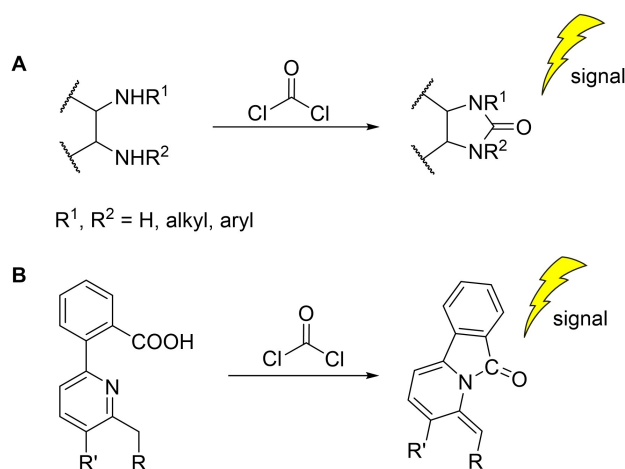
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Scheme 1. A) Typical phosgene sensing reaction for the sensors reported in the literature, based on diamines; B) The new phosgene sensing reaction reported here.

philic attack from the phosgene. These sensors usually show small Stokes shifts^[26] making signal crosstalk more likely, thus leading to possible inaccuracies in the analyte detection.

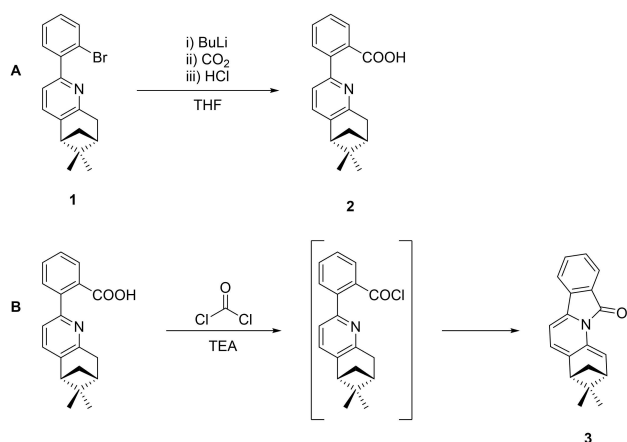
In order to avoid these issues, we have developed a phosgene sensor based on a 5,6-phenyl-pinenepyridine derivative functionalized with a carboxylic acid group. The sensing reaction involves the fast formation of a pyrido-[2,1-a]isoindolone and an off-on colorimetric and fluorescent response, both in solution and in solid state.

Results and Discussion

Synthesis of the sensor and the sensing reaction

The sensor **2** was easily synthesized as previously reported by our group,^[33] starting from the brominated derivative **1**,^[34] which underwent lithiation and carboxylation with gaseous CO₂, as shown in Scheme 2. The sensing reaction involves the activation of the carboxylic acid by phosgene in the presence of triethylamine (TEA). We hypothesize that the reaction involves the formation of an acyl chloride intermediate (not isolated), which undergoes a fast nucleophilic attack from the pyridinic N, followed by deprotonation of the pinene unit, similarly to the mechanism elucidated in our recent work.^[33]

The photophysical properties of the sensor **2** (Figure S1) and its corresponding isoindolone-type product **3** make this sensing reaction an efficient and promising candidate for the detection of phosgene in solution and in gas state. The absorption of **2** shows a $\lambda_{\text{max}} = 294$ nm, with no emission band when excited at 474 nm. In contrast, compound **3** absorbs in the visible region, with a broad absorption band at $\lambda_{\text{abs}} = 474$ nm. The excitation of this band leads to an emission band centred at around 590 nm. The large Stokes shift (superior to 100 nm), efficiently eliminates the signal crosstalk and allows for a high detection accuracy.



Scheme 2. A) Sensor synthesis and B) the phosgene sensing reaction.

