Central European Journal of Energetic Materials, **2009**, *6*(3-4), 303-311.
ISSN 1733-7178

Fluorescence Analysis as an Effective Method Used in Micro/Trace Explosive Detection

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Abstract: There are many kinds of explosives, and their detection methods vary. Nitroaromatic compound is one of the composition of the explosives commonly used. The fluorescence will be quenched when they touch the fluorescent conjugated polymers. General methods for explosives detection have been summarized in this paper, in addition the application of novel fluorescence analysis technique in explosives detection has been introduced. Fluorescent conjugated polymer as chemical sensing material for explosive detection has been reviewed in detail, also a novel fluorescent sensing film self-assembled by fluorescent small molecule pyrene and homogeneous fluoroimmunoassay have been presented briefly. The development of fluorescence analysis used in the area of determining explosives has been prospected.

Keywords: micro/trace explosive detection, fluorescence analysis, conjugated polymer, sensing materials

Introduction

In recent years, as a whole the international situation is stable, whereas local war still going on. Since the terrible incident taking place in America on September 11, 2001, necessary measures have been taken in various countries,

in order to cope with the terrorism. Baggages should be checked in the frontier inspection station and the airport, so as to make sure whether there are explosives or not. Any way, explosives are dangerous and their usage ought to be restricted. Therefore, the job of detecting explosives is important and necessary during the security inspection.

There are many kinds of explosives, and their detection methods vary. Each method just has the ability to determine a certain class or part of explosives. So far, there is no method which could determine all kinds of explosives accurately without mistakes. With the development of the general methods used for detecting explosives, novel technologies appear, such as fluorescence analysis technique. This method has many advantages, namely speed, demanding little of sample and high sensitivity. More and more researchers show greatly interest in it, and more countries focus on this area.

Nowadays, fluorescence analysis technique used for detecting explosives has been investigated by many countries and institutes, such as Massachusetts Institute of Technology (MIT). Michigan State University, Naval Research Laboratory, Jilin University and Shan xi Normal University. Especially, at MIT Swager and his co-workers have great achievements on explosive detection, also their research results attracted more attention.

Techniques of explosive detection

2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene(2,4-DNT) and 2,6-dinitrotoluene (2,6-DNT) are ingredients of most explosive formulations, which are aromatic compounds containing several nitro groups. Besides TNT, there are other explosives, such as picric acid, potassium nitrate, peroxide, azides, ammonium nitrate and so on. Explosive is a hidden danger to human beings and the environment, so it is necessary to develop new techniques for explosives detection.

General methods for explosive detection

General methods for detecting explosives have been used widely in daily life, including neutron detection technique [1, 2], X-ray method [3], chromatography [4] and so on. Recent activity at the US Naval Research Laboratory resulted in a portable fiber-optic competitive immunosensor for rapid on-site detection of TNT [5].

General methods have both advantages and disadvantages. For example, cumbersome and expensive instruments based on X-ray imaming or thermal neutral analysis have been introduced for the detection of hidden explosives [6]. In addition, the chromatographic techniques are commonly used for laboratory measurements of explosives in water samples [7, 8]. Several methods are taken into practice to assure the results reliability. If there has suspicious substance in the baggage, samples will be taken for further study.

Novel technique of fluorescence analysis for explosive detection

Fluorescence analysis technique for detecting explosives has been developed in the last few decades. Analysis technique based on fluorescence has many features: high sensitivity and selectivity, speed, good reproducibility, easily sampling and needing fewer samples. Therefore, this method is especially suitable for micro/trace explosive detection. Fluorescence analysis technique would be applied to explosive detection, and it is a new trend in this area.

Conjugated polymers detection technique based on fluorescence

With unique semiconducting and photoelectrical properties, conjugated polymers have been explored for a wide range of novel applications, such as organic light emitting diodes [9], the film transistors [10], solar cells [11], as well as chemosensors [12, 13]. More and more researchers show great interest in studying conjugated polymers, which contain fluorophore in its structure.

The principle of conjugated polymer detection technique

The electron cloud of conjugated polymers surrounds together, so the electrons tend to come in or out this system, when conjugated polymers contact the analyte. As a result, the distribution of electron cloud of the polymer would change greatly. Swager and his co-workers [14] assume that "molecular wire effect" may exist in conjugated polymers, when electron transfer occurs in the conjugated system. The special "molecular wire effect" has the ability to amplify the signals from sensors, without changing functional groups in its structure and altering identification molecules binding constant, i.e., "one point touch, multi-point response" [15].

Fluorescence intensity changes acutely in fluorescent conjugated polymers, because of their amplification effect. When nitroaromic explosives contact with the conjugated polymers, charge transfer will occur between the electron-rich polymers and the electron-poor nitroaromatic quenchers. After the binding sites

in conjugated polymers are occupied by nitroaromic explosive molecules, the electrons could not transfer any more, so the fluorescence intensity of the system decreases sharply.

