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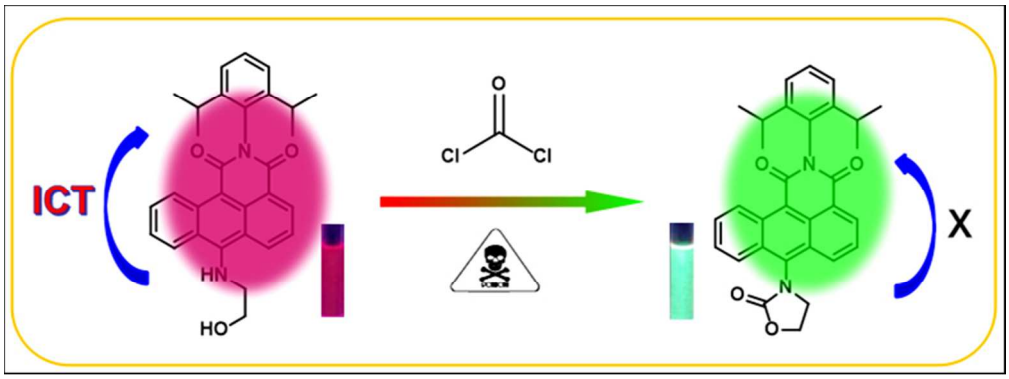

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A Colorimetric and Ratiometric Chemosensor for Visual Detection of Gaseous Phosgene Based on Anthracene Carboxyimide Membrane

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ABSTRACT.

In this work, we reported an anthracene carboxyimides-based chemosensor (AC-Phos) for colorimetric and ratiometric fluorescence detection of highly toxic phosgene, which displayed rapid response (< 5 min) towards phosgene with high selectivity and low detection limit (2.3 nM). Furthermore, a facile testing membrane with polystyrene immobilizing chemosensor has been fabricated for real-time visualizing gaseous phosgene.

KEYWORDS: Anthracene carboxyimide, Ratiometric, Chemosensor, Phosgene, Test membrane

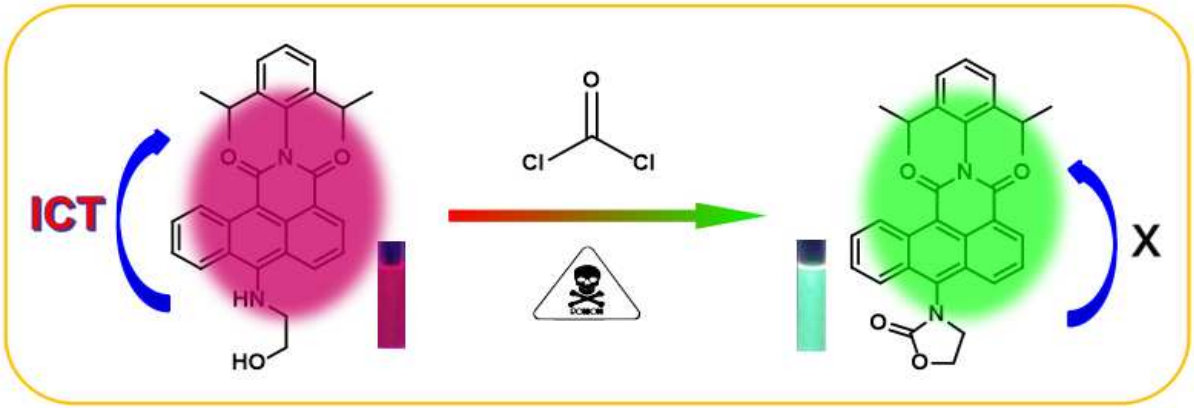
INTRODUCTION

Phosgene ($COCl_2$) is a colorless and high toxic gas, which has ever been used as a lethal chemical warfare agent during World War I. It has been disclosed that exposure to 20 ppm phosgene can cause lung injuries within 2 minutes, and exposure to 90 ppm for 30 minutes is fatal[1] for human and all animals. Nevertheless, such a toxic phosgene is also an essential industrial material for production of drugs, dyes and polymers. For public safety and health,[1,2] it is of great importance to develop facile, low cost, portable, selective and sensitive method for alerting industrial phosgene leakage and phosgene-based chemical warfare terrorism attack.

