

TECHNICAL NOTE

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Selective Detection of Trace Nitroaromatic, Nitramine, and Nitrate Ester Explosive Residues Using a Three-Step Fluorimetric Sensing Process: A Tandem Turn-off, Turn-on Sensor*

ABSTRACT: Detection of trace quantities of explosive residues plays a key role in military, civilian, and counter-terrorism applications. To advance explosives sensor technology, current methods will need to become cheaper and portable while maintaining sensitivity and selectivity. The detection of common explosives including trinitrotoluene (TNT), cyclotrimethylenetrinitramine, cyclotetramethylene-tetranitramine, pentaerythritol tetranitrate, 2,4,6-trinitrophenyl-N-methylnitramine, and trinitroglycerin may be carried out using a three-step process combining “turn-off” and “turn-on” fluorimetric sensing. This process first detects nitroaromatic explosives by their quenching of green luminescence of polymetalloles ($\lambda_{em} \approx 400\text{--}510$ nm). The second step places down a thin film of 2,3-diaminonaphthalene (DAN) while “erasing” the polymetallole luminescence. The final step completes the reaction of the nitramines and/or nitrate esters with DAN resulting in the formation of a blue luminescent triazole complex ($\lambda_{em} = 450$ nm) providing a “turn-on” response for nitramine and nitrate ester-based explosives. Detection limits as low as 2 ng are observed. Solid-state detection of production line explosives demonstrates the applicability of this method to real world situations. This method offers a sensitive and selective detection process for a diverse group of the most common high explosives used in military and terrorist applications today.

KEYWORDS: forensic science, explosives, TNT, RDX, HMX, PETN, Tetryl, TNG, fluorescence, luminescence, metallole polymers, explosives detection, trace explosives, explosives residue, turn-on fluorescence sensors

Explosives detection plays a key role in areas such as minefield remediation (1), crime scene investigations (2), and counter-terrorism applications such as personnel or baggage screening, facility protection, and cargo screening (3). Techniques at the forefront of the detection industry include gas chromatography coupled with mass spectrometry (4), gas chromatography-electron capture detection (2), surface-enhanced Raman spectroscopy (5), mass spectrometry (6), X-ray imaging, nuclear quadrupole resonance, thermal neutron analysis, and ion mobility spectrometry (7). These approaches use both bulk and trace detection methods to analyze suspect materials. Although these have been found to be effective for the applications mentioned above, they may prove inadequate in the area of counter-terrorism.

The recent rise in global terrorism has required that the methods for explosives detection be sensitive and at the same time low cost. The most important requirements for successful sensors are early detection, elimination of false positives, and efficient sampling methods for a variety of substrates. Conventional spectroscopic and imaging techniques, such as those mentioned above, are available in some airports and other high traffic areas. These large, stationary instruments perform bulk or vapor phase sampling in most cases.

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As described in a previous report (8), vapor sampling may be problematic due to the low volatility of most explosives at room temperature. Nitroaromatic explosives, such as TNT, have moderate vapor pressures (7×10^{-6} Torr at room temperature for TNT), but at low surface concentrations, the vapor concentration of TNT molecules is significantly lower than its equilibrium vapor pressure (9). Explosives such as cyclotrimethylenetrinitramine (RDX) and cyclotetramethylene-tetranitramine (HMX) have substantially lower vapor pressures (5×10^{-9} and 8×10^{-11} Torr, respectively) than TNT, which makes vapor detection of these compounds challenging (10).

An alternative method is to sample solid particulates that remain after the handling of explosive materials. It is known that widespread contamination results from the manufacturing and handling of explosives, and that trace contamination remains present and detectable, even after extensive cleaning of the contaminated areas (11). The advantage of solid-state detection is the ability to analyze samples even if concentration levels are too low to produce noticeable vapor concentrations. Sampling solid particulates directly rather than vapor may pave the way for low cost, portable devices with low detection limits for rapid on-site evaluation of suspicious materials.

Two low cost, portable technologies currently exist in the field of explosives detection. They are colorimetric detection (e.g., ExPray from Plexus Scientific) and fluorimetric detection (e.g., Fido from Nomadics, Inc.). Fluorescence detection methods have been widely regarded as the more sensitive approach (12,13); however, they typically require a liquid or vapor

sampling matrix. It has been previously demonstrated that trace explosives detection by solid-state fluorescence quenching provides sensing with low detection limits (8). However, this “turn-off” method, which relies on the electron-accepting ability of the explosive analytes, has historically been limited to the more easily reduced nitroaromatic explosives. In contrast, “turn-on” methods may be preferred because they eliminate the need for background fluorescence that may lead to false positives and may improve signal-to-noise in detection. In an engineered system, sensor sensitivity may be optimized because it is possible to amplify single photons against a dark background. In fact, “turn-on” fluorescent immunoassays are frequently used in enzyme detection systems to eliminate background fluorescence that may decrease sensitivity and produce false positives (14). They may also be more sensitive, and have the potential to be applied to a wider variety of explosive classes.

