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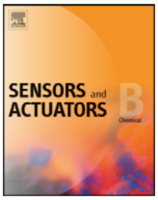

Imine-functionalized, turn-on fluorophore for DCP

Hyun Jung Kim[a], Seunghyun Jang[b], Wen Xiu Ren[a], Richard A. Bartsch[c], Honglae Sohn[b,*], Jong Seung Kim[a,*]

[a] *Department of Chemistry, Korea University, Seoul 136-701, Republic of Korea*
[b] *Department of Chemistry, Chosun University, Gwangju 501-759, Republic of Korea*
[c] *Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA*

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ABSTRACT

A monopyrene-imine derivative **1** is a highly selective and sensitive "turn-on" fluorogenic probe for diethyl chlorophosphate (DCP), a stimulant for organophosphorus nerve agents. Upon addition of DCP to a solution of **1**, a phosphoramidate was formed which exhibited an enhanced fluorescence emission at 425 nm. When exposed to DCP in the vapor phase, **1** impregnated on silica gel showed a sky-blue fluorescence.

1. Introduction

Today, chemical warfare agents are divided into two major categories: lethal agents (including nerve agents, vesicants, choking agents, and blood agents) and incapacitating agents [1,2]. Among them, nerve agents, a class of phosphorus-containing organic chemicals (Fig. 1) that disrupt the mechanism by which nerves transfer messages to organs, have been studied extensively due to their rapid and severe effects on human and animal health systems [3].

Many detection methods for nerve agents have been developed based on potentiometry [4], colorimetry [5], surface acoustic wave spectroscopy [6], gas chromatography/mass spectrometry [7], and interferometry [8]. However, these methods suffer from limitations, such as slow response, lack of specificity, limited selectivity, low sensitivity, operational complexity, non-portability, difficulties in real-time monitoring, or false positive readings [9a–d]. Therefore, simple and efficient detection methods for nerve agents remain of high interest.

Owing to their extremely hazardous nature of nerve agents, diethyl chlorophosphate (DCP) (Fig. 1) has been widely used in laboratories as a safe simulant since it displays a reactivity similar to those of nerve agents, such as Sarin, Soman, and Tabun, yet lacks their toxicity. Since DCP is hydrolyzed in water within a few minutes, a number of reported sensors for DCP were evaluated only in organic media, which limits their subsequent applications [9e–g].

2. Experimental

2.1. Instruments and reagents

Fluroescence and UV–Vis absorption spectra were recorded with Shimadzu RF-5301PC and Sinco S-3100 spectrophotometers, respectively. NMR and mass spectra were recorded with Varian (400 MHz) spectrometer and JMS-700 MStation mass spectrometer, respectively.

Reactants 1-aminopyrene and benzaldehyde and organophorphorus compounds of dichloro chlorophospate (DCP), pinacolyl methylphosphonate (PMP), dimethyl methylphosphonate (DMMP), triethylphosphate (TEP), and tributylphosphate (TBP) (Fig. 1) were purchased from Aldrich and used as received. All solvents were analytical reagent grade chemicals from Duksan Pure Chemical Co. Ltd. For fluorescence spectra, MeCN was HPLC reagent grade with no fluorescent impurity.

2.2. Synthesis

Compounds **1** [10a], **2** [10b], and **3** [10b] were prepared by adaptation of reported procedures.

Diethyl pyren-1-ylphosphoramidate **(6)**. To a solution of 1-aminopyrene (0.1 g, 0.46 mmol) in 100 mL of dried $CHCl_3$, diethyl chloro phosphate (0.07 mL, 0.46 mmol) was added. The reaction

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[*] Corresponding authors. Tel.: +82 2 3290 3143; fax: +82 2 3290 3121.
E-mail addresses: hson@chosun.ac.kr (H. Sohn), jongskim@korea.ac.kr (J.S. Kim).

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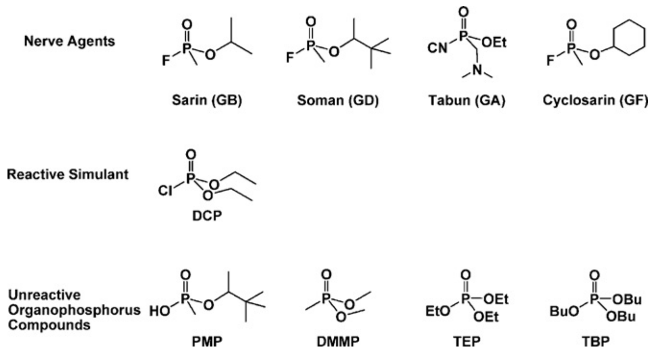


Fig. 1. Chemical structures of nerve agents, a reactive simulant, and other organophosphorus compounds.

mixture was stirred for 30 min, and then triethylamine (0.06 mL, 0.46 mmol) was added. The reaction mixture was stirred for an additional 2 h. The solution was washed with water, and the organic layer was dried over anhydrous $MgSO_4$. Removal of the organic solvent *in vacuo* afforded a yellow solid. Column chromatography on silica gel with EtOAc-hexane (1:3) as eluents gave 0.1 g (62.5%) of 6. M.p.: 110–115 °C; IR (deposit from CH_2Cl_2 solution on a KBr plate, cm^{-1}): 1204 (P═O). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.21–7.94 (m, 9H), 6.49 (d, J = 7.79 Hz, 1H), 4.14–4.30 (m, 4H), 1.28–1.35 (t, J = 7.02 Hz, 6H). FAB MS m/z (M^+) calcd 353.12, found 352.20.

