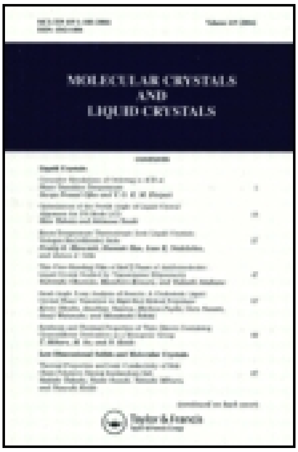

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Explosive Sensing Using Polymer Lasers

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Explosive Sensing Using Polymer Lasers

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Conjugated polymers are attractive materials that have been used to make a wide range of optoelectronic devices. Recently they have been used as explosive sensors as there is currently an urgent need for high sensitivity explosive detection due to the increased security issues across the world. This review outlines the attractive properties of organic polymers as gain media in lasers, and then focuses on the use of such lasers for explosive sensing applications. The combined advantages of fluorescent polymers and lasing promise explosive sensors with strongly enhanced sensitivity.

Keywords Conjugated polymer; distributed feedback laser; explosives; fluorescence quenching; sensor

Introduction

Over the last two decades, conjugated polymers have been an important class of solution-processable semiconductors [1–5], that have attracted a great deal of interest. The combination of novel semiconducting optoelectronic properties with simple processing from solution and the possibility of flexible devices has opened up many directions for research and applications. The potential of these materials for a wide range of optoelectronic devices has been investigated, including organic transistors [6–8], light-emitting diodes (LEDs) [9,10], photodetectors and photovoltaics [11–14]. As the field has developed, new materials and devices have emerged which in turn have led to new applications [15,16]. A current field of considerable interest is organic semiconductor lasers (OSLs) [17–20].

The first conjugated polymer laser was reported in 1992 by Moses [21] it consisted of a solution of poly[2-methoxy, 5-(2′ ethyl-hexyloxy)-*p*-phenylenevinylene], MEH-PPV, pumped by a frequency doubled Q-switched pulsed Nd:YAG laser. This led the way for solid-state conjugated polymer lasers which were reported four years later [22–25]. It was found that lasing could occur in simple structures containing sub-micrometer organic semiconductor films, indicating that light-emitting polymers had both strong absorption and high gain. In addition to the efficient absorption and emission, i.e., high photoluminescence quantum yield (PLQY), these materials have many attractive features for lasing including their scope for simple fabrication [26] and flexibility [27]. Moreover, the broad vibronic bandwidth also promises much shorter output pulse widths and larger tunability ranges compared to inorganic semiconductor lasers [17,28–30]. These advances of conjugated

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*Address correspondence to Ifor D. W. Samuel, Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews, KY 16 9SS, UK. Tel.: (+44) 133446 1618; E-mail: idws@st-andrews.ac.uk polymers have opened and continue to open the way for more novel optical and electrical applications. In this article, we focus on and review progress towards using conjugated polymers for trace explosive sensing.

Explosive Sensing by Fluorescence Quenching of Organic Semiconductors

A critical need for trace explosives detection continues to attract both public and government attention, including the need to clear minefields left by past wars. To meet this need devices with high sensitivity are desired so to avoid omission (i.e. the missing of potentially dangerous objects). Most explosives consist of organic compounds, containing nitro or nitroaromatic groups that release low concentration vapour or gases even when unexploded, for example 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT) and 1,4-dinitrobenzene (DNB) [31].

