

TECHNICAL NOTE

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Visual Detection of Trace Nitroaromatic Explosive Residue Using Photoluminescent Metallole-Containing Polymers

ABSTRACT: The detection of trace explosives is important for forensic, military, and homeland security applications. Detection of widely used nitroaromatic explosives (trinitrotoluene [TNT], 2,4-dinitrotoluene [DNT], picric acid [PA]) was carried out using photoluminescent metallole-containing polymers. The method of detection is through the quenching of fluorescence of thin films of the polymer, prepared by spray coating organic solutions of the polymer, by the explosive analyte. Visual quenching of luminescence ($\lambda_{em} \approx 400\text{--}510\text{ nm}$) in the presence of the explosive is seen immediately upon illumination with near-UV light ($\lambda_{ex} = 360\text{ nm}$). Detection limits were observed to be as low as 5 ng for TNT, 20 ng for DNT, and 5 ng for PA. In addition, experiments with normal production line explosives and their components show that this technology is also able to detect composition B, Pyrodex[®], and nitromethane. This method offers a convenient and sensitive method of detection of trace nitroaromatic explosive residue.

KEYWORDS: forensic science, explosives, TNT, fluorescence, luminescence, metallole polymers, explosives detection, trace explosives, explosives residue

The interest in explosives detection is important for forensic investigation (1), military applications (2), minefield remediation (3), and homeland security purposes (4). The effort to detect trace explosive residue is made more compelling given the rising threat of global terrorism. After the collapse of the Soviet Union, a large black market for explosives, particularly military-grade trinitrotoluene (TNT), developed in central and southern Europe (5). In addition, TNT is an inexpensive component of at least 15 other explosive blends (6). For instance, tritonal is a mixture of TNT and Al powder, amatol is a mixture of TNT and ammonium nitrate, pentolite is a mixture of TNT and PETN, and composition B is a blend of TNT and RDX. The widespread use and availability of TNT makes it an explosive of concern, and subsequently makes it an important target molecule for detection.

There are several physical methods for trace detection of nitroaromatics with low detection limits. These include gas chromatography coupled with mass spectrometry (7), gas chromatography-electron capture detection (3), surface-enhanced Raman spectroscopy (8), mass spectrometry (9), and ion mobility spectrometry (IMS) (10). These methods lack the ability to be manufactured into an inexpensive, low-power portable device for *in situ* detection. In addition, many are limited to sampling the vapor phase, which is problematic given the low volatility of many explosives. For instance, the vapor pressure of TNT (5 p.p.b. (11) at room temperature) may be up to six times lower when

enclosed in a bomb or mine casing or when present in mixtures with other explosives (12). For this reason, solid-state sensing may be desirable for trace residue detection on contaminated surfaces. It is known that trace amounts of explosives often adhere to the surface of packaging materials and clothing present when preparing explosive devices. One commercially available solid-state detection kit is ExPray (Plexus Scientific, Alexandria, VA), which is a three-step colorimetric explosives detection system for a wide range of explosive compounds, with sensitivity purported down to the tens-of-nanogram level; however, performance evaluation tests by Sandia National Laboratories show a practical detection level for TNT at 200 ng, and many false positives are known to occur (13).

Nitroaromatics, such as trinitrotoluene, are oxidizers due to a low-energy unoccupied π^* orbital, which can accept an electron from the excited state of luminescent polymers (14). The detection of nitroaromatic vapor has been achieved using fluorescent polymers, including various functionalized organic polyacetylenes (15), polyphenylenevinyls (16), and polyphenyleneethynyls (17), as well as inorganic polysilanes (18) and polymetalloles (19). Polymetalloles have been shown to detect nitroaromatics in organic solution (19), and nanoparticles of polysilole can detect TNT in aqueous media (20) through electron-transfer photoluminescence quenching. Reported herein is the visual detection of trace residue on surfaces of the nitroaromatics TNT, 2,4-dinitrotoluene (DNT), and picric acid (PA) using thin films of luminescent metallole-containing polymers. Detection limits as low as 5 ng are observed. Polymetalloles have the advantage of being inexpensive, easily prepared, and their application uses simple equipment readily fielded for on-site explosives detection.

