

Trace Detection of Explosive Particulates with a Phosphole Oxide

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ABSTRACT Phosphole oxides exert the ability to detect explosives, especially nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT), by fluorescence quenching. In the image sensing of explosives sprayed with phosphole oxide, fluorescence quenching permits the visual determination of the lower detection limits of the nitroaromatic explosives in the nanogram level.

KEYWORDS: chemosensor • explosive • fluorescent • imaging • phosphole oxide

Because the threat of increased use of explosive materials in terrorism is a major global concern, detection methods for trace explosive materials are in strong demand in the field of security screening (1). A variety of explosive-detection methods such as gas chromatography–mass spectrometry, Raman spectroscopy, X-ray imaging, and ion mobility spectroscopy have been developed (2). These instrumental techniques are highly selective, but some are expensive and others are not easy to operate and are not portable for use in the field. On the other hand, Swager and co-workers reported the detection of nitroaromatic explosives in the vapor phase using fluorescence quenching of conjugated polymers (3). The mechanism of fluorescence quenching for explosive detection is attributed to the photoinduced electron transfer from the excited polymer donor to the explosive acceptors. This method offers a simple, exquisitely sensitive, and rapid detection of explosives in the vapor phase and is now an established technology (4). As an alternative to vapor sampling, Troglor and co-workers recently reported an image-sensing method for explosive particulates using silole-based polymers (5). This imaging method for explosive particulates is useful because explosive materials usually have low vapor pressures, which makes vapor detection difficult. Despite intensive and extensive efforts made during the past decade (6), the development of π -conjugated materials for sensitive, convenient, and precise explosive detection is still required.

Among a variety of π -conjugated systems, phosphacyclopentadienes, phospholes, and phosphole oxides are interesting building blocks (7). This is because the incorporation of a phosphorus atom, especially a phosphine oxide (P=O) group, into the π -conjugated framework results in orbital interactions that lower the lowest unoccupied molecular orbital (LUMO) energy level. We have recently reported the synthesis and photophysical properties of phos-

phole- and phosphole oxide-cored dendrimers (8). The dendritic phosphole oxides displayed an intense bluish-green emission in the aggregated and solid states. On the basis of the photophysical properties of the dendritic phosphole oxides, we anticipated that phosphole oxides could be an alternative sensory element for explosive detection. In addition, the high chemical stability of the phosphine oxide (P=O) group permits facile handling as stable materials. Here, we disclose the potential utility of phosphole oxides for trace detection of explosive particulates. In the image sensing, the phosphole oxide detects explosives, especially nitroaromatics, with a detection limit at the ng cm^{-2} level by fluorescence quenching.

