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An ESIPT Fluorescence Probe and a Nanofiber Platform for Selective and Sensitive Detection of a Nerve Gas Mimic

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An ESIPT based fluorescence probe, containing a hydroxyphenyl-benzothiazole fluorophore and an oxime reaction site, serves as a selective probe for the nerve gas mimic, diethyl cyanophosphonate (DECP), in solutions and the gas phase. The probe undergoes more than a 60-fold fluorescence enhancement in the presence of the target, has a limit of detection of 1.3 nM and displays high selectivity toward DECP over closely related substances, including sulfur mustard stimulants and other nerve agent mimic. Moreover, composite nanofibers with relatively low concentrations of the probe (0.45% w/w) undergo distinct color and fluorescence changes upon exposure to DECP vapor.

Members of the organophosphate family of compounds referred to as nerve agents were widely used as chemical warfare agents (CWAs).[1] When delivered as liquids, aerosols or vapors, these substances cause severe effects on human health. The deleterious effects are a consequence of the ability of nerve agents to stop acetylcholinesterase (AChE) activity by the phosphylation of its active serine residue, a critical central nervous system enzyme that hydrolyzes the neurotransmitter acetylcholine.[2] This inhibition results in an accumulation of acetylcholine at synaptic junctions, which blocks muscle relaxation. Sulfur mustard (SM) is a kind of powerful vesicant and has been used in wars since the beginning of the 20th century.[3] Due to the ability to alkylate the guanine nucleotide in DNA, it usually causes mutagenic, antimitotic, teratogenic and carcinogenic effects.[4] For this reason, nerve agents and sulfur mustard are serious threats to military personnel as well as to public health. As a result, the availability of practical methods for selective detection of these toxic substances with detection limits below the safety margin is of great importance.

To date, many efforts have been devoted to developing sensing systems for these substances, including those that rely on the use of gas chromatography (GC), high performance liquid chromatography (HPLC), surface acoustic waves (SAW), electrochemistry, interferometry and enzyme assays.[5] However, these traditional methods suffer from one or more limitations including the need for complicated sample pretreatment and expensive instrumentation, along with poor selectivity. In contrast, fluorescence probes for sensing nerve agents have received great attention owing to their operationally simple nature, naked eye detection capability, high selectivity and ability to detect these agents in living systems under special circumstances.[6] The commonly used fluorescence probes for detection of nerve agents have been designed using a number of different strategies such as those involving formation of cyclic quaternary ammonium salts,[7] direct phosphorylation reactions of amines or alcohols[8] and reactions that cause restricted bond rotation,[9] as well as those that rely on the "covalent-assembly" approach[10] and cyclization-induced emission enhancement (CIEE).[11]

In addition to the approaches listed above, strategies that take advantage of super nucleophilic oximate-containing substances,[12] especially salicylaldehyde oxime,[13] have attracted attention because of their high selectivity and pH-independence. However, these new methods also have disadvantages including the need for lengthy procedures for probe synthesis and generally high detection limits. More importantly, the potential of fluorescence probes to detect nerve agents in the gas phase is of prime importance. Thus, the development of efficient fluorescence probes that have high sensitivities and can be applied in a practical and inexpensive manner remains highly desirable.

Owing to their large Stokes shifts and high photostabilities, the familiar excited state intramolecular proton transfer (ESIPT) fluorophore, 2-(2'-hydroxyphenyl)-benzothiazole (HBT), has been widely used to construct fluorescent probes.[14] HBT derivatives are easily synthesized and functionalized. Inspired by previous studies in our laboratory and those of others, we designed the new benzothiazole based, nerve agent probe **1**, which contains a salicylaldehyde oxime group as the reactive site (Scheme 1). In the study described below, we demonstrated that the hydroxyl group in the oxime moiety undergoes nucleophilic substitution at the phosphorus (V) center of DECP, which promotes a large enhancement of fluorescence. Specifically, probe **1** in the solution state undergoes more than a 60-fold fluorescence enhancement upon addition of DECP with the detection limit as low as 1.3 nM. Moreover, we found that exposure of probe **1** composited filter

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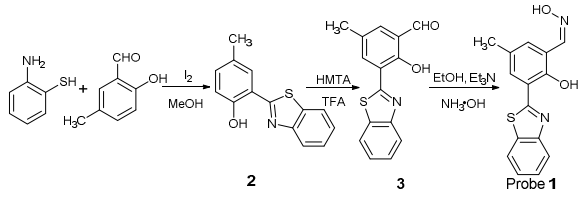
papers and spin coaters to DECP vapor also promotes a fluorescence enhancement. Finally, nanofibers, fabricated by using the electrospinning technique and containing relatively low concentrations of fluorescence probe **1**, can be employed to detect DECP vapor in a sensitive and practical manner. Herein, we wish to communicate the development of this effort.



