

## Development of polymer-based sensor systems for explosives vapour detection

R.N. Gillanders, P.O. Morawska, H. Nguyen, F. Chen, I.A. Campbell, I.D.W Samuel, G.A. Turnbull\*

Organic Semiconductor Centre, SUPA, School of Physics & Astronomy, University of St Andrews, St Andrews, Fife KY16 9SS, Scotland

\*Corresponding author. Email: [gat@st-andrews.ac.uk](mailto:gat@st-andrews.ac.uk)

### Abstract

This paper presents an overview of progress towards the development of compact polymer-based explosives vapour sensors for the detection of landmines. The sensors, under development within the TIRAMISU project, work by detecting a change in the light emission from a semiconducting polymer film when exposed to the vapours of TNT and related materials. The response of the sensor films to vapours of TNT, DNT, RDX and other relevant materials is presented. Portable, robust instrumentation for in-field explosives-vapour sensing integrating these semiconducting polymer films has been prototyped and results of initial tests in a simulated landmine environment are presented.

### Introduction

New technologies are required by the humanitarian mine action community to address the many challenges associated with the removal of buried landmines. Close-in detection of buried landmines commonly uses metal detectors, though these can suffer from high false alarm rates due to innocent fragments of metal. Combined use of metal detectors with ground penetrating radar and prodders can help to reduce false detections, but it would be very desirable to detect directly the chemical presence of the buried explosive itself.

Chemical detection of explosives in humanitarian demining is currently mostly based on the use of trained dogs, to detect vapours of the explosives. The animals are used in two main modes of operation: firstly by walking detection dogs across a section of a minefield, to determine whether that section should be selected for systematic close in detection with metal detectors. Secondly, they are used in a technical survey operation called remote explosive scent tracing (REST) [1], in which a target area of ground is surveyed by sampling air and dust in a filter, which is subsequently presented to the animal to detect vapours of explosives. The REST approach has been successfully implemented with animals by Mechem and others, but there could be advantages in using a sensitive electronic detector that can quantify the explosive residue in the filter, or even identify the constituents. Commercial vapour detection technologies, e.g. the fluorescence-based Fido sensor (Flir Systems) and ion mobility spectrometers, are used in military and airport applications but have not so far been adopted for humanitarian demining.

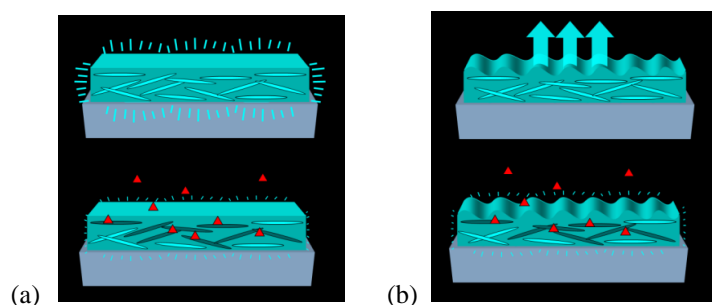
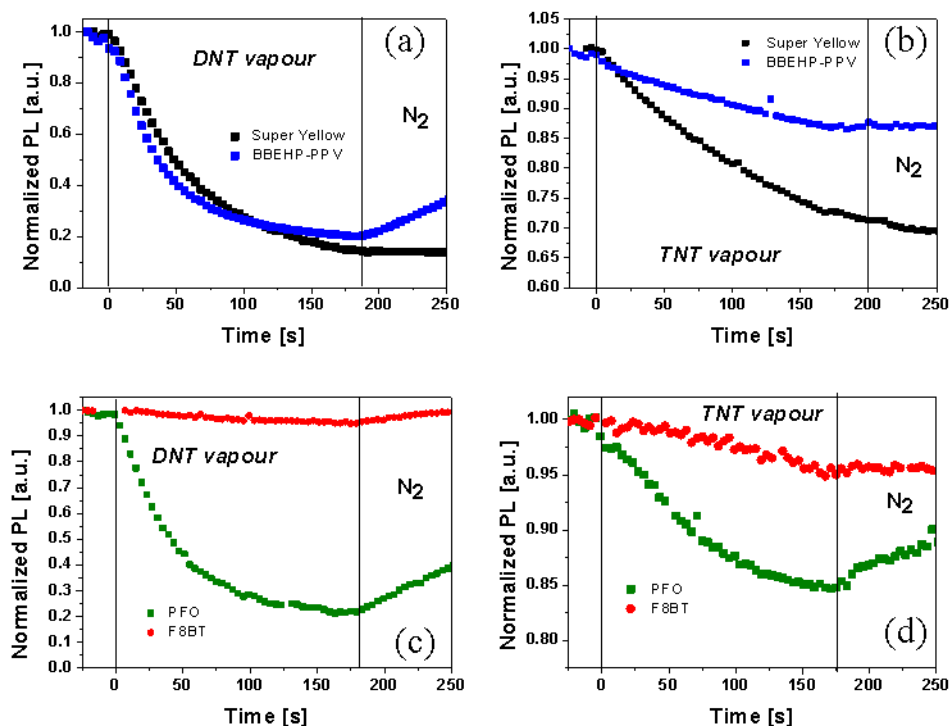