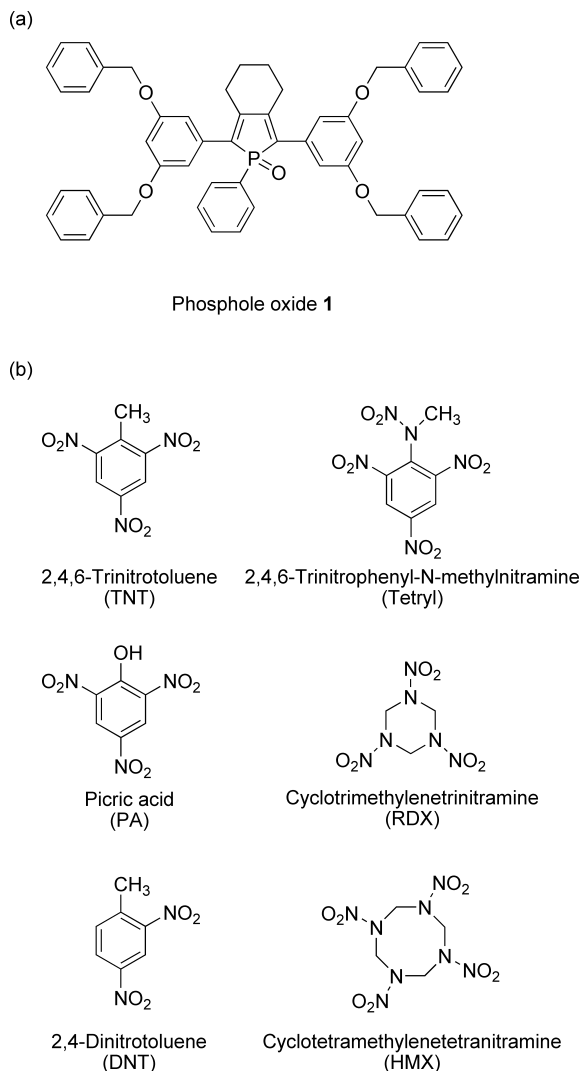
To demonstrate the ability of phosphole oxides for detection of explosives, we first performed fluorescence quenching experiments using phosphole oxide **1** (Chart 1) with nitroaromatics such as 2,4,6-trinitrotoluene (TNT), picric acid (PA), and 2,4-dinitrotoluene (DNT) in solution. Upon the addition of nitroaromatics to a 10% tetrahydrofuran (THF) aqueous solution of **1**, where **1** aggregates with a diameter of ca. 100 nm to show an intense emission at about 500 nm (9), the fluorescence is quenched efficiently. Figure 1 shows the fluorescence response of **1** to TNT in a 10% THF aqueous solution. On the basis of fluorescence titration, the detection limit of TNT with **1** is found to be 8 ppm under these conditions. The first linear part of the Stern–Volmer plots allows determination of the quenching constants (K_{sv}) to be 3900 M^{-1} for TNT, $20\,300 \text{ M}^{-1}$ for PA, and 1700 M^{-1} for DNT (Figure 1b; see also Figure S1 in the Supporting Information). These values for the quenching constants of nitroaromatics are comparable with previously reported values (10). Although a further detailed description of fluorescence quenching of phosphole oxide by nitroaromatics, such as fluorescence lifetime measurements, requires further studies, the linear Stern–Volmer plots suggest that fluorescence quenching involves a static quenching mechanism in the case of lower concentrations of nitroaromatics. Details will be reported in due course. On the other hand, when 1,4-benzoquinone (BQ) is used as a reference for electron-deficient compounds for the analyte, fluorescence quenching is also

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Chart 1. Chemical Structures of (a) Phosphole Oxide 1 and (b) Nitro Explosives


observed (Figure S2 in the Supporting Information), but the quenching constant is quite small (80 M^{-1}). This suggests that phosphole oxide shows high quenching sensitivity and improved selectivity to the nitroaromatic explosives.

Considering the high sensitivity of phosphole oxide to the explosive materials, an image sensing of trace explosive particulates was examined, aiming at practical applications. In the sensing study, TNT, PA, DNT, 2,4,6-trinitrophenyl-*N*-methylnitramine (Tetryl), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX) were used as the analyte for the explosives (Chart 1). The explosive solutions at various concentrations were spotted onto test pieces of filter paper (6 mm in diameter). After evaporation, a THF solution of **1** was sprayed onto the test pieces spotted with trace explosives. After drying the test pieces, quenching of phosphole oxide, under irradiation with UV light of 365 nm, was imaged with a digital camera. As Figure 2 shows, phosphole oxide **1** (control test pieces without explosives) emits bluish-green light under UV irradiation. However, trace amounts of the explosives quench the emission, resulting in lowered intensity, where the degree of

