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This work explores the use of a green-light-emitting copolymer as a chemosensor to detect nitroaromatic-based explosive vapors by recording photoluminescence (PL) and time-resolved PL decay. We show successful detection of 10 ppb 1,4-dinitrobenzene (DNB) vapor. Both a conventional time-correlated single photon counting (TCSPC) device and CMOS time-resolved fluorescence lifetime micro-system are used in the DNB detection. An ultra-portable on-site explosive sensor based on the micro-system has also been demonstrated. This gives rise to the potential for real-time, reliable, inexpensive organic/inorganic hybrid explosives detection. Copyright 2011 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [doi:10.1063/1.3624456]

I. INTRODUCTION

There is currently a critical need for rapid in-field methods of sensing explosive compounds due to the increased security issues and threats across the world. Non-biological sensors1 are being developed to help us detect these dangerous materials. These sensors must fulfill a number of criteria, namely sensitivity, stability, reversibility and a capability for real-time signal processing. For nitroaromatic explosives, sensing of a few parts per billion or less of the analyte is required, with rapid and ideally reversible signal changes in the sensor. For in-field applications, a portable system would be advantageous.

Conjugated polymers have emerged as a promising chemosensory material for detecting nitroaromatic explosive vapours, as they readily transform a chemical interaction into an easily measured optical output with high sensitivity.2,3 The explosive vapour analyte consists of nitrated molecules which are strongly electron-deficient, while the conjugated polymer sensing materials are electron-rich. This means that the lowest unoccupied molecular orbital (LUMO) of the explosive vapour is at lower energy (further from the vacuum) than the LUMO of the polymer. As a result, photoexcitation of the conjugated polymer is followed by electron transfer to the explosive vapour, leading to quenching of the light-emission from the conjugated polymer. Based on this process, several sensing mechanisms such as photoluminescence (PL), amplified spontaneous emission (ASE), and lasing have been explored for explosives detection.4

All of these fluorescence-based sensing techniques measure a reduction in the output power of the light-emission. An alternative approach would be to measure a change in the PL lifetime, because the quenching process increases the non-radiative relaxation of the photo-excited polymer.
This provides a powerful way of measuring dynamic quenching, in which excitations move to a quencher. Measurements of PL lifetime are more readily quantifiable so can be less affected by internal and external environmental factors (for example the number of excited states in the polymer, excitation intensity, collection efficiency and stray light). Recently time-resolved fluorescence lifetime measurements have been reported for detecting nitro-aromatic molecules co-dissolved in solution with conjugated polymers and dendrimers. However, using thin films enables a quenching enhancement, as a single analyte molecule is able to quench many chromophores not only on the same but also on the neighboring polymer chains. In this work, we demonstrate PL lifetime detection of low pressure explosive vapours of 1,4-dinitrobenzene (DNB) using thin films of a fluorescent conjugated copolymer combined with a very compact CMOS time-resolved fluorescence lifetime micro-system. The fluorescent conjugated copolymer is a fluorene based copolymer “CDT Green (CDTG)” supplied by Cambridge Display Technology Limited (CDT Ltd). In addition to standard TCSPC measurements, we also use a two-gate rapid-lifetime determination (RLD) algorithm to compute the PL lifetime in real time. This offers a potentially powerful approach for portable and rapid on-site explosives detection.

II. MATERIALS AND METHODS

A. Photophysical study of the conjugated polymer

The CDT Green (CDTG) copolymer films were spin-coated onto fused silica substrates from toluene solutions (5 – 30 mg/ml) to achieve a range of film thickness varying from 30 nm to 400 nm. The film thicknesses were measured with a Veeco Dektak 150 surface profiler. Absorption spectra were measured with a Cary 300 Bio UV-Vis absorption spectrometer. The PL spectra were measured with a Jobin-Yvon Horiba FluoroMax2 fluorimeter with excitation at a wavelength of 379 nm which is the peak of the absorbance of the films. The solid-state photoluminescence quantum yield (PLQY) was measured with the same excitation wavelength using an integrating sphere in a Hamamatsu Photonics C9920-02 measurement system.

