

Optical amplification in a first-generation dendritic organic semiconductor

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We report a study of a new class of organic semiconductor as an optical gain medium. We demonstrate amplification of violet light by use of stimulated emission in a solution of a first-generation bis-fluorene-cored semiconducting dendrimer. Amplification is also observed in the solid state by means of amplified spontaneous emission in an optically pumped dendrimer planar waveguide. Gains of 36 dB cm^{-1} at 420 nm and 26 dB cm^{-1} at 390 nm in solution and 350 dB cm^{-1} in the solid state are obtained. These results show that semiconducting dendrimers have potential as visible laser and amplifier materials. © 2004 Optical Society of America

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Organic semiconductors are proving to be successful alternatives to inorganic materials for light-emitting diodes, visible lasers, and optical amplifiers.^{1–3} There are three classes of organic semiconductors: thermally evaporated small molecules, solution-processable conjugated polymers, and dendrimers. Of these, dendrimers are the youngest technology and are beginning to attract significant attention. They exhibit high photoluminescence (PL) quantum yields and are easily processed from solution. Semiconducting dendrimers have a modular architecture and consist of a core and dendrons, each of which contain conjugated units, and solubility-conferring surface groups. This allows for the independent tuning of the electrical, optical, and processing properties.^{4,5} Dendrimers have significant advantages over semiconducting polymers, for which attempting to tune the solubility can lead to undesirable changes in the emission properties.⁶ The dendritic structure also allows for a wide range of emissive chromophores that in many cases would be unsuited for use in an unmodified form or as a repeat unit of a polymer. Charge transport in dendrimer films can be controlled by varying the dendrimer generation, which changes the spacing of the cores. Lupton *et al.*⁵ found in a tris(distyrylbenzenyl) amino cored dendrimer a reduction in hole mobility with increasing generation, indicating that hole transport occurs by means of hopping between the cores of the molecules. To date, most semiconducting dendrimer work has centered on light-emitting diodes, and there have been some excellent results.⁷

Nonfluorescent and electrically insulating dendrimers have recently been studied for lasers.^{8,9} The nonfluorescent dendrimers were used to separate molecules of a conventional laser dye to prevent aggregation.⁸ Also, laser emission from a polymer waveguide doped with a rhodamine-cored electrically insulating dendrimer⁹ has been reported. In this Letter we demonstrate strong amplification of light in

a first-generation (G1) dendrimer, which was previously shown to be semiconducting by the time-of-flight technique.¹⁰ The molecular structure of the G1 dendrimer is shown in the inset in Fig. 1(b). The core consists of a bis-fluorene unit capped with two G1 triphenyl-based dendrons containing 2-ethyl-hexyloxy surface groups. It was made by coupling the G1 boronic-acid-focused dendron with 7,7'-dibromobisfluorene using palladium catalysis. The absorption and PL spectra of the G1 dendrimer solution (10^{-4} M in a 1-cm cell) are shown in Fig. 1(a). The absorption maximum is centered at 350 nm, whereas the PL has two peaks (390 and 425 nm) and two shoulders (450 and 475 nm).

To establish the presence of gain, a solution of the G1 dendrimer was used to amplify a weak probe pulse to an intense pulse.³ A nitrogen laser (500-ps pulses, 337 nm) was used as a common excitation source for both the amplifier and probe dye laser. Its output was split into two beams of $\sim 600\text{-}\mu\text{J}$ pulses that were then focused to a stripe of $200 \mu\text{m} \times 10 \text{ mm}$ to transversely pump the cells containing the dendrimer and stilbene 3 laser dye solutions. The output beam from the dye laser was attenuated by use of neutral-density filters and focused through the excited region of the 10-mm-long amplifier cell. The probe beam was then detected with either an optical energymeter or a CCD spectrograph.

To measure the magnitude of the gain, a solution containing 0.31 g/l (1.83×10^{-4} M) of bis-fluorene G1 dendrimer in toluene was used as an optical amplifier. The intensity of the probe beam was measured before and after passing through the 1-cm path-length amplifier cuvette. The gain achieved as a function of probe intensity is shown in Fig. 1(b). The maximum gain achieved is 36 dB cm^{-1} at 420 nm and 26 dB cm^{-1} at 390 nm. Solutions of different concentrations yielded lower gains, and we believe that the reduction in gain at higher concentrations is due to a poor overlap of