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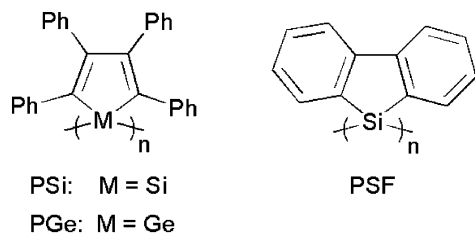


FIG. 1—Chemical structures of polymetalloles.

Methods and Materials

Polymer Syntheses

Polysilole (PSi) and Polygermole (PGe)—PSi and PGe were prepared according to the literature (19, 21). The structures of these polymers are shown in Fig. 1. The λ_{max} of emission for PSi and PGe are 510 nm and 500 nm, respectively, at $\lambda_{\text{ex}} = 360$ nm.

Poly(1,4-Diethynylbenzene)2,3,4,5-Tetraphenylsilole (PDEBSi), Poly(1,4-Diethynylbenzene)2,3,4,5-Tetraphenylgermole (PDEBGe), Poly(1,4-Diethynylbenzene)Silafluorene (PDEBSF), and Polysilafluorene (PSF)—These compounds were prepared by catalytic hydrosilation of diethynylbenzene (22). The structures of the copolymers are shown in Fig. 2, and a short-chain oligomer PSF is shown in Fig. 1. At $\lambda_{\text{ex}} = 340$ nm, the emission maxima are as follows: PDEBSi (495 nm), PDEBGe (475 nm), PSF and PDEBSF (360 nm).

Laboratory Explosives

The method of explosives detection is through luminescence quenching of the polymetalloles by the nitroaromatic analyte. Three common explosives were tested: TNT, DNT, and picric acid. Stock solutions of the explosives were prepared in toluene. Three aliquots (1–5 μL) of the stock (containing 5–100 ng analyte) were syringed onto either Whatman[®] (Middlesex, U.K.) filter paper or a CoorsTek[®] (Golden, CO) porcelain spot plate and allowed to dry completely, along with one aliquot of a toluene blank to serve as a control. The spots were between 3 and 10 mm in diameter, producing a surface concentration of not more than 64 ng/cm² and not less than 17 ng/cm². Solutions of the polymers (0.5–1% w:v) were prepared in acetone (PSi, PGe), 1:1 toluene:acetone (PDEBGe), 2:1 toluene:acetone (PDEBSi, PSF), or toluene (PDEBSF). A thin film of a polymer, amounting to approximately 2.5 $\mu\text{g}/\text{cm}^2$ was applied to the substrate by spray coating a polymeric solution with an air brush onto the substrate and air drying. The coated substrates were placed under a black light ($\lambda_{\text{ex}} \sim 340$ nm) to excite the polymer fluorescence. Dark

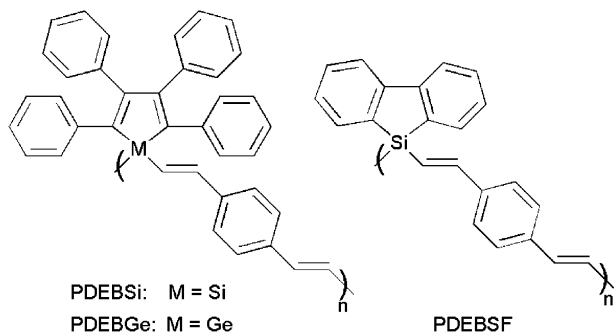


FIG. 2—Chemical structures of copolymers of metalloles and diethynylbenzene.

spots in the film indicate luminescence quenching of the polymer by the analyte.

