

## Chemosensing of 1,4-dinitrobenzene using bisfluorene dendrimer distributed feedback lasers

S. Richardson,<sup>1</sup> H. S. Barcena,<sup>2</sup> G. A. Turnbull,<sup>1</sup> P. L. Burn,<sup>2,a)</sup> and I. D. W. Samuel<sup>1,a)</sup>

<sup>1</sup>Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews KY16 9SS, United Kingdom

<sup>2</sup>Centre for Organic Photonics and Electronics, School of Chemistry and Molecular Biosciences, Chemistry Building, The University of Queensland, Queensland 4072, Australia

(Received 28 January 2009; accepted 7 July 2009; published online 14 August 2009)

We report the trace vapor detection of the molecule 1,4-dinitrobenzene, a model analyte for the explosive substance 2,4,6-trinitrotoluene, via fluorescence quenching of a first generation conjugated dendrimer containing a 2,2'-bis[9,9-di-*n*-hexylfluorene] core. We show that much greater sensitivity can be obtained by using the material as a surface emitting distributed feedback laser. We find that the slope efficiency of the laser is a convenient and sensitive indicator of the presence of the analyte. The slope efficiency decreases by a factor 50 in the presence of 1,4-dinitrobenzene.

© 2009 American Institute of Physics. [DOI: 10.1063/1.3189286]

There is currently a great demand for advanced chemical sensors for applications such as security, process control and environmental monitoring. One such success story is the use of semiconducting conjugated polymers (CPs) in the trace detection of explosive vapor,<sup>1-6</sup> where their efficient emissive and excitonic transport properties make them ideally suited for fluorescence based chemical sensing.

Detection occurs when the high electron affinity nitroaromatic analytes bind to the polymer surface introducing nonradiative deactivation pathways<sup>2</sup> that quench the fluorescence by an electron transfer mechanism. CPs have already been demonstrated to exhibit strong optical amplification<sup>7,8</sup> and are highly promising laser materials.<sup>9-11</sup> Rose *et al.*<sup>5</sup> have shown that microring lasers based on a poly(*p*-phenylene vinylene) derivative can have enhanced sensitivity for the detection of explosive vapors when operated close to threshold. A disadvantage of microring lasers is that they emit light in all directions, and so in this paper we explore the feasibility of explosive detection using a distributed feedback organic semiconductor laser, which has the advantage of giving well-defined surface emission.

In addition to investigating the suitability of an alternative laser geometry we also explore a new class of gain material for laser-based chemical sensing, namely light-emitting dendrimers. Dendrimers are solution-processable organic semiconductors that have been shown to be promising for applications in organic light-emitting diodes<sup>12</sup> and lasers.<sup>13-15</sup> They consist of a core, conjugated dendrons, and surface groups, and their properties can readily be tuned by appropriate selection of these units.<sup>12,16</sup> We show that a combination of a bis(flourene)-based chromophore and a convenient distributed feedback laser geometry are suitable for this purpose. We find that the change in slope efficiency is much greater than the change in photoluminescence or lasing threshold, providing an alternative way of enhancing detection sensitivity.

An important materials requirement both for lasing and for measurement of fluorescence quenching is to have a material with high photoluminescence quantum yield (PLQY)

in the solid state.<sup>2</sup> In order to achieve this, we selected a 2,2'-bis[9,9-di-*n*-hexylfluorene]-cored first generation dendrimer with biphenyl dendrons and 2-ethylhexyloxy surface groups (structure shown in the inset of Fig. 1). Although only first generation dendrons are used, they are effective in preventing concentration quenching and the solid state PLQY of this material is 92%. The analyte used was 1,4-dinitrobenzene (DNB), which resembles explosives such as trinitrotoluene (TNT) in being strongly electronegative, possessing a similar reduction potential ( $E_{1/2} = -1.2$  V versus the ferrocenium/ferrocene couple) and having a very low vapor pressure ( $\sim 30$  ppb).<sup>3</sup>

To perform the analyte sensing, dendrimer films of  $\sim 200$  nm thickness (as determined by spectroscopic ellipsometry) were fabricated under clean room conditions by spincoating from chloroform solution (25 mg/ml) onto planar and corrugated fused silica substrates. The planar substrates were used for absorption and photoluminescence (PL) studies while the corrugated substrate was used for the laser measurements. This dendrimer was previously shown to form distributed feedback (DFB) lasers with low threshold and high slope efficiency.<sup>14,15</sup> The grating structure used here

