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# A naphthalimide-based probe for phosgene sensing based on the phosgene-induced beckmann rearrangement

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ABSTRACT

A new probe for selective and sensitive phosgene sensing in acetonitrile was developed. The sensing mechanism was based on the mechanism of the phosgene-induced Beckmann rearrangement of the naphthalimide fluorophore. An electron-withdrawing ketoxime, which was used as the phosgene receptor, was attached to the 4-position on the 1,8-naphthalimide chromophore to constituted a nonfluorescent probe. The reaction of phosgene with ketoxime induced a Beckmann rearrangement, which was followed by conversion of the nonfluorescent probe into the 4-acetamido-1,8- naphthalimide fluorophore, which emits bright blue fluorescence at 488 nm. The probe exhibited a detection limit of 6.3 nM for phosgene. In addition, the probe-loaded filter stripe for successful monitoring of gaseous phosgene was also demonstrated.

## 1. Introduction

Phosgene exhibits highly toxic lung irritation effects, including pulmonary edema and asphyxia [1,2]. First used in World War I, phosgene is a classical chemical warfare agent. Phosgene is also an important starting material and is widely used in the synthesis of many organic compounds, particularly in the plastics, pharmaceuticals and pesticides industries; therefore, phosgene is available because of its common use. Phosgene leakage can pose a great threat to public health and safety during production, storage and transportation processes. Thus a rapid, sensitive and selective method for the detection of phosgene is urgent in cases of potential security threats arising from industrial accidents as well as chemical terrorist attacks.

Conventional assays have been employed to detect phosgene, such as electrochemical methods and gas chromatography [3,4]; however, some of these methods have shortcomings, including handling complexity, low sensitivity, poor portability, time-consuming methodology, and inconvenience in real-time detection, which limit their further application.

Though colorimetric and/or fluorometric molecular probes are well-known to be low-cost systems capable of simply performing qualitative or quantitative analyses, there are currently only a few papers on spectroscopic chemosensors for phosgene sensing [5]. Most of these papers are based on phosgene-induced carbamylation of various amine-containing fluorophores, such as bodipy [6–8], naphthalimide [9–11], coumarin [12–14], rhodamine [15–17], pyronin [18], benzothiadiazole [19], tetraphenylethene [20], or others [21,22]. In addition, a small number of interesting examples have been reported, based on the unconventional reaction characteristics of phosgene, such as the reaction of phosgene with Harrison's reagent [23], or intramolecular dehydration by the extremely reactive phosgene to furnish lactone [24] or cyano group [25–27].

In the current study, we developed a new strategy for generating a phosgene probe employing 1,8-naphthalimide as a chromophore. We introduced an electron-withdrawing ketoxime group to the 4-position of the 1,8- naphthalimide chromophore to obtain the probe which is nonfluorescent. After adding phosgene, the reaction of phosgene with ketoxime on the probe induced a Beckmann rearrangement and converted the nonfluorescent probe into the 4- acetamido-1,8- naphthalimide fluorophore, which emits bright blue fluorescence.

## 2. Experimental

### 2.1. Materials and instrumentations

All reagents were purchased from J & K Science Ltd and used with no further purification. Compound **3** was synthesized according to the literature [28]. NMR spectra were recorded on Bruker AV400 NMR.

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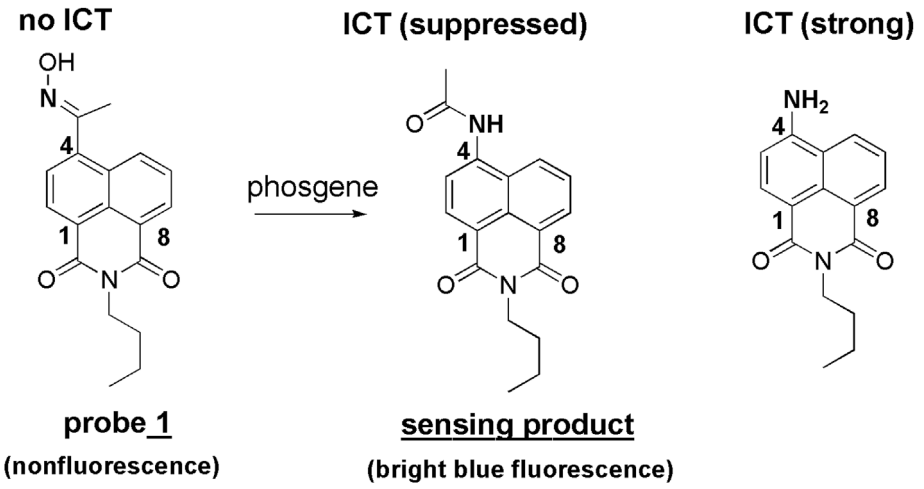
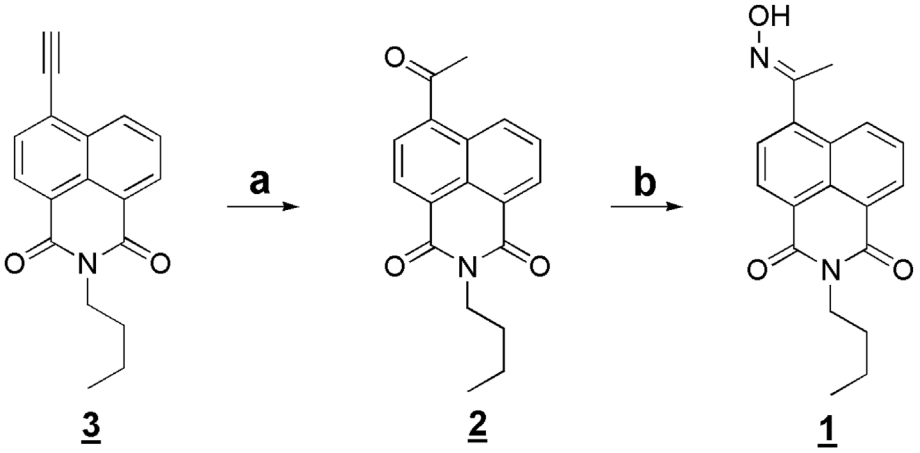