The fluorescence decay lifetime of the solid-state CDTG copolymer was first measured with a conventional time-correlated single photon counting (TCSPC) system (shown in Figure 1(a)). Excitation was provided by a pulsed nitride LED (Picoquant PLS-8-2-066) which provided pulses of duration 1.2 ns at a wavelength of 457 nm, with a repetition rate of 100 kHz. The emitted light was collected by a lens and passed through a monochromator to a micro-channel plate photomultiplier tube (MCP-PMT, Hamamatsu RU-3809U-50). The output of the MCP-PMT passed through an amplifier; a constant fraction discriminator (CFD) connected to a time to amplitude converter (TAC) linked to a multi channel analyzer (MCA); and a PC loaded with analysis software. The full width at half maximum (FWHM) of the instrument response function (IRF) was 1.1 ns. The time-resolved data were fitted using iterative reconvolution to a bi-exponential decay:

\[ y(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \]  

An average fluorescence lifetime is defined by:

\[ \tau_{avg} = \frac{A_1 \tau_1 + A_2 \tau_2}{A_1 + A_2} \]  

The fitting was performed using IBH Ltd. decay analysis software FMAS DAS6.

B. Fluorescence lifetime measurement with the CMOS micro-system

The design of the CMOS-based micro-system and its application for time-resolved fluorescence lifetime measurements of colloidal quantum dot and Rhodamine dyes in solution was previously reported in reference. The system combines a CMOS-driven LED-array excitation source, photodetector and lifetime signal processing circuitry, providing a compact, potentially low-cost approach for measuring the fluorescence decay lifetime of the polymer (see Figure 1(b)). All results from the micro-system were performed with an excitation peak at 450 nm achieved using pixels of an 8 × 8 array of AlInGaN micro-LEDs, where the pixels were of diameter...
72 μm. The CMOS-driven LED pulse width was adjusted to be 1.2 ns (FWHM). The time-resolved analysis system on a second CMOS chip includes a fully addressable array of $16 \times 4$ single-photon avalanche diode (SPAD) detectors (aligned to the micro-LED device), integrated with on-chip timing and signal processing circuits. A 514 nm long pass filter (Semrock, LP02-514RU-25) was inserted between the micro-LEDs and the SPAD chip to block residual excitation. With the copolymer film inserted between the two chips, the lifetime decay was then captured within a series of gated count
FIG. 2. (a) Illustration of a fluorescence lifetime decay histogram; (b) Illustration of the two-gate rapid-lifetime determination technique, using two equal time gates.

windows. The time-gate width was selected to be approximately 460 ps. The photon count values obtained in each time gate were captured and used to build a histogram of the decay curve (shown in Figure 2(a)); this was then displayed on a laptop computer. The IBH software was used to fit the measured decay curves as described in section IIA.

A rapid lifetime determination (RLD) method was developed in which it is assumed the transient PL of the polymer sample can be approximated by a single-exponential decay, the lifetime $\tau$ of which is determined by:

$$I(t) = I_0 \exp(-t/\tau)$$  \hspace{1cm} (3)

where $I(t)$ is fluorescence intensity at time $t$, $I_0$ is initial fluorescence intensity ($t = 0$). In the RLD measurements with the two-chip micro-system, the accumulated counts ($A_1$ and $A_2$ shown in Figure 2(b)) detected in two equal-time windows $\Delta t$ ($\Delta t = 4 \times 460$ ps time-gate in this experiment) were recorded, taking into account a background reading measured beforehand. The starting time for $A_1$ was set to be immediately after the excitation pulse. The decay lifetime $\tau$ is calculated using Equation (4).

$$\tau = \frac{\Delta t}{\ln(A_1/A_2)}$$  \hspace{1cm} (4)

For an exposure time for each window of 4 s, the RLD measurement takes approximately 15 s. The program-controlled system can take 20 RLD measurements continuously, allowing lifetime changes to be observed in near real-time.

C. Ex-situ sensing of explosives based on PL (as a reference) and lifetime

The explosive nitroaromatic analyte, 1,4-dinitrobenzene (DNB), was used during this investigation as it is chemically similar to the explosive TNT and highly electron-deficient. In the PL sensing experiments, the CDTG copolymer thin films were placed inside a chamber with a valve-controlled gas port, allowing the flow of DNB vapor or clean nitrogen into the chamber. A valve-controlled exhaust port from the chamber was connected to a bubbler. With this configuration the chamber can either be filled with $\sim 10$ ppb by volume DNB vapor and sealed, or be ‘cleaned’ using a nitrogen flow. The films were excited by a 355 nm pulsed Nd:YVO$_4$ laser at 500 Hz repetition rate with an average power of 80 $\mu$W. Light emission spectra from the samples, before and after a 15 minute exposure to DNB, were detected using a fibre-coupled charge-coupled device (CCD) spectrograph and were integrated manually across the whole fluorescence wavelength range. A few different thicknesses were studied to investigate the dependence between film thickness and sensing efficiency.
A conventional TCSPC system was used to measure the fluorescence lifetime before and after the 15-minute exposure. To recover the fluorescence lifetime, clean nitrogen with a similar flow-rate to that used in the exposure process, was flowed through the chamber for a further 15 minutes. The CMOS lifetime analysis micro-system was also used to detect the DNB vapor. The CDTG copolymer films were sandwiched between the micro-LED and SPAD chip. A histogram of the time-resolved decay curve of the pre-exposed, post-exposed and recovered CDTG copolymer films was recorded respectively, under the same exposure and recovery conditions as that in the conventional TCSPC sensing measurements.