Spectral response of the sensor towards phosgene

The response of the sensor **2** to phosgene was tested by UV-Vis and emission spectroscopy. In order to avoid the handling of gaseous phosgene, 1 equivalent (equiv.) triphosgene was used for the generation of 3 equiv. of phosgene in situ.^[35] Assays were performed by titrating at 20 °C a solution of **2** containing TEA (2.2 equiv.) with aliquots of 0.025 equiv. of triphosgene (forming 0.075 equiv. phosgene in situ). The UV-Vis and emission titrations experiments indicated the formation of the pyrido-[2,1-a]isoindolone **3** with the addition of triphosgene. In the UV-Vis spectrum (Figure 1), a broad band with a maximum at 474 nm starts to appear with addition of various increments of phosgene, producing an orange colorimetric response. Moreover, an off-on fluorescence response is observed when phosgene is present, leading to a broad emission band with a maximum at 590 nm. A linear correlation between the emission intensity and the concentration of phosgene was observed (Figure S2). This allowed for the determination of a limit of detection LOD of 9.7 nM, by using the formula $3\sigma/k$,^[27] where σ is the standard deviation of a series of blank measurements ($n = 12$) and k is the slope of the calibration curve. This value is

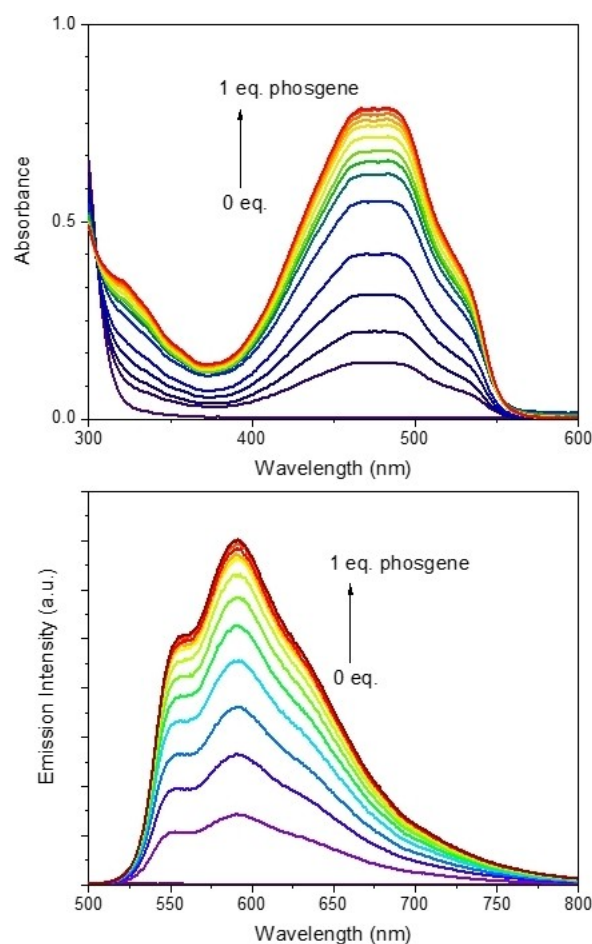


Figure 1. UV-Vis (top) and emission ($\lambda_{\text{ex}} = 474$ nm, bottom) spectra of 0.056 mM sensor and TEA (2.2 equiv.) solutions in THF, in the presence of various amounts of phosgene (0.0–1.0 equiv.).

one of the lowest reported to date. The typical LODs found in the literature are between 1–50 nM for sensors based on fluorophores such as BODIPY^[15] or 1,8-naphthalimides.^[17,19,36] Moreover, the response time was tested for a 1 mM sensor solution containing 2.2 equiv. of TEA, to which 0.33 equiv. triphosgene were added, generating 1 equiv. phosgene in situ. After the addition, an immediate change in colour and fluorescence is observed (see videos in the Supporting Information), which stabilizes in approximately 5 s. The present sensing reaction is remarkably faster than the reported ones based on sensors like o-diamines of BODIPY type (15 s)^[15] or those based on naphthalimides (10–20 minutes).^[19,36]

Selectivity of the sensor

The selectivity of the sensor in solution was investigated by UV-Vis and emission spectroscopy in the presence of 50 equiv. of various chlorinated analytes: diethyl chlorophosphite (DCP), CH₃COCl, tosyl chloride (TsCl), SOCl₂, SO₂Cl₂, POCl₃, (COCl)₂ and HCl versus 5 equiv. triphosgene/TEA. Only phosgene produces a colorimetric response (Figure 2a) leading to the appearance of a

band with a λ_{max} of 474 nm, characteristic for **3**, while in the emission spectrum, no significant changes in the spectrum of the sensor were observed in the testing conditions (Figure 2a). Only in the presence of phosgene a broad emission band centred at 590 nm is observed (Figure 2b). These results indicate a high-selectivity of the sensor towards phosgene. Very important in view of applications, the sensor is showing a strong visual off-on response, clearly visible with the naked eye, either under visible or UV light (366 nm), as seen in Figure 2(c and d).