Gas chromatography is the most widely used assays for determination of phosgene. Unfortunately, it is often limited by poor portability. Optical sensors are advantageous as they offer the possibility of real-time visual detection of analytes. So far, a few fluorescent chemosensors for phosgene have been developed based on nucleophilic substitution reactions with alcohol hydroxyl or amine groups,[4-8] because phosgene can mediate with alcohol hydroxyl or amine groups in chemosensors to form hetero cross-linking or cyclization,[9-14] which block the photo-induced electron transfer (PET) and promote generation of detectable fluorescence enhancement signal.[15, 16] Although these chemosensors are elegant, most of these chemosensors have some limitations such as unsatisfactory selectivity and without observable color changes in response to phosgene. Besides, these chemosensors just displayed fluorescence enhancement at a single emission wavelength, which might be suffered from the interference from environmental conditions and instrumental efficiency. Colorimetric and ratiometric fluorescent chemosensors are highly desirable due to their some good merits such as dual signal output, high sensitivity and visual feature. Nevertheless, development of ratiometric fluorescent chemosensors with high sensitivity and selectivity, fast response and observable color changes still remains a challenge. A good stimuli-responsive fluorescence chemosensor should fulfill these requirements: (1) a high fluorescence contrast to detect trace amounts of analyte, (2) rapid response, and (3) a high recognition specificity to achieve excellent detection selectivity.[17-18]

In order to visually determine phosgene, we make attempt to develop a colorimetric and ratiometric chemosensor (**AC-Phos)** with the advantage of high selectivity and sensitivity, fast response, noticeable color change as well as portability.[19-21] In this work, anthracene carboxyimide was employed as the fluorescence reporter in view of its fascinating photo-physical properties, such as high fluorescence quantum yield, visible absorption and emission

with a large Stokes shift.[22-24] In particular, the UV-vis absorption and fluorescence spectra of this electron-withdrawing anthracene carboxyimide could be easily modulated by tuning the electron properties of substituent groups at 10-position. To construct a ratiometric chemosensor, herein, an electron-donating ethanolamino was covalently fixed at the 10-position of anthracene to form a donor-π conjugation-acceptor (D-π-A) structure, which would lead to a large red-shift in the UV-vis absorption and fluorescence spectra. On the other hand, the -NH- and -OH groups in ethanolamine provide two active reaction sites for coupling with electrophilic phosgene, which would achieve high sensitivity and specificity for phosgene. It was envisioned that phosgene would simultaneously couple with the -NH- and -OH groups in chemosensor to form a five-member ring, which inhibits intramolecular charge transfer from amine to anthracene carboxyimide. Hence, a noticeable colorimetric and ratiometric fluorescence response would be observed (**Scheme 1**).



Scheme 1. The design strategy of chemosensor **AC-Phos** for sensing phosgene

EXPERIMENTAL SECTION

General Information

Unless otherwise noted, all reagents for synthesis were bought from commercial sources (Aladdin-Reagent, Sigma-Aldrich, TCI) and used without further processing. All solvents were purified and dried before use by conventional methods. The solvents used in spectrum analysis were of HPLC grade. All reactions were monitored by layer chromatography (TLC) using 0.25 mm silica gel plates with UV indicator (GF-254) and column chromatography was performed on silica gel (mesh 200-300), both of which were purchased from the Qingdao Haiyang Chemical Co., Ltd. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX 500 NMR

spectrometer with tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were recorded on a HP-1100 LC-MS spectrometer. UV-vis absorption spectra were recorded on a Hitachi UV-3310 spectrometer. Fluorescence spectra were recorded on a Hitachi FL-4500 fluorometer. The solvents used for UV-vis absorption and fluorescence measurements were of HPLC grade. The fluorescence quantum yields were measured by optical dilute method ($A < 0.05$) using Rhodamine B ($\Phi = 0.65$ in ethanol) and fluorescein ($\Phi = 0.92$ in 0.1M NaOH) as reference. [22]

AC-Phos probe for phosgene sensing in solution

Since phosgene is a high toxic gas, a non-volatile and less toxic precursor triphosgene instead of phosgene gas was employed to *in situ* produce phosgene in chloroform. Stock solution of the **AC-Phos** probe (1 mM) was diluted to 10 μM in chloroform (HPLC grade) as the test solution. Stoke solutions (1 mM) of triphosgene, toluenesulfonyl chloride (TsCl), diethyl chlorophosphate (DCP), $C_2Cl_2O_2$, CH_3COCl, $SOCl_2$, $POCl_3$ were prepared in chloroform. In the assay experiment, predetermined amount of triphosgene chloroform solution and other analytes (nerve gas mimics) solutions were added into the **AC-Phos** probe solution for phosgene/analytes detection, respectively. All spectroscopic measurements were performed at room temperature; the solutions were put in 10.0 mm path length quartz fluorescence cuvette for all UV-vis absorption and fluorescence emission measurements.

