Low-threshold organic laser based on an oligofluorene truxene with low optical losses

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A blue-emitting distributed feedback laser based on a star-shaped oligofluorene truxene molecule is presented. The gain, loss, refractive index, and (lack of) anisotropy are measured by amplified spontaneous emission and variable-angle ellipsometry. The waveguide losses are very low for an organic semiconductor gain medium, particularly for a neat film. The results suggest that truxenes are promising for reducing loss, a key parameter in the operation of organic semiconductor lasers. Distributed feedback lasers fabricated from solution by spin-coating show a low lasing threshold of 270 W/cm^2 and broad tunability across 25 nm in the blue part of the spectrum. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3152782]

Organic semiconductor lasers have made great progress since the early demonstrations of lasing in conjugated polymers.[1–3] New materials are being synthesized that offer improvements in key photophysical properties such as photoluminescence quantum yield (PLQY), optical gains and optical losses, leading to organic lasers with lower lasing thresholds.[4–8] Most of the research in the field revolves around creating materials with higher optical gain per unit length, as this allows for stronger amplification of the emitted light that increases the output of a laser and reduces the lasing threshold.[4] The optical losses that light experiences as it travels through an organic thin film are equally important as they significantly affect the lasing threshold and efficiency but have been investigated to a lesser degree than optical gain and usually in the context of the additional losses introduced by metal contacts for electrical excitation of organic films.

The lowest optical loss values reported for neat films of organic semiconductors are in the range of 3.5–6 cm^{-1}, all of which are reported on fluorene-based materials.[5,9,10] The low lasing thresholds that these materials achieve are partly due to these low waveguide loss coefficients. Lower optical losses have only been demonstrated by using guest-host energy transfer in blends. This increases the separation between optical absorption and emission thereby reducing the reabsorption of the emission and hence the waveguide loss.[5,11–13] However, in blends the composition needs to be accurately controlled and phase separation can be a problem, particularly in solution-processed materials such as conjugated polymers.

In this letter we report an oligofluorene truxene material that can be spin coated to make neat films with very low waveguide losses. We present a study of its amplified spontaneous emission (ASE) properties that allows us to determine key photophysical properties such as optical gain and waveguide losses. We find that the low optical losses are combined with other favorable properties for lasing, notably high PLQY, resulting in a solid-state organic laser that has a low lasing threshold of 270 W/cm^2 and is tunable across 25 nm in the blue part of the spectrum.

The chemical structure of oligofluorene truxene T4 studied here can be seen in Fig. 1(a). The molecule consists of a hexahexylated truxene core onto which fluorene arms are attached, with each arm consisting of four 9,9-dihexylfluorene units.[14] The absorption and fluorescence spectra are plotted in Fig. 1(b), with an absorption maximum

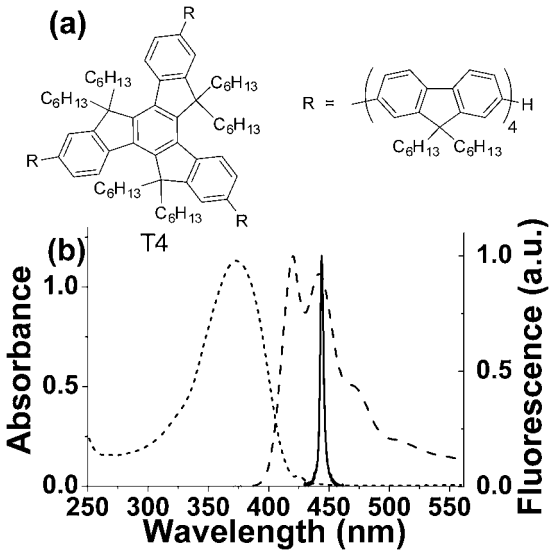

FIG. 1. (a) Chemical structure of the T4 oligofluorene truxene (b) Absorption (dotted line) and fluorescence (dashed line) spectra of T4 truxene, along with the ASE spectrum (solid line).