**Scheme 1.** The design conception.




**Scheme 2.** The synthesis route of probe **1**
(a) $HgSO_4/H_2SO_4$, $CH_2Cl_2$, refluxed for 12 hs; (b) $NH_2OH{\cdot}HCl$, NaOAc, $CH_3CH_2OH/H_2O$, refluxed for 2hs.

Mass spectra were measured with a JEOL JMS-T100LC mass spectrometer (ESI + ). Fluorescence spectra were performed on a Hitachi F7000 fluorescence spectrometer (Tokyo, Japan). Absorption spectra were recorded on a Shimadzu UV2700 spectrophotometer.

### 2.2. Preparation and characterization of probe *1*

#### 2.2.1. Preparation and characterization of compound *2*

Compound **3** (100 mg, 0.36 mmol, 1.0 eq)was dissolved in dichloromethane; then, silica-supported $HgSO_4/H_2SO_4$(40 mg)was added, and the mixture was refluxed under a $N_2$ atmosphere for 6 h. The mixture was filtered, and the residue was washed 3 times with dichloromethane. The filtrate was removed, and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1, v:v) to obtain milky white solid **2** (0.100 g, 94%).

$^1$H NMR (400 MHz, $CDCl_3$) δ: 8.97 (d, $J$ = 8.0 Hz, 1H), 8.66 (d, δ8.67/8.65, $J$ = 8.0 Hz, 1H),8.65 (d, δ8.66/8.64, $J$ = 8.0 Hz, 1H), 8.14 (d, $J$ = 8.0 Hz, 1H), 7.86 (m, 1H), 4.20 (t, $J$ = 8.0 Hz, 2H), 2.83 (s, 3H), 1.75 (m, 2H), 1.47 (m, 2H), 1.00 (t, $J$ = 6.0 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 201.04, 163.68, 163.41, 140.09, 132.41, 131.52, 129.79, 128.75, 128.58, 128.53, 128.02, 125.62, 122.73, 40.42, 30.16, 30.07, 20.37, 13.75.

HRMS spectra of **2**. Cal. for $C_{18}H_{17}NO_3$ + Na, (M + Na): 318.11061; found: 318.11047.

#### 2.2.2. Preparation and characterization of compound *1*

Compound **2** (50 mg, 0.17 mmol, 1.0 eq)was dissolved in 10 mL ethanol; then, $NH_2OH{\cdot}HCl$(47.09 mg, 0.68 mmol, 4.0 eq), NaOAc (41.69 mg, 0.51 mmol, 3.0 eq)and 2.5 mL of water were added. The mixture was refluxed under a $N_2$ atmosphere for 2 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1, v:v) to obtain milky white solid, probe **1** (0.026 g, 50%).

$^1$H NMR (400 MHz, $CDCl_3$) δ: 8.65 (d, $J$ = 8.0 Hz, 1H), 8.62 (m, 1H), 8.51 (d, $J$ = 8.0 Hz, 1H), 8.30 (brs, 1H), 7.79 (m, 1H), 7.74 (m, 1H), 4.21 (t, $J$ = 8.0 Hz, 2H), 2.45 (s, 3H), 1.74 (m, 2H), 1.47 (m, 2H), 1.00 (t, $J$ = 8.0 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$) δ: 164.11, 163.83, 156.88, 141.33, 131.94, 131.34, 130.57, 129.29, 128.61, 127.25, 126.64, 122.94, 122.93, 40.34, 30.17, 20.36, 16.37, 13.81.