AC-Phos polymeric membrane for visualized phosgene sensing

Polystyrene (2 g) was added into a solution of probe **AC-Phos** (2.5 mg) in chloroform (30 mL), which was stirred by a magnetic stirrer until it formed a transparent and homogeneous solution. A certain amount of the solution was further poured into a glass plate until the solution was fully covered on the plate, then it was dried in air at ambient temperature for 5 h. Finally, the polymeric membrane was cut into some pieces of strips.

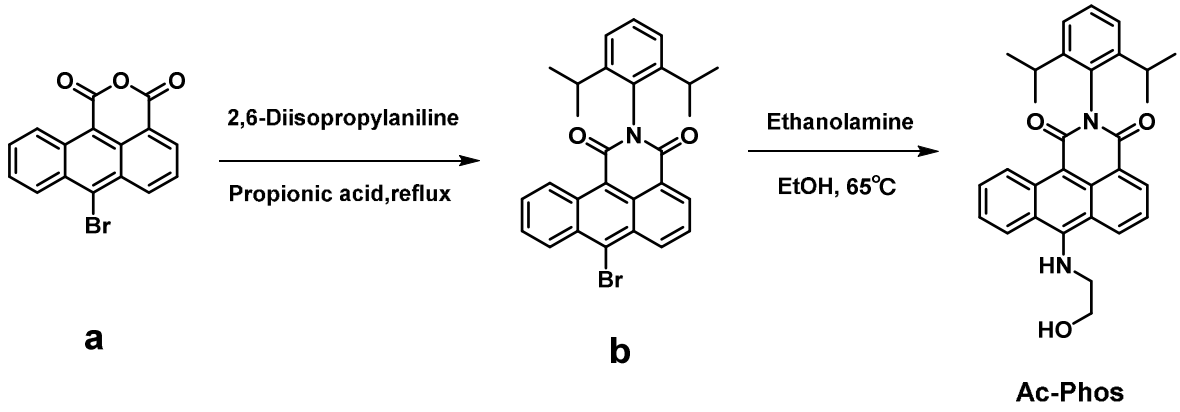
For visualized detection of phosgene and other analytes vapors using **AC-Phos** polymeric membrane, predetermined amount of triphosgene (0−100 ppm) and other analytes (100 ppm) chloroform solutions were placed into centrifuge tubes and vaporized at room temperature for 5 min, respectively, then the **AC-Phos** polymeric membrane was put inside each tube and the lid was quickly closed. Upon exposure to the gas for 5 min, the fluorescence color change of the

AC-Phos polymeric membrane was photographed under 365 nm light.

RESULTS AND DISCUSSION

Synthesis and characterization

Chemosensor **AC-Phos** was easily prepared from 9-bromoanthracene carboxylic acid anhydride (**a**) by two steps, as depicted in **Scheme 2**. 9-Bromoanthracene carboxylic acid anhydride reacted with 2,6-diisopropylaniline to give N-(2,6-Diisopropyl)phenyl-6-bromo-anthracene carboxyimide (**b**), which was further reacted with excessive ethanolamine to afford the chemosensor **AC-Phos** (yield: 36.5%) as a purple solid. The structure of the chemosensor **AC-Phos** was fully characterized by ^{1}H, ^{13}C NMR and HR-MS, and the detailed experimental procedure and characterization data were provided in the Electronic Supporting Information (NMR and MS data shown in **Fig. S1-S2**).



Scheme 2. The synthetic routes and molecular structure of probe **AC-Phos**

Sensing Properties of Probe AC-Phos in Solution

Firstly, we investigated the sensing behavior of **AC-Phos** towards phosgene in chloroform. As shown in **Figure 1a**, the chemosensor **AC-Phos** exhibited a strong absorption band centered at 502 nm. Upon addition of increasing triphosgene, the absorption band at 502 nm gradually blue-shifted to 434 nm. As a result, **AC-Phos** solution displayed obvious color change from deep-red to orange, which can be observed by the naked eyes. This dramatic blue-shift might be ascribed to that the intramolecular charge transfer from NH to anthracene carboxylimde was inhibited after the electrophilic phosgene coupled with -OH and –NH. Then, we examined the fluorescence response of the chemosensor **AC-Phos** towards phosgene. As expected, the