Illuminated plates were examined by an independent observer to determine whether quenching was discernible. Detection limits are reported as the lowest amount of explosive necessary for the independent observer to notice quenching visually. The blind detection study was carried out five times for the three explosive analytes with each polymer on both substrates. Digital images were recorded with a Canon Powershot 110 2.0 megapixel digital camera (Canon Inc., Tokyo, Japan), or a Sony 2.0 megapixel digital camera (Sony Corporation, Tokyo, Japan) as black and white images. No representative images of the silafluorene polymers (PSF and PDEBSF) were obtained due to their low fluorescence yield in the visible spectral region and the difficulty of imaging deep blue emission with the use of a conventional digital camera.

Production Line Explosives

The ability of the polymers PSi and PDEBSi to detect normal production line explosives and their components through luminescence quenching was also researched at a Department of Defense-approved explosives testing range operated by NEWTEC Services Group Inc. The nitro-based explosives tested were TNT, Comp B, Pyrodex[®] (Hodgdon Powder Co., Shawnee Mission, KS), and nitromethane. Contaminated filter paper samples were prepared by contacting a gloved hand with an explosive (either solid, pellet, or powder form, or liquid swab for nitromethane), removing the excess on the glove, and then contacting the filter paper. Alternatively, thumb print samples were prepared by contacting a bare thumb to the explosive, and then contacting the contaminated thumb to filter paper 5 successive times. A thin film of a polymer was applied to the filter paper by airbrushing an acetone or toluene solution, and quenching was visually observed under near-UV illumination from a black light.

Results and Discussion

Laboratory Explosives Detection

The detection of nanogram quantities of the explosives is possible using thin films of the luminescent polymers. Detection is achieved through luminescence quenching by the nitroaromatics. The silole and germole polymers fluoresce green, with λ_{max} of emission at 510 nm for PSi, 495 nm for PDEBSi, 500 nm for PGe, and 475 nm for PDEBGe. The metallole rings of the silafluorenes, PSF and PDEBSF, are functionalized differently from the siloles and germoles, which results in λ_{max} of emission at 360 nm. Illumination with near-UV radiation from a black light ($\lambda_{\text{ex}} \sim 340$ nm) excites the fluorescence of all polymers. The blue luminescence of the silafluorenes is weak in the visible, 390–420 nm, but is sufficient to observe quenching by eye. Luminescence quenching in the presence of the explosives is observed immediately upon illumination. The polymers are photodegradable, however, and luminescence begins to fade after a few minutes of continual UV exposure. Regardless, detection of the explosives is effected immediately. Figure 3 shows sample black and white digital images of the luminescence quenching of four polymers by TNT observed on a porcelain plate, at TNT concentrations of 200, 100, 50, and 10 ng, respectively. Quenching was observed at 10 ng for each polymer. Figures 4 and 5 show photoluminescence quenching on porcelain plates of the same four polymers by DNT and PA, respectively, at the same analyte concentrations. Quenching was observed as low as 50 ng for all polymers. Detection

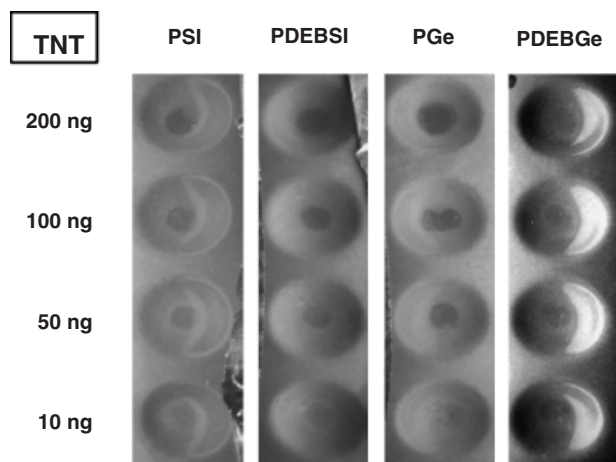


FIG. 3—Luminescence quenching of polymers polysilole (PSi), poly(1,4-diethynylbenzene)2,3,4,5-tetraphenylsilole (PDEBSi), and polygermole (PGe), by 200, 100, 50, and 10 ng trinitrotoluene (TNT) on porcelain plates.

limits depend on the nitroaromatic analyte, the substrate (porcelain or filter paper), and on the polymer used. Table 1 summarizes the detection limits of TNT, DNT, and PA using the six metallole-containing polymers synthesized—PSi, PDEBSi, PGe, PDEBGe, PSF, and PDEBSF.