ESI-MS: calcd. for $C_{18}H_{19}N_2O_3$ (**1** + H): 311.1, found: 311.5.

#### 2.2.3. Synthesis of sensing product by reaction of probe *1* with phosgene

An acetonitrile solution of triphosgene (1.2 eq) containing TEA (5% equiv. of triphosgene) was added dropwise to the acetonitrile solution containing probe **1** (30 mg, 1.0 eq) at room temperature. The mixture was stirred under a $N_2$ atmosphere at 45 °C overnight. The solution was removed under reduced pressure, and the residue was purified by silica gel chromatography to get sensing product in ca.85.3% yield.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ: 10.39 (s, 1H), 8.69 (dd, $J$ = 8.0, 4.0 Hz, 1H), 8.51 (d, $J$ = 8.0 Hz, 1H), 8.46 (d, $J$ = 8.0 Hz, 1H), 8.30 (d,

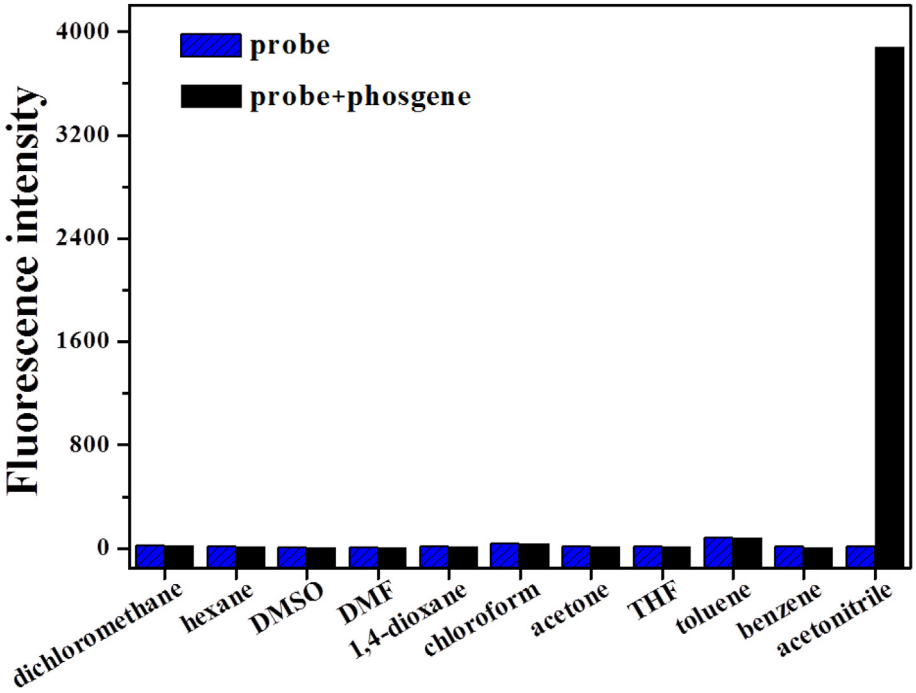



**Fig. 1.** The effect of the type of organic solvent on the reaction of probe **1** (50 μM) with phosgene (10 μM). Data were measured after 30 min reaction. $\lambda_{ex}$ = 367 nm; slit: ex/em = 2.5 nm/2.5 nm.

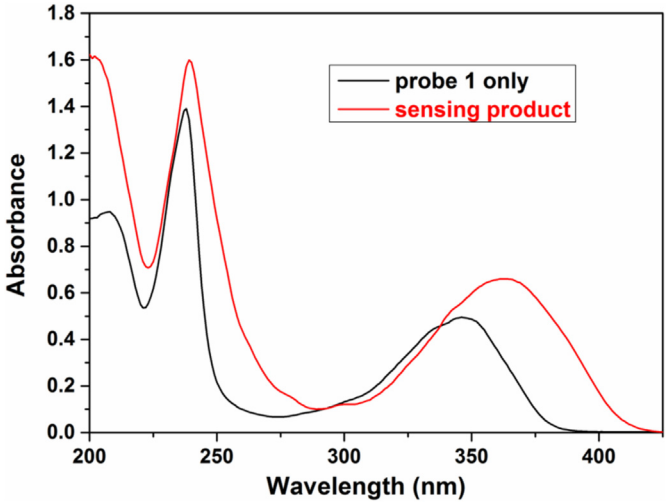



**Fig. 2.** The absorption spectra of 50 μM of probe **1** and the sensing product (reaction of probe **1** with phosgene) in $CH_3CN$ solution.