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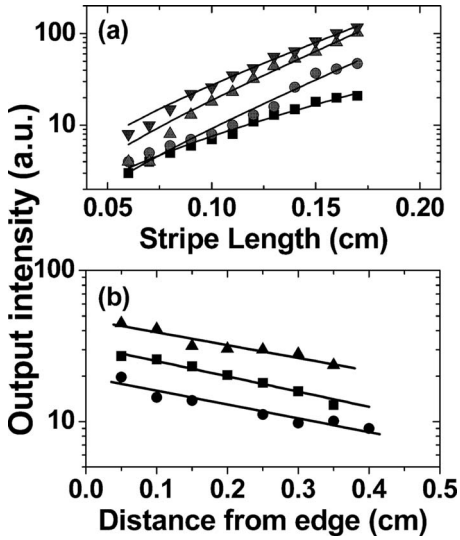

FIG. 2. ASE measurements on the T4 oligofluorene truxene showing (a) optical gain measurements and (b) waveguide losses. The gain was measured at pump intensities of 4.3 kW/cm^2 (squares), 6.5 kW/cm^2 (circles), 10.3 kW/cm^2 (upward triangles), and 16.3 kW/cm^2 (downward triangles).

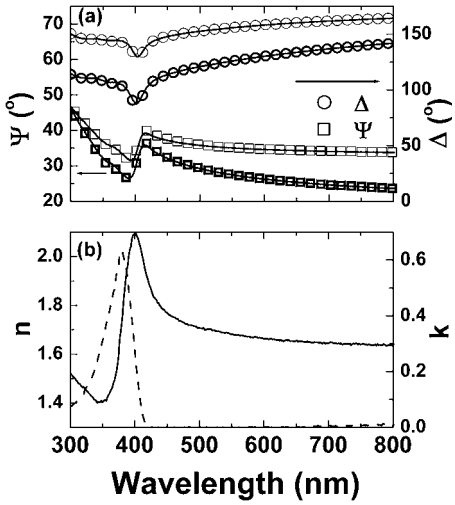

FIG. 3. Ellipsometry data from T4 oligofluorene truxene films in the region of 300–800 nm showing (a) the experimentally measured Ψ (squares) and △ (circles) values for 45° (thin outlines) and 60° (thick outlines) angles, along with the fitting results (solid lines) for an isotropic model. (b) Refractive index n (solid line) and extinction coefficient k (dashed line) for thin films of T4 truxene.

at 375 nm and the main emission features at 420 nm (0-0 transition), 440 nm (0-1 transition), and 467 nm (0-2 transition).

PLQY measurements performed on thin films spin coated from a toluene solution (20 mg/ml) using cw excitation at 325 nm showed a PLQY value of 73%, indicating that the T4 truxene is a very efficient light emitter in the solid state. ASE is another important parameter in evaluating the suitability of a material for lasing, as it demonstrates the material's ability to strongly amplify light over a range of wavelengths, with low ASE thresholds corresponding to low lasing thresholds. To investigate the ASE properties of T4, thin films of T4 were excited at 375 nm, the peak of the material's absorption, by an optical parametric oscillator that produced 4 ns pulses at 20 Hz repetition rate. The pump beam was focused to a spot of 2.3×0.1 mm^2. When the excitation power was increased, the emission spectrum of T4 changes from the normal broad fluorescence spectrum to the narrower ASE spectrum centered at 440 nm, as seen in Fig. 1. The ASE threshold was 4 kW/cm^2, a value substantially lower than the corresponding value of 58 kW/cm^2 reported for polyfluorene,[15] indicating effective amplification of light by the truxene material.

ASE is also very useful as the means to determine the available optical gain and waveguide losses from a thin film of material using the variable stripe technique.[6] When a thin film of material is illuminated by a narrow stripe of changing length, the intensity of the emission detected from the edge of the film as a function of the stripe's length allows for the optical gain of the material to be measured. The gain measurements based on the above technique can be seen in Fig. 2(a) for a range of different pump energy densities, with a maximum gain value of 23 cm^{-1}, a value that is comparable to other fluorene-based organic semiconductors.[16]

If instead of changing the length of the stripe we vary the distance between the stripe and the edge of the film, the output intensity I_{out} is given by $I_{out}=I_0 \exp(-\alpha x)$, where α is the optical loss coefficient and x is the distance from the end of the stripe to the edge of the film. The corresponding data for such a measurement in T4 can be seen plotted in a logarithmic scale in Fig. 2(b), where the slope of the graph corresponds to an optical loss coefficient of 2.3 cm^{-1}. This is the lowest waveguide loss coefficient reported for solution-processed neat films of organic semiconductors indicating that the light traveling within the T4 truxene thin film experiences very few losses either from scattering or reabsorption by the truxene molecules. In comparison to polyfluorene, one of the benchmark blue-emitting organic semiconductor laser gain materials, the optical losses within a thin film waveguide are reduced by more than a third.[15]

