Low threshold Amplified Spontaneous Emission properties in deep blue of poly[(9,9-dioctylfluorene-2,7-dyil)-alt-p-phenylene] thin films

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Abstract

Amongst the different optoelectronic applications of conjugated polymers, the development of new active materials for optically pumped organic laser is still an open question particularly in the blue-near UV spectral range. We investigate the emission properties of poly[(9,9-dioctylfluorene-2,7-dyil)-altp-phenylene] (PFP) neat films under nanosecond pump. We demonstrate that thanks to the introduction of a phenylene moiety between two fluorene units it is possible to obtain Amplified Spontaneous Emission (ASE) with a

lower threshold and a blue shifted wavelength with respect to poly(9,9dioctylfluorene) (PFO). We demonstrate efficient ASE with a minimum threshold as low as 23 μJcm^{-2} and a minimum ASE wavelength of 436 nm. A maximum net optical gain of about 26 cm^{-1} is measured at an excitation density of 0.23 mJcm^{-2}. These results make the PFP a good active material for optically pumped deep blue organic lasers.

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1. Introduction

During the last couple of decades many studies have been performed to fully understand the optical and electronic properties of organic conjugated molecules, with lot of efforts dedicated to the optimization of various chemical and electronic parameters in order to obtain the best performance of such class of compounds in low cost photonic and optoelectronic applications. In particular several organic molecules have demonstrated the capability to amplify the luminescence emission, under strong enough optical pumping, with evidence of a strong line narrowing of the luminescence spectrum and exponentially growing intensity as the excitation density increases. The nature of this effects has been well established to be originated, in thin films, by the process of Amplified Spontaneous Emission (ASE) supported by waveguiding effect in the organic layer sandwiched between different materials with lower index of refraction [1, 2, 3] (in the

simplest configuration a glass substrate at the bottom and air on the top). The presence of ASE is a direct evidence of optical gain in the material, thus the investigation of the ASE properties of new materials is strictly connected to the development of new active materials for optically pumped organic lasers.

In this frame great efforts have been thus devoted to the development of materials simultaneously showing low ASE (or lasing) threshold and high optical gain [4, 5, 6, 7], leading in some cases to organic lasers demonstrators close to the performances needed in real devices [8, 9]. One of the open issues in the development of active materials for organic lasers is the realization of organic molecules with good gain properties in the blue-near UV spectral range, that would be strategic for optical data storage applications, for bluelaser-light therapy against antibiotic-resistant bacteria [10], as well as for excitation source in spectroscopy experiments.

To date the most common blue-emitting polymers are based on the fluorene moiety, among which the well known poly(9,9-dioctylfluorene) (PFO) exhibits good film forming properties and high optical gain [11, 12] between 446 nm and 466 nm, depending on the waveguide thickness and on the PFO aggregation phase [13]. However PFO samples suffer of poor stability under optical pumping, with fast quenching of the blue emission and with a variation of the luminescence spectra lineshape, due to the formation of green emitting keto-defects [14, 15] as a results of photo-oxidation. Moreover PFO is a mesomorphic molecule showing two different phases with different blue emission spectra, typically coexisting in solution processed thin films, and strongly affecting the emission spectra of the films [16].

Considering the good optical properties of pristine PFO, some groups worked on the chemical functionalization of the polymer backbone, in order

to modify its photoluminescence and ASE properties. Several funtionalization approaches have been developed, allowing to improve the ASE properties in terms of threshold and/or wavelength reduction. To date the best results have been obtained in a (3,5-di(tert-butyl)phenoxy)sulfonyl functionalized polyfluorene, showing ASE at about 423 nm with a threshold of about 11 μJcm^{-2} under nanosecond pump [17], while even lower threshold has been obtained, but at considerably higher wavelength, down to about 3 μJcm^{-2} at 469 nm in a fully arylated poly(indenofluorene)[18].

In this frame it has been recently reported that the phenyl functionalization of the fluorene moiety allows to blue-shift the absorption spectra, to increase the oxidation potential, and to increase the photoluminescence quantum yield with respect to PFO, preserving the charge mobility [19]. These properties have been exploited to realize efficient deep blue OLEDs at 405 nm, with a remarkable 5.03% external quantum efficiency and stable emission color [10].

In this paper we investigate the emission properties of poly[(9,9-dioctylfluorene2,7-dyil)-alt-p-phenylene] (PFP) thin films under strong optical pumping. We demonstrate the presence of ASE with a threshold about 3 times lower than PFO, in a wavelength range between 436 nm and of 446 nm. We also demonstrate that PFP shows, at a common excitation density, an optical gain about 2.2 times higher than PFO. These results propose PFP as an interesting active material for organic deep blue optically pumped lasers.