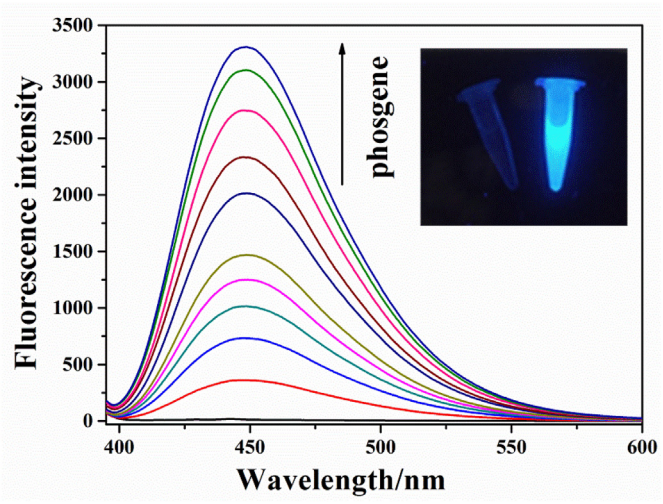



**Fig. 3.** The fluorescence spectra of probe **1** (50 μM) upon adding various concentrations of phosgene in $CH_3CN$ solution. Spectra were measured after 15 min reaction. [phosgene] = 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 μM, respectively. Inlet: Visual fluorescence change before (left) and after (right) reaction with phosgene. $\lambda_{ex}$ = 367 nm; slit: ex/em = 2.5 nm/2.5 nm.

$J$ = 8.0 Hz, 1H), 7.87 (dd, $J$ = 8.0, 4.0 Hz, 1H), 4.03 (t, $J$ = 8.0 Hz, 2H), 2.28 (s, 3H), 1.61 (m, 2H), 1.35 (m, 2H), 0.92 (t, $J$ = 8.0 Hz, 3H).

$^{13}$C NMR (400 MHz, DMSO-$d_6$) δ: 169.99, 163.84, 163.27, 140.73, 131.99, 131.19, 129.55, 128.67, 126.70, 124.32, 122.65, 119.60, 117.79, 39.71, 30.12, 24.54, 20.26, 14.15.

ESI-MS: calcd. for $C_{18}H_{18}N_2O_3$, 310.1, found, 309.7.

### 2.3. Fluorescent detection of phosgene in acetonitrile solution

To avoid handling toxic and volatile phosgene, nonvolatile and safe triphosgene was employed. Triphosgene is a trimer of phosgene, and decomposes into phosgene *in situ* in the presence of trimethylamine (TEA) [29]. A stock solution of phosgene was prepared by mixing triphosgene and TEA (5.0% equiv. of triphosgene) in $CH_2Cl_2$ and letting the mixture sit for 30 min.

Acetonitrile ($CH_3CN$) was used as the solvent for all assays. A fluorescence assay was carried out by titrating aliquots of the phosgene stock solution into a $CH_3CN$ solution of probe **1** (50 μM) at room temperature (25 °C). The changes of the fluorescence spectra (λex = 367 nm) were then recorded after 15 min reaction.

### 2.4. Selective detection of phosgene over selected analytes

In addition to phosgene, we also studied the fluorescence responses of probe **1** to other analytes including: 1) hydrochloric acid (HCl); 2) nerve agent mimics: diethyl chlorophosphate (DCP) and diethyl cyanophosphonate (DCNP); and 3) various acylating/phosphorylating agents: thionyl chloride ($SOCl_2$), sulfuryl chloride ($SO_2Cl_2$), phosphorus

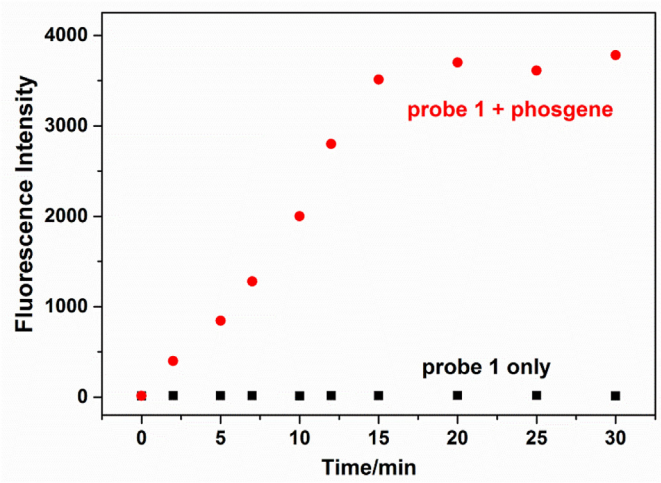



**Fig. 4.** Time-dependence of fluorescence changes at 448 nm for probe **1** (50 μM) in the absence and presence of phosgene (10 μM) in $CH_3CN$ solution. Monitored at 448 nm $\lambda_{ex}$ = 367 nm; slit: ex/em = 2.5 nm/2.5 nm.