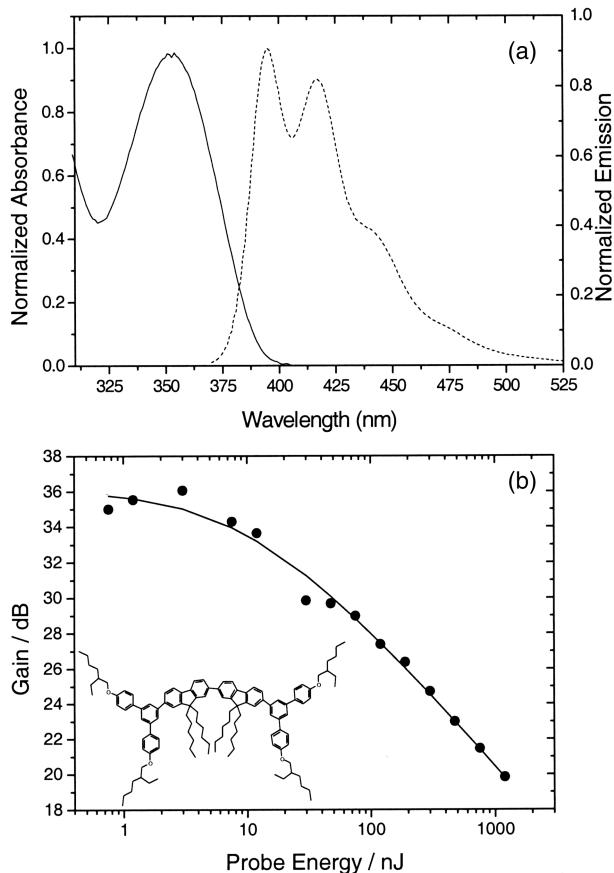


Fig. 1. (a) Absorption and emission spectra of the dendrimer solution. (b) Gain (at 420 nm) versus probe energy of the dendrimer optical amplifier. Inset, dendrimer structure.

the probe beam with the small excited region of the solution. At lower concentrations, meanwhile, the pump beam was too weakly absorbed to yield the excitation density necessary for substantial amplification.³ As the probe energy was increased, the amplifier gain was found to drop as a result of gain saturation. The curve in Fig. 1(b) is a theoretical fit to the 420-nm data using the well-known expression for a homogeneously saturated pulsed amplifier¹¹:

$$E_{\text{OUT}} = E_S \ln\{1 + [\exp(E_{\text{IN}}/E_S) - 1]\exp(G)\}. \quad (1)$$

Here G is the small signal gain coefficient, E_S is the saturation energy, E_{OUT} is the energy extracted from the amplifier, and E_{IN} is the unamplified probe energy. We found that the data can be convincingly described by Eq. (1), and from the fit we obtained a small signal gain of 36 dB cm^{-1} .

Amplification in organic semiconductors arises from stimulated emission in a four-level system similar to organic laser dyes.¹ The stimulated emission cross section σ for the bis-fluorene dendrimer can therefore be determined from $G = \sigma N_{\text{ex}} l$, where N_{ex} is the excitation density and l is the amplifier length. We estimate the gain cross section to be $\sigma \approx 3.4 \times 10^{-18} \text{ cm}^2$. The accuracy of this value is limited by incomplete knowledge of the excitation density as the probe pulse travels through the amplifier. These

values compare reasonably well with the gain of 44 dB cm^{-1} and the cross section of $5.3 \times 10^{-17} \text{ cm}^2$ at 600 nm obtained with poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-paraphenylenevinylene] ($\text{OC}_1\text{C}_{10}\text{-PPV}$)³ and $5.0 \times 10^{-17} \text{ cm}^2$ at 420 nm in *t,t'*-dicycloxy-II-distyrylbenzene laser dye.¹² However, dendrimers are less-developed materials than dyes and conjugated polymers, leaving considerable scope for improvement. This illustrates the potential of semiconducting dendrimers for substantial gain in compact amplifiers.

Although high gain can be obtained in dendrimer solutions, liquids are inconvenient for use in practical devices. We therefore investigated the potential for amplification in the solid state. Dendrimers have important advantages over dyes for solid-state amplification. They can be spin coated to give good quality films, and the dendritic structure greatly reduces quenching caused by aggregation. These dendrimers are semiconductors with the potential for electrically pumped amplification in the future.

Slab waveguides were formed by spin coating the G1 dendrimer solution onto quartz substrates to produce 200-nm-thick films, which yield high absorption of the pump beam. The waveguides were optically pumped at 337 nm by the nitrogen laser described previously, which was focused to a 280- μm -wide stripe near the edge of the film. The energy of the pump pulse was controlled by neutral-density filters, and light emitted from the waveguide edge was collected with an optical fiber and analyzed by a CCD spectrometer.

