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REVIEW ARTICLE

Advances in Chemiluminescence based Explosive Detection

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ABSTRACT

CONTEXT: Detection of explosives is indeed crucial for the fact that it has harsh impact upon peace in the community as well as its nature as a contaminant in the environment. As of now there have been numerous additions due to clandestine synthesis of explosive materials which are not up to date with the spectral library of various spectrometric techniques. For the detection of explosives new mechanism are often required which should have advantages like sensitivity, selectivity, rapid response, low cost, remote sensing and sensors made with ecofriendly material. Techniques which are commonly utilized areIon Mobility spectrometry, Gas Chromatography – Mass Spectrometry, Fido-XT for sensing explosives like Trinitrotoluene (TNT), Trinitrophenol (TNP), and Dinitrotoluene (DNT) etc. Apart from that, military agencies, police and forensics are still having a hard time to detect the trace amount of explosives like RDX, PETN, Tetryl and HMX etc. selectively. Recent upbringing in Chemiluminescence based explosive detection showed quite a reliable way for detecting these compounds. In Chemiluminescence based detection various materials are used namely conjugated fluorescent polymers, small molecule fluorophores, supramolecular system, Bio-inspired fluorescent materials, Aggregation induced emission active materials. These techniques if combined with various techniques like electronics, imaging and sensor design then it would provide deployment over real field for explosive detection which includes buried land mines, environmental contamination by explosive material. This review article may help the readers in order to get insight about what is explosive, various types of explosive, and mechanism of explosion and explosive detection techniques.

KEYWORDS | explosive, detection, detection technique, chemiluminescence

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INTRODUCTION

THE THREAT OF IMPROVISED EXPLOSIVE DEVICES (IEDs) is a major concern in the twenty-first century. Explosive devices, which are frequently used by extremists and revolutionary groups, can be created by using commercial detonators, and scrap elements from leftover army munitions. Undeployed munitions from current and historical warzones are a source of munitions. Bomb sniffing canines are commonly employed to locate hidden munitions, and even when they are incredibly successful, they have drawbacks in concerns of maintenance, instruction, expense, and temperament. An explosive has 4 fundamental properties: 1) It is a chemical substance or blend which is triggered by heat, shock, impact, friction, or a combined effect of such circumstances; 2) It decays swiftly in a detonation; 3) There is indeed a sudden discharge of thermal energy as well as massive amounts of high-pressure gaseous substances that expand speedily with considerable power to surmount constraining factors; and 4) The energy generated by detonation has four main consequences: a) stone shattering, b) stone dislocation, (c) earth tremor, and (d) atmospheric shockwave.[1] According to a theoretical perspective of explosive, the explosion of the explosive materials generates a large blast wave as well as a massive discharge of gases. The blast wave fractures and compresses the rocks around the explosive, resulting in dozens of splits. The expanded gas subsequently fills in the fractures. The gaseous substances keep filling and extend the fractures till the compressed gases become too low to allow the fractures to enlarge any more or until they are expelled from the stone.[1]

Almost all high explosives contain at least one nitro-functional group. In general, nitroaromatic compounds including TNT, DNT and NT are one of the main explosive materials used primarily by army and as one of the main constituents present in the buried underground mines nationwide. Nitramines and nitrate esters (e.g., 3,5-trinitroperhydro-1,3,5-triazine and pentaerythritol tetranitrate, are main components of highly energetic plastic explosives, such as C-4 (91% cyclonite) and Semtex (40–76% pentaerythritol tetranitrate). Because nitrogen group containing explosives are particularly responsive to shock, friction, and impact, detecting techniques that allow for contact-free examination are preferred.[1] Furthermore, the need to identify concealed munitions in transit stations and underground bombs in conflict areas has sparked strong interest in low-cost, supersensitive explosive identification technologies. In comparison to recognition in liquid and solid phases, identification of nitro group containing explosive in vapor state is more difficult because most of them have very low volatility.1 Despite the fact that modern nitro-explosive vapor monitoring depends mainly on Ion-mobility Spectrometry and Gas Chromatography combined with Mass Spectrometry (GC-MS), their intricate methods, low accessibility, and increased price have limited their widespread applicability As a result, there is a considerable requirement for revolutionary sensor devices that are inexpensive, simple to use, hypersensitive, and discriminatory for a wide range of nitro-explosives. Some of the currently used techniques for explosive detection are discussed below.