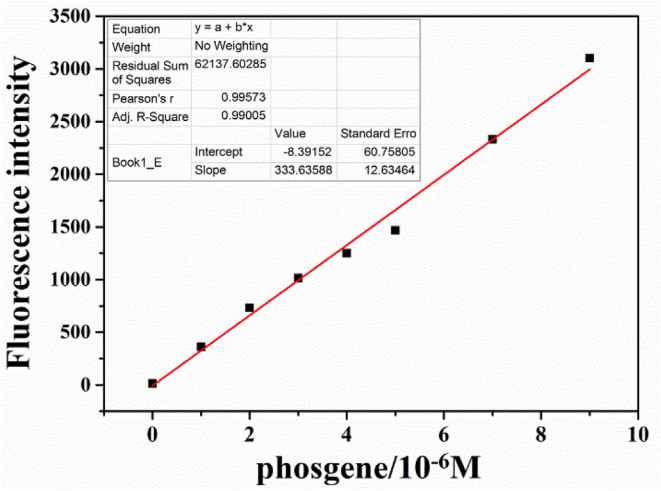



**Fig. 5.** Fluorescence intensity of probe **1** (50.0 μM) *vs.* concentrations of phosgene in $CH_3CN$ solution. Data were measured after 15 min reaction. Monitored at 448 nm $\lambda_{ex}$ = 367 nm; slit: ex/em = 2.5 nm/2.5 nm.

oxychloride ($POCl_3$), oxalyl chloride (ClCOCOCl), acetyl chloride ($CH_3COCl$), p-toluenesulfonyl chloride (p-TsCl) and triphosgene.

### 2.5. Detection of gaseous phosgene by test strip

A small piece of filter strip was immersed in an ethyl acetate solution of **1** (2500 μM) and then air-dried, leaving a small amount of the sensor dispersed on the paper. Gaseous phosgene at 0, 0.2 and 1.0 ppm was prepared as follows: the triphosgene stock solution (7 mM) and TEA (5.0% equiv. of triphosgene) were prepared using $CH_2Cl_2$ as the solvent; then 0, 5.0 and 25 μL of the stock solution were added to 50 mL centrifuge tubes. Next, the probe-loaded filter papers were placed into the above mentioned centrifuge tubes, and the lids were immediately closed. The filter papers were exposed to gaseous phosgene for 5 min and then removed and photographed by an iPhone 6S under handheld UV lamp set to 365 nm.

## 3. Results and discussion

### 3.1. Design of the probe

Our approach for the fluorescence detection of phosgene relies on utilizing internal charge transfer (ICT) within a dye platform to promote emission upon reaction with phosgene. It is known that the Beckman rearrangement converts the ketoxime group into an amide group. Therefore, we attached a ketoxime group to the 4-position on the 1,8-naphthalimide chromophore to obtain a nonfluorescent probe. Because of the electron-withdrawing ketoxime group at the 4-position on the 1,8-naphthalimide chromophore, there is no inner ICT process (Scheme 1). After reaction with phosgene, the ketoxime group is converted into an amide group to form the sensing product, 4- acetamido −1,8-naphthalimide fluorophore, which has an inner ICT process (in the ICT suppressed state, Scheme 1) and bright blue fluorescence is thus emitted. The synthesis route for probe **1** was showed in Scheme 2, and $^1H$ NMR, $^{13}C$ NMR, MS spectra were showed in Figs. S3–S8.

### 3.2. Effect of an organic solvent as the reaction media

We initially found that the type of organic solvent utilized as the reaction medium exerted a significantly effect on the response of phosgene. The solvents we chose were dichloromethane, n-hexane, dimethyl sulfoxide (DMSO), N, *N*-dimethylformamide (DMF), 1, 4-dioxane, chloroform, acetone, tetrahydrofuran (THF), toluene, benzene and acetonitrile, respectively. It can be seen from Fig. 1 that probe **1** only exhibited a strong response to phosgene in acetonitrile. This preference for acetonitrile as a solvent can be ascribed to the mechanism [30] that various electrophilic reactive intermediates of Beckman rearrangement can be stabilized by the lone pair electrons of nitrogen atom in acetonitrile molecule, which leads to the solvation of these reactive intermediates and thus promotes the further reaction.

### 3.3. Spectral response study

A detailed study of the response characteristics of probe **1** towards phosgene was carried out in an acetonitrile solution. The absorption spectra of probe **1** and the sensing product were recorded first. As shown in Fig. 2, the acetonitrile solution of probe **1** showed three major peaks centred at 208, 238 and 346 nm. After reaction with phosgene, the sensing product also exhibited three peaks; the peaks of the former two were almost unchanged in contrast to those of probe **1**, and the third was redshifted to 362 nm.

Furthermore, the reaction of probe **1** with phosgene also produced noticeable changes in the fluorescence emission spectra. Probe **1** itself showed minimal emission, but after the addition of 10 μM phosgene, the resulting maximum emission at 448 nm was greatly increased by 260 times with respect to the maximum excitation at 367 nm (Fig. 3). In addition, the fluorescence response of the phosgene could be conveniently observed with the naked eye (Fig. 3, inset). When exposed to a handheld UV lamp set to 365 nm, the solution of probe **1** alone appeared to be nonfluorescent; the solution of probe **1** with 10 μM phosgene, however, was bright blue.