Low loss organic semiconductors should avoid crystallization as the presence of crystalline domains can increase scattering losses. Differential scanning calorimetry experiments show that T4 is an amorphous solid under ambient conditions, with a glass transition temperature of 116 °C. Cross-polarization microscopy of a thin film of T4 during heating and cooling cycles did not reveal any liquid crystalline phases and the material retains its glassy amorphous state on cooling below its glass transition temperature.[14] In addition, the optical constants of the thin films of T4 truxene were investigated using variable-angle spectroscopic ellipsometry. This technique provides insight into the way molecules are arranged in a thin film, including the presence of birefringence that can occur due to crystallization of the organic molecules.[17] The formation of crystalline domains within the volume of a film can have a detrimental effect on the optical losses as the different domains scatter light at their interfaces.[9] For the T4 material a set of six samples of varying thicknesses were prepared by spin-coating from a toluene solution onto silicon wafers. Ellipsometric measurements were performed over a spectroscopic range of 200 to 1700 nm for angles of 45° to 75° in steps of 5°. The results were first fitted with an isotropic Cauchy model between 450–1700 nm to determine the film thickness. The excellent agreement between the isotropic model and the ellipsometry data, as seen in Fig. 3(a), indicates that the T4 truxene films measured were all isotropic, meaning that the T4 molecules arrange themselves in random directions within the film. The absence of crystalline phases is consistent with the reduced

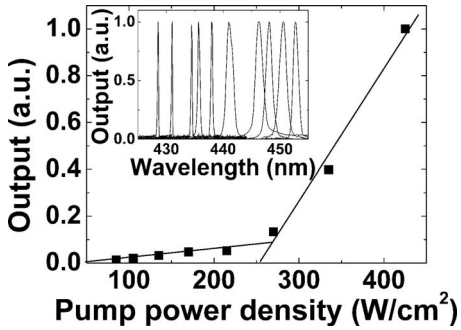

FIG. 4. Optical output as a function of pump power density for the best T4 oligofluorene truxene DFB laser emitting at 446 nm. The lines are guides to the eyes. Inset: Tuning range of T4 DFB lasers (428–453 nm) for different combinations of grating period and film thickness.

waveguide losses within these films, and suggests truxenes are promising laser materials. The ellipsometry data also allows the calculation of the refractive index n of the material and the extinction coefficient k across a wide range of wavelengths, as seen in Fig. 3(b).

Knowing the refractive index of the material makes it possible to calculate the effective refractive index n_{eff} that a waveguided mode would experience when traveling through a thin film. This is very important for distributed feedback (DFB) lasers, as the wavelength for which lasing is supported occurs near the Bragg wavelength as determined by $\lambda_{\text{Bragg}}=2n_{\text{eff}}\Lambda/m$, where n_{eff} is effective refractive index of the laser medium, m the Bragg order and Λ the grating period. A value of $m=2$ means that the laser emission will be perpendicular to the plane of the film, leading to fabrication of surface-emitting DFB lasers.

To make the T4 oligofluorene truxene DFB lasers, a thin film of the material was spin coated from toluene solution (20 mg/ml) on top of corrugated silica substrates ($\Lambda=270-301$ nm). The samples were then placed within a vacuum chamber (10^{-4} mbar) and excited with 10 ns pulses from a frequency-tripled Nd:YVO_4 laser beam focused to a spot of 1.6 mm diameter.

Upon increasing the optical pump power density, lasing from the T4 truxene DFB laser occurs over a threshold value of 270 W/cm^2 as seen by the change in the slope of the emission as a function of pump power density in Fig. 4. This is a very promising result for a new laser material. We note that an even lower threshold has been achieved in a fluorene copolymer in a more sophisticated resonator with first and second order feedbacks.[7,18] However, it is important to emphasize that the lasing threshold presented here is largely due to the very low waveguide losses of the films, making the truxene molecules a promising route to solid-state organic lasers with reduced waveguide losses.

By changing the period of the corrugated substrate between 270 and 301 nm, extensive tuning of the output wavelength of the laser was possible over 25 nm, from 428 to 453 nm, as seen in the inset of Fig. 4. The lasing peaks at wavelengths longer than 440 nm were recorded using a different charge-coupled device spectrograph with a shorter focal length and therefore have lower resolution. This wide tunability in a single material is one of the most attractive features of organic semiconductor laser materials.

In summary, we report a low-threshold organic semiconductor laser based on the star-shaped oligofluorene truxene T4. The low optical losses of 2.3 cm^{-1} that the material demonstrates lead to a very low ASE threshold of 4 kW/cm^2. Low optical losses in neat films are important for the development of organic semiconductor lasers, as confirmed by the low lasing threshold of 270 W/cm^2 achieved in truxene DFB lasers.

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