The application of conjugated polymer in explosive detection

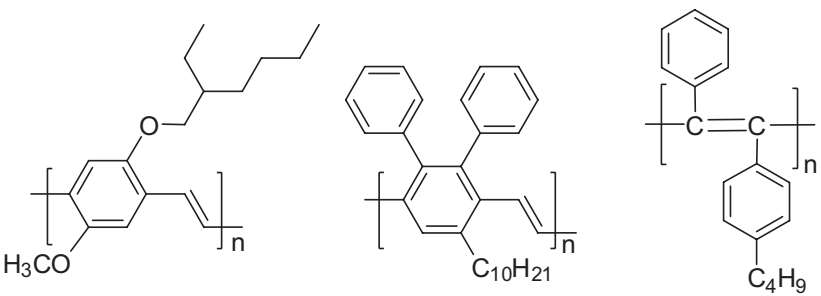

Figure 1. Chemical structure of typical conjugated polymers [16].

The fluorescent quenching response between three typical conjugated polymers (see Figure 1) and the explosives (TNT, 2,4-DNT, 2,6-DNT) and benzo quinone have been investigated by Chang and his co-workers [16]. Results show that MEH-PPV [17], DP10-PPV [18] and BuPA [19, 20] display high sensitivity to TNT and other explosives. The fluorescence quenching percentage of MEH-PPV, DP10-PPV, and BuPA films (25Å) to TNT by 1200 s, is 91%, 70% and 54% respectively. It means that these polymers are potential candidates chemosensor materials for detecting landmines. The sensitivity of fluorescence quenching by analytes depends on factors, such as the solubility parameters, the interchain charge transfer quenching the exciton and the binding strength (polymer-analyte interactions). High fluorescence quenching implies that polymer thin films should have adequate porosity or free volume to accommodate TNT-like small molecules.

An artificial porous polymers **2** has been reported (shown below) by Yang et al. [21]. It contains the rigid three-dimensional pentiptycene moieties **1** [22-24], which prevent π-stacking or excimer formation. **3** is the porous planar polymer.

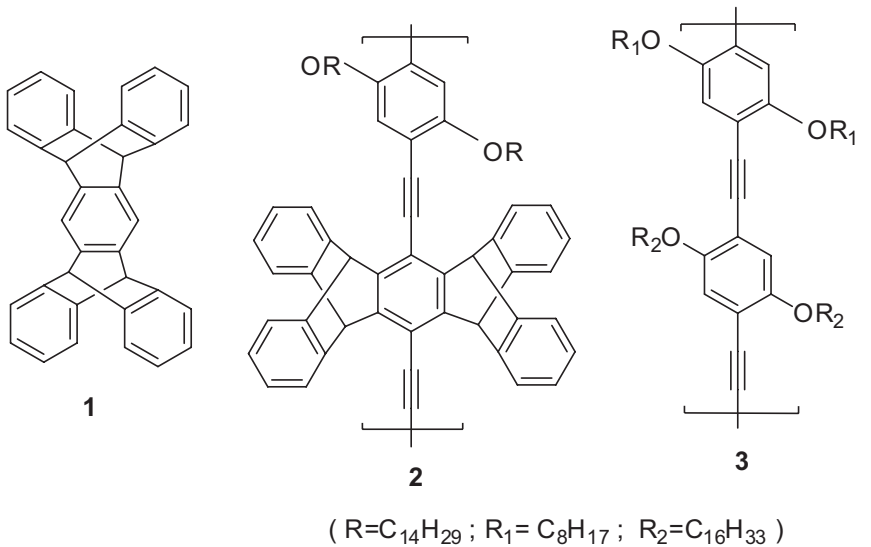

Figure 2. The rigid three-dimensional pentiptycene moieties 1, Porous shape fluorescent polymers **2** and **3** [21].

It can be concluded that solubility of **2** is 100 times larger than that of **3** in organic solvents. The fluorescence quantum yield of **2** is 3.5 times larger than that of **3** in the thin films. Results show that pentiptycene polymer **2** display enhanced fluorescene quantum yield and stability.

The porous property of pentiptycene polymers has been reported by Swager [12, 14, 21]. Many advantages gain when polymers contain the rigid three-dimensional pentiptycene moieties. First, they prevent π-stacking of the polymer backbones and thereby maintain high fluorescence quantum yields and spectroscopic stability in thin films. Second, reduced interpolymer interactions dramatically enhance the solubility of polymers. Third, the cavities generated between adjacent polymers are sufficiently large to allow diffusion of small organic molecules into the films.