Moreover, the time-dependence of the reaction of probe **1** with phosgene in an acetonitrile solution was also evaluated (Fig. 4). We found that approximately 15 min was required for 10 μM of phosgene to promote the generation of maximum fluorescence.

To further evaluate the analytical response of the probe to the concentration of phosgene, titrations with different concentrations of phosgene were conducted (Fig. 5). When monitored using an excitation wavelength of 367 nm, the fluorescence titration curve revealed that the fluorescence intensity at 448 nm increased with increasing concentrations of phosgene, with the correlation coefficient $R^2$ = 0.9900. The limit of detection of phosgene was calculated to be 6.3 nM based on the definition by IUPAC [31] (CDL = 3Sb/m) from eleven blank

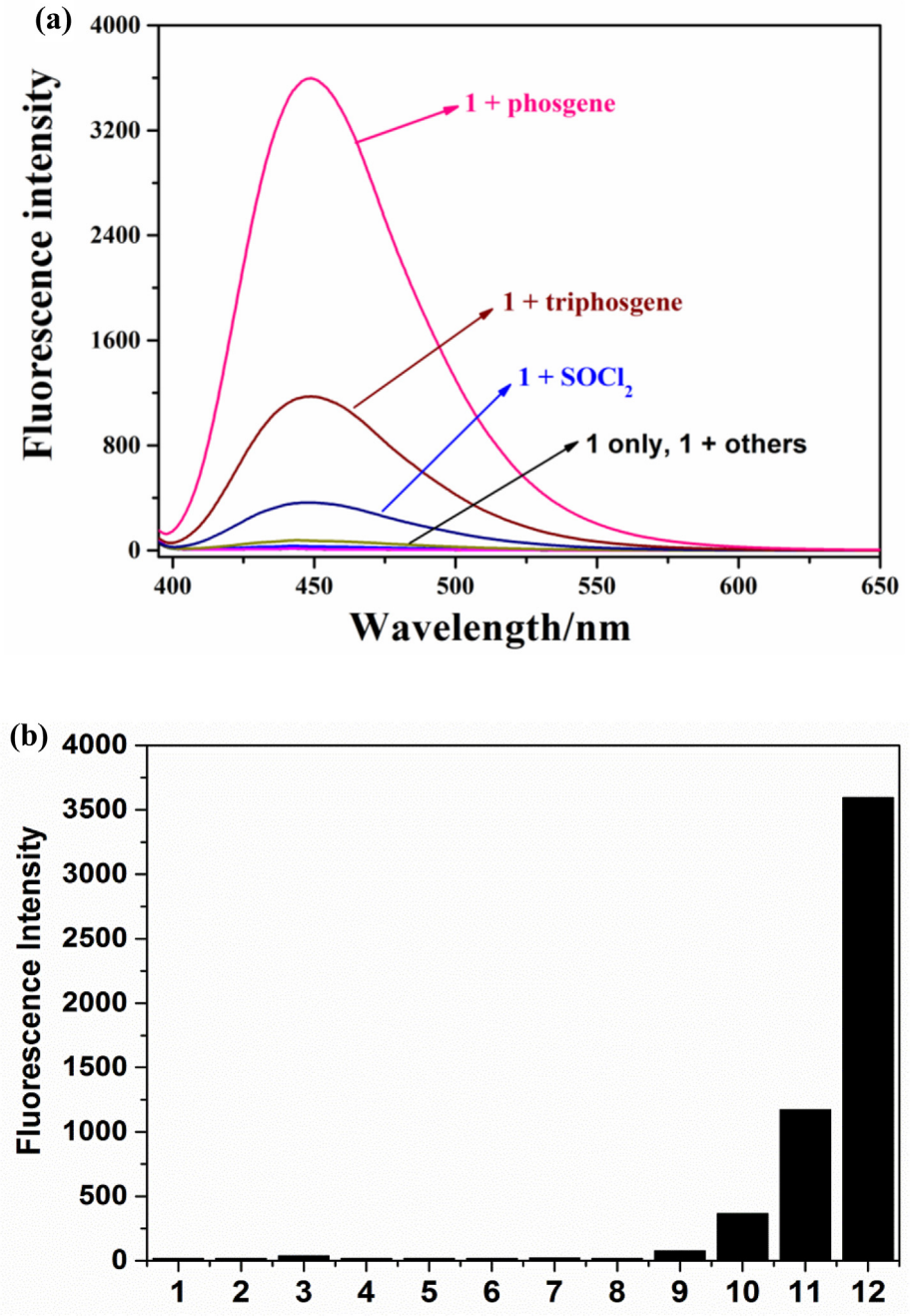
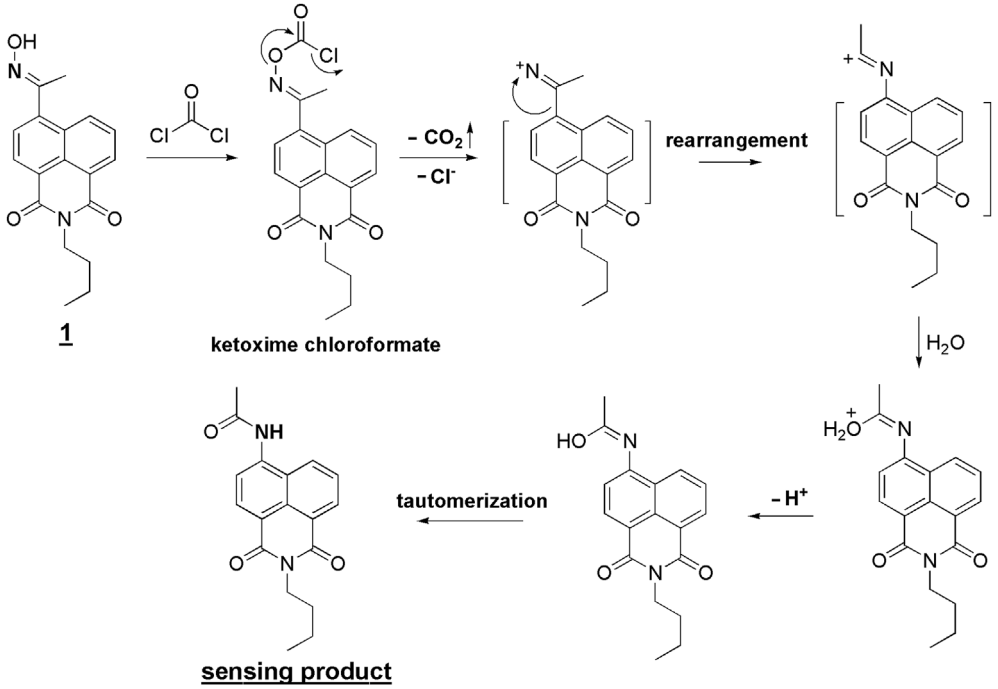