Fluorescent conjugated polymers have emerged as one of the most promising candidates for sensing explosives of small magnitude, in particular for sensing nitroaromatic-based explosives [15,32–38]. The highly nitrated molecules in these explosives make them ‘electron-deficient’ so that when these electron acceptors come into contact with ‘electron-rich’ conjugated polymers, photoinduced electron transfer occurs between the lowest unoccupied molecular orbital (LUMO) of the polymer and the LUMO of the analyte (explosive) molecule with lower energy state. This charge transfer causes efficient quenching of fluorescence, as shown schematically in Fig. 1. The world’s first fluorescent

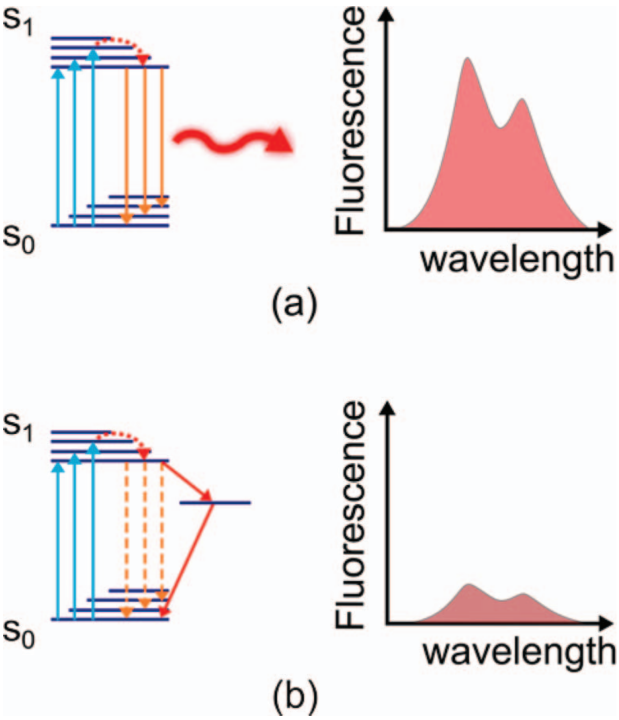

Figure 1. Energy levels and fluorescence for (a) organic semiconductor; (b) organic semiconductor and explosive analyte.

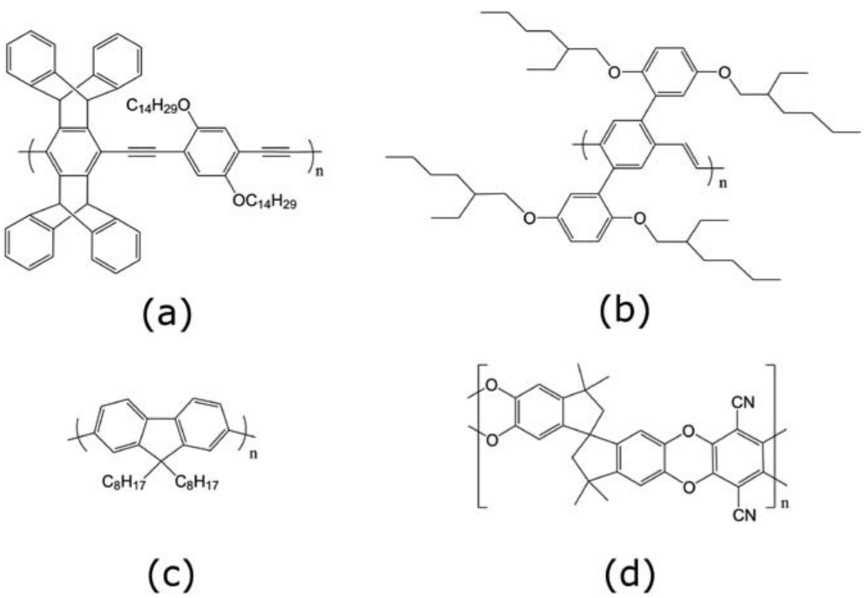

Figure 2. Chemical structures of polymers used for explosive sensing. (a) Pentiptycene-derived phenyleneethynylene polymer designed for use in the sensing of TNT in [15]; (b) polymer used within the micro-ring laser sensor [46]; (c) commercially available polyfluorene; (d) polymer of intrinsic microporosity PIM-1 [53].

polymer films, used as TNT chemosensors, were demonstrated in 1998 by Yang and Swager [15,32]. A group of fluorescent pentiptycene-derived phenyleneethynylene polymers, shown in Fig. 2a, was designed to be highly sensitive to TNT vapour as their rigid three-dimensional pentiptycene moieties in the polymer backbone both prevented self-quenching in the solid state and also provided porosity in thin films for analyte binding.