Visual detection studies were performed by preparing substrates that were spotted four times, including three spots of an explosive solution and one spot of a solvent blank. An independent observer was asked to identify dark spots in the polymer thin film. Detection studies were performed for each explosive at each contamination level (50, 40, 30, 20, 10, and 5 ng). Detection limits were noted as the lowest concentration of explosives that enabled the independent observer to notice quenching. The probability of detection is reported as the probability that the independent observer was able to identify quenching correctly in the areas of explosives contamination. The false-positive rate is defined as the probability that the independent observer identified quenching in an area without contamination. The detection limits depend on the quality of the polymer thin film. High-quality films evenly cover the substrate surface and have a uniform thickness. Poor-quality films are characterized by an uneven coverage that may lead to either areas of higher concentration, or areas lacking full coverage of the polymer. Under UV light, these nonuniform films luminesce

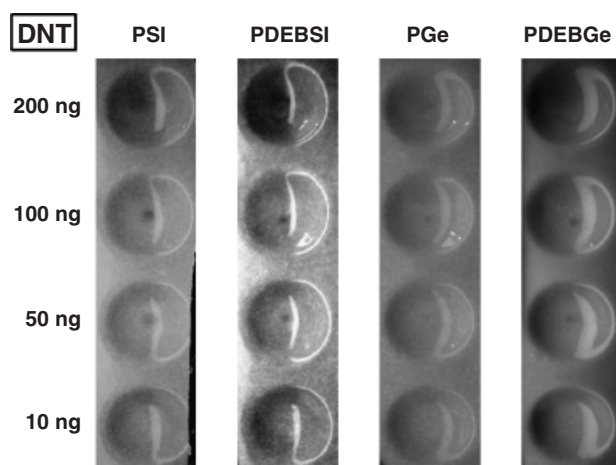


FIG. 4—Luminescence quenching of polymers polysilole (PSi), poly(1,4-diethynylbenzene)2,3,4,5-tetraphenylsilole (PDEBSi), and polygermole (PGe), by 200, 100, 50, and 10 ng dinitrotoluene (DNT) on porcelain plates.

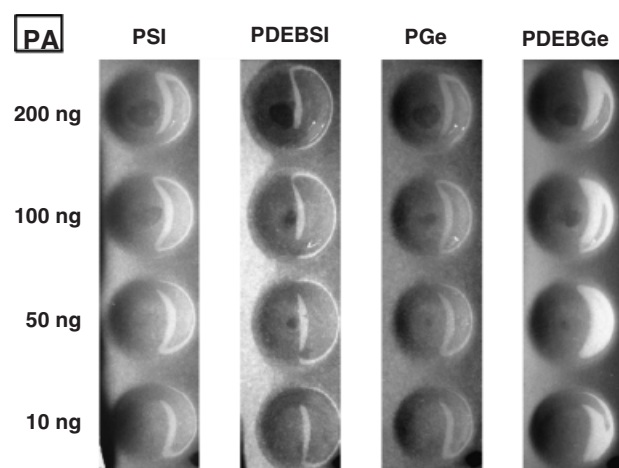


FIG. 5—Luminescence quenching of polymers polysilole (PSi), poly(1,4-diethynylbenzene)2,3,4,5-tetraphenylsilole (PDEBSi), and polygermole (PGe), by 200, 100, 50, and 10 ng picric acid on porcelain plates.

