

The portable detector of nitro-explosives in vapor phase with new sensing elements on a base of pyrimidine scaffold

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Abstract. In this paper, the new sensors based on the C(4) or/and C(5) mono(heteroaryl) and di(heteroaryl) substituted pyrimidines are described. The effect of different substituents in pyrimidine ring on the detection limits and selectivity for prepared sensors are explained. The results of detection towards various nitro-explosives and volatile interferents at room temperature with use of the portable detector “Nitroscan” are shown.

1. Introduction

Development of an efficient and cost-effective method for detection of nitroaromatic explosives is highly desirable, since there are considerable environmental and security needs, especially with the surge of international terrorism and an enhanced use of explosives in terrorist attacks [1-3]. There are a number of handled sniffers (sensors working as an artificial dog's nose) using advantage of materials which are capable of searching explosives through smell of these compounds [4]. The most famous artificial nose for nitroaromatics has been launched successfully into the market, as “FIDO” by Nomadics Inc [5]. “Nitroscan”, a Russian portable detector of nitro-explosives, has been designed and produced by “Promautomatika” Plant in collaboration with “UralProektAvtomatika” and “Security Intermolecular System” (Ekaterinburg, Russia) [6]. The main device functions are as follows: excitation of sensor element stationary luminescence and measuring its intensity in the absence of explosive vapors; registration of changes in the intensity of sensor element luminescence in time at the contact of its surface with explosive vapors; creation of external conditions for efficient interaction of the sensor element surface with explosive vapors. The device contains a ventilator for pumping air through the sensor element, an exciting luminescence light source, a photo element for luminescence intensity recording, an electronic tract, that converts the light flux into an electrical signal, the analog-digital converter and a microcontroller unit for control and display. Alarm on explosive detection is realized as a sound emitter and quantitative indicators are presented on the symbol display [7]. The development and investigation of new sensors for the device “Nitroscan” was the aim of our work.

2. Results and discussion

Recently, three types (A-C) of new push-pull dyes based on pyrimidines, bearing thiophene or/and phenyl linkers, have been studied as sensing fluorophores (figure 1). These compounds A-C have been



obtained by using a combination of the Suzuki cross-coupling and nucleophilic aromatic substitution of hydrogen (S_N^H) reactions [8-10].

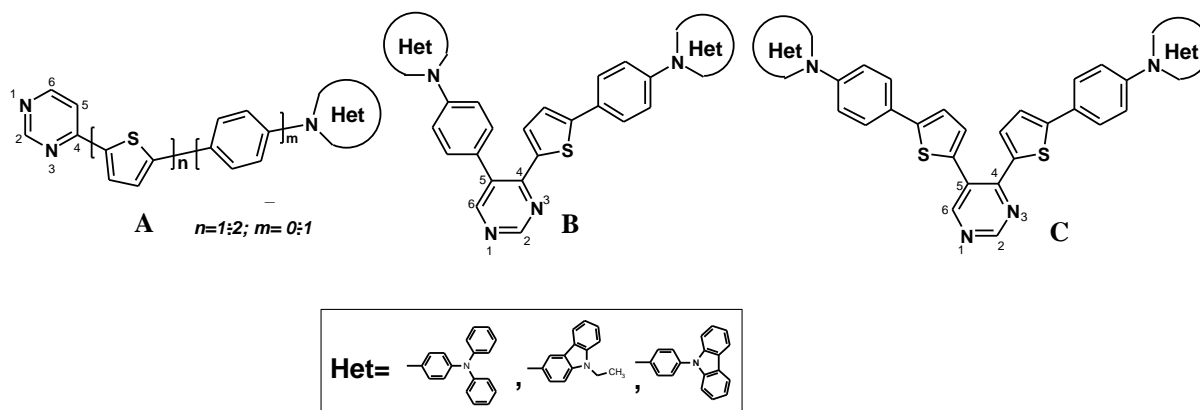


Figure 1. Molecular structures of the donor- π -acceptor organic dyes A-C on a pyrimidine scaffold.

To evaluate the utility of the fluorophores A-C for the detection of nitroaromatic explosives, the corresponding fluorescence measurements of the fluorophores A-C were carried out in acetonitrile solutions containing measured quantities of the compounds shown in figure 2, which serve as quenchers of the fluorescence.