DETECTION TECHNIQUE

Ion-Mobility Spectrometry

Explosive material recognition has become one of the primary causes for the establishment of IMS technique (together with toxic warfare weapon identification). The blend of responsiveness and toughness gave a powerful resolution to the challenging problem of explosive counter terrorism.[2] Nevertheless, ignorance about instrumentation and contextual variables with IMS has resulted in a less-than-ideal use of the approach. The machine's effectiveness has improved as the IMS's skill set of complicated gaseous phase ion-molecule dynamics has developed. The ongoing implementation of IMS technology into terminals across the U. S. highlights IMS's capabilities in the implementation of flight safety. This technique and the rules governing reaction have advanced to the point that testing strategy is becoming the primary shortcoming in deployments. One can confidently predict that IMS sensors will get compact and inexpensive in the near future, while the consequences for munition identification is still unknown.[2]

Gas Chromatography Mass Spectrometry

This study is the initial publication on the LVI-GC-MS analysis method that intends to evaluate isolated explosive materials and associated substances and allows for the convenient injection of 20 microlitre specimen quantities in a split-less configuration into a universal PTV injector.[3] This approach was proved to produce minimal identification sensitivity of 0.1 picogram/milli-litre for substances with a diverse variety of volatile substances, particularly volatile chemicals which are not normally susceptible to LVI testing.[3] Regarding air examination, sorptive pipes avoiding the need of a suitable solvent, along with TDS assessment, are often favoured for achieving low limit of detection. The technique's usefulness was proved effectively in the minute analysis of chemicals from

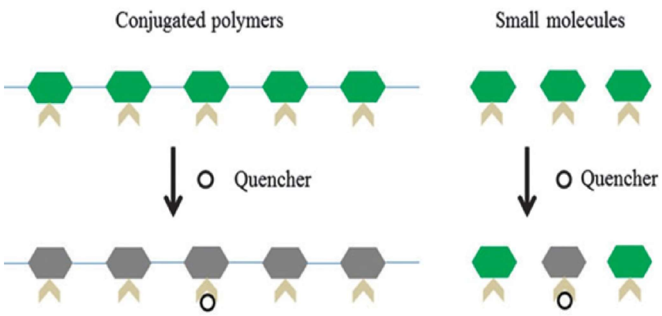

Figure 1: The schematic illustration of molecular wire theory.

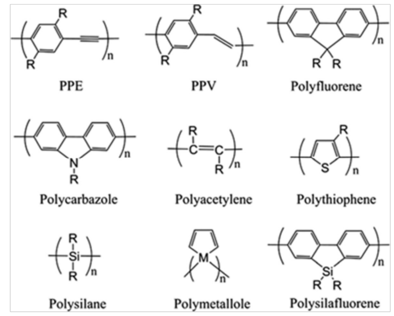

Figure 2: Basic backbone structures of the Conjugated Polymers.

specimens collected from ground in the likeness of inevitable atmospheric interventions. All investigated substances were detected reliably at a minimal concentration value of 0.5 nanogram/gram.[3]

Materials for Explosive Sensors

Conjugated Fluorescent Polymers

Fluorescent conjugated polymers (CPs) was lately been utilized efficiently in detecting nitro based explosives.[4] They feature a longer charge carrier propagation channel and excellent electronic transmission among quenchers along the polymeric matrix as opposed to ordinary small molecule fluorophores. The delocalized ϖ* exciton enhances excited state transfer and hence boosts the electro-static contact between the polymer and electron-deficient nitro-explosive solute, making CPs efficient electron donor. In instance of Conjugated Polymeric fluorescence sensory materials.

According to Swager *et al.,* engaging single receptor location resulting in an excellent dampening of all radiating subunits in a complete chained polymer molecule compared to single molecular system. This magnification is described as the "molecular wiring" phenomenon, or the "single spot touch, multiple-point action" impact, as shown in Fig. 1. In practice, luminous polymeric substances can be classified as organic or inorganic based on underlying fundamental spine architectures, as shown in Figure 2.