chemosensor also exhibit significant ratiometric fluorescence changes in response to phosgene. As shown in **Figure 1(b-c)**, **AC-Phos** itself displays an emission peak at 615 nm with red fluorescence (Φ = 3.3% in chloroform). With the increasing of phosgene, the emission band of **AC-Phos** centered at 615 nm gradually decreased and a new emission band emerged at 482 nm. As a consequence, the chemosensor exhibits dramatic fluorescence changes from red to bright green (Φ = 20.3% in chloroform). The ratios of the fluorescence intensity at 482 nm and 615 nm (F_{482}/F_{615}) showed a good linear relationship (R^2 = 0.9938) with the concentration of phosgene ranging from 0 to 20 μM (**Figure 1d**), and the limit of detection was calculated to be 2.3 nM based on the signal-to noise ratio (S/N = 3, **Fig. S3**). These results demonstrate that the **AC-Phos** could be employed as a ratiometric fluorescent chemosensor for quantitative detection of phosgene.

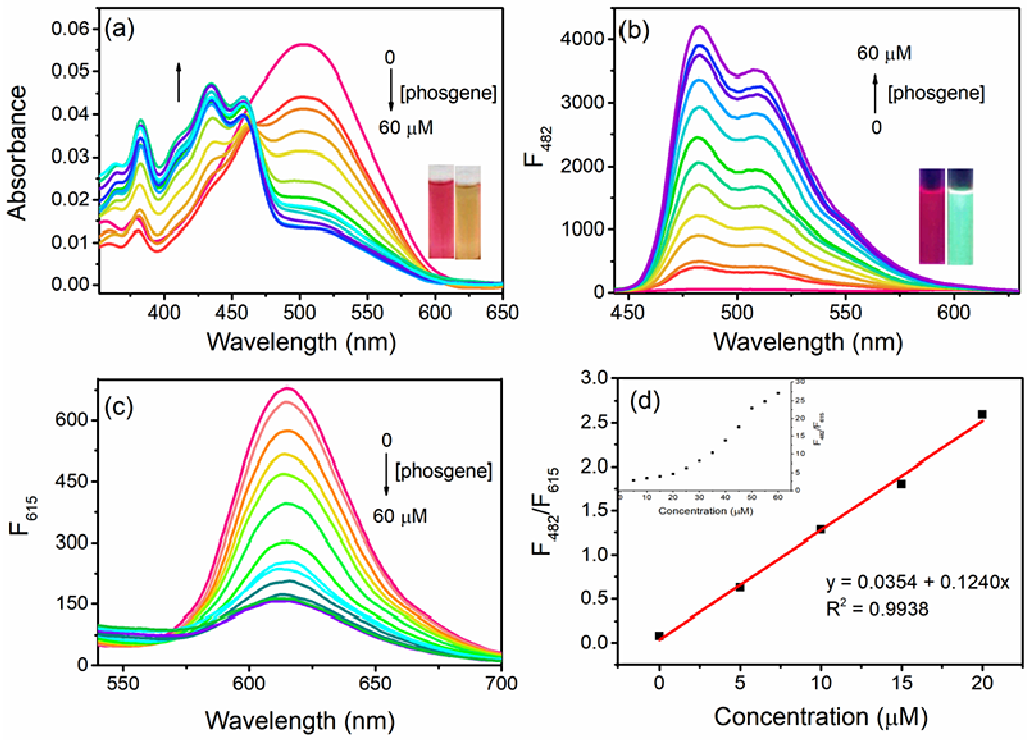


Figure 1. (a) UV-vis absorption spectra and (b,c) fluorescence spectra of chemosensor **AC-Phos** (10 μM) in chloroform upon addition of increasing amount of phosgene (0-60 μM). Inset: (a) the color and (b) (c) fluorescence images of chemosensor **AC-Phos** in the absence/presence of phosgene (b: λ_{ex} = 502 nm, slits: 5/5 nm; c: λ_{ex} = 434 nm, slits: 2.5/5 nm). Each spectra was recorded after 5 min at 25 °C. (d) Linear relationships of fluorescence intensity ratios (F_{482}/F_{615}) for chemosensor **AC-Phos** (10 μM) *versus* concentrations of phosgene in chloroform solution.

The time-dependent fluorescence enhancement of **AC-Phos** (10 μM) was examined and recorded by every 30 s after addition of triphosgene (6 equiv). As shown in **Figure 2**, the fluorescence intensity at 482 nm increased dramatically and reached to a plateau within 5 min after addition of triphosgene, implying that the chemosensor **AC-Phos** might be utilized to determine phosgene in real time.