Nitramine and nitrate ester-based compounds make up a large portion of explosive formulations, such as Composition C-4 and Semtex-H (15–17). These compounds, which include RDX, pentaerythritol tetranitrate (PETN), cyclotetramethylene-tetranitramine (HMX), 2,4,6-trinitrophenyl-N-methylnitramine (Tetryl), and trinitroglycerin (TNG), can be used pure or as mixtures. Many improvised explosive devices (IEDs) used by terrorists include such explosive materials (10,17). In fact, 42 kg of RDX was recovered in multiple sting operations in India in July 2006 (18). These explosives are found in military munitions, which are the primary type used in IEDs in the Iraq terrorist conflict. Nitramine-based explosives (e.g., RDX, HMX, Tetryl) are of particular concern because they require almost no confinement (19), can be mixed and molded without loss of reactivity (20), have high energy yield per unit weight (21,22), and are readily available (23). Nitrate ester-based explosives (e.g., PETN, TNG) vary in their properties depending on their chemical structure. A high detonation velocity is one common feature, making them attractive materials to terrorists (17).

Colorimetric explosives detection techniques, such as ExPray, have proven effective in detecting nitramine and nitrate ester-based explosives, and have the ability to distinguish them from nitroaromatics. ExPray causes the chemical release of nitrite from the explosives upon exposure to a basic matrix followed by a reaction of nitrite with a colorimetric reagent in an acidic medium. Detection of nitramine and nitrate esters based on the detection of nitrite gives the sensor its chemical specificity. There are biological assays which are also specific for nitrite sensing. These assays are performed to detect nitrate, but do so by reducing the nitrate to nitrite, and further reacting the nitrite with 2,3-diaminonaphthalene (DAN) in an acidic environment to form the fluorescent 1-[H]-naphthotriazole (24–26). These assays are most commonly performed in solution. Detection is observed by monitoring a shift in the fluorescence spectra from $\lambda_{em} = 375$ nm (DAN) to $\lambda_{em} = 450$ nm (triazole).

Reported herein is the visual detection of a range of nitramine and nitrate ester-based explosives using DAN in a two-step fluorimetric process. Detection limits as low as 2 ng are observed for this turn-on luminescent sensor. This process may also be combined with fluorescence quenching technology (8,27) to establish a three-step fluorimetric sensing system to include the detection of nitroaromatic-based explosives. Sequential determination of explosives classes may be a beneficial feature in rapid on-site detection, as it may allow the analyst to quickly evaluate the threat or choose an appropriate disposal procedure (28). The approach described herein provides a low-cost, selective fluorescence sensing method for a diverse group of the most common explosives used in military and terrorist applications today.

Methods and Materials

Polysilole (Reagent A)

Polysilole (PSi) was prepared by catalytic dehydrocoupling of 1,1-dihydrido(tetraphenyl)silole using H_2PtCl_6 . A typical procedure involves refluxing 100 mg of 1,1-dihydrido(tetraphenyl)silole in 5 mL of dry toluene for 48 h. Subsequent removal of toluene under vacuum and re-precipitation of the residue from tetrahydrofuran (THF)/methanol yields PSi as a yellow powder (28). Reagent A is a solution of PSi (0.2 mg/mL) in acetone. Polymer solutions are made fresh prior to use.

2,3-Diaminonaphthalene (Reagent B)

DAN was purchased from Aldrich (St. Louis, MO) (97% purity) and used as received. Reagent B is a solution of DAN (4.0 mM) and KOH (0.75 M) in a 2:9:9 ratio of dimethylsulfoxide (DMSO):acetone:ethanol, respectively. The light brown reagent is made fresh prior to use.

Acidic Solution (Reagent C)

Reagent C is a 2:1 solution of ethanol and phosphoric acid.

