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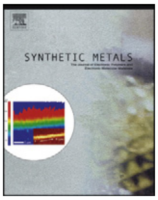

Broadly tunable deep blue laser based on a star-shaped oligofluorene truxene

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ABSTRACT

We report amplified spontaneous emission (ASE) and optically pumped deep-blue-emitting distributed feedback (DFB) lasers based on a star-shaped oligofluorene truxene molecule. A low ASE threshold of 2.1 kW/cm^2 at 439 nm was achieved. The material exhibits a high net gain of 38 cm^{-1} and also low optical loss coefficient of 3.5 cm^{-1}. Second-order DFB lasers show tuning of the emission wavelength from 422 to 473 nm, and a minimum threshold density of 515 W/cm^2. This is the broadest tuning range (51 nm) reported for organic deep-blue/blue lasing materials.

1. Introduction

Over the past decade, the development of organic semiconductors has attracted a great deal of interest [1–4]. They have become very attractive materials for a range of photonic devices including light-emitting diodes [5], photovoltaic cells [6], organic field effect transistors [7] and lasers [4]. The solution processing of these materials promises low-cost optoelectronic devices and simplified fabrication of wavelength-scale structures. This is particularly relevant for organic semiconductor lasers which have been demonstrated in a wide range of novel resonator structures allowing low-threshold optical pumping by lasers or even LEDs [8,9]. One of the most interesting properties of organic semiconductor gain materials is that they have broad emission spectra and a selection of materials can cover the whole visible spectrum [10–15].

While many of the advances in organic semiconductor lasers have used conjugated polymers as the gain medium, conjugated oligomers offer some advantages. Oligomers are monodisperse and characterized by a well-defined and uniform molecular structure, and can have superior chemical purity [16]. However, one-dimensional conjugated oligomers can be prone to aggregation which can quench light emission [17,18]. This issue can be addressed by attaching the oligomers to a truxene (10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene), which is a polycyclic aromatic system with C_3 symmetry [19]. The truxene core is crowded by six hexyl groups that are perpendicular to the fused aromatic rings, therefore aggregation (through π–π stacking) is suppressed in such structures. The two-dimensional molecules form high-quality amorphous films [16], leading to a promising new class of oligomeric organic laser material [20,21]. Here, we report a systematic study of the photophysics, gain and lasing behaviour of the T3 oligomer, having a truxene core with three fluorene units on each of its three arms. We have found that the material T3 has high photoluminescence quantum yield (PLQY) and low ASE threshold. Solid-state distributed feedback (DFB) lasers have also been fabricated with T3 with low-threshold and very broad tuning. Indeed the T3 lasers demonstrate the broadest tuning range (51 nm) reported for organic deep-blue/blue laser materials.

2. Experimental

The chemical structure of the truxene oligofluorene molecule studied (T3) is shown in Fig. 1a. The molecule consists of a central truxene core with three fluorene arms attached, and contains long-chain *n*-hexyl substituents on both truxene core and fluorene arms that makes the material soluble in organic solvents with good film-forming properties. Each arm consists of three 9,9-dihexylflurorene units. The synthesis of T3 has been described elsewhere [16]. Films of 80–130 nm thickness were made by spin-coating from 20 mg/ml toluene solutions on quartz substrates. The film thicknesses were

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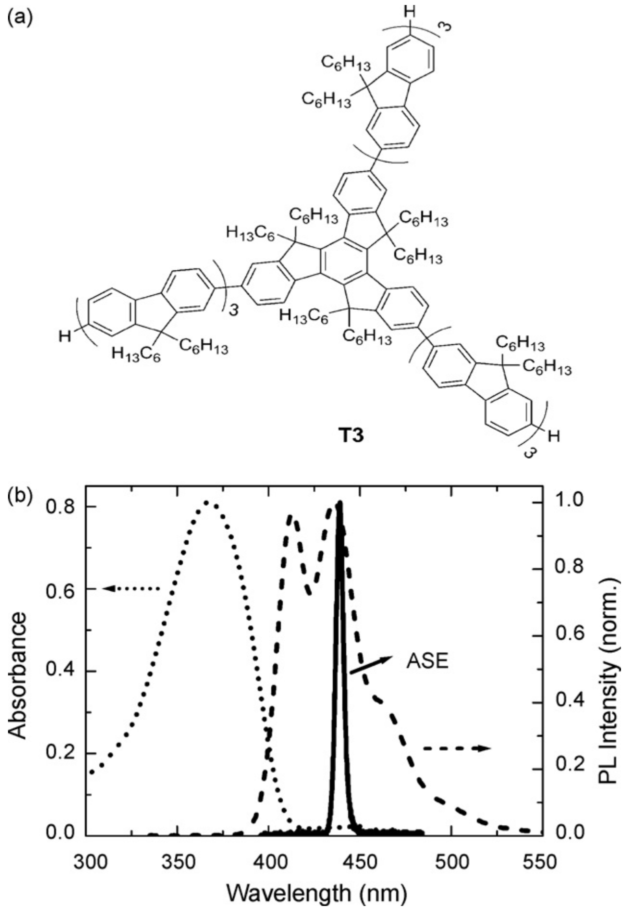

Fig. 1. (a) Chemical structure of the T3 oligofluorene truxene. (b) Absorption (dotted line) and photoluminescence (dashed line) spectra of T3 truxene, along with the ASE spectrum (solid line)

measured with a Veeco Dektak 150 surface profiler. Absorption spectra were measured with a Cary 300 UV-Vis spectrophotometer and PL spectra were measured with a Jobin Yvon FluoroMax2 fluorometer. PLQY measurements of thin films (of approximately 130 nm thickness) were made using the method of Greenham et al. [22], with the 325 nm output of a He–Cd laser for excitation. The photoluminescence (PL) lifetime was measured with a streak camera in the spectral window of 400–500 nm.