The sensing mechanism

To confirm the sensing reaction in the presence of phosgene, ¹H NMR titrations were performed on a sensor **2** solution in the presence of 2.2 equiv. TEA. As it can be seen in Figure 3, the characteristic signals of the sensor **2** start to disappear, while the typical proton signals of the isoindolone derivative **3** (5.95 and 6.31 ppm) appear progressively as more phosgene is present. The equivalence point is reached at 1 equiv. phosgene. At this point a spectrum corresponding to the pure compound **3** is obtained (Figure S3). It indicates a 1:1 reaction between the sensor **2** and phosgene and supports our hypothesis of an acyl chloride intermediate.

Detection of phosgene in the gas phase

In order to test the possible use of our sensor for the detection of the phosgene in the gas phase the sensor was immobilized on paper strips using TEA and polyethylene oxide, using a simple procedure, similarly to other literature reports.^[37] After exposing the paper strips to various phosgene concentrations in closed vials for 2 minutes, a visual response (colourless in the absence of phosgene, orange when phosgene is present) was clearly observed with the naked eye as well as under UV radiation (366 nm). The color change is visually detected for phosgene concentrations as low as 0.1 ppm (Figure 4). The strips were also analysed by solid state emission spectroscopy and the characteristic 590 nm emission band was evidenced as well (Figure S4). The phosgene concentrations detected by the strips are much lower than the median lethal dose LC₅₀ (500 ppm) or even the low lethal concentration LC_{LO} (3 ppm).^[38] Our sensor is thus suitable for the fabrication of mobile devices like detection badges to be used in typical working conditions. Moreover, the 0.1 ppm value is precisely the TWA (10 h^[5]) for humans, so the possibility of detecting the phosgene at these concentrations is of high importance.

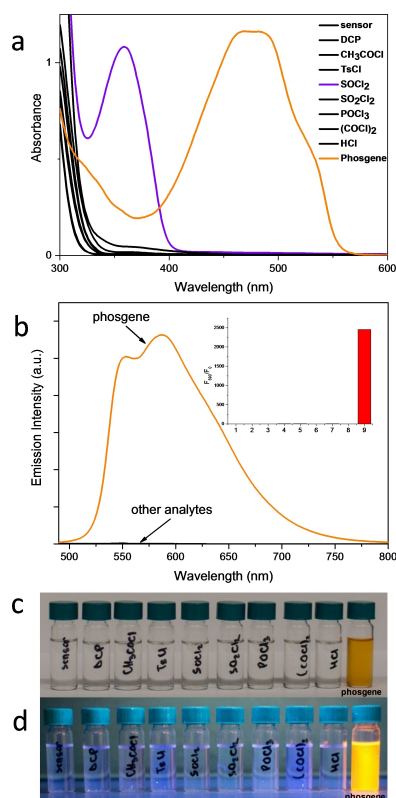


Figure 2. a) UV-Vis and b) fluorescence emission spectra of sensor solutions (0.1 mM in THF) containing TEA (2.2 equiv.), in the presence of triphosgene (5 equiv., 0.5 mM) or various analytes (50 equiv., 5 mM) (DCP, CH₃COCl, TsCl, SOCl₂, SO₂Cl₂, POCl₃, (COCl)₂, HCl). $\lambda_{\text{exc}} = 474$ nm with inset showing the relative emission intensity at 590 nm upon addition of the analytes (1–8) and triphosgene/TEA (9). c) and d). Photos of solutions of sensor (0.1 mM) and TEA (2.2 equiv.) in THF c) under visible light and d) under a 366 nm lamp, in the presence of 50 equiv. (5 mM) of various analytes (in the following order: DCP, CH₃COCl, TsCl, SOCl₂, SO₂Cl₂, POCl₃, (COCl)₂, HCl, phosgene).