Laboratory Explosives

Initial visual detection studies of nitramines and nitrate esters (RDX, HMX, TNG, PETN, and Tetryl) were performed by preparing substrates spotted with explosive solutions, prepared from diluted analytical standards purchased from Cerilliant® (Round Rock, TX), using acetonitrile as the solvent. The explosive solutions were spotted onto Whatman® 2 filter paper at the desired concentration level using a glass microsyringe. A solvent blank was spotted next to each explosive. All depositions were prepared from a 5 μ L volume, producing a spot of *c.* 1 cm in diameter, to insure consistent analysis. Upon evaporation of the acetonitrile, the substrate is airbrushed at a rate of 0.5 mL/sec with Reagent B for *c.* 2 sec. Heat is applied with a heat gun, followed by application of Reagent C. Upon a final heating process, an independent observer (randomly ordering samples and solvent blanks) identified the appearance of the blue/green luminescent product when illuminated with a black light ($\lambda = 360$ or 302 nm). Whatman filter paper was selected for these studies because of its low background fluorescence. Detection studies were performed for each explosive at contamination levels of 200, 100, 50, 10, 8, 6, 4, and 2 ng. The detection limits were noted as the lowest concentration of explosive that enabled the independent observer to notice luminescence.

Detection of nitroaromatics, as well as nitramines and nitrate esters, was carried out in a three-step process. Whatman filter paper samples were prepared as stated above, but with an additional spot of TNT at concentrations equal to the nitramine and nitrate ester explosives. The sample was then airbrushed with Reagent A and analyzed for TNT by monitoring the quenching of luminescence under a black light ($\lambda = 360$ or 302 nm), according to a previous procedure (8). Subsequent analysis of nitramine and nitrate ester-based explosives was carried out by applying Reagents B and C as described above.

Production Line Explosives

Thumbprint samples of production line explosives were prepared at a Department of Defense approved explosives testing range

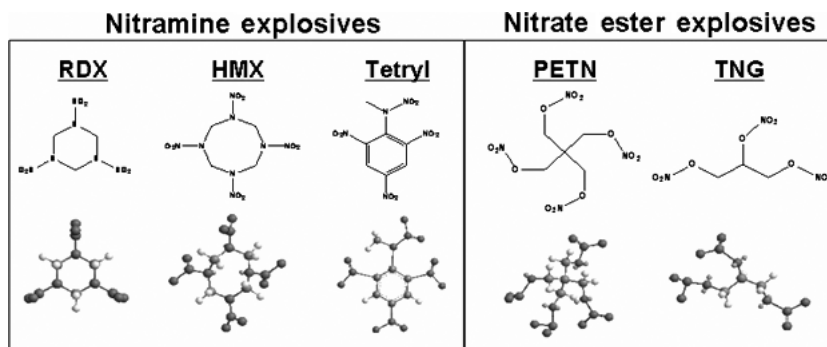


FIG. 1—Chemical structures of explosives.

operated by Newtec Services Group, Inc. Contaminated filter paper samples were prepared by contacting a finger or a hand with an explosive (TNT, RDX, PETN, C-4, or PE-4), removing the excess, and then contacting Whatman® 2 filter paper five successive times to prepare five generations of prints. C-4 is a mixture of RDX (91% by weight) and plasticizer (9% by weight). PE-4 is the British equivalent of C-4 with the only difference being the type and composition of plasticizer used. Detection using Reagents A–C was performed directly on these samples, as described above for the laboratory explosives.

Results and Discussion

Detection of Nitramines and Nitrate Esters (Two-step)

The five explosives studied were RDX, HMX, Tetryl, PETN, and TNG. The structures of these explosives are shown in Fig. 1. The common feature seen in these explosives, and in many other highly energetic materials, is an N–NO₂ (for nitramines) or O–NO₂ (for nitrate esters) functionality. These energetic bonds are also the target site for the detection of these classes of explosives. Detection relies on the detection of nitrite (NO₂⁻) and is achieved through the successive application of two reagents (Reagents B and C). Reagent B, which is applied in the first step in this “two-step” detection process, causes the release of nitrite from the explosive through a reaction with base. The hydroxide base deprotonates the explosive at a position alpha to the N or O in the nitramine or nitrate ester, respectively. Nitrite is subsequently released as a double bond forms between the α carbon and N or O. Reagent B also includes DAN and several organic solvents, which aid in the solvation of both the explosive and DAN to allow for necessary mixing. Heat is applied to provide the energy necessary to promote the reaction, as well as to aid in solvent evaporation. Immediately following the heating process, Reagent C is applied. The acid in Reagent C reacts with nitrite to form nitrous acid, which then reacts with the DAN applied in Reagent B to form the luminescent 1-[H]-naphthotriazole (Fig. 2). The luminescent material is visualized by exciting the molecule with an inexpensive blacklight (λ ~360 nm). Slightly better resolution is achieved using a short-wave