Figure 1. (a) concept of explosive vapour sensing using fluorescent polymer films (a) and polymer lasers (b). (a) Top panel shows blue fluorescence from a film of polymer molecules (blue rods). Bottom panel shows effect of TNT vapour exposure- when the TNT molecules (red triangles) come into contact with the polymer chains they switch off much of the light emission. (b) Top panel shows a blue laser beam emitted from a corrugated film of the polymer. Bottom panel shows effect of TNT vapour exposure, switching off the laser emission, leaving only weak fluorescence.

Within the TIRAMISU project, we are developing novel polymer-based sensors for detecting explosive vapours from landmines. These sensors work by detecting a change in the light emission from a semiconducting polymer film [2]. When exposed to very dilute vapours of TNT-like compounds, the explosive molecules are sorbed into the film and turn off the light emission due to a reversible electronic interaction between the molecules (Figure 1). The speed of response and sensitivity to TNT can be increased by generating laser light in the polymer film instead of fluorescence to detect explosives [3-6]. In this paper we describe progress towards the development of a compact polymer-based explosives vapour sensor that could be used for on-field mine detection. We describe the response of the polymers to nitroaromatic explosives and other relevant materials, and implementation of compact prototype sensor systems for single sensor and array detection.

### Polymer Response to Explosive Vapours

We have studied the response of a number of light-emitting polymer sensor materials to a selection of explosives and related materials including TNT, 2,4-DNT, 1,4-DNB, RDX, DMDNB and PETN. Figure 2 shows the change in light emission observed on exposure to ppb-level concentrations of DNT and TNT for example films from two groups of polymers (based on poly(para-phenylenevinylene) (PPV) and polyfluorene backbones). The sensing elements were films of approximately 50 nm thickness, deposited on silica substrates. Each film was exposed to the vapours for 180 s while the light emission was monitored, before being purged with nitrogen gas to remove the surrounding vapour. Each of these polymers significantly responded to the nitroaromatic vapours, with a measurable drop in the light emission within a few seconds after exposure. After removal of the DNT vapours, the light emission recovers as the DNT molecules are desorbed from the film. For the case of Merck “Super Yellow” polymer, no recovery is observed at room temperature, but the sensor can be ‘reset’ by heating the film. We observe that TNT molecules more strongly bind to the films but also show recovery of light emission at room temperature in some materials (e.g. PFO).



**Figure 2** Change in photoluminescence (PL) of four sensor polymers to vapours of (a), (c) DNT and (b), (d) TNT. The response of PPV-group polymers BBEHP-PPV and Merck “Super Yellow” are shown in (a) and (b) and the response of polyfluorene-group polymers PFO and F8BT are shown in (c) and (d).

The response of these polymers to a wider set of explosives is summarized in Table 1. These show fast response to ppb-level vapours, with measurable changes within a few seconds. One interesting result to note is that F8BT has much higher response to DNB than to DNT molecules, despite DNT having higher vapour pressure. Such variations in sensitivity to different explosives could be exploited to distinguish the detected chemicals.

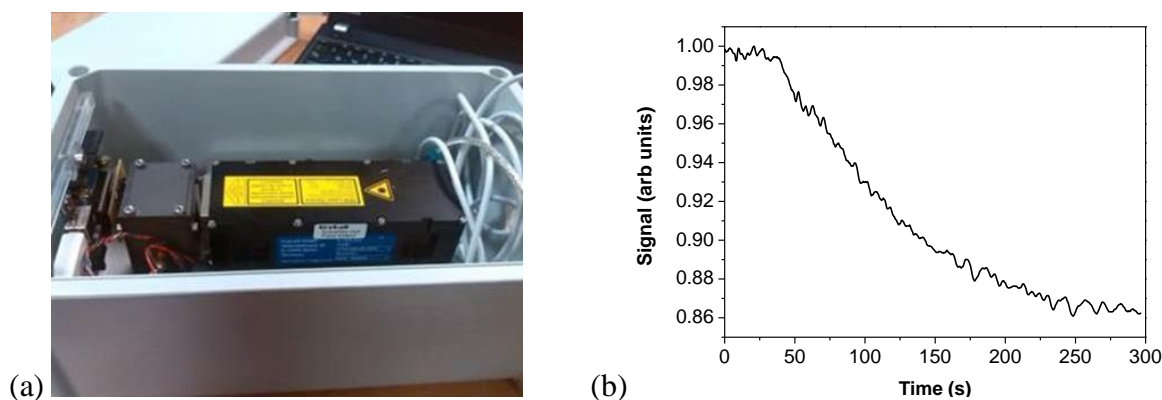
**Table 1:** Summary of the response (percentage change in the light emission output) of a selection of polymers following exposure to vapours of different explosive-related materials. 1,4-dinitrobenzene (DNB); 2,4-dinitrotoluene (DNT); trinitrotoluene (TNT); cyclotrimethylenetrinitramine (RDX).

