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Research paper

A low-cost, portable optical explosive-vapour sensor

Ross N. Gillanders*, Ifor D.W. Samuel, Graham A. Turnbull

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

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ABSTRACT

Humanitarian demining requires a broad range of methodologies and instrumentation for reliable identification of landmines, antipersonnel mines, and other explosive remnants of war (ERWs). Optical sensing methods are ideal for this purpose due to advantages in sensitivity, time-of-response and small form factor. In this work we present a portable photoluminescence-based sensor for nitroaromatic vapours based on the conjugated polymer Super Yellow integrated into an instrument comprising an excitation LED, photodiode, Arduino microprocessor and pumping mechanics for vapour delivery. The instrument was shown to be sensitive to few-ppb concentrations of explosive vapours under laboratory conditions, and responds to simulated buried landmine vapour. The results indicate that a lightweight, easy-to-operate, low-cost and highly-sensitive optical sensor can be readily constructed for landmine and ERW detection in the field, with potential to aid worldwide efforts in landmine mitigation.

1. Introduction

Global conflicts over decades have seen a legacy of landmines and Explosive Remnants of War (ERWs) left buried and active long after the conflicts themselves may be over. In addition to their inherent danger, the presence of mines prevents trade, communication and land use among local peoples. While several demining techniques are presently used successfully, there is still a pressing need in current humanitarian demining for rapid-response in-situ measurement techniques appropriate to a wide range of environments, since existing methods are not necessarily able to operate over extended periods of time in the field. Common methods such as canines have stringent and limited working practice in the field, in addition to occasional unpredictability or fitness-to-work of the canines [1,2]. Other commonly-used techniques, such as metal detection, can flag false positives like harmless fragments of metal [3]; others have intrinsic high danger, such as prodders which require a deminer to physically push at the landmine. Detection of vapours given off by landmines, such as tri-nitrotoluene (TNT) or its derivative di-nitrotoluene (2,4-DNT), can potentially complement the above methods to mitigate these issues, since the non-contact nature of vapour detection allows one to identify a landmine that may be missed by other methods, for instance a plastic mine being missed by a metal detector. A hand-held, in-situ and sensitive system based on explosive vapour sensing would provide an extremely useful tool in the field for demining.

In the development of a low-cost and field-serviceable instrument, an Arduino Uno, from the Arduino family of off-the-shelf development kits that have been receiving increasing interest since their release in 2012, can be a suitable microprocessor to handle signal capture and A/D conversion. Recent work has shown Arduino platforms integrated into optical sensing systems, for instance for Copper (II) ions [4] and Volatile Organic Compounds in seawater [5]. Another advantage to these platforms is that the device can be flashed with firmware allowing the device to function without the need for external control software from e.g. a laptop computer. Simple functionality such as this allows for an "on/off" version of the system, where an alert can be made by buzzer or warning light to indicate the detection of explosive vapours, allowing a simple deployment.

There have been extensive studies on conjugated polymer films for explosives detection [6–12]. Conjugated polymers have great potential for humanitarian demining due to the high sensitivity of their light emission to the presence of nitroaromatic compounds. The sensing mechanism is based on the transfer of an electron from a photo-excited exciton state in an electron-rich polymer to an electron-deficient adsorbed molecule from the vapours, resulting in a loss of light emission. The light emission is quenched, in proportion to the level of nitroaromatic vapour present, as this photo-induced electron transfer provides a non-radiative pathway for the exciton to relax. This reduction in light intensity can subsequently be monitored using a photodiode, aiding development of low-cost, compact optical sensors. Since the polymers are typi-

* Corresponding author.
E-mail address: rg89@st-andrews.ac.uk (R.N. Gillanders).

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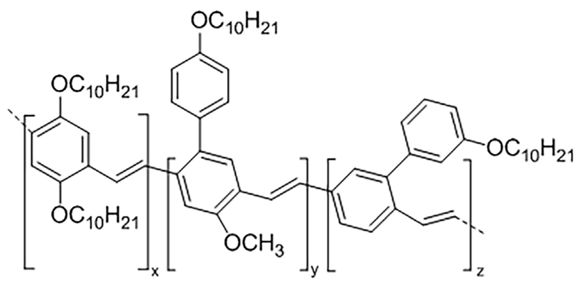

Fig. 1. Chemical structure of Merck Super Yellow, with x:y:z = 1:12:12.

cally spin-coated to give films a few tens of nm thickness on glass substrates, the sensor films can be produced in large enough quantities for disposable use after positive identification of explosives. The commercially-available polymer Merck Super Yellow, part of the PPV group of conjugated polymers and illustrated in Fig. 1, has previously been shown to have a high PLQY [13]. The chemical properties of this material has been characterised in other work for applications as polymer LEDs (PLEDs) [14], and displays high sensitivity to nitroaromatic vapours with 2,4-DNT giving a significant quenching effect [12].

In this work we present a small-form, low-cost, robust, easy-to-use and field-serviceable optical sensor for explosive vapours to help address the challenges involved in humanitarian demining. It is anticipated to be able to be used in conjunction with established humanitarian demining technologies to aid in reduction of false negatives and contribute to a more comprehensive surveying suite of technologies.