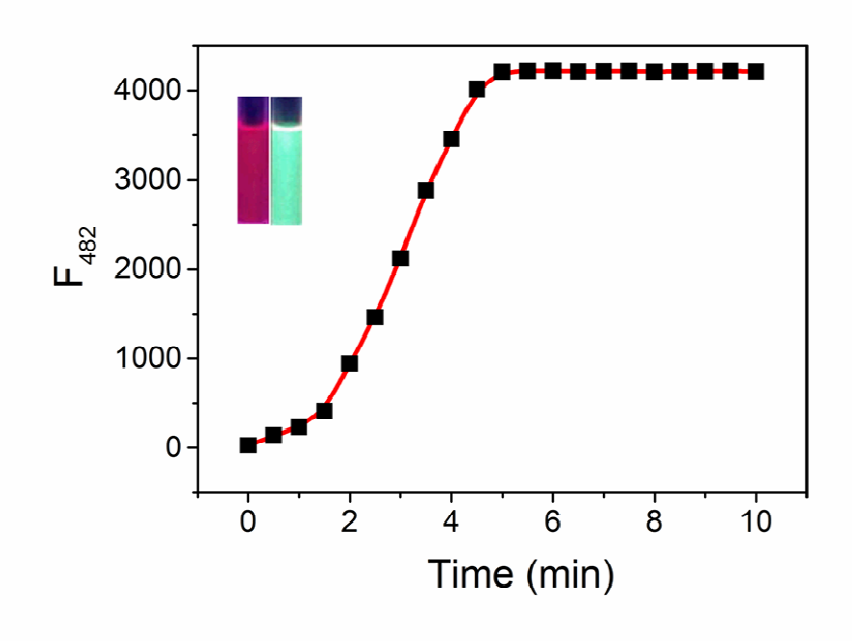


Figure 2. Time-dependent fluorescence response of chemosensor **AC-Phos** (10 μM) to phosgene (60 μM) in chloroform. λ_{ex} = 502 nm, slits: 5/5 nm.

To evaluate the selectivity of **AC-Phos** for phosgene, we examined the fluorescence response of **AC-Phos** to some similarly reactive toxic chemicals such as acryl chlorides, diethyl chlorophosphate (DCP), $SOCl_2$, $POCl_3$ and TsCl. As shown in **Figure 3**, among triphosgene and these interfering substances, only triphosgene induced obvious color change from deep-red to light yellow along with a large fluorescence enhancement. By contrast, the fluorescence emission of **AC-Phos** probe remained unchanged or was only slightly increased in the presence of various interfering substances (**Fig. S4**). Although diethyl chlorophosphate (DCP), $SOCl_2$, $POCl_3$ and TsCl can react with -NH group, they cannot influence the fluorescence of **AC-Phos** because –OH also can bind with these compounds to prevent the subsequent reaction with -NH. The high specificity for phosgene was attributed to the -NH- and -OH groups in **AC-Phos,** which provide two active reaction sites for coupling with electrophilic phosgene. The results showed that the

chemosensor **AC-Phos** possesses high selectivity to phosgene over other nerve-gas mimics and acryl chlorides.