Conclusion

In conclusion, we have developed a highly sensitive and selective sensor based on 5,6-pinenepyridine, leading to isoindolone formation. The sensing reaction leads to a colorimetric and fluorescent response, both visible with the naked

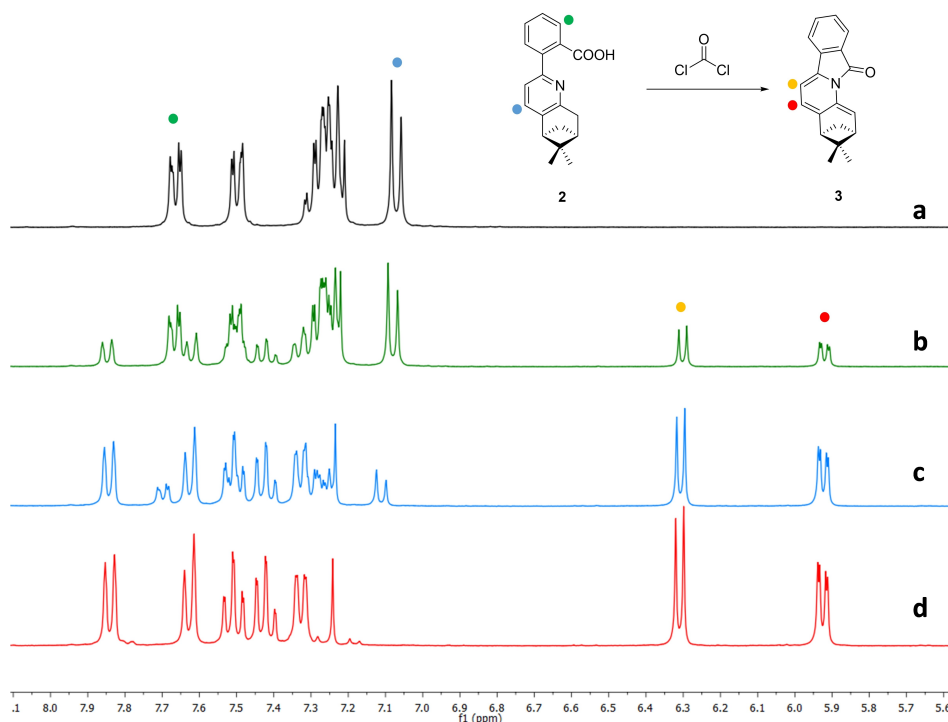


Figure 3. Aromatic region of the ^1H NMR spectra (in CDCl_3) of solutions containing **2** and 2.2 equiv. TEA titrated with various equivalents of phosgene: a) 0 equiv., b) 0.3 equiv., c) 0.75 equiv. and d) 1.0 equiv. phosgene (0.33 equiv. triphosgene produces 1 equiv. phosgene in the presence of TEA).

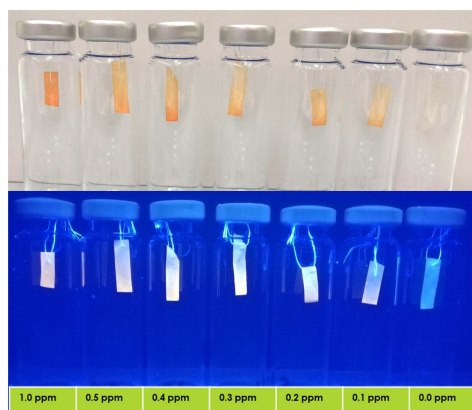


Figure 4. Photographs of test papers exposed for 2 min to various phosgene.

eye. The sensor has a limit of detection of 9.7 nM in solution, lower than most reported sensors to date and displays high selectivity in the presence of various chlorinated analytes. Remarkably, the sensor demonstrates a fast response (about 5 s), almost 3 times faster than the sensing reactions already reported. Furthermore, the sensor was immobilized on a solid substrate and gas sensing of phosgene was possible down to 0.1 ppm gaseous phosgene, which is far below the critical dangerous concentrations. Based on the results obtained, we demonstrated that this new sensing approach for phosgene is very promising and paves the way towards a new class of fluorophores for the specific detection of phosgene.