Figure 2(a) shows the normal PL of a dendrimer film and the line-narrowed spectrum when the film is pumped at an energy of $0.12 \mu\text{J mm}^{-1}$. Comparing the PL spectra of the solution and the solid state shows that the shoulders and peaks of the two spectra are the same and the small differences could be due to self-absorption of emission in the film or differences in the dielectric environment between the solution and the solid state. The film PL quantum yield is 40%, suggesting that aggregation does not dominate the photophysics. The emission spectrum was found to narrow significantly with increasing pump energy and was accompanied by a superlinear increase in intensity of the output radiation. The linewidth dropped from 53 to 3.3 nm. The spontaneously emitted photons were waveguided and amplified by stimulated emission, a process known as amplified spontaneous emission^{1,13} (ASE). ASE preferentially occurs where the gain exceeds the absorption and scattering losses by the greatest amount. The ASE peak is at 425 nm, which is at a longer wavelength than the PL maximum (418 nm) because the ground-state absorption is reduced.

To quantify the level of gain from the ASE measurements described above, an adjustable slit was placed in the pump beam¹³ to allow the length of the pumped stripe to be varied. The emission was then measured as the pump stripe length was increased from 0.3 to 1.8 mm and the pump energy from 20 to 120 nJ mm^{-1} . Figure 2(b) shows the emission intensity at 425 nm as a function of stripe length. The data were fitted using $I(\lambda) = [(AP_0)/g(\lambda)]\exp[g(\lambda)l] - 1$ (Ref. 14) to extract a value for the net gain coefficient $g(\lambda)$. The emission intensity is $I(\lambda)$, AP_0 is the spontaneous emission

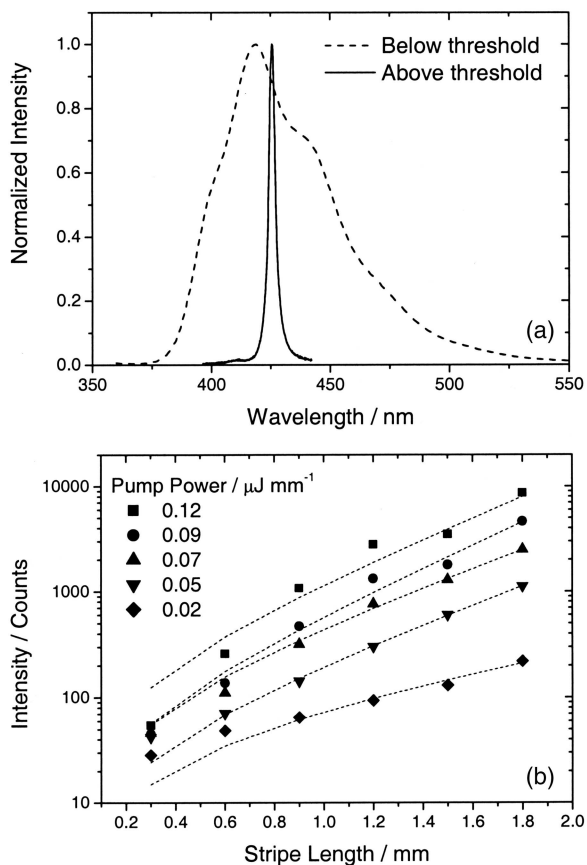


Fig. 2. (a) Emission spectrum of a bis-fluorene dendrimer film below and above ASE threshold. (b) ASE intensity as a function of pump energy and stripe length.

proportional to the pump energy, and l is the pump stripe length. At low pump energy (20 nJ mm^{-1}) the net gain was found to be 10 cm^{-1} . At higher energy (120 nJ mm^{-1}), net gains of 46 cm^{-1} were observed. A maximum gain of 79 cm^{-1} (350 dB cm^{-1}) was achieved while pumping with $30 \mu\text{J mm}^{-1}$. These results compare well with values reported for other materials, e.g., 74 cm^{-1} for polyfluorene with a pump energy of $9 \mu\text{J}$.¹⁵ The loss coefficient of the dendrimer waveguide at 425 nm was measured to be 1.4 cm^{-1} (6 dB cm^{-1}).

In summary, we have demonstrated strong amplification in both solutions and thin films of a new class of organic semiconductor. Gains of 36 dB cm^{-1} in solution and 350 dB cm^{-1} in the solid state have been obtained. A loss coefficient of 1.4 cm^{-1} has been

measured. These values are comparable with other organic semiconductors, such as conjugated polymers. Dendrimers offer considerable scope for molecular design, e.g., changing the core chromophore should make it possible to tune the gain across the visible spectrum in a similar way to dendrimer light-emitting diodes.⁴ We therefore conclude that light-emitting dendrimers show promise as a gain medium for optical amplifiers.

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