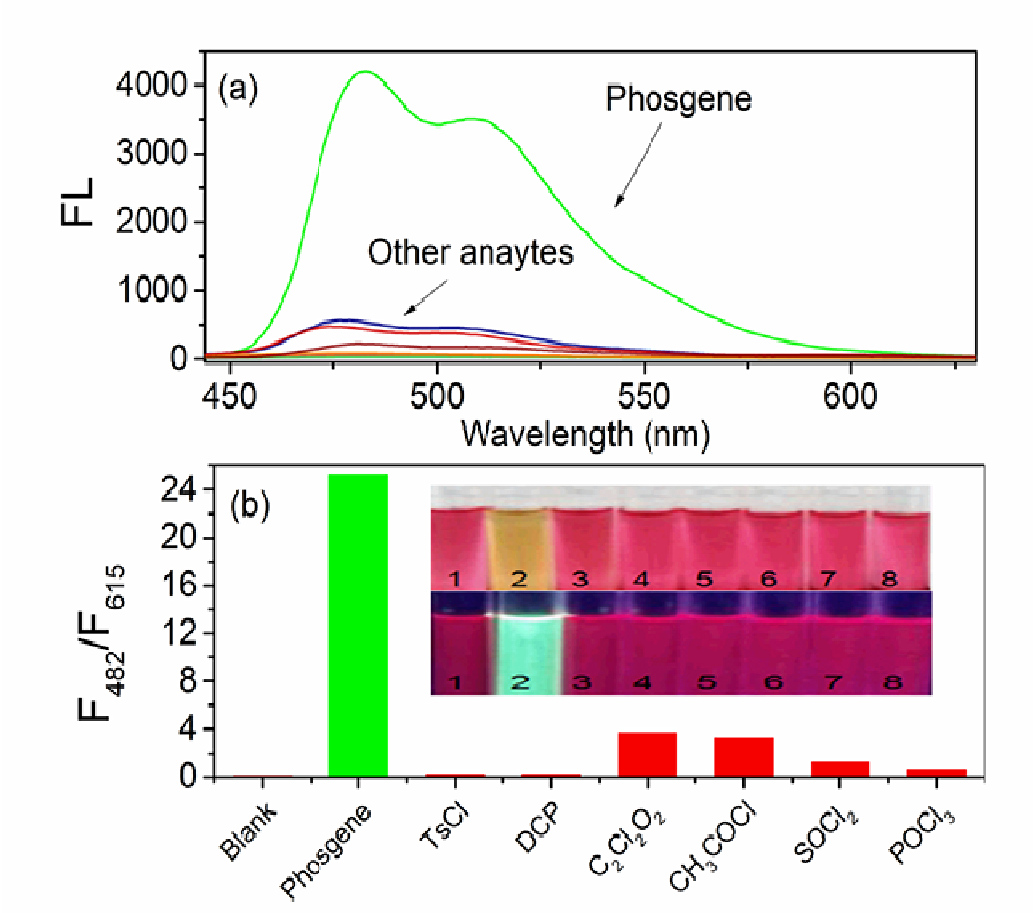


Figure 3. (a) Fluorescence spectra and (b) fluorescence intensity ratios (F_{482}/F_{615}) of **AC-Phos** (10 μM) to triphosgene (6 equiv) , and other analytes (250 μM) for 5 min:(1) blank, (2) triphosgene, (3) toluenesulfonyl chloride (TsCl), (4) diethyl chlorophosphate (DCP), (5) $C_2Cl_2O_2$, (6) CH_3COCl, (7) $SOCl_2$, (8) $POCl_3$. Each spectrum was recorded after 5 min. Inset: the color (top) and fluorescence images (bottom) of chemosensor in the presence of above analytes in chloroform solution.

Sensing Mechanism Study

To confirm the sensing mechanism depicted in **Scheme 1**, **AC-Phos** was reacted with 6 equivalents of triphosgene in chloroform for 5 min, and then the major green fluorescence product was separated by silica gel column for ^{1}H NMR and MS analysis. As shown in **Figure 4**,

the chemical shifts at 7.6 ppm and 4.6 ppm were assigned to the proton signals of –NH (Ha) and –OH (Hd), respectively. These proton signals disappeared along with obvious downfield-shift of the H_b and H_c signals on ethylene (N-CH_2-CH_2-O) group after **AC-Phos** reacted with triphosgene. Moreover, ESI-MS spectrum (Fig. S5) showed a dominant peak at m/z value of 493.2126, which was corresponding to compound **1**(calculated for $[C_{11}H_8O_2 + H]^+$, 493.2049). According to ^{1}H NMR and MS spectra, we concluded that electrophilic phosgene readily couple with the –NH and –OH groups in **AC-Phos** to from a five-member lactam ring *via* hetero-atom cyclization. Since –NH group in **AC-Phos** has been transformed into amide, the strong electron-donating property of amine was reduced and the intramolecular charge-transfer (ICT) was greatly weakened, which contributed to a significant blue-shift in the UV-vis absorption and fluorescence spectra of **AC-Phos**. Hence, **AC-Phos** displayed a noticeable color change and fluorescence change in the presence of phosgene.