Experimental Section

General: Reagent grade chemicals were purchased from Sigma Aldrich and Acros Organics and used without further purification. Yields reported are for isolated, spectroscopically pure compounds. UV-Vis spectra were measured at 20 °C on an Evolution 220 spectrometer equipped with a thermostat, using quartz cuvettes with a 10 mm path length. Fluorescence spectra were recorded at 20 °C on a Fluoromax 4 spectrometer from HORIBA equipped with a thermostat, using triangular quartz cuvettes with 10 mm catheti. Solid state emission spectra and quantum yields (integrating sphere) were measured on an Edinburgh Instruments spectrofluorometer. NMR spectra were recorded on a Bruker Advance DPX 300 spectrometer using TMS or the residual solvent proton as internal standard. HRMS spectra were recorded on FTMS 4.7T BioAPEX II and Waters Synapt G2-Si.

Synthetic procedures

Synthesis of 2: Compound **2** was synthesised as previously reported.^[33] A solution of **1** (4.07 g, 12.4 mmol, 1 equiv.) in anhydrous THF (40 mL) was treated under inert atmosphere, at -78°C , with 1 equiv. BuLi (5.7 mM, 2.2 M in hexane). After stirring for 2 h at -78°C , gaseous CO_2 was bubbled into the reaction mixture until discoloration. The reaction mixture was left to warm to RT and was afterwards quenched with H_2O . The solvents were removed under reduced pressure. HCl 1 M was added until pH 7. The mixture was extracted with CH_2Cl_2 (3×40 mL), the combined organic phases were dried over MgSO_4 and afterwards the solvent was removed under reduced pressure. The obtained solid was triturated with pentane to give the desired product as a white solid (2.37 g, 65%). ^1H NMR (300 MHz, CDCl_3) δ = 8.34–8.21 (m, 1H, H3), 7.70–7.39 (m, 5H, H4, H5, H6, H9, H10), 3.23 (d, J = 2.9 Hz, 2H, H15), 2.91 (t, J = 5.6 Hz, 1H, H12), 2.79 (dt, J = 9.8, 5.8 Hz, 1H, H13a), 2.46

(tt, $J=5.9, 2.9$ Hz, 1H, H14), 1.47 (s, 3H, H18), 1.35 (d, $J=9.9$ Hz, 1H, H13b), 0.71 (s, 3H, H19). ^{13}C NMR (75 MHz, CDCl_3) δ 170.2 (C1), 154.3 (C16), 154.1 (C11), 142.8 (C2), 136.4 (C_{arom}), 136.2 (C_{arom}), 136.2 (C_{arom}), 134.3 (C3), 133.3 (C_{arom}), 131.7 (C_{arom}), 130.8 (C_{arom}), 129.3 (C_{arom}), 121.8 (C_{arom}), 46.3 (C17) 46.2 (C12), 39.9 (C14), 34.9 (C15), 32.0 (C13), 26.0 (C18), 21.5 (C19). HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{20}\text{NO}_2^+$ $[\text{M}+\text{H}]^+$, 294.1489, found 294.1478. $[\alpha]_{\text{D}20} = -90^\circ$ ($c=1$ in CH_2Cl_2).

