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## Amplified spontaneous emission and lasing properties of bisfluorene-cored dendrimers

J. C. Ribierre, G. Tsiminis, S. Richardson, G. A. Turnbull, and I. D. W. Samuel<sup>a)</sup>  
*Organic Semiconductor Centre and Ultrafast Photonics Collaboration, SUPA, School of Physics  
 and Astronomy, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9SS, United Kingdom*

H. S. Barcena  
*Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, OX1 3TA  
 Oxford, United Kingdom*

P. L. Burn  
*Centre for Organic Photonics and Electronics, Chemistry Building, University of Queensland, St. Lucia,  
 Queensland 4072, Australia*

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A study of the amplified spontaneous emission (ASE) properties of three bisfluorene-cored dendrimers in the solid state is reported. The results show that the dendron type has a strong impact on the photoluminescence quantum yield and affects the ASE threshold, the optical gain, and loss coefficients. Optically pumped distributed feedback lasers operating in the blue spectral region were fabricated by spin coating the dendrimer films on top of a two-dimensional corrugated fused silica substrate. A best lasing threshold of  $4.5 \mu\text{J}/\text{cm}^2$  and a slope efficiency of 8.3% were obtained, which demonstrate the high potential of these materials for laser applications. © 2007 American Institute of Physics. [DOI: 10.1063/1.2761833]

Over recent years, semiconducting conjugated dendrimers have attracted considerable attention for their application in organic light-emitting diodes (LEDs).<sup>1</sup> These branched macromolecules with a well-defined structure are typically composed of a light-emitting core and dendrons to which surface groups are attached. Their electronic properties are controlled by the core, which can be chosen from a large range of luminescent chromophores. The dendron type and generation provide a fine tuning of the intermolecular interactions between the cores and thus play an essential role in the charge transport, exciton diffusion, and photophysical properties of these materials. Finally, the surface groups enable the dendrimers to be processed from solution. The high potential of this approach has been clearly illustrated by the demonstration of green electrophosphorescent devices based on iridium(III) complex-cored dendrimers with external quantum efficiencies as high as 16%.<sup>2</sup> So far, most attention has been focused on the development of phosphorescent dendrimers for LEDs but the forbidden transitions are not suitable for high gain laser materials. Dendrimers also have potential for organic semiconductor lasers and amplifiers,<sup>3–5</sup> but this would require fluorescent dendrimers. In previous work, high optical gain was measured in solutions and thin films of a fluorescent bisfluorene-cored dendrimer.<sup>6</sup> Recently, a distributed feedback (DFB) laser using a second generation bisfluorene-cored dendrimer as gain medium was fabricated by soft lithography and showed a lasing threshold of 60 nJ/pulse together with a high slope efficiency of 14%.<sup>7</sup> We also note that nonfluorescent dendrimers were previously used as host to prevent aggregation of laser dyes<sup>8</sup> and an electrically insulating rhodamine-cored dendrimer was blended into a polymer waveguide to obtain laser emission.<sup>9</sup>

In this work, we explore the effect of dendron structure on the potential of fluorescent dendrimers for lasing in a

family of first generation bisfluorene-cored dendrimers. As shown in the inset of Fig. 1, the dendrons attached to the bisfluorene core were biphenyl (BP), biphenylcarbazole (BPCz), and *E*-stilbenyl (ES). We show that strong variations observed in the amplified spontaneous emission (ASE) threshold, the optical gain, and the loss coefficient are attributed to the effects of the dendrons on the intermolecular interactions and the associated photoluminescence quantum yield (PLQY). We also report the fabrication and detailed characterization of optically pumped solid state distributed feedback lasers using the bisfluorene-cored dendrimer with the biphenyl dendrons as gain medium.

Dendrimer films were fabricated under clean-room conditions by spin coating from a chloroform solution with a typical concentration of 25 mg/ml. Planar and corrugated fused silica substrates were used for the ASE measurements and the fabrication of dendrimer lasers, respectively. The corrugation was formed by holography in a photoresist and dry etched into the silica.<sup>10</sup> The grating structure consisted of a two-dimensional “egg box” with a periodicity of around 260 nm in both directions and a depth of 30 nm. The dendrimer film thicknesses were measured by spectroscopic ellipsometry to be typically around 200–220 nm in the planar structure.