2. Experimental

Poly[(9,9-dioctylfuorene-2,7-diyl)-alt-p-phenylene] (PFP) was synthesized as previously reported [19, 10]. Since purity is essential for

optoelectronic materials we carefully purified the polymer. The crude polymer was filtered on Celite and precipitated in methanol. In order to eliminate residual catalyst PFP was purified by means of an Aldrich Pd scavenger and the precipitation in MeOH, after dissolution in toluene, was repeated until a white precipitate was obtained.

Table 1: Measured sample thickness T and standard deviation σ.

Sample	Thickness T	σ
PFP$_A$	180 nm	30 nm
PFP$_B$	67 nm	9 nm
PFP$_C$	31 nm	5 nm
PFO	184 nm	15 nm

PFO has been purchased from American Dye Source (ADS129BE) and used as received. PFP has been dissolved in toluene with three different concentrations, namely 7.5, 15 and 25 mg/ml, in order to change the film thickness. PFO has been dissolved in toluene with a concentration of 20 mg/ml. PFO solutions have been placed on an hot plate at 60 C during the first 10 minutes of stirring in order to avoid the formation of the β-phase [20]. All the solutions have been then stirred overnight up to their use.

Thin films have been realized by spin coating 100 μl of each solution onto thin microscope cover glasses (from Bresser, certified thickness 130÷170μm) at 2500 rpm. The thickness has been measured by a DEKTAT AlphaStep profilometer and the obtained values are reported in Tab. 1.

PL, ASE and optical gain have been characterized using an experimental set-up similar to the one described by Shaklee and Leheny [21].The samples

have been excited by a rectangular laser spot (variable length and height of about 100μm) obtained by a cylindrical lens, while the PL has been collected from the sample edge in a waveguide configuration. PL and ASE experiments have been performed under vacuum of about 10^{-2} millibar at room temperature (18 C). The pumping laser was a Nitrogen laser emitting 3 ns pulses at 10 Hz, 337 nm. The excitation power density has been changed by a variable circular neutral filter. PL signal has been collected by a multimodal optical fiber connected to a PC controlled ACTON SpectraPro-750 spectrometer equipped with a Peltier cooled ANDOR CCD (spectral resolution of about 0.5 nm). Absorption spectra have been collected by a Varian Cary 500 spectrophotometer.

3. Results and discussion

PFO is one of the most representative optical amplifying polymers whereas its derivative PFP have been only scarcely studied. The insertion of a phenyl group between two dialkyl fluorene moieties improve the film stability both from a morphological point of view , in fact it does not present the multiphases problem and from a chemical point of view because the fluorenone defect could not be formed on a simple phenylene unit. Thought we have obtained thin film of excellent optical quality that in combination with efficient solid state blue emission [10][10] (about 77%) makes the material a promising candidate for ASE.

The absorption spectrum of PFP samples (see Fig. 1) shows a main absorption resonance peaked at 367.6 nm (3.37 eV), with a Full Width at Half Maximum (FWHM) of 63 nm (0.59 eV). The only visible effect of the thickness variation is on the absorbance values, without notable lineshape differences.

The photoluminescence spectra of the PFPₐ sample (see Fig.1) shows, at
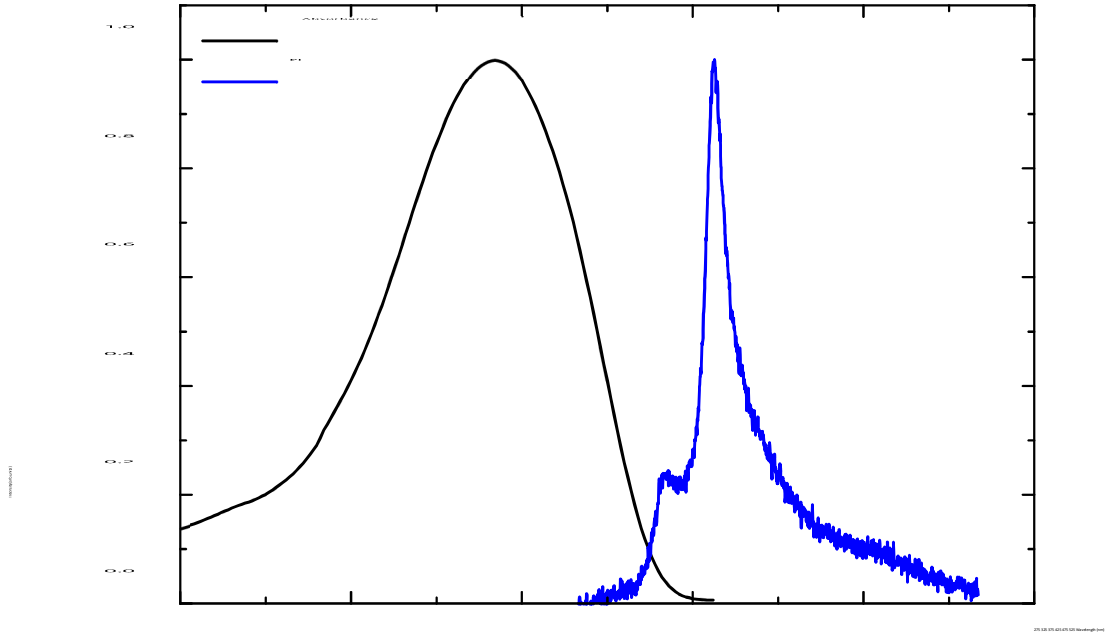low excitation density, a first peak at about 417 nm, ascribed to the 0-0 tran-