Synthesis of 3: Under inert atmosphere, a solution of **2** in anhydrous THF (30 mg, 0.1 mmol, 1 equiv.) was treated with solid K_2CO_3 (138 mg, 1 mmol, 10 equiv.). The mixture was stirred at RM for 30 minutes. Over this, solid triphosgene (10 mg, 0.033 mmol, 0.33 equiv.) was added over. The mixture turned orange immediately. The reaction mixture was stirred under inert atmosphere for 30 minutes and filtered under inert atmosphere with supplementary washings of the precipitate with anhydrous THF. The solvent was removed under reduced pressure and the orange solid was dried under high vacuum to give 25 mg of compound **3** in 90% yield. ^1H NMR (300 MHz, CDCl_3) δ = 7.93 (dt, $J=7.5, 1.0$ Hz, 1H, H3), 7.69 (dt, $J=7.7, 1.0$ Hz, 1H, H6), 7.58 (td, $J=7.5, 1.2$ Hz, 1H, H5), 7.49 (td, $J=7.4, 1.1$ Hz, 1H, H4), 7.41 (dd, $J=6.9, 1.7$ Hz, 1H, H15), 6.37 (d, $J=6.4$ Hz, 1H, H9), 5.99 (dd, $J=6.5, 1.7$ Hz, 1H, H10), 2.84 (t, $J=5.9$ Hz, 1H, H12), 2.68–2.61 (m, 1H, H13b), 2.58 (dd, $J=6.7, 5.5$ Hz, 1H, H14), 1.69 (d, $J=8.3$ Hz, 1H, H13a), 1.42 (s, 3H, H18), 0.93 (s, 3H, H19). ^{13}C NMR (75 MHz, CDCl_3) δ 165.5 (C1), 145.1 (C16), 134.6 (C11), 132.7 (C8), 131.5 (C5), 131.4 (C2), 128.9 (C4), 128.1 (C7), 123.4 (C3), 119.6 (C6), 116.5 (C15), 113.8 (C10), 104.5 (C9), 50.8 (C12), 44.4 (C17), 42.8 (C14), 35.3 (C13), 26.4 (C18), 22.6 (C19). HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{18}\text{NO}^+$ $[\text{M}+\text{H}]^+$ 276.1383, found 276.1383. $[\alpha]_{\text{D}20} = -359$ ($c=0.276$ in CH_2Cl_2). IR (neat, cm^{-1}): 2924 (C–H), 1661 (C=O), 1429, 1203, 1126, 800, 758, 722, 696. UV-Vis (THF): $I_{\text{max}}(\epsilon)$: 288 (7200 $\text{M}^{-1}\text{cm}^{-1}$), 470 nm (2600 $\text{M}^{-1}\text{cm}^{-1}$).

UV-Vis and fluorescence titrations on the sensor: A 0.56 mM sensor solution in THF was prepared by mixing 16.5 mg sensor (0.056 mmol) with 2.2 equiv. TEA (1.2 mM, 172 μL) in a 100 mL volumetric flask and completing with anhydrous THF. This was further diluted 10 times to reach the final 0.056 mM sensor concentration which was used for the measurements. The exact concentration of the sensor was determined by UV-Vis. Samples of the 0.056 mM sensor solution (1.5 mL) were titrated with the appropriate aliquots from a 15 mM solution of triphosgene in THF, which was prepared by dissolving triphosgene (44.5 mg, 0.15 mmol) in anhydrous THF.

Selectivity tests: Solutions of identical concentration (150 mM) of chlorinated analytes (DCM, CH_2COCl , TsCl , SOCl_2 , SO_2Cl_2 , POCl_3 , $(\text{COCl})_2$, HCl) were prepared in anhydrous THF.

1.5 mL sensor solution (0.1 mM) containing 2.2 equiv. TEA was treated with 50 equiv. chlorinated analytes through the addition of 50 μL analyte solutions (150 mM). For phosgene, 1.5 mL sensor solution (0.1 mM) containing 2.2 equiv. TEA was treated with 1.67 equiv. phosgene (5 equiv. triphosgene) by the additions of 50 μL triphosgene solution (15 mM). The spectra and photographs were recorded 2 minutes after exposure.

^1H NMR titration of the sensor: A 83 mM sensor solution (15 mg, 0.05 mmol) was prepared in 0.6 mL CDCl_3 . Over this, 15 μL anhydrous TEA (2.2 equiv.) were added over. This solution was titrated with the appropriate aliquots of 0.2 M triphosgene solution in CDCl_3 .

Detection in the gas phase: A suspension in CH_2Cl_2 containing 50 mg (0.17 mmol) of **2**, 25 μL (excess) TEA, 10 mg polyethylene oxide ($M_w=10^6$) was made. Filter paper strips were immersed in this mixture and afterwards left to dry in air for 10 h.

Phosgene vapours at various concentrations were prepared starting from a commercially available 15% phosgene solution in toluene. Five concentrations of phosgene solutions were prepared (193 mM, 97 mM, 77 mM, 58 mM, 39 mM and 19 mM) corresponding to gaseous concentrations of 1.0–0.1 ppm. The gaseous concentrations of phosgene in the vials were calculated by using the Antoine equation. The paper strips were exposed to these solutions in closed glass vials for 2 minutes.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: colorimetric sensor · fluorescent probe · gas sensing · paper test strips · phosgene

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