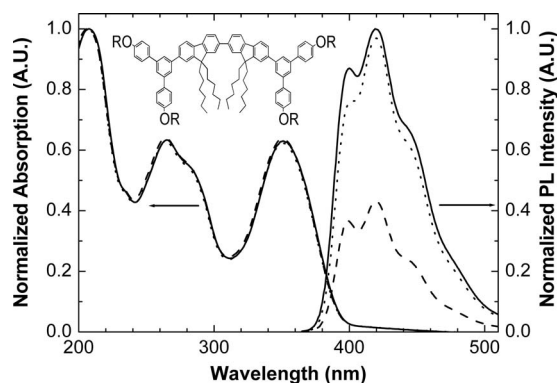


FIG. 1. Absorption and PL spectra for a thin film of dendrimer before (solid curves) and after (dashed curves) a 60 min exposure to DNB. The absorption and PL for the same sample after recovering in nitrogen is also shown (dotted curves). While there is little effect upon the absorption, the quenching of the PL after exposure to DNB is clearly evident. The structure of the bisfluorene dendrimer is shown in the inset,  $R=2$ -ethylhexyl.

<sup>a)</sup>Electronic mail: idws@st-and.ac.uk.

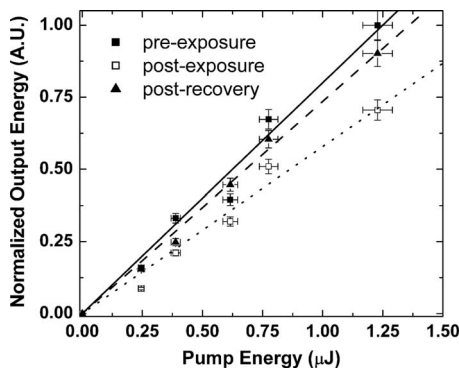


FIG. 2. PL emission (normalized) from the bisfluorene film as a function of pump energy before exposure to DNB (filled squares), after exposure (open squares) and after recovery in nitrogen (filled triangles).

consisted of a two-dimensional square array “egg-box” with a periodicity of  $\sim 260$  nm in both directions and a depth of  $\sim 30$  nm and was formed by holography in photoresist before reactive ion etching into silica. Surface emitted output coupling and in-plane feedback were provided by first order and second order Bragg scattering, respectively.

Absorption and PL measurements were performed with a Cary 300 Bio UV-visible spectrophotometer and a Jobin Yvon Fluoromax 2 spectrometer, respectively. For the laser measurements, samples were pumped with the 337 nm output of a nitrogen laser at 10 Hz (pulse duration=0.5 ns). Pump pulse energy was attenuated using calibrated neutral density filters. Output from the dendrimer film was collected close to normal incidence using a fiber-coupled charge coupled device (CCD) spectrometer with resolution  $\sim 0.7$  nm at full width at half maximum. All optical measurements were made with the sample exposed to air.

For the exposure,  $\sim 10$  mg of DNB crystals were introduced to an air-filled chamber containing the bisfluorene film. The chamber had an approximate volume of  $400$  cm<sup>3</sup>. The configuration was such that there was no contact between the sample and the DNB. While practical applications of this technology require only small changes in the PL output of the film within a short timescale, at such low vapor pressures, it is difficult to precisely control the concentration. Hence, we allowed the atmosphere within the chamber to saturate over a period of 60 min allowing the vapor and film to approach equilibrium, before again measuring the output. Following this characterization, the dendrimer films were isolated in a nitrogen atmosphere for 16 h to demonstrate the ability of the film to show a recovery of the PL.