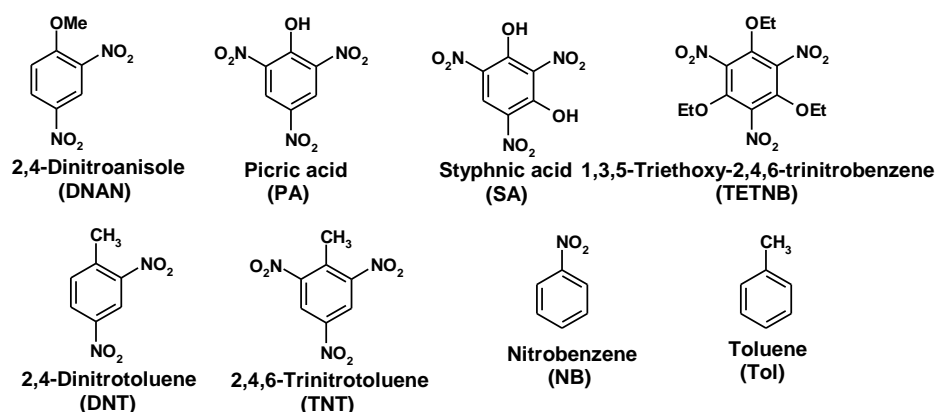


Figure 2. Structures of used quenchers and interferents.

Detection limits (DL) of the fluorophore to the analytes in acetonitrile solution were determined and calculated according to the following functions:

$$s_b = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (1)$$

$$S = \frac{\Delta I}{\Delta c} \quad (2)$$

$$DL = \frac{3s_b}{S} \quad (3)$$

Firstly, the standard deviation (s_b) was calculated by measuring the intensity of the fluorophore in the blank solution for more than 10 times and then the average intensity (\bar{x}) was obtained. By fitting

the data into Function 1, the value of standard deviation (S_b) was obtained. Secondly, a certain amount of analyte such as DNAN, PA, SA, TETNB, DNT, TNT, TATB, NB or Tol was added into the blank solution and the resulting variation of the intensity (Δc) was recorded. By fitting the data into function 2, where ΔI is the variation of intensity, and Δc is the variation of quencher concentration, the value of precision S was calculated. Finally the detection limit, DL, was calculated according to function 3. The ranges of detection limits for different nitroaromatic compounds are given in table 1.

Table 1. Detection limits (DL) of DNAN, PA, SA, TETNB, DNT, TNT, TATB, NB and Tol towards fluorophores A-C in CH_3CN .

Dye	DL ($\text{mol}\times\text{L}^{-1}$)							
	DNAN	PA	SA	TETNB	DNT	TNT	NB	Tol
A	-	5.8×10^{-6} $\pm 2.4\times 10^{-7}$	-	-	8.4×10^{-5} $\pm 1.2\times 10^{-6}$	1.7×10^{-4} $\pm 1.4\times 10^{-6}$	-	-
B	2.6×10^{-4} $\pm 1.2\times 10^{-5}$	1.7×10^{-5} $\pm 1.8\times 10^{-7}$	5.0×10^{-6} $\pm 2.1\times 10^{-6}$	1.1×10^{-4} $\pm 3.5\times 10^{-6}$	4.6×10^{-4} $\pm 3.6\times 10^{-5}$	2.0×10^{-4} $\pm 6.5\times 10^{-5}$	2.7×10^{-4} $\pm 4.3\times 10^{-5}$	-
C	2.0×10^{-3} $\pm 2.9\times 10^{-5}$	6.9×10^{-4} $\pm 4.0\times 10^{-5}$	7.15×10^{-4} $\pm 3.7\times 10^{-5}$	1.5×10^{-3} $\pm 4.7\times 10^{-5}$	5.4×10^{-4} $\pm 2.9\times 10^{-5}$	5.9×10^{-4} $\pm 3.0\times 10^{-5}$	1.3×10^{-4} $\pm 3.8\times 10^{-3}$	5.1×10^{-3} $\pm 1.1\times 10^{-4}$

As can be seen in Table 1, detection limits are decreased for fluorophores from type A to type C. We suggest that an additional aryl substituent at C(5) causes a significant steric hindrance which has to be proceeding at the neighboring C(4) position of the pyrimidine ring. This steric hindrance deteriorates interaction of fluorophore with quencher and also interrupts π -electron conjugation in push-pull system.