polymer	polymer type	DNB	DNT	TNT	RDX
<b>BBEHP-PPV</b>	phenylene-vinylene	50%	80%	13%	5%
<b>Super Yellow</b>	phenylene-vinylene	77%	86%	29%	12%
<b>F8BT</b>	fluorene	35%	5.2%	5%	0%
<b>PFO</b>	fluorene	50%	79%	15.5%	11%

### Instrumentation Design

The explosives vapour detector is intended for deployment in two main scenarios: close-in detection of individual mines (in support of metal detector / GPR) by a deminer or robot, and for wide-area technical survey in combination with REST filters in a side-of-minefield configuration. A simple “yes/no” configuration allows the system to be stand-alone with a visual or aural alert if explosives are detected, while the full system has real-time monitoring of sensor emission via laptop or PC. For these two applications we have designed a modular system with the option for different vapour delivery to the sample chamber. However, the principle of the detection instrumentation for both applications is the same. In the laser/PL configurations the basic tool consists of the following elements:

- A thin-film polymer sensing element deposited on a glass/plastic substrate;
- A laser or LED excitation source that illuminates the luminescent polymer film;
- A light-detection module that monitors the intensity of the light emission from the polymer;
- A method to ensure satisfactory vapour/polymer contact;
- Control electronics/software for the light source and detector;
- Stand-alone operation with interface for computer communication.



**Figure 3:** (a)  $\alpha$ -prototype of explosive vapour detector with laser head; (b) Detection response of  $\alpha$ -prototype to DNT vapour (using a Super Yellow polymer film); vapour source switched on after 50 s.

The general principle of operation of the instrument, sees vapour drawn through a gland at the front end of an IP67 enclosure, passed through an air-tight chamber containing the polymer film sensor, and out an exhaust gland at the back. The system is shown on the left in Figure 3, with the lid off to show the components inside the box and laptop in the background for data capture and display. The sensor is excited by incident light from a Philips LED or compact pulsed laser, and the emission response is monitored by a Hamamatsu photodiode interfaced to an Arduino microprocessor which converts the signal from analogue to digital. The microprocessor sends the data via USB to LabView hosted on a laptop with real-time display, data saving options, and laser control software.

The sensor system has been used to detect vapours at ppb levels, and also for initial tests on buried vapour sources where a positive detection to DNT has been made. Measurements are ongoing to test for buried samples

of TNT, DNT and RDX. For simulated REST samples, the sensors have detected vapours from particles of TNT with masses as low as 250 ng, and made initial positive detections on contaminated REST filters.

### **CMOS Image Array for Selective Detection**

As discussed above, the sensor system responds to a range of nitroaromatic materials and other target explosives. To improve the selectivity of the sensor, a CMOS camera-based system for multi-sensor array detection is in initial development stages. By monitoring multiple sensor films in parallel this detection module should offer the possibility to “fingerprint” the explosive, enhancing selectivity. The imaging system approach should be low-cost, low footprint and give future potential to integrate the hardware and software with smartphones. Since each polymer material has a different response to each explosive, a combinatorial approach using multiple materials can yield a selective measurement to try to identify the particular explosive and give information about its concentration. Ultimately, a database could be built for explosives, pesticides, and other in-situ contaminants by mapping the unique pattern obtained from multiple sensor spots. The imaging sensor has been tested with the polymers listed in table 1 to successfully detect DNT vapour. We have also developed composite films based on molecularly imprinted polymers in which binding sites for DNT are specifically imprinted into a film of the light-emitting sensor polymer. These imprinted materials show a preferential response to DNT, TNT over potential interferants including some agricultural pesticides.

### **Conclusions**

Polymer-based explosive vapour sensors for mine / UXO detection have been developed which use sensing mechanisms based on both spontaneous emission and lasing in thin polymer films. A portable, compact version of the vapour sensor has been developed and the initial prototype is currently being tested. An input stage suitable for outside use has been made and following initial tests on buried explosives is currently being redesigned. Studies to optimise the sensor material response time and sensitivity have been undertaken. Approaches to optimise the design and processing of sensing materials for target vapours of TNT, DNT and RDX have been explored and evaluated. We have also developed strategies to increase the chemical selectivity including use of a multiple sensor array and light-emitting materials incorporated in molecularly imprinted polymers. The chemical sensors have successfully detected vapours from very small particles of explosives and detected vapours above sources that had been buried for several weeks. Assessment and validation of performance is ongoing and will continue into 2015, including measurements of response speed, range and limit of detection of nitro-aromatic vapours, and detection of buried explosives for use in realistic field conditions.

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