In Fig. 1, the absorption and PL spectra are given for a bisfluorene film before (solid curve) and after (dashed curve) a 60 min exposure to the DNB. It can be seen that there is a clear reduction in the PL while the absorption remains unchanged. After exposure to nitrogen, the PL recovers most of its initial intensity. As laser studies involved measuring the output energy as a function of input energy following excitation by a pulsed nitrogen laser at 337 nm, we also performed PL measurements (using planar films) with this excitation source. The results are shown in Fig. 2 which shows the PL differential slope efficiency. In the figure, the output from the bisfluorene film before exposure to DNB has been normalized to one. After a 1 h exposure to DNB, the slope efficiency of the PL has been reduced to 0.7 of the initial

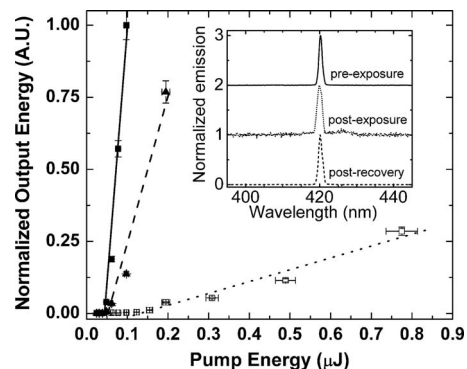


FIG. 3. Dendrimer DFB laser emission curves showing the response of the bisfluorene film before (filled squares) and after (open squares) exposure to DNB. The open triangles demonstrate the recovery of the laser emission after isolation in nitrogen. Laser threshold in each case is indicated by an abrupt change in the slope of the curves. The quenching of the stimulated emission and reduction in slope efficiency after exposure is clearly evident. Inset: laser spectrum before exposure to DNB, after exposure to DNB, and after recovery in nitrogen. The linewidth is limited by the resolution of the spectrometer used.

value. After recovery in nitrogen, we observe a recovery in the efficiency to 0.9 of the pre-exposed value.

The relatively low level of quenching of the PL at equilibrium (30%) could potentially be explained by one of two reasons: either the lowest unoccupied molecular orbital (LUMO) of the analyte is not sufficiently below the LUMO of the dendrimer to facilitate exciton dissociation or the dendrimer film is too dense to allow diffusion of the DNB throughout the relatively thick films. The dendrimer was found to undergo one chemically reversible oxidation with an  $E_{1/2}$  of 0.8 V (relative to the ferrocenium/ferrocene couple). By adding the energy corresponding to the first  $\pi$ - $\pi^*$  transition from the UV-visible spectrum the reduction potential was estimated to be  $-2.7$  V. Therefore, the reduction potential of the dendrimer is significantly more negative than that of DNB, which has an  $E_{1/2}$  of  $-1.2$  V. The difference of 1.5 eV between the reduction potentials (electron affinities) of the dendrimer and DNB means that efficient electron transfer should occur from the exciton on the dendrimer to the DNB. This therefore suggests it is slow diffusion through the thick dendrimer film that is responsible for the less than 100% quenching of the luminescence. This is consistent with the good charge mobility determined by the time-of-flight technique, which suggests a good deal of order within the bisfluorene-cored dendrimer film.<sup>17</sup> We note from our observations that the recovery is not complete, which is likely to be due to some DNB remaining in the film.

We next studied the effect of exposure to DNB on DFB lasers made from the same dendrimer. It was first necessary to establish that exposure to air did not affect the laser operation, and so the laser output was measured immediately after fabrication and after 1 h in ambient air. The threshold and slope efficiency were identical, indicating the negligible effect of the atmosphere and photo-oxidation on our experiment over this timeframe. We then proceeded to test the effect of exposure to DNB and the results are shown in Fig. 3. The observed emission wavelength and threshold of our test laser before exposure were  $\lambda = 415$  nm and 40 nJ, respectively. After exposure to DNB, the threshold of our laser increased by 3.6 times to 145 nJ and showed a 300-fold quenching in laser emission (for a pump energy of

0.1  $\mu\text{J}/\text{pulse}$ ) compared to the pre-exposed value. A large reduction in output close to the threshold has also been reported in CPs.<sup>5</sup> However, in addition, we observe a large reduction in the laser slope efficiency (50 times) after exposure. Following recovery in nitrogen, we observed a substantial increase in the output energy and slope efficiency from the film by a factor of 43 and 12 times, respectively, compared to the values obtained postexposure. We attribute the incomplete recovery of the slope efficiency to some DNB remaining in the dendrimer film. The laser threshold after recovery was 45 nJ/pulse, very similar to the initial value. The reduction in slope efficiency of the dendrimer laser is 35 times greater than the corresponding reduction when measuring PL emission. It is also much larger than the corresponding change in lasing threshold, suggesting that the presence of the DNB leads to a reduction in the surface output-coupling from the laser. The relatively large change in laser slope efficiency is thus an attractive quantity to use for organic semiconductor laser-based sensing. While large changes can also be observed in the laser output close to threshold, this is effectively a single point measurement, and will be very sensitive to any change in threshold for any reason. In contrast, the slope efficiency draws on several points and need not be measured in the delicate regime close to threshold. We can estimate the lowest concentration of DNB we could potentially detect by noting that a vapor pressure  $\sim 30$  ppb gives a change in slope efficiency of a factor of 50. Assuming the change in slope efficiency is proportional to DNB concentration and that we can measure a 5% change in slope efficiency, we should be able to detect 0.03 ppb of DNB. Unfortunately we were not able to vary DNB concentration to test this estimate.