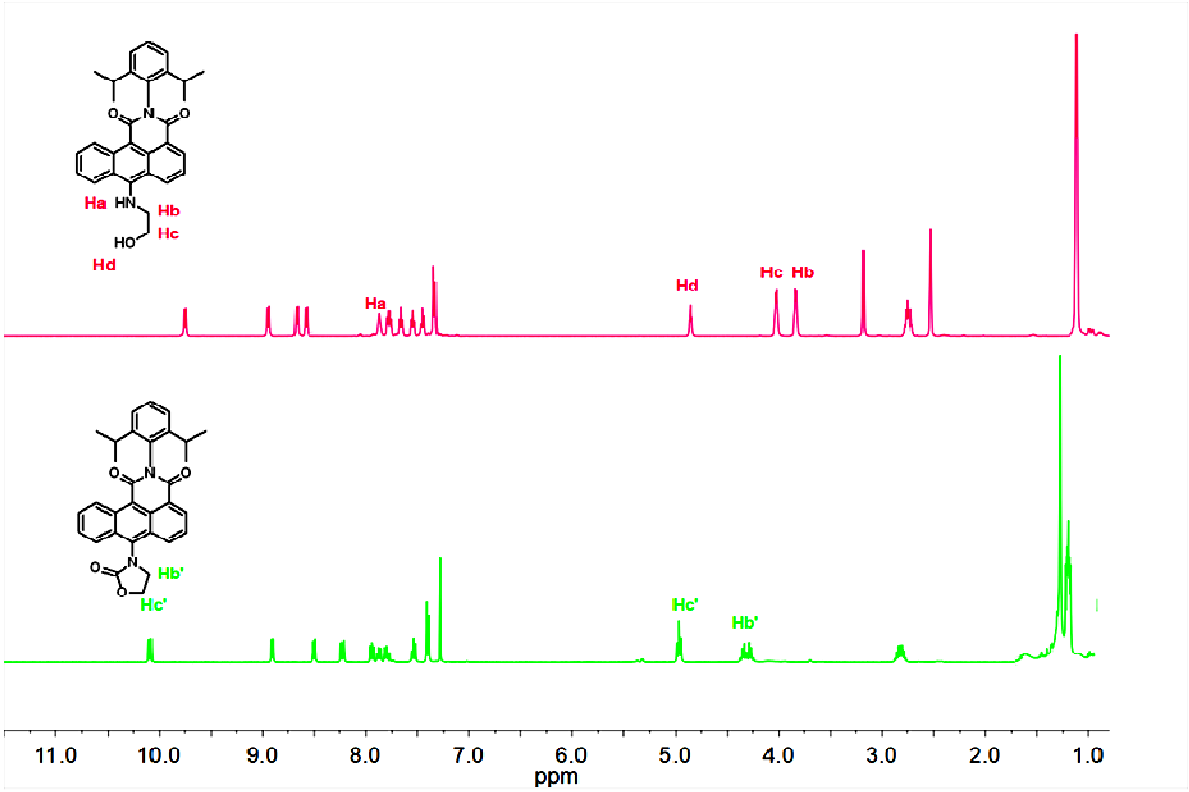


Figure 4. ^{1}H NMR spectrum of **AC-Phos** (top) in DMSO-d_6 and its reaction product compound **1** (bottom) in $CDCl_3$ (500 MHZ).

AC-Phos-loaded Membrane for Phosgene Detection

To obtain fast and portable detection kit for phosgene, **AC-Phos** (0.125% w/w) was further

loaded into polystyrene to prepare **AC-Phos** membrane with deep-red color. Upon exposure to various amounts of phosgene (0-100 ppm) for 5 min (**Figure 5**), the color of test membrane changed from deep-red to light yellow accompanied with noticeable green fluorescence lighting up, which could be observed by the naked eyes. It has been disclosed that 20 ppm concentration of phosgene can cause lung injuries[3]. Delightfully, the **AC-Phos** membrane could detect trace amounts of phosgene within the dangerous range (20-90 ppm), which enables it to be a fast and portable and highly sensitive test kit for visible detection of phosgene gas.