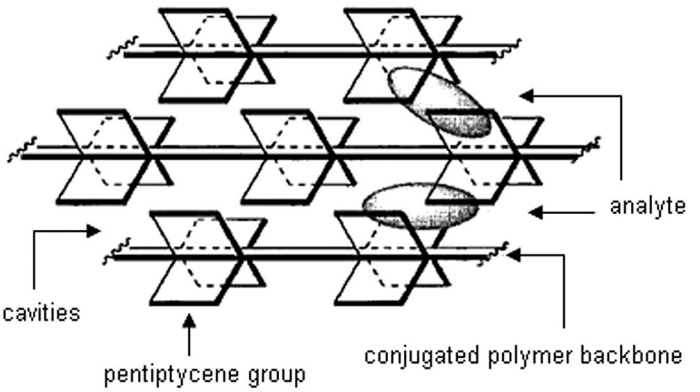

Figure 3. Schematic illustration of polymers containing pentiptycene group and resulting porous structure [12, 14, 21].

The author used a SPEX fluorolog-τ2 fluorometer (model FL112, 450 W xenon lamp) for fluorescence studies. Preparation of polymer materials and testing methods were introduced in the literature [12].

Characteristics of fluorescent conjugated polymers used for detecting explosive

Fluorescent conjugated polymers quickly quench their fluorescence and display high sensitivity to analytes, such as TNT, when the vapor of explosive comes across the thin film, due to its "molecular wire effect". Gao et al. [15] pointed out that the molar extinction coefficient of fluorescence conjugated polymers could be 10^6 L·mol^{-1} cm^{-1}, and the electron transfer or energy transfer occurs within femto-second. The shortcoming is that these polymers just response quickly to nitroaromic explosives, therefor other kinds of explosives may not be available.

Technique of small fluorescent molecule pyrene in explosive detection

Preparation of fluorescent films by multi-step reactions and self-assembled on glass have been investaged by Li et al. [25]. This film was made from pyrene and linking groups containing triethyltetramine moieties. As a result, many factors affect the response sensitivity between films and nitroaromic explosives, such as the length of linking groups, the vapor saturated pressure and molecular volume of nitroaromic compounds. Larger vapor pressure and molecular volume can enhance the speed of fluorescence response between fluorescent

films and nitroaromatic compounds. The detection limit is 7.14×10^{-12} g/ml and 5.49×10^{-11} g/ml respectively, when the films contact with TNT and 2,4-DNT in air.

Technique of homogeneous fluoroimmunoassay in explosive detection

Goldman et al. [26] used homogeneous fluoroimmunoassay to determine the concentration of TNT in solid and water samples. The principle of this method is that the fluorescence intensity in the system decreases sharply, when TNT combines with anti-TNT antibody which was labeled by fluorescent substance. The process is shown in Figure 4.

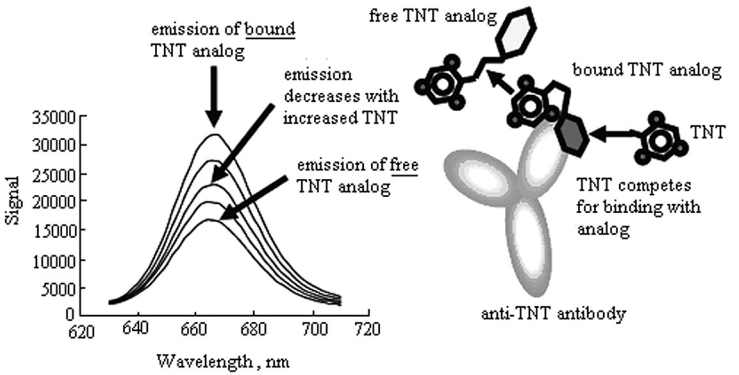

Figure 4. Schematic illustration of fluorescent emission decreases as the antibody binds TNT in place of the fluorescent TNT analogue [26].

It can be concluded that the fluorescence-emission is the strongest in this system, when TNT combines with anti-TNT antibody. As TNT analog competes with TNT, fluorescence intensity decreases. Methods of homogeneous fluoroimmunoassay and HPLC had been studied by the author, in order to determine the concentration of TNT in the same samples. They analyze the data by linear regression analysis and relative percentage difference (RPD). The correlation coefficient of the data from two methods is 0.9997 by linear regression analysis. RPDs ranged from -28% to 22%. These results indicate a good agreement between the two methods.

In a word, lots of methods are used to detect explosives, and each one has its merits and shortcomings. With the development of the techniques, it is a new trend to use fluorescence analysis technique for explosives detection.

Prospect

More and more researchers show great interest in fluorescence analysis technique used for micro/trace explosive detection. Preparation of polymer is easy, so fluorescent conjugated polymers are potential chemical sensing materials in explosive detection. Preparing fluorescence material with excellent performance is the key point to put it into practice. Conjugated polymers with cavities, which can transfer the electrons effectively between the polymers and the analytes, may be feasible. Works should be done by this principle. This kind of polymers would make the instrument miniaturization, display high sensitivity and meet with the needs of on-line detection.

Acknowledgments

The authors gratefully acknowledge fund support from Institute of Chemical Materials No. 626010926 and No. 626010917.

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