In conclusion, we have demonstrated the detection of DNB, a model analyte with similar characteristics to the explosive TNT through use of a bisfluorene-cored dendrimer.

Our results show that the very convenient DFB laser geometry is suitable for sensing, and gives a much larger response than the PL. The reduction in slope efficiency after exposure is 35 times greater than the corresponding change when measuring photoluminescence emission from the film, offering a robust method, with excellent sensitivity, for the trace-detection of analytes, commonly found in explosive vapor.

<sup>1</sup>S. W. Thomas III, G. D. Joly, and T. M. Swager, *Chem. Rev.* **107**, 1339 (2007).

<sup>2</sup>J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.* **120**, 5321 (1998).

<sup>3</sup>J.-S. Yang and T. M. Swager, *J. Am. Chem. Soc.* **120**, 11864 (1998).

<sup>4</sup>C. J. Cumming, C. Aker, M. Fisher, M. Fox, M. J. la Grone, D. Reust, M. G. Rockley, T. M. Swager, E. Towers, and V. Williams, *IEEE Trans. Geosci. Remote Sens.* **39**, 1119 (2001).

<sup>5</sup>A. Rose, Z. Zhu, C. F. Madigan, T. M. Swager, and V. Bulovic, *Nature (London)* **434**, 876 (2005).

<sup>6</sup>S. J. Toal and W. C. Trogler, *J. Mater. Chem.* **16**, 2871 (2006).

<sup>7</sup>J. R. Lawrence, G. A. Turnbull, and I. D. W. Samuel, *Appl. Phys. Lett.* **80**, 3036 (2002).

<sup>8</sup>G. Heliotis, M. Goossens, S. Richardson, G. A. Turnbull, I. D. W. Samuel, and D. D. C. Bradley, *Appl. Phys. Lett.* **85**, 6122 (2004).

<sup>9</sup>N. Tessler, *Adv. Mater. (Weinheim, Ger.)* **11**, 363 (1999).

<sup>10</sup>M. D. McGehee and A. J. Heeger, *Adv. Mater. (Weinheim, Ger.)* **12**, 1655 (2000).

<sup>11</sup>I. D. W. Samuel and G. A. Turnbull, *Chem. Rev. (Washington, D.C.)* **107**, 1272 (2007).

<sup>12</sup>P. L. Burn, S.-C. Lo, and I. D. W. Samuel, *Adv. Mater. (Weinheim, Ger.)* **19**, 1675 (2007).

<sup>13</sup>J. R. Lawrence, G. A. Turnbull, I. D. W. Samuel, G. J. Richards, and P. L. Burn, *Opt. Lett.* **29**, 869 (2004).

<sup>14</sup>J. C. Ribierre, G. Tsiminis, S. Richardson, G. A. Turnbull, I. D. W. Samuel, H. S. Barcena, and P. L. Burn, *Appl. Phys. Lett.* **91**, 081108 (2007).

<sup>15</sup>J. R. Lawrence, E. B. Namdas, G. J. Richards, P. L. Burn, and I. D. W. Samuel, *Adv. Mater. (Weinheim, Ger.)* **19**, 3000 (2007).

<sup>16</sup>S.-C. Lo and P. L. Burn, *Chem. Rev. (Washington, D.C.)* **107**, 1097 (2007).

<sup>17</sup>J. P. J. Markham, T. D. Anthopoulos, I. D. W. Samuel, G. J. Richards, P. L. Burn, C. Im, and H. Bässler, *Appl. Phys. Lett.* **81**, 3266 (2002).