METHOD

Small Molecule Fluorophore

Shanmugaraju and Mukherjee demonstrated current notable instances of small molecule - electron-rich turn-off fluorescence sensing materials employed for nitro-explosive sensing.[5] Small molecule fluorophores are attractive sensor substances for detection of nitroaromatic compounds due to their synthetic simplicity, ease of functionalization, and broad array of recognition ability for chemical explosives. Moreover, the excellent solubility of small molecule-based fluorescence sensor in conventional solvents allows for simple synthesis for potential implementation. The effectual charge-transfer (donor-acceptor) complex formation of electron-rich small molecule fluorescence sensor with electron-deficient nitroaromatic explosive is responsible for their medium to considerable dampening effectiveness.[5] Although their great discrimination and effective monitoring ability small molecule fluorescence sensor are poorer to conjugated polymeric sensor. Because many charge carrier emission can be suppressed by one molecule of quencher via far range exciton diffusion all along polymer chains, linked polymeric sensor are incredibly effective. Small molecule sensor fluorescence, on the other hand, is dampened in a stoichiometric manner of one fluorophore per analyte. One proposed solution is to create supramolecular sensor

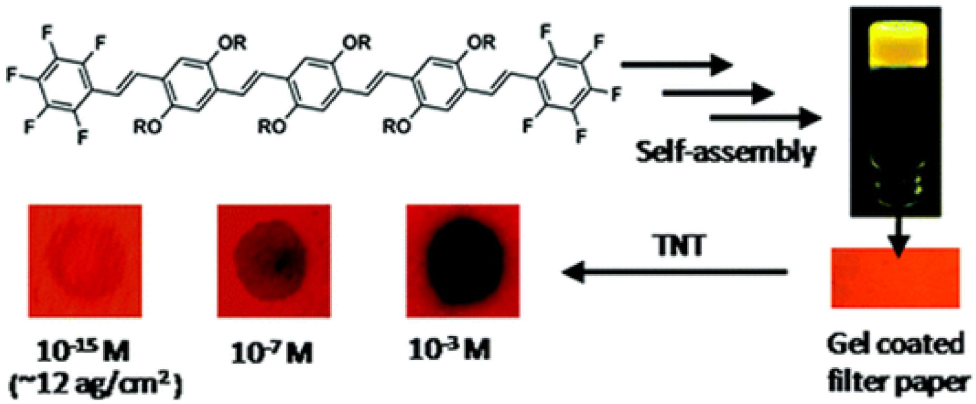

Figure 3: Molecular structure of OPVPF and its self-assembly to gel-coated filter films and the ability for attogram TNT detection in contact mode.

by connecting basic fluorophores via several supramolecular contacts.

Metal Organic Framework

Ning He *et al.,* developed a prominent fluorescent Eu-MOF and utilized it to sense Picric Acid, Trinitrotoluene, and Tetryl having a low sensing level (20-140 g/mL), excellent sensitive having stern volmer constant value of 104-105 M-1, and remarkable reusability.[7] Furthermore, utilizing UV-vis absorbance spectrum interpretation, the process of the fluorescence signal was studied, and the process may be attributed to competing absorbance among Eu-MOF and analytes. Ning He *et al.,* also created a test strip for detecting TNT and were able to obtain visual detection and fast field identification. As a conclusion, Eu-MOF is a perfect candidate to be used in explosive sensing results since it has a better selectivity for detecting Picric acid, Trinitrotoluene, and Tetryl.[7] There seems to be an ongoing necessity for explosive sensing devices that are simple to use on the site and produce accurate outcomes. Unfortunately, maintenance support would be required before such a technology could be functional and useful for forensic investigations. A development procedure is required that would have to recognize nitro aromatic, nitro amines, and nitro esters in contrast to NACs, which could have an appropriate false positive and false negative probability.[8] Furthermore, in the sector of mankind relief when field bomb identification is required, a TNT-only sensing method may discover applicability, however sensing in the gaseous state may be required. As a result, the research is mostly a technical challenge.[2] Here a visual self-explanatory (Fig. 4) is given to show how metal organic framework behaves with/without the presence of various type of molecule.

