Chemical Physics Letters 478 (2009) 37–41

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Amplified spontaneous emission in optically pumped neat films of a polyfluorene derivative

Jiu Yan Li [a,*], Frédéric Laquai [b,*], Gerhard Wegner [b]

[a] State Key Laboratory of Fine Chemicals, Dalian University of Technology, 158 Zhongshan Road, Dalian 116012, PR China
[b] Max-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

ARTICLE INFO

Article history:
Received 5 May 2009
In final form 6 July 2009
Available online 9 July 2009

ABSTRACT

We report the emissive properties of a fluorene-based polymer, PF-1SOR, in planar asymmetric waveguides under optical pumping. A laser beam homogenizer setup was applied to achieve the flat-top intensity profile of the excitation light. Amplification of deep blue light via stimulated emission (SE) occurred at an energy threshold of 11 μJ cm^{-2} and the amplified spontaneous emission (ASE) peak could be tuned from 411 to 423 nm. A net gain coefficient of 19.8 cm^{-1} was obtained by means of the modified variable stripe length (VSL) method. The PF-1SOR thin films delivered a remarkably low loss coefficient of 1.5 cm^{-1}, among the lowest ever reported for a single component polymer waveguide.

1. Introduction

Polymeric and organic semiconductor materials have attracted considerable interest as active materials in solid-state organic lasers and light-emitting diodes due to their high photoluminescence efficiencies and easy colour-tuning possibilities [1–5]. Optically pumped organic lasers have been realized with various resonator geometries and have stimulated intensive research aimed at realizing electrically pumped laser diodes [6–9]. In the absence of a resonator for the coupling of modes which would be a prerequisite for a true laser, the thin film of the active material coated on a substrate forming an asymmetric optical waveguide confines the emitted light within the film, thus making stimulated emission (SE) processes possible which result in gain narrowing of the emission spectra and amplification of spontaneous emission [10]. In order to realize a practical and efficient laser device, low energy thresholds for amplified spontaneous emission (ASE) and laser action are necessary. A large Stokes shift of the active material is desirable to minimize the self-absorption losses and to lower the ASE threshold. The Stokes shift of organic molecules or polymer materials can be adjusted by modifying the chemical structure of the molecules or the polymer main chain, thus the energy of electronic transitions. A variety of light-emitting polymers have been developed for application in optically and electrically pumped solid-state laser devices. For a potential use in semiconductor injection lasers, highly luminescent conjugated polymers are superior to organic molecules doped inert matrix systems due to higher charge carrier mobility [11], as well as to polymer blends due to the absence of phase separation problems that frequently occur in the latter [12]. In particular, fluorene-based polymers have been widely investigated due to their good thermal and oxidative stability, high quantum efficiencies of blue light-emission and low ASE thresholds [13–15].

In this Letter, we report the optical gain properties of a novel fluorene-based conjugated polymer, PF-1SOR, in thin film waveguides under optical excitation. The chemical structure of PF-1SOR is shown in the inset of Fig. 1a. The synthesis has been reported elsewhere [16]. The previous spectroscopy investigation of PF-1SOR films showed an absorption maximum at 350 nm, a fluorescence (FL) peak at 419 nm and a large Stokes shift of 69 nm. In contrast to the traditional polyfluorenes, PF-1SOR and its analogues emit stable blue fluorescence in the absence of any contamination by the well-known 'green' band that has usually been observed in the emission spectra of fluorene-based polymers. The electron withdrawing nature and the scavenging effect of the (3,5-di(tert-butyl)phenoxy)sulfonyl side groups were suggested to be responsible for the improved spectral stability. Here, the ASE properties of PF-1SOR were studied in form of planar asymmetric waveguides under pulsed laser excitation, with particular attention being focused on the ASE gain and loss properties. The variable stripe length (VSL) technique was modified to minimize the experimental error when it was used to measure the net gain of PF-1SOR waveguides. A deviation of the ASE data of PF-1SOR from the established ASE equation has been observed and was interpreted. The loss coefficient of the polymer waveguides was determined and tuning of the ASE peak position by varying the film thickness was also demonstrated.