unevenly. Film quality depends on the concentration of the polymer in solution and the quality of the airbrush. The independent observer was able to identify correctly the presence of explosives at the detection limits reported in Table 1, on average for all analytes, more than 75% of the time when film quality was poor, with an approximate false-positive rate of 10%. However, in cases when high-quality, uniform films are prepared, quenching is more clearly discernable. A probability of detection >90% was obtained at the detection limits reported in Table 1; probabilities of detection at the detection limit are also listed parenthetically in Table 1. At contamination levels 10 ng above the reported detection limits, 100% probability of detection was achieved, with no false positives.

In all cases, the detection limit of the explosives was as low or lower on the porcelain surface than on paper. This is not surprising as the dissolved analyte may be carried deep into the paper fibers during deposition, thus lowering the amount of explosive analyte available on the surface after solvent evaporation. Less explosive would therefore be present to visibly quench the luminescence from the thin film of polymer on the surface. This situation will be less of a problem in real applications, because explosive traces are expected to be in the form of residual particulates transferred from the solid phase rather than by deposition from solution.

As the method of detection is through electron-transfer luminescence quenching of the polymer luminescence by the analytes, the ability of the polymers to detect explosives depends on the oxidizing power of the analytes. The oxidation potentials of the analytes follow the order TNT > PA > DNT. Both TNT and PA have three electron-withdrawing nitro substituents on the aromatic ring that account for their higher oxidizing and quenching potential relative to DNT, which has only two nitroaromatic substituents. PA has a lower oxidation potential than TNT due to the electron-donating power of the hydroxy substituent.

Fluorometric detection is highly sensitive, and these polymers offer a method to detect nitroaromatic explosives at detection limits lower than those obtained from performance evaluation tests using the colorimetric detection system ExPray. The first step in the ExPray system detects nitroaromatics, while the second and third steps encompass nitramines, nitrate esters, and inorganic nitrates. One advantage of polymetalloles is that, like many commercial colorimetric schemes including ExPray, they may potentially be combined with other detection methods as part of a

TABLE 1—Detection limits (ng) and probabilities of detection (listed parenthetically) of nitroaromatic explosives (TNT, DNT, PA) with luminescent metallole-containing polymers.

	TNT		DNT		PA	
	Porcelain	Paper	Porcelain	Paper	Porcelain	Paper
PSi	10 (100%)	30 (100%)	40 (100%)	50 (100%)	40 (93%)	40 (93%)
PDEBSi	10 (100%)	30 (100%)	20 (100%)	50 (100%)	20 (87%)	30 (93%)
PGe	5 (93%)	30 (100%)	30 (87%)	50 (100%)	30 (100%)	30 (87%)
PDEBGe	10 (100%)	30 (87%)	50 (100%)	50 (93%)	30 (87%)	30 (93%)
PSF	5 (87%)	30 (93%)	20 (87%)	40 (93%)	5 (100%)	5 (100%)
PDEBSF	10 (93%)	20 (93%)	20 (93%)	40 (93%)	5 (100%)	5 (100%)

PSi, polysilole; PDEBSi, poly(1,4-diethynylbenzene)2,3,4,5-tetraphenylsilole; PGe, polygermole; PDEBGe, poly(1,4-diethynylbenzene)2,3,4,5-tetraphenylgermole; PSF, polysilafluorene; PDEBSF, poly(1,4-diethynylbenzene)silafluorene; TNT, trinitrotoluene; DNT, 2,4-dinitrotoluene; PA, picric acid.

more comprehensive explosives detection system, encompassing nonnitroaromatics, while enabling a much higher sensitivity to nitroaromatics.