D. Ultra-portable explosive sensing using the CMOS micro-system

To measure the dynamic response of the sensing process, a two-gate RLD method was used to monitor the fluorescence lifetime in real time using the two-chip micro-system. The whole micro-system with CDTG films was all placed in a 20 × 13 × 7 cm$^3$ customized sensing box (shown in Figure 3). Several CDTG films of different thicknesses were exposed to ~ 10 ppb DNB vapor one at a time, allowing us to study the effect that film thickness has on sensing efficiency. The lifetime of each film was calculated on-chip every 15 seconds for 15 minutes continuously. Following exposure, the gas port of the box was switched to clean nitrogen allowing the kinetics of the lifetime recovery to be monitored. All this suggests the micro-system has the potential to perform a near-real-time on-site detection of low vapor pressure explosives.

III. RESULTS AND DISCUSSION

To study the photophysical properties of the CDTG copolymer, absorption and PL spectra of a 250 nm thick film were measured (see Figure 4). The figure shows that the absorption and emission
are peaked at 379 nm and 538 nm, respectively. The solid-state PLQY was measured to be 61% ± 6% when excited at 379 nm. The PL lifetime was measured with a conventional TCSPC system with an excitation from a 457 nm LED. By fitting the time-resolved PL decays to a bi-exponential decay curve, we measured a steady-state PL lifetime with a fast component 1.3 ns ± 0.5 ns (pre-exponential factor 0.80) and a slow component 3.5 ns ± 0.2 ns (pre-exponential factor 0.20). We note that the fast component is less accurate because it is close to the IRF.

The PL emission was found to be quenched when the CDTG films were exposed to the 10 ppb DNB vapor (results shown in Table I). After a 15-minute continuous exposure, the spectrally-integrated emission intensity dropped by 38% on average ($\Delta_{PL}$) over the three different thickness samples. Figure 5(a) shows the PL decay curves from the same sample #3 (150 nm thick) measured with a conventional TCSPC system; again quenching was observed under the influence of the DNB molecules. The lifetime values in Table I were extracted from the decay curves by the fitting of double-exponential expressions deconvolved with the instrument response individually. After a 15-minute exposure the average lifetime of the 150 nm thick sensor measured with the conventional TCSPC decreased from 1.78 ns to 1.11 ns, dropping by 38% ($\Delta_{\tau_{avg}}$), in good agreement with the change in PL intensity ($\Delta_{PL}$). After exposure, the PL intensity and lifetime were fully recovered by the flowing of clean nitrogen through the optical chamber (data not shown in Table I).

Corresponding TCSPC measurements were also performed using the CMOS micro-system. From Table I we can see that the lifetimes measured with the two different methods are relatively consistent, showing that the CMOS micro-system can provide a compact and easy-to-operate approach for fluorescence lifetime measurements. Figure 5(b), the PL decay as measured by the CMOS micro-system, clearly shows a decrease in the PL lifetime after the film is exposed to the DNB vapor, and that a full recovery of the lifetime is achieved after purging with nitrogen. By fitting the data to the double-exponential expressions the average lifetime was calculated to be 2.66 ns before exposure and 1.63 ns after exposure, reducing by 38%. The percentage changes in lifetime are consistent with the results measured with conventional TCSPC. Quenching can potentially be “static” in which the fluorophore and quencher bind together to form a nonemissive state, or “dynamic” in which an
FIG. 5. (a) Conventional TCSPC lifetime sensing with sensor #3 (i.e. thickness of 150 nm); (b) CMOS micro-system sensing results from the same sensor.
TABLE I. Comparison of the change in emission intensity (ΔPL) and lifetime measured with both the conventional TCSPC and the CMOS micro-system, before exposure (pre-exp) and after a 15-minute exposure to DNB (post-exp). Pre-exponential factor are shown in brackets. Also shown is the change of average lifetime in percentage (Δτ_avg). The film thicknesses of sample #1, #2 and #3 are 50 nm, 95 nm and 150 nm, respectively.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Film thickness</th>
<th>ΔPL</th>
<th>Pre-exp</th>
<th>Post-exp</th>
<th>Δτ_avg</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>50 nm</td>
<td>36%</td>
<td>1.3 ns</td>
<td>0.97 ns</td>
<td>32%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.4 ns</td>
<td>2.9 ns</td>
<td></td>
</tr>
<tr>
<td>#2</td>
<td>95 nm</td>
<td>40%</td>
<td>1.3 ns</td>
<td>1.0 ns</td>
<td>30%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.5 ns</td>
<td>3.0 ns</td>
<td></td>
</tr>
<tr>
<td>#3</td>
<td>150 nm</td>
<td>38%</td>
<td>1.3 ns</td>
<td>0.91 ns</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.3 ns</td>
<td>2.9 ns</td>
<td></td>
</tr>
</tbody>
</table>