Scheme 1. Synthesis of probe **1**.

As shown in Scheme 1, probe **1** was synthesized using a simple three-step sequence. Initially, intermediate **2** was prepared by I_2 promoted, benzothiazole forming, reaction between commercially available 2-aminothiophenol and 2-hydroxy-5-methylbenzaldehyde. The aldehyde moiety in **3** was then introduced using hexamethylenetetramine. Finally, probe **1** was generated by reaction of **3** with hydroxylamine in the presence of Et_3N. (Scheme 1 and Scheme S1). Notably, in this sequence both **2** and probe **1** are isolated in nearly pure form by using simple filtration and only **3** needs to be purified by using column chromatography.

The capability of using probe **1** to sense nerve agents was initially assessed using fluorescence spectroscopy, along with 100 equivalents of sulfur mustard stimulant (CEES), and various nerve gas mimic including diethyl methylphosphonate (DEMP), diethyl chlorophosphate (DCP), diethyl fluoridophosphate and diethyl cyanophosphonate (DECP). As shown in Figure 1, the free probe **1** displays weak fluorescence owing to photoinduced electron transfer (PET) from nitrogen in the oxime moiety to the benzothiazole fluorophore.[13c,13d,15,16] Only addition of DECP and none of the other nerve agents to a solution of probe **1** in DMF leads to a large enhancement in the intensity of the emission band at 480 nm.

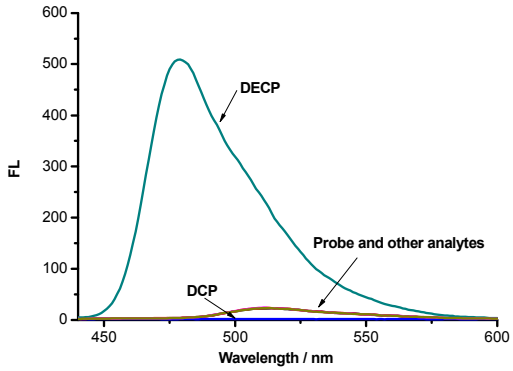


Figure 1. Fluorescence spectra of **1** (10 μM in DMF) was obtained upon additions of different never agents and sulfur mustard (1.0 mM) in DMF; λ_{ex} = 430 nm.

In order to investigate this response further, probe **1** (10 μM in DMF) was utilized to detect different concentrations of DECP in the range of 0-15 μM. In the presence of increasing concentrations of DECP, the intensity of the absorption band of **1** at 480 nm decreases in concert with a large increase in the intensity of a new peak at 450 nm (Figure S1). The DECP concentration dependent fluorescence spectral changes of probe **1** are displayed in Figure 2. Specifically, increasing concentrations of DECP induce increases in the intensity of the fluorescence peak of **1** at 480 nm. Unfortunately, a smaller Stokes shift (~30 nm) was observed as compare to the normally ESIPT fluorophores. It might result from the presence of the cyano group which will affect the acidity of the phenolic –OH group and disable the ESIPT process. Consequently, the emission was strongly hypsochromically shifted, which in turn led to a smaller Stokes shift.[17] Moreover, a linear relationship exists between the emission intensity at 480 nm and concentrations of DECP in the 0-2.5 μM range (Figure S2A). Finally, the detection limit of probe **1** for DECP was determined to be 1.3 nM based on the formula 3δ/k. Importantly, this detection limit for DECP is far lower than those of oxime-based probes for this nerve agent developed to date.[12b-12d,13] Moreover, in order to determine the photostability and response time of probe **1** for its reaction with DECP, time-dependent fluorescent response was determined. As shown by viewing the results in Figure S3A, addition of DECP (5 μM) to the DMF solution of probe **1** leads to a distinct fluorescence enhancement which reaches the maximum after 4 min. The pseudo-first-order rate constant (k_{obs}) of probe **1** with DECP is calculated as 1.1×10^{-1} min^{-1} based on the kinetic data (Figure S3B). As expected, the reaction rate can be correspondingly increased when higher concentration of DECP is used. In consideration of the real-world applications, sensing DECP in aqueous solutions was further investigated. As the results shown in Figure S4, upon additions of DECP, under the excitation of 410 nm, a remarkable fluorescence enhancement was also observed at approximately 480 nm. The results indicate that probe **1** can selectively detect nerve agent stimulant, DECP, in both organic solvents and aqueous media.