The Swager group has also shown that strong quenching of conjugated polymer fluorescence can result from relatively few nitroaromatic quenching molecules [39,40]. In conjugated polymers the photoinduced emissions are dramatically influenced by small numbers of binding events, i.e., a single explosive molecule can quench many repeat units of the polymer chain. In addition neighbouring polymer chains can also be quenched as in the film, interchain exciton transport enables excitons formed on one chain to move to quenching sites on other chains. Time-resolved spectroscopy has shown exciton diffusion lengths in thin films of some poly(*p*-phenylene vinylene) (PPV) based polymers to be on the order of 5 nm to 8.5 nm [41,42].

The most convenient way of using a conjugated polymer to detect explosive vapour is to measure its change in fluorescence intensity. Changes in fluorescence intensity from 10% to 80% in 1 minute have been reported for polymer films on exposure to a few parts-per-billion (p.p.b.) TNT vapours [15,37,38]. A more sophisticated approach is to make a time-resolved photoluminescence (PL) measurement [43,44]. The non-radiative relaxation of the excitons from the photo-excited polymer to the analytes results in a shorter fluorescence lifetime of the polymer. This can be measured in a convenient portable way by using a complementary metal–oxide–semiconductor (CMOS) based PL lifetime micro-system [45]. A fluorene-containing polymer was excited by a nitride micro-LED array, driven by short pulses from a CMOS chip. Fluorescence was detected by an array of CMOS single photon avalanche photodiodes, enabling time-correlated single photon counting (TCSPC). A change in PL lifetime of approximately 40% has been achieved after a 15 minute exposure to DNB vapour and this corresponded to the change in steady-state fluorescence.

Explosive Sensing by Quenching of Microring Lasers

In 2005, Bulovic, Swager and co-workers reported an organic microring laser providing high sensitivities to nitroaromatic analytes [46]. A poly(*p*-phenylene vinylene) based material (molecular structure shown in Fig. 2b) which showed high PLQY of 80% was designed to detect TNT and DNT. Amplified spontaneous emission (ASE) was studied within a glass-parylene-polymer-air planar structure where the parylene layer in combination with the polymer formed a waveguide. The change in ASE of the polymer on exposure to DNT was 30 times greater than the change of PL, which indicated that lasing (stimulated emission) would further enhance this sensitivity. By using a ring-mode lasing structure, illustrated in Fig. 3a, made by dip-coating a 25 μm diameter silica fibre with polymer solution, 5 p.p.b. TNT was detected by observation of attenuation in the lasing action before any change of the fluorescence could be measured. Moreover, the authors suggested that to get the highest sensitivity, the pump power should be set to just above the threshold of the unexposed polymer laser. The authors' reason for using a microring laser configuration for sensing rather than the more conventional distributed feedback (DFB) resonator was due to the limited penetration depth (up to 15 nm) of the analytes into the neat polymer film.

However, a microring is an inconvenient laser geometry, because it emits light in all directions, rather than as a beam. Subsequent work has explored whether the effect occurs in other polymers, whether other resonator geometries can be used, and key performance parameters such as response time.

Explosive Sensing by Quenching of DFB Lasers

More recently, polyfluorene (PFO, see Fig. 2c), a widely available prototypical polymer, has been used in the convenient DFB resonator configuration, illustrated in Fig. 3b, to detect low vapour pressure nitroaromatics-based explosives [47]. After the PFO laser was exposed to 9.8 p.p.b. 1,4-dinitrobenzene (DNB) for 5 minutes, the lasing threshold was seen to increase by 1.8 times from 6.8 to 12.5 μJ/pulse due to the quenching states introduced by the DNB molecules. Sensing enhancement was also observed here compared to a pure fluorescence sensing scheme using thin films. The output intensity against input power