**Fig. 6. (a)** Fluorescence selectivity of probe **1** (50.0 μM) at 448 nm to various analytes in $CH_3CN$ solution. Spectra were measured after 15 min reaction. Others including: HCl, $POCl_3$, DCP, DCNP, p-TsCl, ClCOCOCl, $CH_3COCl$, $SO_2Cl_2$.
(b) Selectivity of probe **1** (50.0 μM) at 448 nm to various analytes in $CH_3CN$ solution. Analytes are: (1) none, (2) HCl, (3) $POCl_3$, (4) DCP, (5) DCNP, (6) p-TsCl, (7) ClCOCOCl, (8) $CH_3COCl$, (9) $SO_2Cl_2$, (10) $SOCl_2$, (11) triphosgene, (12) phosgene.

solutions.

### 3.4. Selectivity of probe

The selectivity of probe **1** (50 μM) to phosgene (10 μM) and various analytes in a $CH_3CN$ solution was determined. The analytes included: 1) HCl (100 equiv. of phosgene); 2) nerve agent mimics (100 equiv. of phosgene): diethyl chlorophosphate (DCP) and diethyl cyanophosphonate (DCNP), and 3) various acylating/phosphorylating agents (10 equiv. of phosgene): oxalyl chloride (ClCOCOCl), acetyl chloride ($CH_3COCl$), p-toluenesulfonyl chloride (p-TsCl) and phosphorus oxychloride ($POCl_3$). Furthermore, thionyl chloride ($SOCl_2$) and triphosgene (1.0 equiv. of phosgene, respectively) were also used to test the selectivity. As shown in Fig. 6 (a and b), a large fluorescence enhancement only occurred for phosgene, and large excesses of acid and nerve agent mimics did not cause potential false positive responses. Triphosgene also caused a moderate increase in fluorescence, since it is a trimer of phosgene, and has the same chemical properties as phosgene, but is less reactive than phosgene [32]; thus, triphosgene might follow the same mechanism as phosgene to initiate the Beckmann rearrangement and had a moderate fluorescence enhancement. These results indicated the high selectivity of probe **1** for phosgene over acid, nerve agent mimics and various acyl chlorides.