Steady-state PL spectra were collected by a Jobin Yvon Fluoromax 2 fluorimeter. The PLQY of the dendrimer thin films was measured using an integrating sphere under a flowing nitrogen atmosphere.<sup>11</sup> The samples were excited at 325 nm and with an excitation power of around 0.15 mW using a helium-cadmium laser. To study the ASE properties, the dendrimer films were pumped at 350 nm with an optical parametric oscillator delivering 4 ns pulses at a repetition rate of 20 Hz. The energy of the excitation pulses was varied using a set of neutral density filters. A cylindrical lens was employed to focus the excitation beam into a stripe of dimension  $175 \mu\text{m} \times 4 \text{ mm}$ . The emission was collected from

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

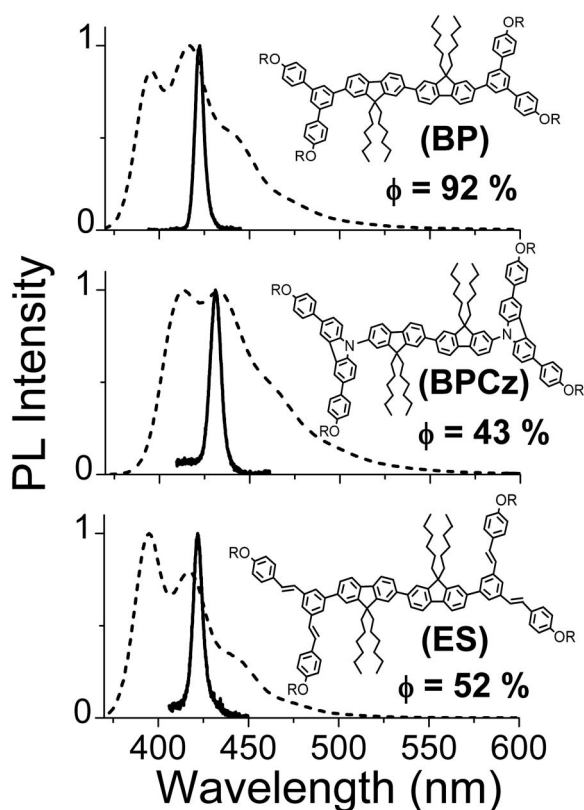


FIG. 1. Steady-state PL spectra (dashed line) and ASE emission spectra (solid line) of neat bisfluorene-core dendrimer films. The spectra were normalized at their peak wavelength. In the insets are shown the chemical structure of the dendrimers and their photoluminescence quantum yield (PLQY) values  $\phi$  measured in the solid state.  $R=2$ -ethylhexyl.

the waveguide edge using a fiber-coupled grating spectrometer equipped with a charge coupled device detector. For the characterization of the dendrimer lasers, the samples were optically pumped at 355 nm by a Nd:YVO<sub>4</sub> microchip laser that generates 1 ns pulses at a repetition rate of 5 kHz. The excitation beam was incident upon the device at a slight angle and focused onto a stripe of dimensions 650  $\times$  200  $\mu\text{m}^2$ . The emitted radiation was detected in this case normal to the film surface. In order to reduce photodegradation and avoid oxidation of the dendrimer films, the samples were placed in a vacuum chamber with a pressure lower than 10<sup>-4</sup> mbar.

Figure 1 shows the emission spectra of the bisfluorene dendrimer films below and above the ASE threshold. At low excitation densities ( $<15 \mu\text{J}/\text{cm}^2$ ), the PL spectra are broad and show vibronic peaks characteristic of the spontaneous emission, and are independent of the pump intensity. At high excitation densities, ASE occurs and a spectral narrowing of the emission band is observed.<sup>3</sup> Amplification occurs at 431 nm in BPCz while in BP and ES it occurs at 421 and 422 nm, respectively. The redshift in the emission of BPCz is due to the fact that it has carbazolyl units as part of the chromophore compared to the phenyl units in BP and ES. The full width at half maximum drops in our samples from 50–60 to 5–6 nm [see Fig. 2(a)]. This effect is caused by spontaneously emitted photons, which are waveguided in the films and exponentially amplified by stimulated emission. We observed that the line narrowing occurs in bisfluorene dendrimer films near the 0-1 vibronic transition of the PL spectra, a situation which corresponds to a quasi-four-level

