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Optical gain in fluorenyl-thiophene co-oligomer thin films

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Abstract

We report on the emission properties of thin films of a fluorenyl-thiophene co-oligomer under strong optical excitation. A clear line narrowing is observed in the emission spectra as a function of the excitation density, due to a Stimulated Emission band attributed to Amplified Spontaneous Emission (ASE). The ASE threshold of about 150 $\mu J\,cm^{-2}$ is comparable with the best values reported for other oligomeric and/or co-oligomeric films or crystals. A maximum gain value of about 8 cm^{-1} is obtained for an excitation density of about 940 $\mu J\,cm^{-2}$. These results propose fluorene-thiophene co-oligomers as interesting materials for high performance optically pumped laser devices.

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Keywords: Stimulated emission; Organic film; Amplified spontaneous emission

1. Introduction

In the last few years a lot of studies have been performed to understand and describe the optical properties of organic conjugated molecules for low cost photonic and optoelectronic devices. Concerning optically pumped lasers, optical gain has been demonstrated in several different compounds, including homopolymers [1–3], copolymers [4,5], short molecules both in disordered films and crystals [6–9], and dendrimers [10]. Among this wide family of materials showing optical gain two classes of compounds revealed promising optical properties for high performances devices applications, namely thiophene-S,S-dioxide oligomers and fluorene based polymers. Thiophene-S,S-dioxide oligomers present clearly improved optical properties with respect to standard oligothiophenes [11–13], good solubility in standard organic solvents, high gain cross section [14] and tunable optical gain in the visible spectrum [15] in thin films. These features have been exploited to realize optically pumped lasers with low lasing threshold and good external efficiency [14,16]. Similar results have been demonstrated on fluorene based homopolymers [17] and copolymers [18], showing tunable Amplified Spontaneous Emission in the blue–red spectral range [18] with optical gain up to 74 cm^{-1}, and good optically pumped laser performances in Distributed Feedback (DFB) laser both in one and two dimensional devices [19–21]. However, light emitting devices with polyalkylfluorenes as active materials suffer from chemical degradation during operation, which

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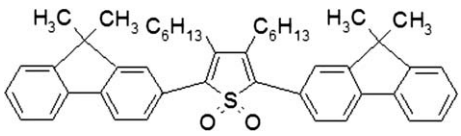

Fig. 1. Chemical structure of the FTS molecule.

leads to the appearance of low energy emission bands, which affect the color and intensity stability of emitted light. Possible solutions for this chemical instability are the functionalization of the fluorene backbone with side-chains as arylene-type dendrons [22], or the realization of copolymers with other conjugated moieties [23], including thiophenes [24,25]. In particular, high photoluminescence and electroluminescence efficiencies have been recently demonstrated in a fluorene-thiophene copolymer and in the corresponding co-oligomer, containing a dioxide-thienyl ring [26]. However, despite the recent demonstration of high optical gain in conjugated co-oligomers single crystals [27–29], optical gain in disordered co-oligomeric thin films has not been observed yet.

In this paper we study the emission properties under strong optical excitation of thin films of a fluorenyl-thiophene co-oligomer having a dioxide thienyl ring between two fluorene units, 2,5-di(9,9-dimethyl)fluorenyl-3,4-dihexyl-thiophene-S,S-dioxide, namely FTS, see Fig. 1. We show that Amplified Spontaneous Emission is present in the spectra with a threshold of about 150 μJ cm^{-2}. A maximum optical gain of about 8 cm^{-1} is obtained for an excitation density of about 940 μJ cm^{-2}. These results are among the best reported for short molecules, both in disordered films and in single crystals, and propose fluorenyl-thiophene co-oligomer as interesting active materials for low cost and high performances optically pumped laser devices.

2. Experimental

FTS has been synthesized as reported in Ref. [26]. Thin films have been prepared by spin coating from a 3.0×10^{-2} M solution in $CHCl_3$ on glass substrates in air and at room temperature, obtaining a film thickness of about 260 nm. The samples have been excited with the third harmonic ($\lambda = 355$ nm) of a Q-switched Nd-YAG laser, delivering 3 ns pulses with a repetition rate of 10 Hz. The excitation beam has been focused on the sample by a cylindrical lens, thus obtaining a rectangular excitation stripe with width of about 100 μm and variable length up to 7 mm. In order to obtain an homogeneous excitation density only the central region of the pump beam has been selected with a variable slit. The sample emission has been collected from the sample edge, dispersed by a TRIAX 320 monochromator, and detected by a Si-CCD. The spectral resolution was about 5 Å. All the measurements have been performed at room temperature in vacuum of about 10^{-5} mbar in order to avoid photo-oxidation.

3. Results and discussion

The emission spectra as a function of the excitation density are reported in Fig. 2. For an excitation density lower than about 100 μJ cm^{-2} only the broad spectrum due to spontaneous emission is present, with a maximum intensity at $\lambda \approx 550$ nm and a Full Width at Half Maximum (FWHM) of about 100 nm. For an excitation density higher than 200 μJ cm^{-2} (corresponding to about 70 kW cm^{-2}) a clear narrow band with a maximum intensity at $\lambda \approx 542$ nm and a FWHM of about 10 nm appears in the spectra. As the excitation density increases the FWHM of the spectrum decreases (inset of Fig. 2) and the intensity of the narrow band relative to the broad one increases. These features are typical of Amplified Spontaneous Emission (ASE) assisted by wave-guiding effect in the film. The observed ASE threshold [30] is about 150 μJ cm^{-2} (corresponding to about 50 kW cm^{-2}). For the sake of comparison, this value is about two times lower than the ASE threshold for quinquethienyl S,S-dioxide (T5OCx) films [32] (about 100 kW cm^{-2}), and it is comparable to the reported ASE threshold for other co-oligomeric compounds like oligothiophene-phenylene crystals [27] (about 400 μJ cm^{-2}, recently improved [28] down to 27 μJ cm^{-2}) and about four times lower than end-capped fluorene/phenylene co-oligomer crystals [29] (about 200 μJ cm^{-2}). Concerning polymers the observed threshold is about four times lower than the threshold observed in DOO-PPV [33] films (about 200 kW cm^{-2}), but about 20 times larger than the typical values found for polyfluorenes [17,18].

In order to determine the net gain spectrum (difference between gain and losses $g = g' - \alpha$) we measured

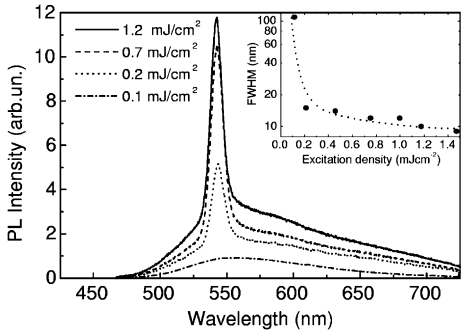

Fig. 2. Emission spectra as a function of the excitation density, the Stimulated Emission band, peaked at $\lambda \approx 542$ nm, is clearly visible for excitation density higher than 200 μJ cm^{-2}. Inset: FWHM of the spectra as a function of the excitation density. The dotted line is a guide for the eyes.