2. Experimental

2.1. Film fabrication & characterisation

Films based on the conjugated polymer Super Yellow (supplied by Merck) were prepared by spin-coating, at 2000 rpm, from a 6.5 mg/ml solution of the polymer in toluene onto 1 cm x 1 cm glass coverslips from Agar Scientific. The film thickness was measured using a Veeco Dektak 150 surface profiler and films were typically 100 nm thick. The film thickness has previously been shown to affect the speed of response to vapours due to molecules penetrating the polymer matrix at a fixed rate [9], and so films of 100 nm thickness were chosen to allow a fast response to the vapour. Photoluminescence Quantum Yield (PLQY) measurements were performed in an integrating sphere [15], using a Hamamatsu Photonics C9920-02 measurement system with an excitation wavelength of 440 nm. Absorption and emission spectra were measured with a Cary 300 Bio UV–vis absorption spectrometer and Edinburgh Instruments FLS980 Fluorescence spectrometer respectively.

2.2. System architecture

The system operates by a polymer film being loaded into an airtight sample chamber with windows on each side to allow excitation by an LED, and collection of photoluminescent emission by a photodiode. The vapour is drawn via the bottom face of the enclosure by a pump, past the polymer film, and out via an exhaust line. The pump and LED are switched on manually by switches on the enclosure, with emission data being processed on an Arduino microprocessor prior to being sent via USB to a laptop.

Fig. 2(a) shows a schematic of the system architecture, with a photograph of the system with lid removed in Fig. 2(b) and a photograph of the sample-loading mechanism in Fig. 2(c). The LED was a high-power Royal Blue LUXEON LED from Philips, driven

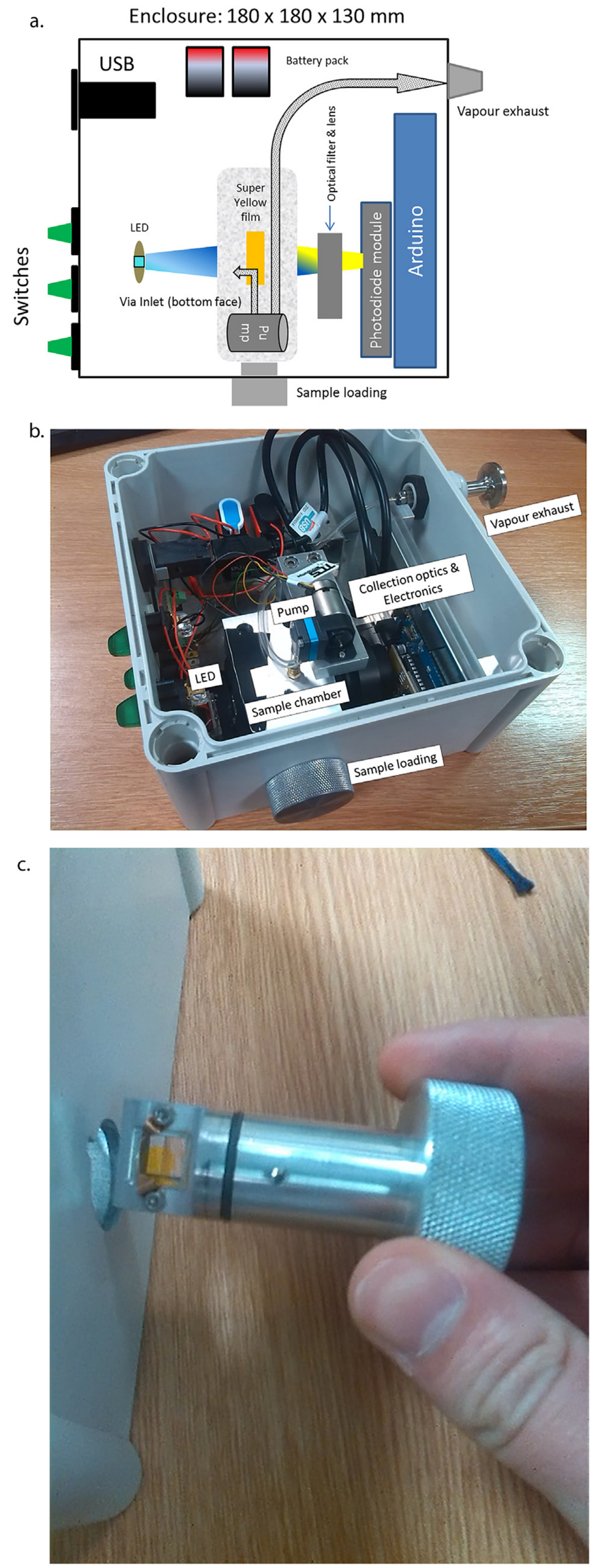

Fig. 2. (a) Schematic of instrumentation (not to scale); (b) Photograph of Enclosure with labelled parts; (c) Loading mechanism with a Merck Super Yellow film.