**Scheme 3.** Phosgene-promoted Beckmann rearrangement in probe **1**.

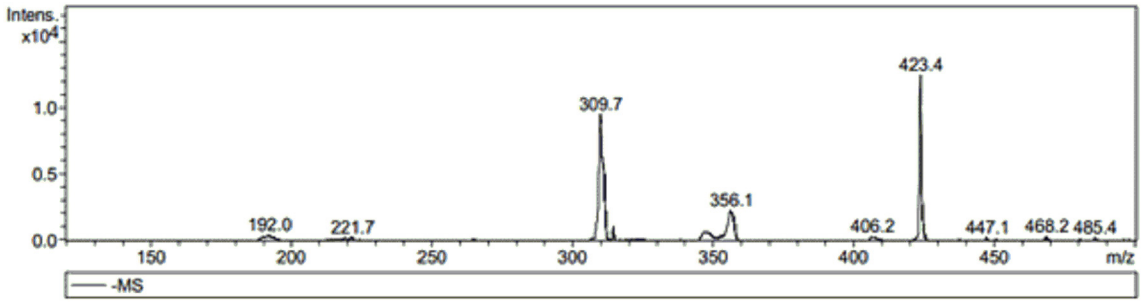



**Fig. 7.** ESI-MS spectra of the sensing product. Calcd. for $C_{18}H_{18}N_2O_3$, 310.1, found, 309.7.

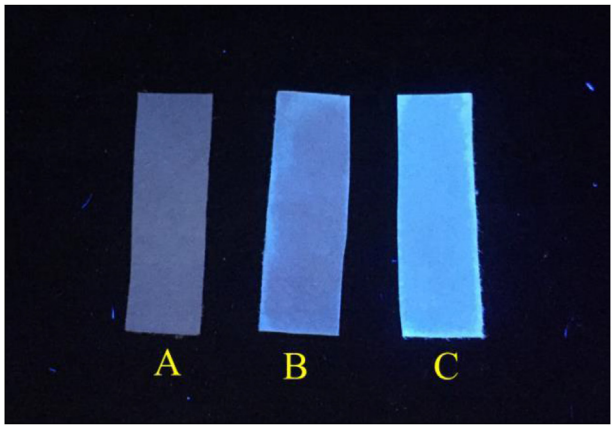



**Fig. 8.** Photographs of fluorescence responses of test stripes loaded with probe **1** upon exposure to different amount of phosgene gas in air (from left to right: 0, 0.2, 1.0 ppm, respectively).

### 3.5. Study of mechanism

As shown in Scheme 3, it is believed that the reaction of probe **1** with phosgene produces the ketoxime chloroformate first; then, a gaseous carbon dioxide ($CO_2$) molecule is released to form a cationic intermediate, which is eventually converted into an amide structure, the sensing product, through a further Beckmann rearrangement and hydration, resulting in a significant enhancement of fluorescence.

To verify the reaction mechanism of probe **1** with phosgene, we first employed the sensing product for ESI-MS experimentation. As expected, the sensing product was confirmed by its mass spectra (ESI-MS): calcd. for $C_{18}H_{18}N_2O_3$, 310.1; experimentally determined, 309.7 (Fig. 7). These data preliminarily proved that the 4-acetamide-1,8-naphthalimide fluorophore was obtained after the reaction of **1** with phosgene.

Moreover, the $^1H$ and $^{13}C$ NMR results further demonstrated the structure of the sensing product (Figs. S1 and S2). Significantly, the —OH proton signal of the oxime group in probe **1** (δ 8.30 proton, broad singlet, 1H, Fig. S6) was converted into the —NH proton signal of acetylnaphthalamide in the sensing product (δ 10.39 proton, singlet, 1H, Fig. S1). These results confirmed the reliability of the reaction mechanism we hypothesized.

### 3.6. Visual fluorescent sensing of gaseous phosgene by test stripes

Furthermore, a portable method for fluorescent visual detection of phosgene vapour with probe-loaded paper stripes was also developed (Fig. 8). Stripes A, B, and C are test papers in the presence of phosgene at concentrations of 0, 0.2 and 1.0 ppm, respectively. Under 365 nm UV light irradiation, the strong bright blue colour of stripe C clearly demonstrates that the test stripe exhibits prominent fluorescent

visualization for 1.0 ppm of phosgene gas. More importantly, this value is below the threshold (2 ppm) value that causes immediate danger to health and life [33].

## 4. Conclusion

In summary, a novel sensing mechanism for phosgene was developed using the skeleton of the 1, 8-naphthalimide chromophore. An electron-withdrawing 4-ketoxime as the phosgene receptor was attached to the 4-position on the 1,8-naphthalimide chromophore to produce a nonfluorescent probe, and the reaction of phosgene with ketoxime induced a Beckmann rearrangement and converted the nonfluorescent probe into the 4- acetamido-1,8- naphthalimide fluorophore, which emits bright blue fluorescence. In addition, the probe showed high selectivity and sensitivity to phosgene with a detection limit of 6.3 nM, and a probe-loaded filter stripe for monitoring gaseous phosgene was also demonstrated. To the best of our knowledge, this probe is the first reported sensor utilizing a phosgene-induced Beckmann rearrangement, and the mechanism offers potential for further applications in designing more effective phosgene probes.

## Acknowledgments

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2019.107854.

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