To assess the potential of T3 as an optical gain medium we first measured amplified spontaneous emission in the films under pulsed optical excitation. The excitation light in the ASE measurements was generated by a Nd:YAG laser pumped optical parametric oscillator (OPO) with 4 ns output pulses at a repetition rate of 20 Hz. The pump wavelength was 375 nm which is close to the absorption maxima of T3. Calibrated neutral density filters were inserted in the beam path to adjust the pump intensity incident on the samples. A cylindrical lens was used to shape the excitation beam into a narrow stripe with a width of approximately 200 μm on the surface of the film. The length of the pump stripe was varied in the range 0.6–2 mm, controlled by an adjustable aperture, between 2 mm and 0 mm. The edge emission from the films was collected and recorded with a fibre-coupled grating spectrograph and a charge coupled device (CCD) detector. During all the measurements, the film was located in a vacuum chamber with a pressure of approximately 10^{-5} mbar. The net gain per unit length, g, was studied using the variable stripe length method [23,24]. For gain measurements, the output intensity was recorded as a function of excitation length, for a range of different pump intensities. In theory, when ASE occurs the output intensity from one end of the pump stripe is given by:

$$I(\lambda) = \frac{AI_{\text{pump}}}{g(\lambda)}(e^{g(\lambda)l} - 1), \tag{1}$$

where l is the length of the pump stripe. To measure the waveguide loss coefficient, α, the pumped stripe on the film was moved away from the edge of the sample without changing its length. The pump stripe was fixed in the measurements to be 4.5 mm × 200 μm. The emission from the edge should then be given by:

$$I = I_0 e^{(-\alpha x)}, \tag{2}$$

where x is the distance between the end of the pump stripe and the sample edge.

The optical constants of the thin films of T3 truxene were investigated by variable angle spectroscopic ellipsometry using a J.A. Woollam Co. Inc. M2000-DI ellipsometer. Eight samples of different thickness (30–50 nm) were prepared by spin coating from a T3 solution (toluene, 10 mg/ml) onto fused silica substrates. Polarised light reflection data were collected for angles of incidence between 45° and 75° in intervals of 5° and in the wavelength range of 190–1700 nm. Transmission at normal incidence was also measured and a general oscillator Cauchy model was fitted to the combined reflection and transmission data.

T3 films were deposited onto corrugated fused silica substrates to form distributed feedback (DFB) lasers. The corrugated structures were formed by holography followed by reactive-ion etching into the silica. These provide laser feedback at a wavelength determined by the Bragg condition, $m\lambda_{\text{Bragg}} = 2n_{\text{eff}}\Lambda$, where λ_{Bragg} is the wavelength of the light, Λ is the period of the resonator structure, n_{eff} is the effective refractive index of the waveguide and m is an integer that represents the order of the diffraction. n_{eff} for the TE_0 transverse mode is calculated from the refractive indices of T3 (n_{T}), the substrate (n_{s}) and air (n_{a}) using the equation:

$$\frac{2\pi d}{\lambda}\sqrt{n_{\text{T}}^2 - n_{\text{eff}}^2} = \tan^{-1}\sqrt{\frac{n_{\text{eff}}^2 - n_{\text{a}}^2}{n_{\text{T}}^2 - n_{\text{eff}}^2}} + \tan^{-1}\sqrt{\frac{n_{\text{eff}}^2 - n_{\text{s}}^2}{n_{\text{T}}^2 - n_{\text{eff}}^2}}. \tag{3}$$

The gratings used in our T3 truxene lasers are designed for second-order ($m = 2$) DFB laser operation, which gives a convenient surface emission and avoids the need for high-quality edge facets. They had periods Λ of 270 nm, 280 nm (feedback in one-dimension, 1D) and 301 nm (square-array, two-dimensional feedback, 2D) and depths of 30–50 nm shown from atomic force microscope (AFM) images. By spin-coating T3 toluene solutions (25 mg/ml or 30 mg/ml) onto the corrugated silica substrates at speeds in the range of 800–1500 rpm, the thickness of the films was varied between 100 nm and 160 nm, and hence, the effective refractive index of the waveguide could be changed to support different laser output wavelengths. The T3 truxene lasers were optically pumped with 355 nm pulses (4 ns pulse width) at a repetition rate of 500 Hz from a frequency-tripled Nd:YVO_4 laser. The DFB laser emission was detected at an angle normal to the waveguide using the fibre-coupled grating spectrograph. The pump beam was incident onto the samples at an angle of 20° to the surface normal to avoid detection of transmitted pump light and it was focused to a 1.1 mm diameter spot (measured with a Coherent Inc. Beam Profiler at the position of the T3 films), which resulted in the excitation area of 0.0095 cm^2.

3. Results and discussions

Fig. 1b shows the absorption, PL excited at 325 nm, and ASE spectra of T3 truxene. The absorption has a maximum at 367 nm and the main emission peaks are at 414 nm (0-0 vibronic transition), and 438 nm (0-1 vibronic transition), with a shoulder near 461 nm (0-2 vibronic transition). By fitting the time-resolved PL decays from