TABLE II. In-situ CMOS lifetime results both before exposure (pre-exp) and after a 15-minute exposure to 10 ppb DNB vapor (post-exp), and after a 15-minute recovery (post-rec), also shown the change of lifetime (Δτ) during the 15 minute periods.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Film thickness</th>
<th>CMOS TCSPC lifetime</th>
<th>Δτ</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>50 nm</td>
<td>2.85 ns 1.70 ns 2.90 ns</td>
<td>40%</td>
</tr>
<tr>
<td>#2</td>
<td>95 nm</td>
<td>2.82 ns 1.80 ns 2.90 ns</td>
<td>36%</td>
</tr>
<tr>
<td>#3</td>
<td>150 nm</td>
<td>2.95 ns 1.93 ns 2.95 ns</td>
<td>35%</td>
</tr>
<tr>
<td>#4</td>
<td>200 nm</td>
<td>3.00 ns 1.92 ns 2.94 ns</td>
<td>36%</td>
</tr>
<tr>
<td>#5</td>
<td>250 nm</td>
<td>3.00 ns 2.05 ns 2.90 ns</td>
<td>32%</td>
</tr>
<tr>
<td>#6</td>
<td>330 nm</td>
<td>2.95 ns 1.95 ns 2.72 ns</td>
<td>34%</td>
</tr>
<tr>
<td>#7</td>
<td>400 nm</td>
<td>3.20 ns 2.00 ns 2.73 ns</td>
<td>38%</td>
</tr>
</tbody>
</table>

excited state moves to a quencher. We observe similar reductions in steady-state and time-resolved PL, which indicates that dynamic quenching dominates.

We next demonstrated real-time explosive sensing experiments with the CMOS micro-system during an exposure and recovery cycle for seven different thicknesses CDTG films (sensors); results are summarized in Table II (sensor #1 - #3 are the same as the ones in Table I). It should be noted that as the rapid-lifetime determination method assumes the fluorescence decay is single-exponential, the CDTG lifetime values are slightly over-estimated in the RLD scheme, but in an acceptable range - the longer lifetime component contributes more to the on-chip calculation of the average lifetime value. Taking sensor #3 for example, Figure 6 shows that the dynamics of the PL lifetime of a 150 nm film in 15-minute exposure to 10 ppb DNB vapor (decreasing from 2.95 ns to 1.93 ns) and 15-minute recovery in nitrogen (increasing back to 2.93 ns). The sensing efficiency (i.e. change in average lifetime Δτ_avg) of sensor #3 in the total 15 minutes is 35%. Additionally Δτ values in Table II were found to be independent of the variation of the thickness of the CDTG films, suggesting that the DNB molecules can penetrate into both thin and thick CDTG films in the 15-min period of the measurements.

IV. CONCLUSIONS

We have shown that the conjugated copolymer CDTG, in combination with a CMOS PL lifetime detection system, can be used as a chemo sensor for detecting low vapor pressure nitro-aromatic molecules. Two different lifetime measurement schemes - conventional TCSPC and CMOS time-resolved fluorescence lifetime analysis – were investigated. For both schemes, successful indication of the presence of the analyte based on the monitoring of the PL lifetime of the copolymer films has been achieved. Compared to the conventional TCSPC, our results show that the CMOS micro-system provides both a simple and reliable technique for PL lifetime measurement, with potential for
FIG. 6. Real-time two gate RLD dynamics during (a) 15-minutes exposure, and (b) 15-minutes recovery, of sensor #3. The scatter points in the figures represent the RLD lifetime values every 15 seconds, the background individual bars represent the average lifetime value every 60 seconds with standard deviation error bars.

practical applications such as in-field explosive detection. A sensing efficiency of approximately 40 % has been achieved with several thicknesses of CDTG films after a 15-minute exposure to 10 ppb DNB vapor. It has also been shown that the PL emission recovers completely with a nitrogen purge over the same period of time. Furthermore, we have shown that in near-real-time, the required time-resolved lifetimes can be monitored with our compact, convenient and ultra-portable CMOS-based micro-system.
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