---

* Corresponding authors.
E-mail addresses: jiuyanli@dlut.edu.cn (J.Y. Li), laquai@mpip-mainz.mpg.de (F. Laquai).

0009-2614/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2009.07.028

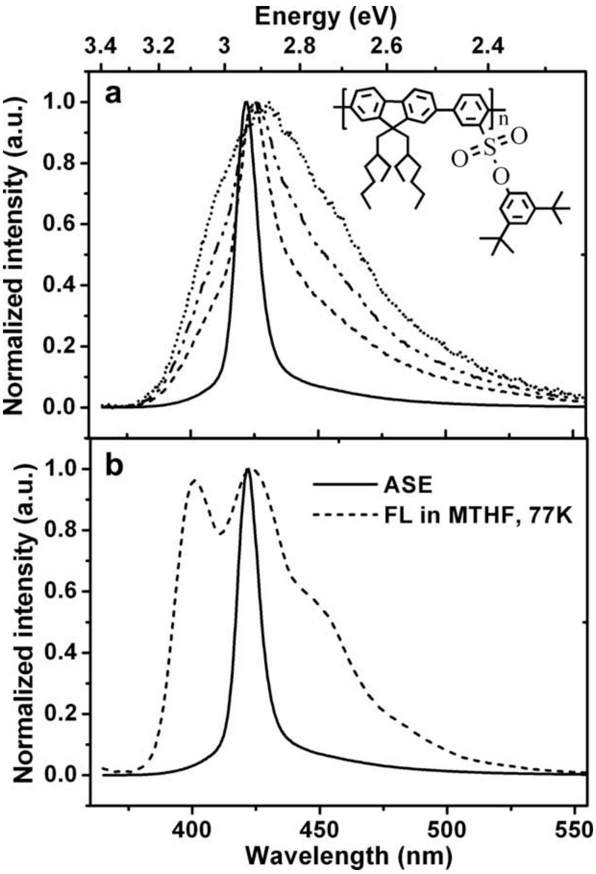

Fig. 1. (a) Evolution of the emission spectra of a PF-1SOR slab waveguide with increasing pump energy density: 6 μJ cm^{-2} (dotted line), 24 μJ cm^{-2} (dashed dotted dotted line, ÷3.57), 48 μJ cm^{-2} (short dashed line, ÷9.07) and 378 μJ cm^{-2} (solid line, ÷35.68); Inset: the chemical structure of PF-1SOR. (b) The fluorescence spectrum in MTHF at 77 K (dashed line) and the ASE spectrum of PF-1SOR (solid line).

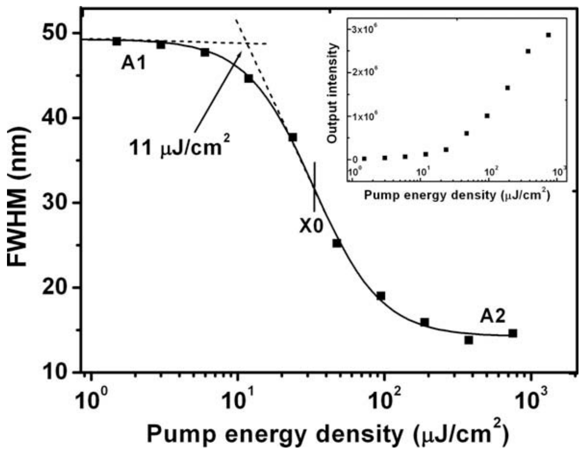

Fig. 2. Illustration of the experimental procedure to determine the ASE onset for a PF-1SOR film of 128 nm. Inset: dependence of the output intensity at the ASE peak wavelength on the pump energy density.