CONCLUSION

Because of the necessity for immigration enforcement and extracting operations, there is a great deal of focus in enhancing explosive identification. Almost all of the requirements necessary for an efficient recognition element, including the tailored properties, high response, compactness, mobility, and cheap price, are likely to be addressed by fluorescence-based technologies.[1] Fluorescent substances combined with complementary techniques such as electronic devices photography, and technology of experiments could play a larger role in real-world explosive identification such as underground minefields and toxic substances in land, freshwater, and saltwater. For bomb identification, the fluorescent technique was used. Nevertheless, in current history, various other approaches, like as surface Raman

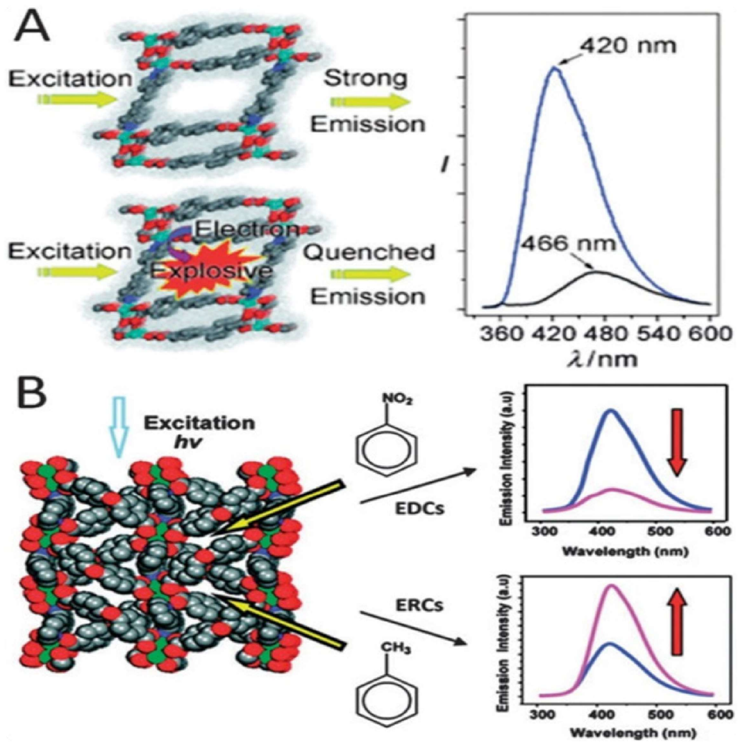

Figure 4: A highly luminescent microporous metal–organic framework, [Zn2(bpdc)2(bpee)] (bpdc = 4,40-biphenyldicarboxylate; bpee = 1,2-bipyridylethene), capable of very fast detection of the vapors of nitroexplosives and the fluorescence spectra before and after exposure to DNMB vapor for 10 s. (B) A highly luminescent 3D microporous MOF, [Zn2(oba)2(bpy)] DMA, demonstrates unique selectivity for the detection of electron-deficient explosives (EDCs) and electron-rich aromatics (ERCs) via a fluorescence quenching and enhancement mechanism.

Spectroscopy, have arisen as formidable instruments and have fiercely challenged with fluorescent techniques for explosive identification, which should not be neglected. Raman spectroscopy has spawned a new area of detection study since its emergence in the 1970s, owing to its advantages such as excellent specificity (molecule fingerprinting) and super-sensitivity (enhanced signals). Several scientists found on the discriminating and precise sensing of Trinitrotolouene using the Raman approach, and Limit of detection was reached at the 100 femto-molar levels as well as at the 15 atto-molar mark, which was significantly less than that of fluorescent based explosive investigative techniques.[6] Though Surface-enhanced Raman-spectroscopy has excellent capability in detecting explosives, it has some drawbacks, including low repeatability and expensive equipment setup. I believe that in the long term, chemiluminescence-based explosive sensing and Surface-enhanced Raman-spectroscopy-based explosive identification will augment each other. Though there are many obstacles in the case of responsiveness, specificity, steadiness, and expense for chemiluminescence-based explosive sensing, I assume that with the recent advancements in structural characterization of sensing substances and advancement in control system and data processing modeling, chemiluminescence-based explosive sensor will have a hopeful and positive experience. Owing to overall higher requirements for immigration control in the face of anticipated terror activity, including the rehabilitation of situations which already pose a serious threat as landmine clearance—the science of explosive sensing is guaranteed to continue an important and broaden the research area. Among the most significant characteristics of such techniques is scalability, and much work is currently done to miniaturize established technology Nanoparticles plays a significant part in this, as well as allowing the adoption of advance equipment. Increasing the responsiveness and selectivity of explosive sensing technologies maintain crucial components; lower limit of sensing for many compounds have grown significantly and studies in such situation continues a prominent subject of inquiry.[2] IJFMP

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