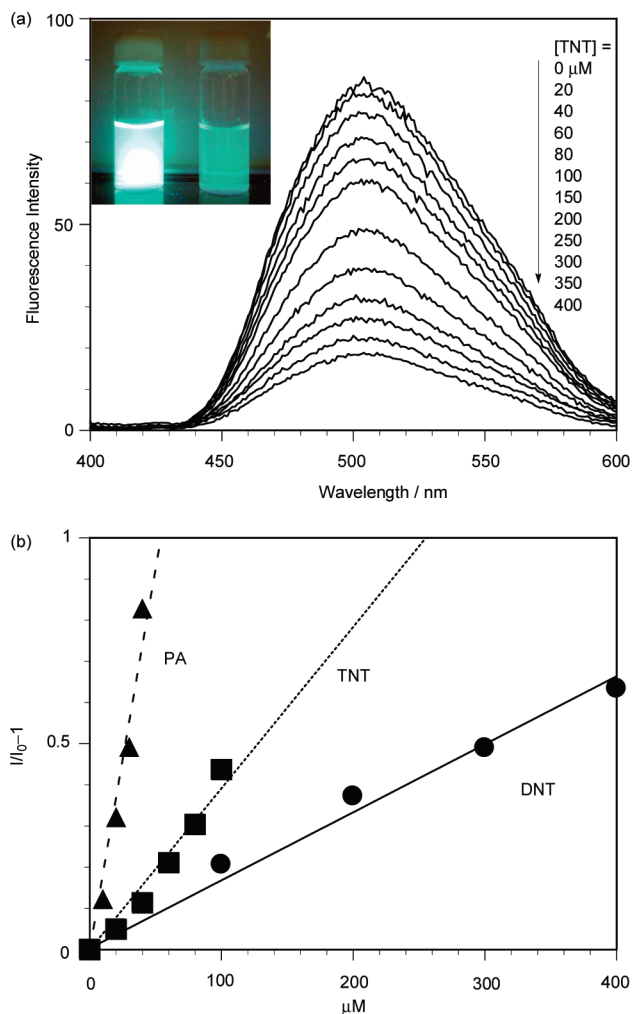


FIGURE 1. (a) Fluorescence quenching of phosphole oxide 1 ($19 \mu\text{M}$) with TNT in a 10% THF aqueous solution ($\text{Ex} = 370 \text{ nm}$). The inset shows photographs of **1** (left) and a mixture of **1** and TNT (right) in a 10% THF aqueous solution under UV irradiation with 365 nm ($[\mathbf{1}] = 19 \mu\text{M}$; $[\text{TNT}] = 400 \mu\text{M}$). (b) Stern–Volmer plots of fluorescence quenching of phosphole oxide 1 ($19 \mu\text{M}$) with TNT, PA, and DNT in a 10% THF aqueous solution.

quenching is highly dependent upon the quantity and the structure of the explosives. Fluorescence quenching is easily confirmed by the naked eye. For example, the ultratrace amounts of nitroaromatics, such as TNT, PA, DNT, and Tetryl, quench the emission of **1** efficiently. The detection limits of the explosives were estimated by analysis of the digital photographs. The lower detection limits of TNT, PA, DNT, and Tetryl were found to be 10, 50, 100, and 50 ng cm^{-2} , respectively (Figures S3 and S4 in the Supporting Information) (11). On the other hand, RDX and HMX also quench the emission of **1**, but the detection limits are much higher (500 ng cm^{-2} and $5 \mu\text{g cm}^{-2}$, respectively) than those of nitroaromatics. The mechanism of fluorescence quenching is primarily attributed to electron transfer from excited phosphole oxide to the analytes, where the LUMO energy of explosive analytes is an important factor in the fluorescence quenching process. Because the LUMO energy level of nitroaromatics is lower than that of RDX and HMX (Figure S5 in the Supporting Information), it is detected with high sensitivity. Further, BQ and benzaldehyde used as analytes