Production Line Explosives Detection

Detection studies were performed at an explosives testing range in order to observe the behavior of this technology in experiments closer to what might be expected in the real world. The explosives available at the range are in their used form, rather than in their purified form as used in the laboratory studies, for instance, with impurities, plasticizers, etc., that would be part of the chemical composition of the explosives as they are actually used. In these range experiments, the solid forms of the explosives (except for nitromethane) were used to contaminate the filter paper, not organic solutions of the explosives. Therefore, although no quantitative data on the amount of explosive present could be determined, the resultant contamination resembles that which might be expected in real-world applications, in terms of surface coverage, particulate size, and size distribution. Figure 6 shows a representative black and white image of the detection of TNT by PSi. A gloved thumb was lightly touched to production line TNT, and then five successive prints were touched to Whatman[®] filter paper, listed as P1 through P5. A thin film of the polymer was

applied to the paper by spray coating an acetone solution of PSi with an airbrush. Under UV illumination, luminescence quenching of the 510 nm emission is clearly observed in the presence of TNT. Although the amount of explosive material deposited through contact lessens with each successive print, there is almost no change in signal to noise between the first and last print. Both PSi and PDEBSi positively identify the presence of TNT and Comp B, which contains TNT in addition to RDX, through luminescence quenching. In addition, nitromethane and the proprietary propellant Pyrodex[®] are detected by PDEBSi. As stated above, these polymers may potentially be used in conjunction with other detection methods to broaden the range of detectable explosives to nitrate esters and nitramines, while taking advantage of the high sensitivity of the polymetalloles with respect to nitroaromatics.

Summary

Polymetalloles have been demonstrated to be an inexpensive, simple, and rapid visual detection method that reliably identifies low nanogram levels of nitroaromatic explosives. These polymers have real potential for lab and field applications for explosives detection. Given that the method of detection is electron-transfer fluorescence quenching, potential interferents that would lead to false positives would be limited to other strongly oxidizing species. Such solid-state materials are not common in everyday use. Strong UV absorbers, such as sunscreen, may present other potential interferents, although not interferents that would lead to false positives. Strong UV absorbers might absorb the majority of the excitation source and prevent the photoluminescence of the polymetallole. The appearance of this interference is qualitatively different from fluorescence quenching. Another feature of this detection method is that identification of fluorescence quenching depends on the subjective judgment of the user, which may be inconsistent between different users at low levels of explosives contamination. However, this method is easily adaptable to a portable device that could be in the field for initial on-site examination with high sensitivity. A positive detection may then be verified by passing samples through an IMS, or other instrument, which can accurately identify the quenching species present. In addition, these polymers are nontoxic and can be used safely when exercising care in controlling the mechanism of spraying on a polymer coating from an organic solution.

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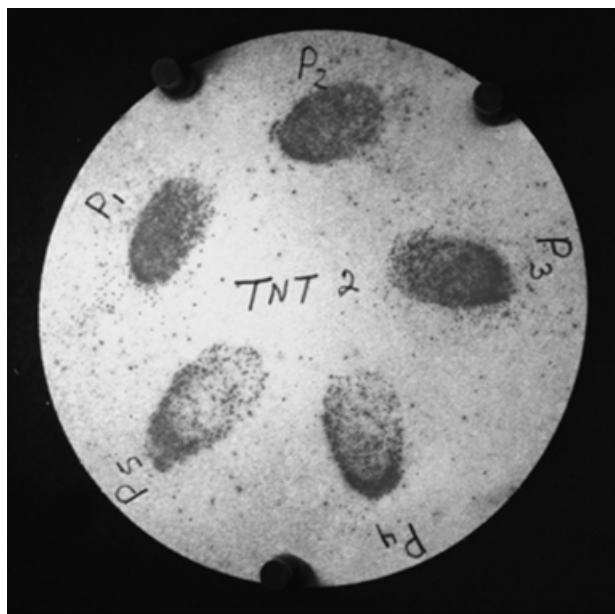


FIG. 6—Black-and-white image under UV illumination of quenching of fluorescence of a thin film of polysilole (PSi) by trinitrotoluene (TNT) on Whatman[®] filter paper.

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