On a base of fluorescence measurements in acetonitrile solutions, the two best fluorophores (see figure 3) have been proposed for fabrication of sensors prototypes and their application in detecting of explosive vapors [9,10].

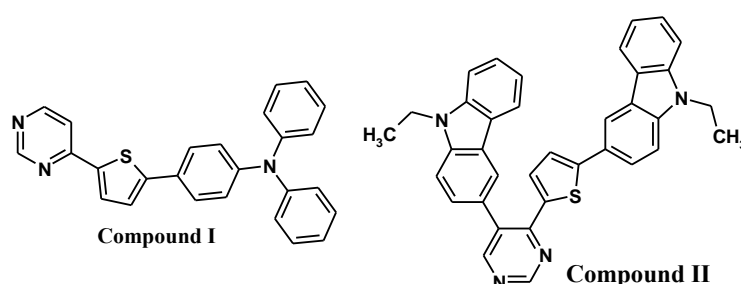


Figure 3. Structures of fluorophores I and II with the best data for detection limits in acetonitrile solutions.

For the fabrication of sensors, a non-woven dry wipe was used as a porous substrate (70% wood pulp, 30% polypropylene, Industrial Wipes purchased from Kunshan Yichen Clean Material Co., Ltd., China). A piece of the non-woven dry wipe (50 mm in diameter) was immersed in the fluorophore solution with a range of concentration: 1.0×10^{-3} (I or II), for 5 min. Then non-woven dry wipe or spunlace with immobilized fluorophore I or II was removed from the solution and dried at 70–80 °C for 30 min. To demonstrate its application as a fluorescence sensor for nitroaromatic compounds detection, the obtained non-woven dry wipe was placed in cartridges.

The resulted sensors have been used to detect nitrobenzene (NB) vapor in a hermetic glow-box (0.8 m \times 0.6 m \times 0.4 m) containing maximum permissible concentration (3 mg/m³) and also 0.3 and 0.03 mg/m³ of NB). It has been shown that all sensors are capable of fast reversible and reusable self-recovering after interruption of exposure to nitroaromatic explosive. Reversibility of the sensing

process for sensors on the basis of fluorophores **I** and **II** in NB vapor was examined by using the following procedure: the device bearing a sensor was inserted into a glow box with NB vapor with various concentrations for 25 s, and then the fluorescence intensity was recorded. After that, the device was removed from the box for 25 s, and the ambient room air was pumped automatically through the sensor in the device. The recovered emission intensity of the sensor was measured. The sensing and pumped process was repeated 3 times, and the results obtained are shown in figure 4. As can be seen, the recovered fluorescence intensity is decreasing with each next cycle but the quenching efficiency does not falls down to a 0 level even up to cycle 30.

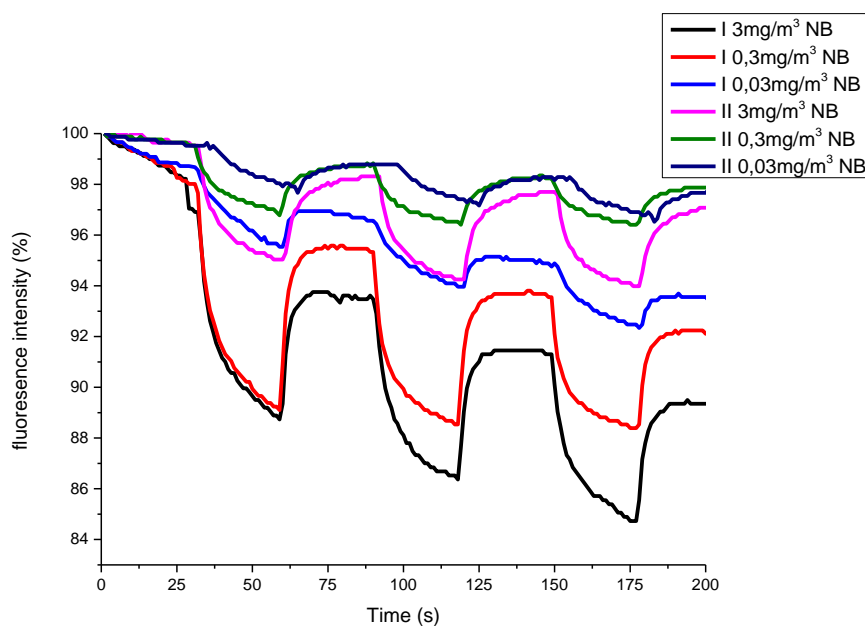


Figure 4. Fluorescent recovery cycles for the sensor on the basis of **I** and **II** in the device “Nitroscan” with exposure to nitrobenzene (NB) vapor with various concentrations.