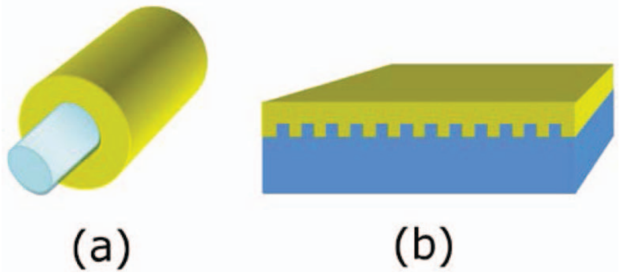

Figure 3. (a) Microring laser i.e. fibre surrounded by optical gain material; (b) DFB laser i.e. corrugated substrate coated with thin film of gain material.

intensity indicated that the slope efficiency of the DFB laser was reduced by a factor of 3, providing an alternative convenient and sensitive way of detecting explosives.

Furthermore, Yang, Turnbull and Samuel found that the PL and lasing could be fully recovered by removal of the analyte molecules [47]. In order to investigate the interaction speed between DNB molecules and the PFO laser, they monitored the temporal dynamics of the laser emission during exposure and recovery. This information is extremely important in terms of practical applications such as security checks and mine detection which require fast and sensitive sensors. While the PFO laser was pumped at 3 times the threshold of the unquenched laser, the lasing output decreased rapidly by 20% in an initial 14-second exposure followed by a 40% drop within 46 seconds, and very little further change after a 5 minute exposure time, which was limited by the diffusion distance of the DNB molecules into the PFO films. The authors also developed a model to determine how far the DNB penetrated into the PFO films. By fitting the experimental data on quenching efficiency in different thickness films to the model, it was shown that DNB could penetrate as deep as 71 nm into PFO films in 5 minutes. Meanwhile the films still gave 15% of their original emission in the presence of DNB molecules as excitons existing outside the exciton diffusion range, from an analyte molecule, could not be quenched.

Materials Developments for Explosive Sensing in Lasers

So far we understand that the degree of fluorescence quenching of polymer films depends on a variety of factors, including the concentration of analytes, the interactions between polymer and analyte, the diffusion of excitons, the penetration of analytes in polymer films and the strength of enhancement. Novel materials for laser explosive sensing applications must therefore fulfil a number of requirements such as: high PLQY, high optical gain, low waveguide loss coefficient, and quenching by explosives in short times, i.e. fast responsitivity.

Besides conjugated polymers there are various fluorescent organic semiconducting materials including small molecules [48], macromolecules [43,49,50], and dendrimers [43,51,52], that have been developed for use in explosive sensors. These results all suggest that the physical shape of the (macro-)molecules and their arrangement in solution or film together play a very important role in the sensitivity of fluorescent explosive sensors.

However, a problem of solid films is that they are fairly dense, which slows down the diffusion of the analyte into the films. The possibility of obtaining faster response by working with a porous film has been investigated [53,54]. The first issue is to find a porous material suitable for lasing. This means the material must support a low loss waveguide mode; hence, it must be porous on a lengthscale much less than a wavelength of light to avoid scattering light. A soluble polymer with a rigid backbone and microporosity (polybenzodioxane PIM-1) [55] addressed this issue. The molecular structure of PIM-1 is shown in Fig. 2d [53]. After 30 minutes exposure to ∼10 p.p.b DNB vapour, the PL intensity was reduced by 85%. Figure 4a shows the comparison of the PL sensing dynamic between PIM-1, a polymer of intrinsic microporosity and, PFO, a linear conjugated polymer, within the first 900 seconds of exposure. The data shows that the PL from a porous film is quenched faster than from a dense non-porous film, i.e. the porosity enables the analyte to penetrate the film and interact more quickly with the chromophores in the sensor.