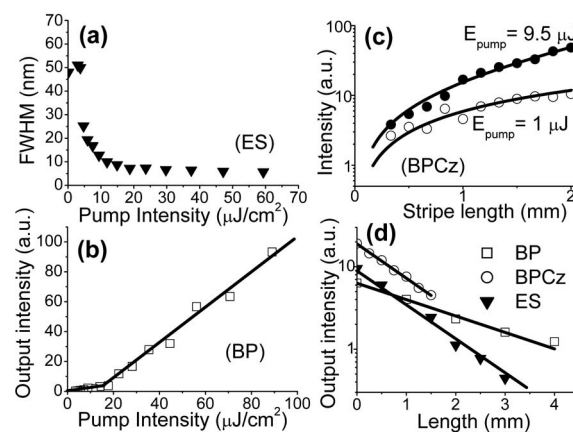


FIG. 2. Panel (a) shows the dependence of the full width at half maximum of the emission spectrum in ES as a function of the pump intensity. Panel (b) shows the total emission intensity from the edge of the BP dendrimer waveguide (integrated over all wavelengths) vs pump intensity. The excitation wavelength was 350 nm. Panel (c) displays the ASE intensity as a function of pump energy and stripe length in the neat film of BPCz. Solid lines are the fits obtained. Panel (d) shows the intensity of ASE vs the distance between the pump stripe and the edge of the sample. Solid lines are the fit obtained from a single exponential decay function.

vibronic system. In the case of BP and ES, the ASE peak is slightly redshifted with respect to the 0-1 vibronic peak, which may be due to some additional self-absorption losses.

Figure 2(b) shows the output light intensity emitted from the edge, integrated over all wavelengths, as a function of the excitation intensity in the dendrimer (BP) film. The abrupt change in slope efficiency is directly associated to the ASE threshold. The dendrimer (BP) presents the lowest threshold with a value of 300 nJ/pulse, corresponding to an excitation density of 16  $\mu\text{J}/\text{cm}^2$ . Among the wide range of fluorene derivatives previously studied,<sup>12–15</sup> poly(9,9-dioctylfluorene) (PFO) presents the closest chemical structure to our dendrimers. An ASE threshold of 29  $\mu\text{J}/\text{cm}^2$  was measured in this conjugated polymer,<sup>15</sup> which is higher than the value measured in BP but is comparable with the value of 25  $\mu\text{J}/\text{cm}^2$  in ES and lower than the value of 50  $\mu\text{J}/\text{cm}^2$  found in BPCz. These ASE thresholds together with the broad PL spectra of these materials show great promise for the fabrication of efficient and tuneable solid state lasers.

The gain and loss characteristics of the dendrimer waveguides were calculated from the ASE measurements using the variable length stripe technique.<sup>3,4</sup> Figure 2(c) shows that the highest gain of 51  $\text{cm}^{-1}$  was obtained in dendrimer (BP) for a pump energy of 9.4  $\mu\text{J}$ , which is comparable with the value of 74  $\text{cm}^{-1}$  reported in PFO for a pump energy of 9  $\mu\text{J}$ .<sup>15</sup> At similar pump energies, the gain was found to be 8 and 21  $\text{cm}^{-1}$  in BPCz and ES, respectively, which confirm the trends observed in the ASE threshold.

Figure 2(d) shows the ASE intensity as a function of the distance between the pump stripe and the edge of the dendrimer films. From these measurements, we calculated the loss coefficients to be  $\alpha=4 \text{ cm}^{-1}$  in BP and  $\alpha=10 \text{ cm}^{-1}$  in BPCz and ES. These small values are comparable with the loss coefficient of 3.5  $\text{cm}^{-1}$  reported in PFO (Ref. 15) and show the excellent quality of the waveguides formed by the dendrimer films.

The PLQY values measured in the dendrimer films are given in the inset of Fig. 1. They show that the dendron chemical structure can play a critical role on the intermolecu-

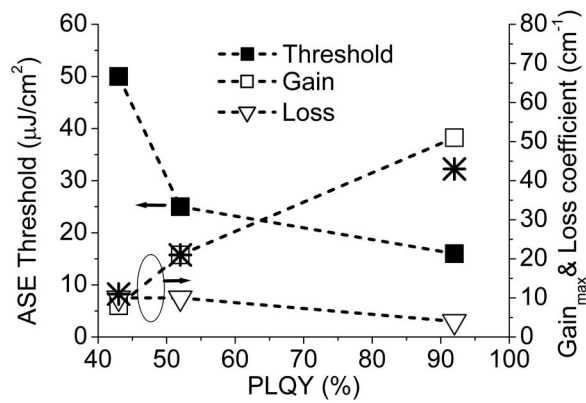


FIG. 3. ASE threshold (solid squares), net gain measured at a pump energy of  $\sim 9 \mu\text{J}$  (open squares), and loss coefficient (open triangles) as a function of the PLQY value in the solid state. The dashed lines are guides for the eyes. The cross symbols correspond to the net gain calculated from the PLQY values.