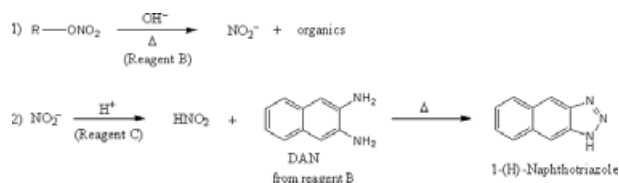


FIG. 2—Reaction scheme for steps 1 and 2 of two-step detection process.

TABLE 1—Vapor pressure and detection limits of the different classes of explosives studied with the three-step fluorimetric sensing process.

Explosive	Class	Vapor Pressure (Torr)*	Detection Limit (ng)
RDX	Nitramine	5×10^{-9}	2
HMX	Nitramine	8×10^{-11}	10
Tetryl	Nitramine	6×10^{-6}	10
TNG	Nitrate ester	4×10^{-4}	10
PETN	Nitrate ester	1×10^{-8}	25
TNT	Nitroaromatic	7×10^{-6}	10^\dagger

*Measured at room temperature (10).

†Based on fluorescence quenching of polysilole (8).

lamp (λ ~302 nm) and UV-transmitting filter (HOYA Optics [Fremont, CA] U-340). Detection limits as low as 2 ng are observed with this method. A summary of the detection limits is given in Table 1.

To demonstrate the selectivity of the two-step process for nitramine and nitrate ester-based explosives, filter paper samples were prepared with both TNT and RDX spots. Only reagents B and C were applied as described above. While RDX shows “turn-on” fluorescence detection as low as 10 ng, TNT does not show any “turn-on” fluorescence even for spot loadings as high as 200 ng (Fig. 3). The slight darkening at 200 ng for TNT is actually a red

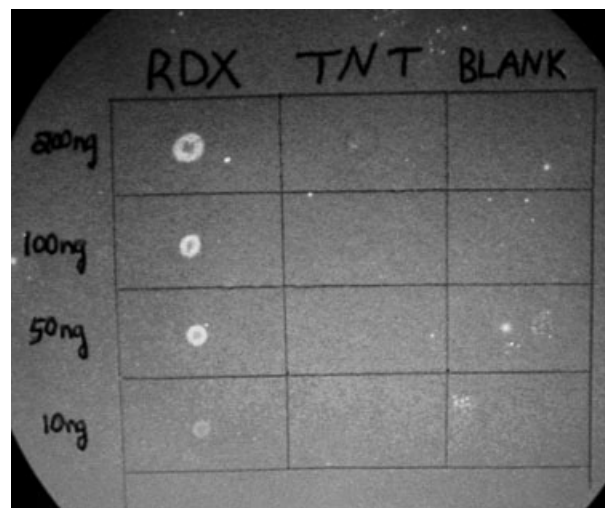


FIG. 3—Turn-on fluorescence detection of cyclotrimethylenetrinitramine (RDX) using the two-step process. TNT is detected by colorimetric analysis at a limit of 200 ng. Blank spots of toluene show no detection.

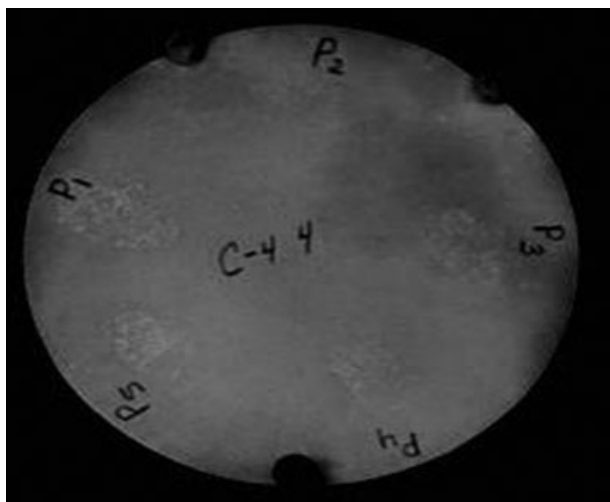


FIG. 4—Turn-on fluorescence detection of five successive fingerprints of cyclotrimethylenetrinitramine (RDX) starting with print 1 (P_1).