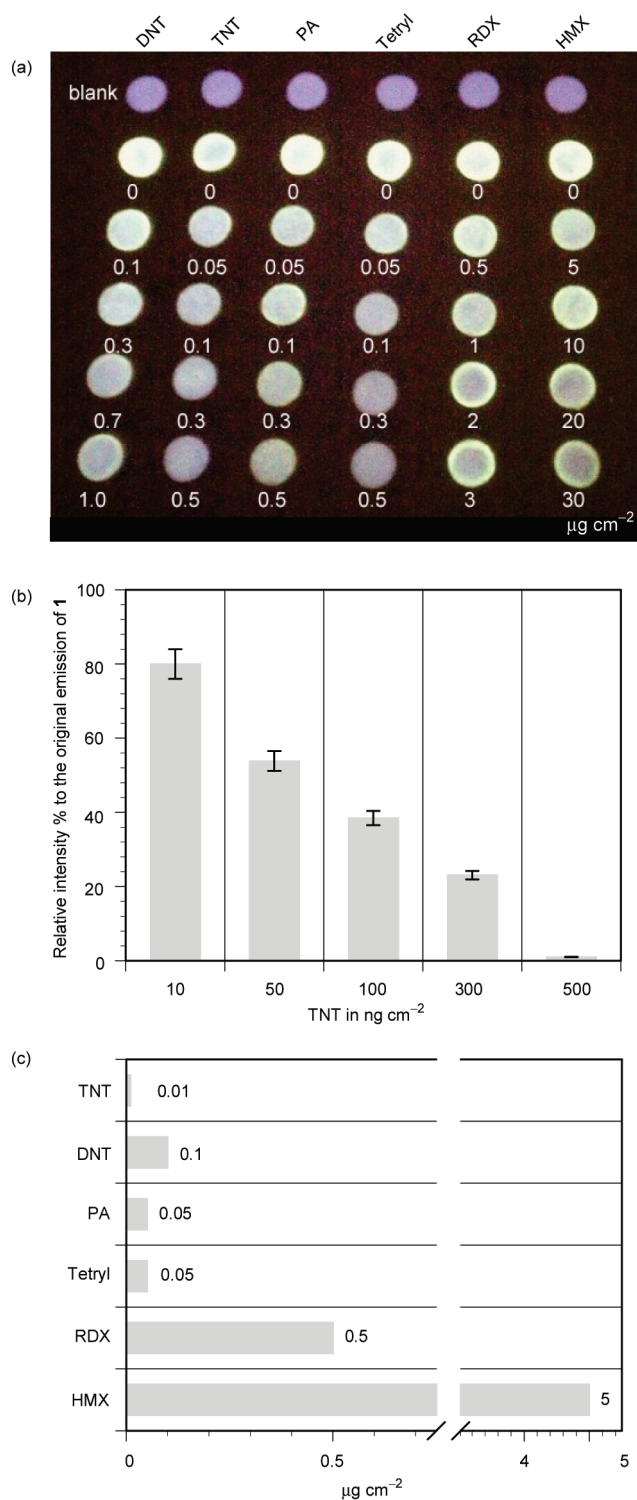


FIGURE 2. (a) Photograph of the image sensing of trace explosive particulates DNT, TNT, PA, Tetryl, RDX, and HMX on the filter paper after spraying with a phosphole oxide **1** solution under irradiation with black light. “Blank” is the sample of the filter paper without spraying with **1** as a reference. The figure gives the concentration of the explosives in $\mu\text{g cm}^{-2}$. (b) Fluorescence quenching percentage of **1** with trace amounts of TNT relative to the original emission intensity analyzed from the digital imaging data shown in part a. (c) Detection limits of the explosives by image sensing with **1**. The figure on the top of the bar is the lower detection limit in $\mu\text{g cm}^{-2}$.

for the image sensing quench the emission of **1** with detection limits of $5 \mu\text{g cm}^{-2}$ (Figure S6 in the Supporting

Information). Again, the phosphole oxide **1** displays a highly selective and sensitive response to nitroaromatics.

We also examined vapor detection of nitroaromatic explosives. Upon exposure to DNT or TNT vapor, the fluorescence of a film of **1** is indeed quenched, but the response is slow, requiring a few minutes for detection of DNT and 1 h for detection of TNT to reach 20% quenching (Figure S7 in the Supporting Information). The present phosphole oxide may not be practical for the real-time vapor detection of DNT or TNT at this stage. This is probably because **1** does not form a good porous film to contact the explosives to produce effective intermolecular interactions.

In summary, we have demonstrated the trace detection of nitrogen explosives using phosphole oxide **1**. Phosphole oxide shows the ability to detect explosives, especially nitroaromatic explosives including TNT, by fluorescence quenching. The detection is clearly visualized in image sensing, which allows the estimation of detection limits as low as 10 ng cm^{-2} for nitroaromatic explosives. The present system shows the improved selectivity for detection of nitroaromatics. Although a modification is required to improve the detection limits, phosphole oxides and related compounds should be more seriously scrutinized as alternative sensory materials with a potential application in the field of explosives detection. Further study is in progress.

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Supporting Information Available: Experimental procedures, fluorescence spectral changes of **1** with PA, DNT, or BQ in solution, details of the image sensing with explosives, and vapor detection of TNT or DNT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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