In addition, both sensors **I** and **II** show a good selectivity to DNT in comparison with some other explosives [2,4,6-trinitrotoluene (TNT), 2,4,6-trinitrophenyl-N-methylnitramine (Tetryl), cyclotrimethylenetrinitramine (RDX), pentaerythritol tetranitrate (PETN)] and interferents, such as ethanol, ethylene glycol, acetone, acetic acid, toluene, nitrobenzene, phenol, and 1,2-dichlorobenzene (see figure 5), since their quenching sensitivities in these vapours are weaker than those in DNT.

3. Conclusion

In summary, fifteen dyes of the push-pull type on the basis of pyrimidines bearing various thiophene or/and phenyl linkers and various electron-donative fragments have been studied as sensing fluorophores. All dyes demonstrate high sensitivity towards nitroaromatic explosives. High fluorescence quenching response makes these fluorophores in vapour be promising fluorescence sensor materials for nitroaromatic explosives with the detecting limit of $\sim 10\text{--}11\text{ g/cm}^3$, as estimated in experiments with NB by utilizing the portable detector “Nitroscan”.

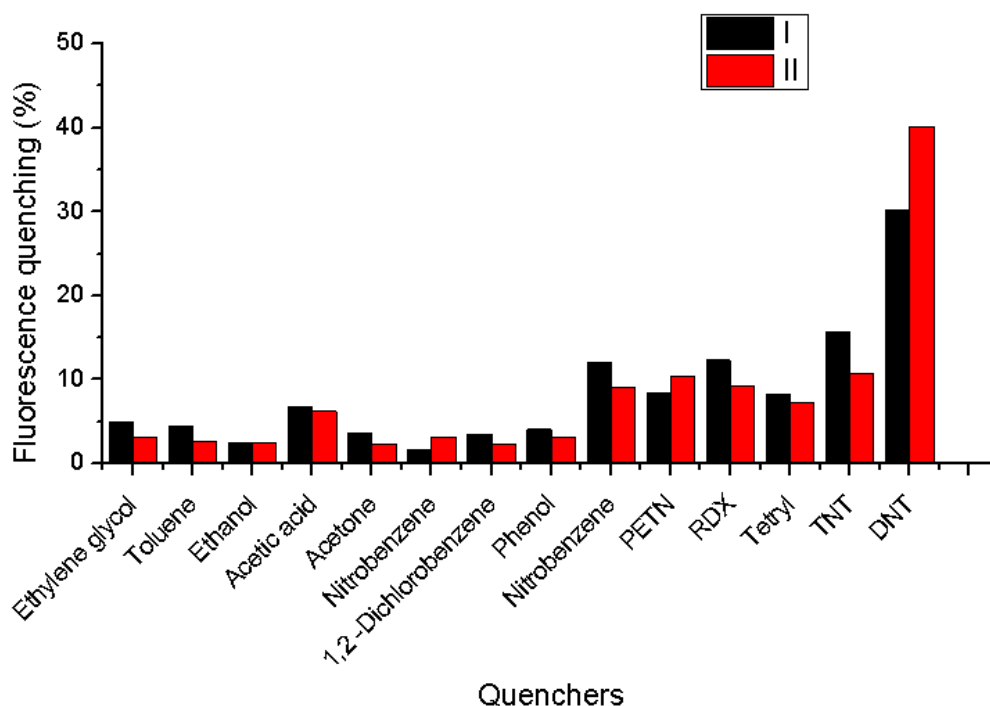


Figure 5. Sensor's I and II fluorescence quenching (%) in the first cycle towards various nitro-explosives and volatile interferents at room temperature.

Acknowledgements

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