Optical gain properties were characterised using thin PIM-1 films and also a second-order DFB PIM-1 laser. The laser was later used in explosive sensing. It was found that after a 5-minute exposure to DNB vapour, there was an increase in the laser threshold of 2.5 times and a reduction of the laser slope efficiency by 4.4 times. For pumping at 2 times

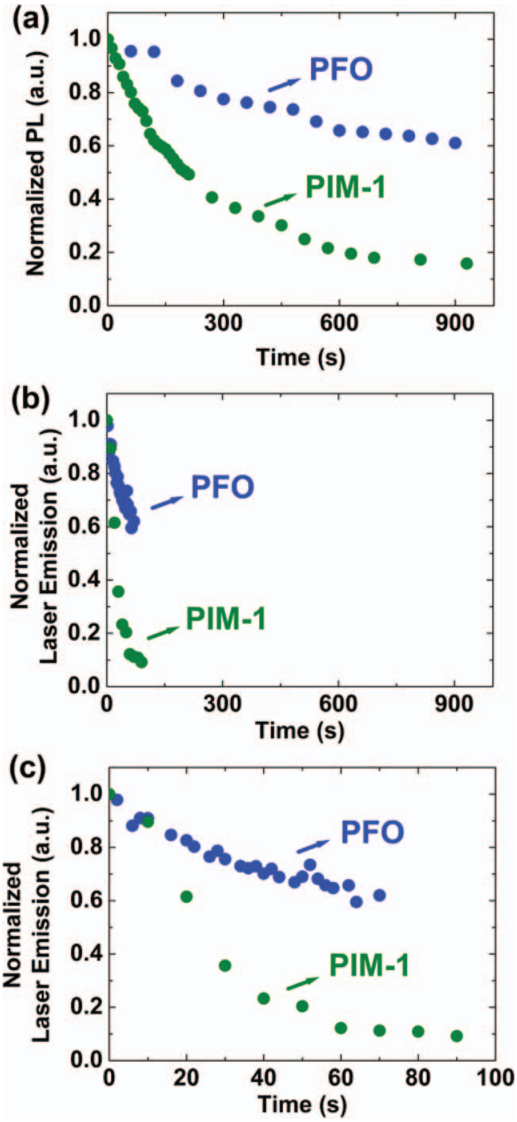

Figure 4. Comparison between PFO and PIM-1 sensing dynamics (a) PL scheme; (b) DFB laser scheme; (c) first 90 seconds of emission from DFB lasers exposed to DNB vapour.

threshold, the laser emission intensity dropped rapidly. There was a 60% fall in 30 s and the lasing action was completely stopped after 60 s exposure to DNB vapour, indicating that PIM-1 has a very fast responsivity and as such has a potential sensing ability for ultra-low-concentration explosives. As shown in Fig. 4b and 4c, by directly comparing the dynamics of the laser output in the presence of the same vapour pressure of DNB between the PIM-1 and PFO laser sensors, the PIM-1 showed more than 2 times higher sensing efficiency in 80 s and a much faster responsivity. Comparing the PL and laser response for these two polymers, both the PIM-1 and PFO laser sensors respond 6 times faster than their PL during the first 80 s. These results prove that the combination of intrinsic microporosity in polymer and DFB laser geometry promises real-time low concentration detection of explosives.

Conclusions

Explosive sensing is a promising, emerging application of polymer lasers. Recent advances have shown that DFB lasers are suitable, and that a change of slope efficiency or laser threshold can be used. As DFB lasers can be readily fabricated by soft lithographic means [56], and as they can also be pumped by LEDs [20], there is the prospect of simple explosive sensors based on these materials. This application further illustrates the differences between inorganic semiconductors and conjugated polymers. In the latter, the gain medium itself can act as the sensor. It has been shown that increasing the porosity can make the sensor respond faster, and substantial changes can be seen in a matter of seconds. Our results show how both materials and device developments can be used to develop polymer sensors. One exciting potential area of application is to clear landmines left after wars. Humanitarian demining is a challenging problem and polymer laser sensors could be used to complement existing technologies such as ground-penetrating radar to improve the detection of hazardous objects.

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