lar interactions and the concentration quenching of the fluorescence. Figure 3 shows the correlations of the ASE threshold and the highest net gain (obtained at similar pump energies close to  $9 \mu\text{J}$ ) with the PLQY. The net gain can be expressed as  $g = \sigma P \Phi / k_R - \alpha$ , where  $\sigma$  is the stimulated emission cross section,  $P$  is the pumping rate and is calculated from the excitation density generated during the 4 ns excitation pulses,  $\Phi$  is the PLQY value, and  $k_R$  is the radiative decay rate. The ratio  $\sigma/k_R$  does not depend on the gain medium considered due to the proportionality of the Einstein A and B coefficients. In dendrimer (BP),  $\sigma$  has been found to be  $3.4 \times 10^{-18} \text{ cm}^2$  and we have measured a  $k_R$  value of  $1.28 \times 10^9 \text{ s}^{-1}$  (data not shown).<sup>8</sup> Taking into account the losses associated with the waveguide modes, we calculated the net modal gain from the PLQY values and found an excellent agreement between the experimental and simulated data, as shown in Fig. 3. These results demonstrate the strong influence of the dendron chemical structure on the photo-physical properties and the ASE performance of bisfluorene-cored dendrimers. In particular, the anticorrelation of waveguide loss and PLQY suggests that dendrons which reduce the level of crystallinity and improve the degree of amorphousness are most useful for the design of efficient fluorescent dendrimers for optical amplifiers and lasers.

In DFB lasers, lasing occurs near the Bragg wavelength  $\lambda_{\text{bragg}} = 2n_{\text{eff}}\Lambda/m$ , where  $n_{\text{eff}}$  is the effective refractive index of the laser medium,  $m$  is the Bragg order, and  $\Lambda$  is the grating period. The period of the grating used in this study was chosen for  $m=2$ , which supports laser radiation emitted in the direction perpendicular to the film surface. We have shown that the dendrimer (BP) exhibits the best ASE performance in the solid state and this material is consequently the best candidate for the fabrication of an efficient optically pumped DFB dendrimer laser. A DFB laser using this material as gain medium and a two-dimensional corrugated fused silica substrate was previously reported, which showed lasing at 408 nm with a threshold of 90 nJ/pulse and a slope efficiency of 0.3%.<sup>12</sup> Fig. 4 shows the output energy from the laser with the best power characteristics ( $\lambda=418 \text{ nm}$ ) as a function of the pump energy. The abrupt change in the slope gives a threshold of 6 nJ/pulse, corresponding to an excitation density of  $4.5 \mu\text{J}/\text{cm}^2$ . Above this threshold, we ob-

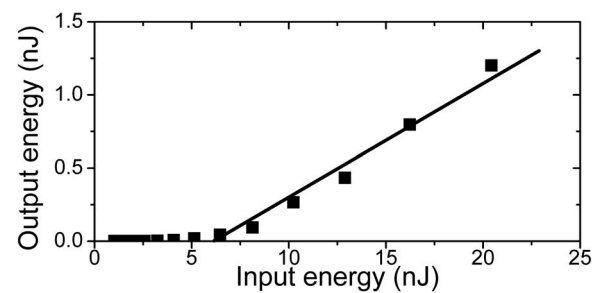


FIG. 4. Output of a (BP) dendrimer DFB laser.

served a linear increase of the output energy with the pump energy and a slope efficiency of 8.3% was measured on one side. These values of lasing threshold and slope efficiency are comparable with those of  $4 \mu\text{J}/\text{cm}^2$  and a combined total of 7.8% from both sides reported in a PFO DFB laser emitting at 454 nm.<sup>10</sup> By changing the dendrimer film thickness from 200 to 220 nm, we turned the lasing wavelength between 412 and 427 nm.

In summary, we have shown how dendron structure plays a crucial role in the PL efficiency and related the measured gain to the PL efficiency. Optically pumped DFB lasers were fabricated using the bisfluorene-cored dendrimer with biphenyl based dendrons as gain medium. The high lasing performance of these devices demonstrates that conjugated dendrimers are promising materials as gain media for future organic semiconductor lasers.

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