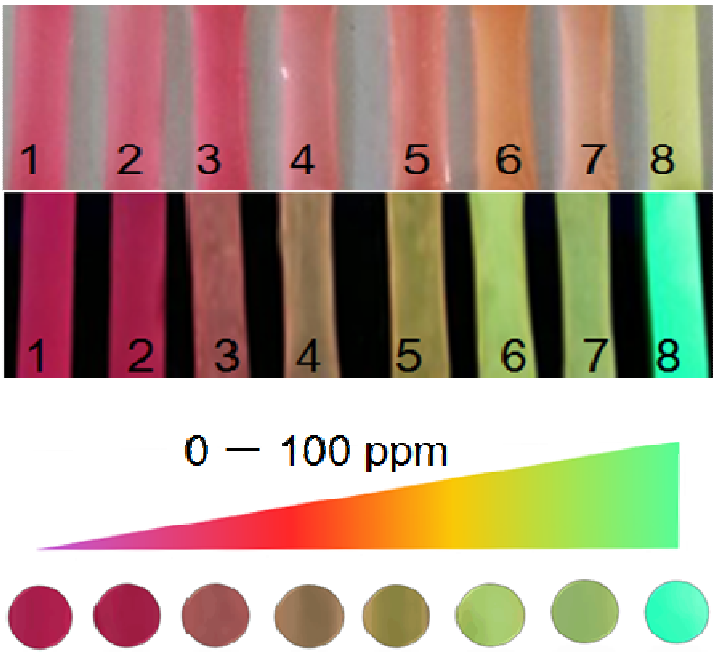


Figure 5. Photograph of color and fluorescence response of **AC-Phos** loaded polystyrene membrane upon exposure to various amounts of phosgene vapor. (1): 0 ppm, (2):15 ppm, (3):30 ppm, (4): 45 ppm, (5): 60 ppm, (6): 75 ppm,(7): 90 ppm, (8):100ppm.

Finally, we examined the selectivity of **AC-Phos** membrane for phosgene among other nerve-gas mimics and acyl chlorides. As shown in **Figure 6**, the color of **AC-Phos** membrane became light yellow from deep-red in the presence of phosgene gas. Meanwhile, the fluorescence color change from deep-red to bright green could be observed under a hand-held UV lamp (365 nm), while various interfering substances did not cause any changes in color and fluorescence of **AC-Phos**. These results imply that the **AC-Phos** membrane may serve as a potential highly selective test kit for real-time detection of phosgene gas/vapor over other nerve-gas mimics.

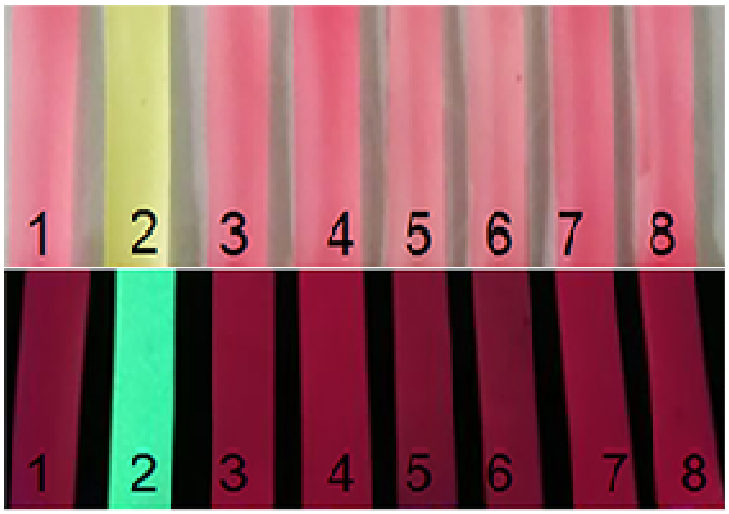


Figure 6. Photograph of color (top) and fluorescence (bottom) response of **AC-Phos** loaded polystyrene membrane upon exposure to 100 ppm phosgene and various nerve-gas mimics and acyl chlorides. (1) blank, (2) triphosgene, (3) toluenesulfonyl chloride (TsCl), (4) diethyl chlorophosphate (DCP), (5) $C_2Cl_2O_2$, (6) CH_3COCl, (7) $SOCl_2$, (8) $POCl_3$ in 2 mL chloroform solutions.

CONCLUSION

In summary, we have rationally designed and synthesized an anthracene carboxyimide-based fluorescent chemosensor **AC-Phos** for visual detection of fatal phosgene, which could bind with phosgene to generate a significant color change from deep-red to orange and remarkable ratiometric fluorescence (F_{482}/F_{615}) enhancement (about 25-fold). **AC-Phos** could quantitatively determine the phosgene (0-70 μM) with good selectivity, high sensitivity, low detection limit (2.3 nM) and fast response (< 5 min). Furthermore, **AC-Phos** loaded polystyrene membrane was prepared to detect trace amounts of phosgene gas (20-90 ppm) over other nerve-gas mimics, which make it a portable, highly sensitive and selective colorimetric and fluorescent test kit for real-time visible detection of environmental phosgene gas.

ASSOCIATED CONTENT

*Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

Conflicts of interest

There are no conflicts to declare.

ACKNOWLEDGEMENTS

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