2. Results and discussion

Fig. 1a shows the edge collected FL spectra of a neat film of PF-1SOR (128-nm-thick) at various pump energy densities. At a low pump energy of 6 μJ cm^{-2}, the emission spectrum is broad and structureless with a peak at 430 nm, similar to the normal FL spectra of spin-coated PF-1SOR films [16]. With increasing pump energy, the emission spectrum collapses into a narrow ASE peak at 423 nm with a full width at half maximum (FWHM) of 9 nm due to an increase in the SE component. A blue shift of the emission peak from 430 nm to 423 nm at high pump energies suggests that the SE occurs on a time scale faster than the spectral diffusion that occurs during the first few tens of picoseconds after photoexcitation [1]. In order to assign the ASE peak to a certain electronic and vibronic transition, the prompt FL spectrum of PF-1SOR was measured in a dilute 2-methyl-tetrahydrofuran (MTHF) glass at 77 K upon excitation at 355 nm. Well-defined vibronic peaks at 401 nm (0-0), 423 nm (0-1) and 450 nm (0-2) were observed in the structured emission spectrum as shown in Fig. 1b. The ASE peak is located in the center of the 0-1 vibronic band in the normal FL spectrum of PF-1SOR, suggesting that the maximum net gain in the present PF-1SOR waveguide occurs during the transition from the lowest vibronic level of the first excited singlet state ($S_{1,0}$) to an excited vibronic level of the singlet ground state ($S_{0,1}$). This corresponds to a quasi-four-level laser system.

The ASE threshold was determined by monitoring the dependence of the FWHM of the emission spectra on the pump energy density as shown in Fig. 2. The plot of the FWHM as a function of the pump energy density (on a semilogarithmic scale) gives a sigmoidal curve, which can be fitted to the following equation [10]:

$$\mathrm{FWHM}(x) = \frac{A1 - A2}{1 + (x/x_0)^p} + A2, \qquad (1)$$

in which x means the pulse energy, $A1$ and $A2$ are the FWHM in the low and high pulse energy limit, x_0 is the pulse energy for FWHM = $(A1 + A2)/2$, and p represents the steepness of the function. The intersection of the tangent at the turning point and the normal fluorescence linewidth (FWHM = $A1$) defines the ASE threshold intensity. In this way the ASE thresholds for PF-1SOR films with different thickness were determined to 11 μJ cm^{-2} for 128 nm, 13 μJ cm^{-2} for 120 nm and 23 μJ cm^{-2} for 93 nm. It should be noted that the ASE threshold of PF-1SOR obtained in this way can only be viewed as the energy for the onset of ASE in the emission spectra, where the normal fluorescence still dominates the emission. Such an ASE threshold of 11 μJ cm^{-2} for PF-1SOR is three times higher than that of the reported poly(tetraoctylarylindenofluorene) [6] and comparable to that of poly(ladder-type tetraphenylene) [17,18].

The inset of Fig. 2 shows the ASE peak intensity at 423 nm as a function of the pump energy density. Again it is evident that such an energy threshold exists in the ASE behavior. The emission intensity from the end of the excitation stripe grows slowly below the ASE threshold. When the pump energy exceeds this threshold, the emission intensity increases abruptly accompanied by a collapse of the spectral linewidth since the stimulated emission instead of the spontaneous emission becomes dominant.

The net gain coefficient of PF-1SOR was measured using the VSL technique by pumping a 232-nm-thick film with energies above the ASE threshold (in the $A2$ region in Fig. 2). The excitation geometry was kept same as before and the excitation stripe length was increased gradually in steps of 0.2 mm by moving the shutter of the laser beam away from the film edge. The edge emission intensity from one end of the excitation stripe at different excitation stripe lengths was fitted to the following equation [1,3–15,19]:

$$I = \frac{AP_0}{g}\{e^{gl} - 1\}, \qquad (2)$$

where AP_0 describes spontaneous emission proportional to the pump energy, g is the net gain coefficient, and l is the length of the excitation stripe. However, fitting the subset of data at short excitation stripe lengths of PF-1SOR waveguide obtained by this traditional method to Eq. (2), resulted in the net gain coefficient g lower than 10 cm^{-1} even at a pump energy density of 238 μJ cm^{-2}.