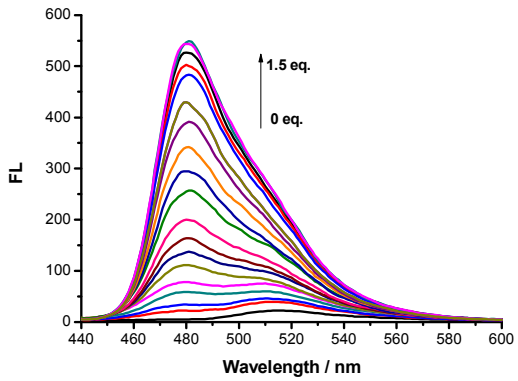


Figure 2. Fluorescence spectra of **1** (10 μM in DMF) was obtained upon additions of DECP (0-15 μM); λ_{ex} = 430 nm.

Based on previous reports describing mechanisms of reactions of the salicylaldoximes,[13a-13c] we propose that the chemical process responsible for sensing by probe **1** begins with nucleophilic phosphoryl substitution by the oxime hydroxyl group with expulsion of CN- (Scheme 2 and Scheme S2). The formed oxime OP ester **4** then undergoes phenolic hydroxyl group assisted phosphate elimination to generate the nitrile-containing product **6** via the benzisoxazole intermediate **5**. The electron withdrawing cyano group present in **6** is responsible for the advent of strong fluorescence because it inhibits the PET quenching process responsible for inefficient emission from **1**. In order to gain evidence for the proposed chemistry, **6** was isolated from the reaction mixture and its structure was assigned using ^1H and ^{13}C NMR spectroscopy. As the partial ^1H NMR spectra shown in Figure

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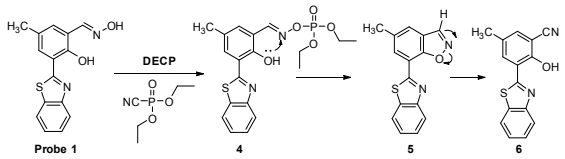
S5A, the characteristic resonance for the oxime CH=N and OH protons in the ^{1}H NMR spectrum **1** resonating at 8.41 and 11.65 ppm, respectively, are missing from the spectrum of product **6**. Moreover, the presence of the electron withdrawing cyano group in **6** promotes down-field shifts of the aromatic and *o*-hydroxyl proton resonances. HRMS was employed to further confirm that **6** forms in the reaction of an equimolar mixture of **1** with DECP (Figure S5B). The spectrum obtained on the reaction mixture contains a major peak at m/z 267.0603, which matches the calculated molecular weight of $[\mathbf{6}+H]^+$ (calcd 267.0592 for $C_{15}H_{11}N_2OS$).



Scheme 2. Sensing mechanism of probe **1** and DECP.

Encouraged by the solution sensing properties of **1**, experiments were conducted to assess the capability of using the probe to detect of DECP in the gas phase. Taking into account the positive features of probe systems that are both portable and operationally simple, we initially explored a filter paper based system. For this purpose, filter papers (0.5 cm x 1.0 cm) were immersed in dichloromethane solutions of probe **1** (0.1 mg /mL) and then air dried. As shown in Figure S6, upon exposure to DECP vapor (0-10 ppm), [7f] the non-fluorescent paper strips immediately emit yellow light when exposed to a 365 nm hand-held UV lamp. In addition, the spin coater system was also used to demonstrate the capability of using **1** to detect gaseous DECP. The fluorescence color of the **1** absorbed on a spin coater becomes gradually yellow when exposed to different amounts of DECP vapor and light from a UV lamp (365 nm) (Figure S7).

Electrospunfibers fabricated using electrospinning are considered to be one of the most effective platforms for high performance nano- and micro-scale sensing of a variety of target analytes.[18] Well-defined nanoscale based systems offer substantial benefits in the context of probes as a consequence of their higher sensitivities and portable nature. To assess the use of this technology for nerve gas sensing, we produced uniformly distributed, composite nanofibers that contain relatively low concentrations of probe **1** by utilizing the electrospinning technique and polyvinylpyrrolidone (PVP) as the matrix. The general scheme of the preparation for the composite nanofibers has been shown in the Figure S8. When the nanofibers are exposed to DECP vapor (10 ppm), both colorimetric (white to brown) and fluorescence (weak to strong yellow fluorescence) changes take place as shown in Figure 3.