2.3. Preparation of plate with 1 impregrated on silica gel

A 5 cm × 5 cm silica gel-coated commercial TLC plate including a phosphor was soaked with a THF solution of **1** (3.25×10^{-4} M). The coated plate was dried under vacuum. For some experiments, the letters DCP were cut into a thin piece of plastic film which was used to cover the impregnated silica gel.

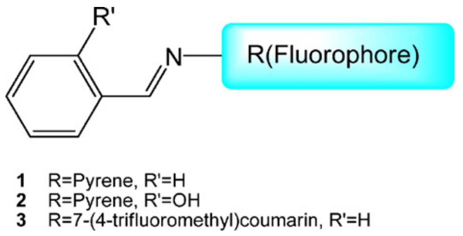
2.4. General procedure for fluorescence studies in solution

Stock solutions (10.0 mM) of the organophosphorus compounds were prepared in MeCN. Stock solutions of **1** (or **2** or **3**) (0.50 mM) were prepared in H_2O/MeCN (5/95, v/v). Titration experiments were performed with 3.0 μM solutions of **1** (or **3**) in H_2O/MeCN (5/95, v/v). Excitation by the Shimadzu RF-5301PC spectrofluorometer was at 382 nm (for **1** and **2**) and 360 nm (for **3**) with excitation and emission slit widths of 1.5 and 3 nm, respectively.

2.5. Instrumentation and procedure for sensing DCP vapor

All manipulations for sensing of DCP vapor were conducted in a well-ventilated fume hood. Fluorescence spectra were obtained with an Ocean Optics S2000 spectrometer fitted with a fiber optic probe. The excitation source was a UV LED (λ_{max} = 382) focused on the sample (at a 45° angle to the normal of the surface). Light was collected along the axis normal to the front surface of the sample with a microscope objective lens and focused onto a fiber optic. Spectra were recorded with a CCD-detector in the wavelength range of 400–900 nm.

The impregnated silica gel, glass-backed TLC plate was placed in a chamber fitted with transparent widows in which it was exposed to a flow of the carrier gas under consideration. The sample was exposed to a flux of DCP (partial pressure of 0.1 Torr or 1300 ppm) in wet air with a flow rate of 1 L/min.



Scheme 1. Structures of **1**–**3**.

3. Detection of DCP in solutions by 1

We have discovered that monopyrene-imine derivative **1** (Scheme 1) shows high selectivity and sensitivity for DCP as a fluorogenic "Turn-On" probe in both hydrous solutions and the vapor phase. Compound **1** was prepared by imination of 1-aminopyrene with benzaldehyde in EtOH. Imino compounds **2** and **3** have been reported in the literature [10b].

Absorption spectra of **1** in the presence of various organophosphorus compounds, including diethyl chlorophosphate (DCP), pinacolyl methylphosphonate (PMP), dimethyl methylphosphonate (DMMP), triethylphosphate (TEP), and tributylphosphate (TBP) (for structures see Fig. 1) in H_2O/MeCN (5/95, v/v), are shown in Fig. 2a. A solution of probe **1** gave a blue shift from 382 to 340 nm in the UV–Vis absorbance spectrum in the presence of DCP. In sharp contrast, the presence of the other organophorphorus compounds did not produce any significant changes under the same conditions. Fig. 2b presents the absorption changes of **1** in detail upon gradual

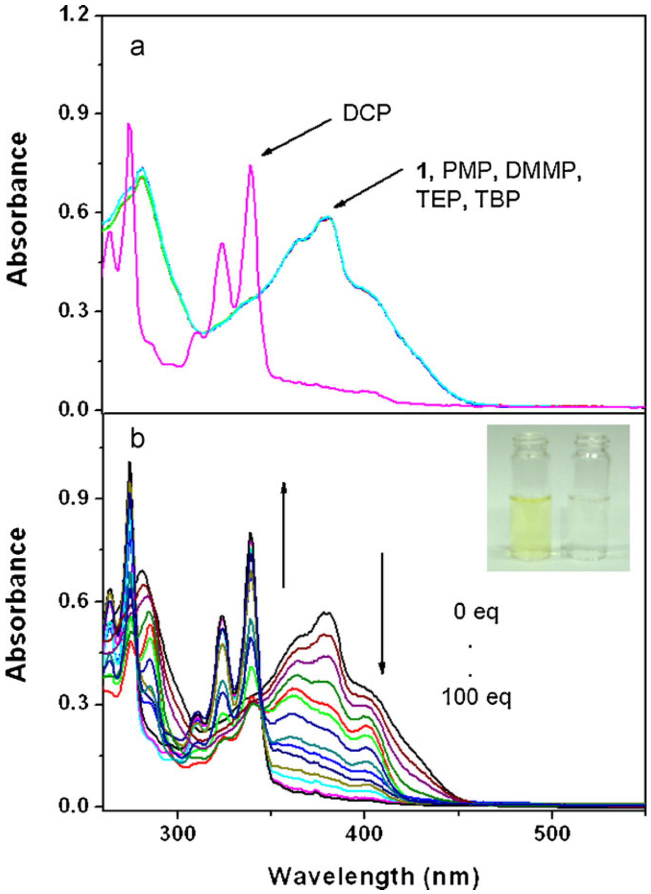


Fig. 2. (a) UV–Vis spectra of **1** (20.0 μM) in H_2O/MeCN (5/95, v/v) upon addition of DCP, PMP, DMMP, TEP, and TBP (10 equiv.). (b) UV–Vis titration spectra of **1** (20.0 μM) in H_2O/MeCN (5/95, v/v) upon addition of varying amounts of DCP.