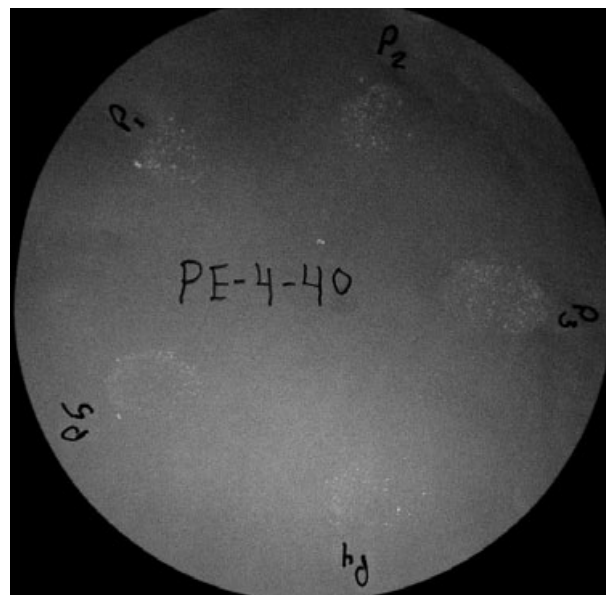


FIG. 5—Turn-on fluorescence detection of five successive fingerprints of PE-4 starting with print 1 (P_1).

spot from the Meisenheimer complex, which results from the reaction of TNT with the base applied in Reagent B (29,30). Detection limits are based primarily on the susceptibility of each explosive to undergo nucleophilic attack from the strong base and to release nitrite. The low detection limits seen in this study can also be attributed to the resulting “turn-on” fluorescence indicator. Reduction in background noise greatly increases the ability to observe a positive result and provides a reduction in false positives.

This process was also carried out on fingerprints placed on filter paper after contact with production line explosives. Detection of production line explosives in real world applications presents challenges not present in controlled laboratory spot tests. Contaminants in both pre- and postblast residues mimic what one would find in the field. These may include various plasticizers, by-products of low-quality synthetic procedures and common natural residues such as oils and dust. This current detection method can readily visualize the first five successive fingerprints made after direct contact with commercial RDX (Fig. 4). Fingerprints of the explosives PETN, C-4, and PE-4 are also detected. Contact with the explosives was limited to one touch of the finger or thumb with the material. An example of the detection of PE-4 is shown in Fig. 5. It is important to note that the concentration of explosive materials deposited in these studies remains well above the detection limits determined by the spot tests. These tests indicate that detection of the explosive materials is possible even in the presence of plasticizers and impurities found in the C-4 and PE-4 explosives and with limited handling of the material.

Three-Step Detection Process

The process of detecting nitramine and nitrate ester-based explosives was combined with previous technology to create a tandem fluorescence sensor that also detects nitroaromatic explosives. It has been previously reported that detection of low nanogram quantities of nitroaromatic-based explosives (e.g., TNT, DNT, and picric acid) may be achieved using fluorescence quenching of PSi by the explosive materials (8). Reagent A may be airbrushed onto a substrate and the presence of nitroaromatic-based explosives is confirmed under UV light. For selectivity purposes, it is noted that Tetryl (Fig. 1) is both a nitroaromatic and nitramine explosive and therefore is detected by both the PSi and the “turn-on” system using

DAN. An example of the two technologies side-by-side is shown in Fig. 6. A handprint of trace particles of tetrabutylammonium nitrite (left) was laid down next to a handprint of trace particles of TNT (right) using nitrile laboratory gloves. RDX was not used directly due to purchasing restrictions. The left portion of the filter paper was exposed to Reagents B and C. The right portion was exposed to Reagent A. This demonstrates how these different detection methods detect the presence of explosive materials.

To demonstrate the effectiveness of the two technologies used in tandem, filter paper samples were prepared onto which TNT and RDX were co-spotted. After application of Reagent A and analysis under UV light, Reagent B is airbrushed onto the substrate. The luminescent polymer in Reagent A is destroyed through degradation of the silicon backbone under basic conditions via a $S_{\text{N}}2$ ring