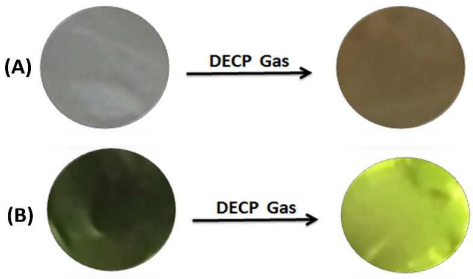


Figure 3. (A) Colorimetric and (B) fluorescence responses of **1**-composited nanofibers upon exposure to DECP gas (10 ppm) DECP gas.

Scanning electron microscope (SEM) imaging before and after exposure **1** composited nanofibers to DECP was carried out to probe surface changes promoted by gaseous DECP. As can be seen by viewing the images in Figures 4 and S9, before exposure to DECP, **1**-composited nanofibers have a typical morphology comprised of one-dimensional fibers with a broad range of diameters (100-700 nm) and a uniform texture. These observations confirm that molecules of **1** are homogenously distributed over the entire PVP polymer matrix. In contrast, after exposure to DECP the surface morphology of the **1**-composited nanofibers is dramatically changed into a rough two-dimensional film. The results suggest that reaction of **1** with DECP on a PVP polymer matrix leads to deformation of the original morphology driven by the severe aggregation among PVP polymer.

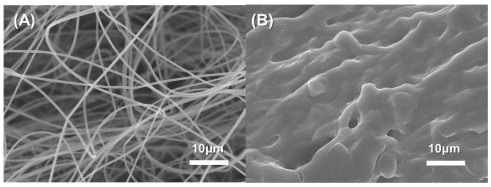


Figure 4. (A) Scanning electron microscope (SEM) images of probe **1**-composited on PVP nanofibers before (A) and after (B) exposure to DECP vapor (10 ppm).

Finally, confocal microscope imaging of **1**-composited nanofibers was carried out before and after exposure to DECP gas (Figure 5). Following exposure to DECP gas, the nanofiber emits strong yellow fluorescence in association with formation of cyano-containing product **6**. In contrast, the non-exposed nanofibers do not fluoresce (Figure 5A). These observations demonstrate that probe **1**-composited nanofibers have the capability of serving as a highly sensitive and compact DECP fluorescent probe.

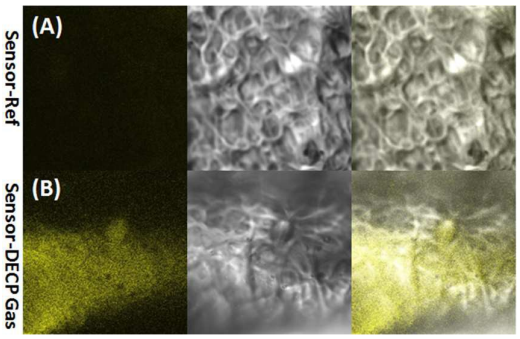


Figure 5. Confocal microscope images of probe **1**-composited nanofibers before (A) and after (B) exposure to DECP gas (10 ppm).

In conclusion, we have synthesized the ESIPT based probe **1** and demonstrated that it can be employed to detect the well-known nerve agent stimulant DECP in a simple, selective and sensitive manner. It is believed that reaction between probe **1** and DECP, resulting in transformation of the oxime group into a nitrile, is the cause of the remarkable fluorescence enhancement. The

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chemical process responsible for sensing was confirmed by using ^{1}H and ^{13}C NMR spectroscopy, and high resolution mass spectrometry. Notably, the high value of probe **1** is a consequence of its low detection limit of 1.3 nM, which is much lower than those of fluorescent probes utilizing salicylaldehyde oximes as the active sites. Moreover, filter paper strips and spin coaters containing composited probe **1** undergo dramatic fluorescence changes upon exposure to gaseous DECP. Finally, the highly efficient DECP sensing activity of **1**-composited nanofibers, containing a relatively low concentration of the probe, further demonstrates the utility of probe **1** in sensing of nerve agents in a simple and compact manner. As a kind of intelligent functional fibers which have attracted much attention in toxic reagent indicators, display, design accessories and protective equipment, the excellent colorimetric and fluorescent responses of **1**–composited nanofibers present the possibilities to produce multi-probe delivery systems with timed programmed release in biomaterials.

Notes and references

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