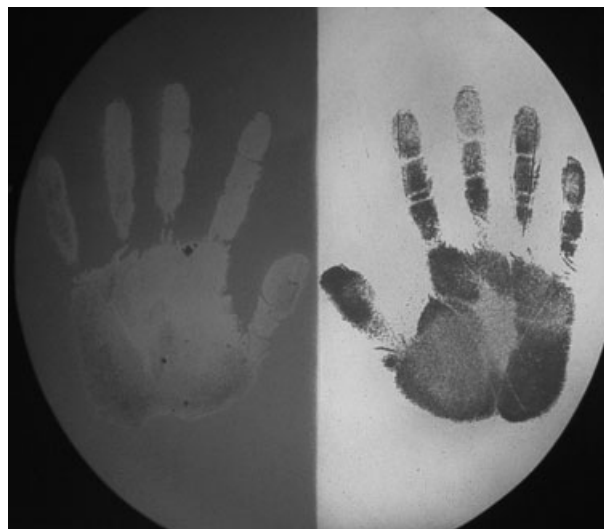


FIG. 6—Side-by-side comparison of two-step turn-on sensor (left) with fluorescence quenching sensor (right). Tetrabutylammonium nitrite was used as the analyte for the turn-on sensor and TNT was used for the fluorescence quenching sensor.

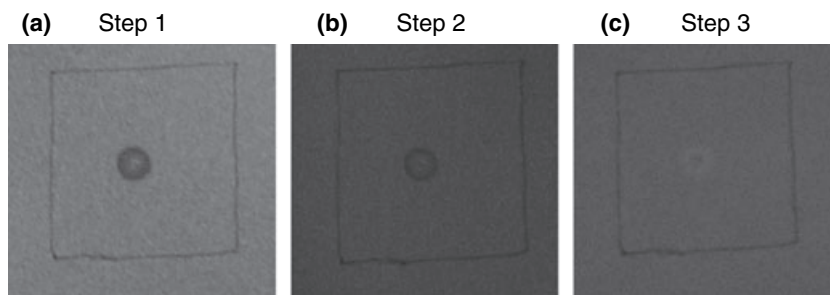


FIG. 7—Three-step detection process on a co-spot of 200 ng of TNT and 200 ng of cyclotrimethylenetrinitramine (RDX). (a) Luminescence quenching of polysilole by TNT; (b) colorimetric confirmation of TNT by a red Meisenheimer complex; (c) turn-on fluorescence of triazole complex confirming the presence of RDX.

opening reaction, eliminating its fluorescing properties. This eradicates the background fluorescence that could create interference in the subsequent turn-on detection process. Basic conditions of Reagent B may also cause the appearance of a red spot resulting from the formation of the Meisenheimer complex when nitroaromatics such as TNT are present, which can be viewed in both ambient and UV light. This is similar to colorimetric testing of these explosives and will work to confirm the presence of nitroaromatic explosives if there is a sufficient quantity present. It is noted that this red spot does not appear at low concentrations (<50 ng) of explosives even when a positive nitroaromatic test result is obtained by the PSi. After the application of Reagent B and subsequent heating, Reagent C is applied to increase the acidity and cause the formation of the luminescent triazole. The detection limits for the nitramine and nitrate ester explosives are not compromised by the initial use of Reagent A, because PSi luminescence is completely removed at this point. An example of this fluorescent “on/off” detection series is shown in Fig. 7.

This three-step explosives detection process is effective on production line explosives as well. The first five fingerprints produced after contact with TNT, RDX, PETN, C-4, and PE-4 were all detected in the three-step process with high signal-to-noise, indicating that contaminants, impurities, and plasticizers do not interfere with detection. Possible interferents in the detection of nitroaromatics by PSi, such as common organic solvents were found to be minimal, while the low abundance of naturally occurring solid-state oxidizers should reduce false-positive results in field tests (8). As the turn-on sensor is based on the specific chemistry of nitramine and nitrate ester-based explosives, very few interferents, other than nitrite salts found in some fertilizer products, are known. Even highly oxidizing materials such as benzophenone, TNT, DNT, and picric acid will not quench the luminescence of the triazole complex. Detection of other nitramine (e.g., CL-20) and nitrate ester (e.g., nitrocellulose) based explosives is expected to be achieved using this system.

Summary

It has been demonstrated that selective detection of nitramine and nitrate ester-based explosives can be achieved using “turn-on” fluorescence technology. In combination with the fluorescence quenching detection of nitroaromatics using PSi, a three-step process was established for selective explosives detection at the low nanogram level. Targeting the specific chemical features of the explosive materials has led to the highly selective and sensitive analysis of samples without the need for preconcentration or pre-treatment of the sampling substrate. The direct *in situ* analysis of solid particulates gives this method of detection an advantage over

conventional sensors. This technology may also be easily integrated into a low power, portable device for low-cost, rapid explosive sensing. The use of fluorescence as the detection method has allowed for the possibility of much lower detection limits than those typically found in colorimetric methods.

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