Figure 1: Absorbance spectrum (black) and PL spectrum at low excitation density (blue) of
PFPₐ thin film (the spectra are normalized to 1 for clarity).

sition, followed by a vibronic replica at about 432 nm, and a weaker shoulder
at about 448 nm. As the excitation density increases a clear line narrowing is
observed (see Fig.2), with the appearance of an ASE band peaked at 446 nm,
showing an intensity superlinearly increasing with the excitation density.
The ASE threshold, estimated as the minimum excitation density that allows

the observation of the ASE band in the spectra, is about 23 μJcm^{-2}. For the sake of comparison we observe that the PFO sample, with comparable thickness, shows ASE peaked at about 455 nm, with a threshold of about 70 μJcm^{-2}. The phenyl functionalization thus results in a blue-shift of the ASE band of about 10 nm, and in a considerable threshold reduction of about 3 times.

In order to explore the ASE tunability range we also realized thinner samples, exploiting the reduction of the maximum waveguided wavelength to tune the ASE band within the gain spectral range of PFP. We observe (see Fig. 3) a progressive blue shift of the ASE peak wavelength as the sample thickness decreases, down to 436 nm in PFP$_C$ sample, and a progressive ASE threshold increase up to 40 μJcm^{-2} in PFP$_B$ sample and up to 125 μJcm^{-2} in PFP$_C$ sample, consistent with the progressive decrease of waveguide mode confinement in the active layer [4].

In order to further compare the PFP gain properties with the PFO ones we determined the optical gain in the samples by using the Variable Stripe Length method at an excitation density 10 times higher than the ASE threshold one (thus at 230 μJcm^{-2} for PFP$_A$ and 700 μJcm^{-2} for PFO), and fitting the stripe length dependence of the ASE peak intensity to the following equation:
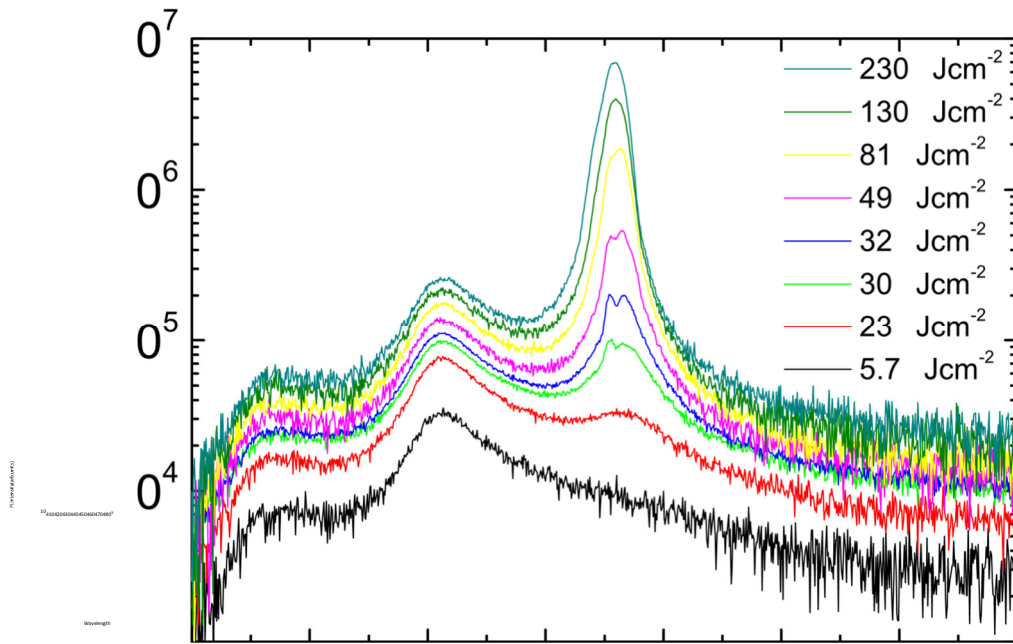
Figure 2: Excitation density dependence of the PL spectra of PFP_A sample. The ASE band at about 446 nm is well visible.
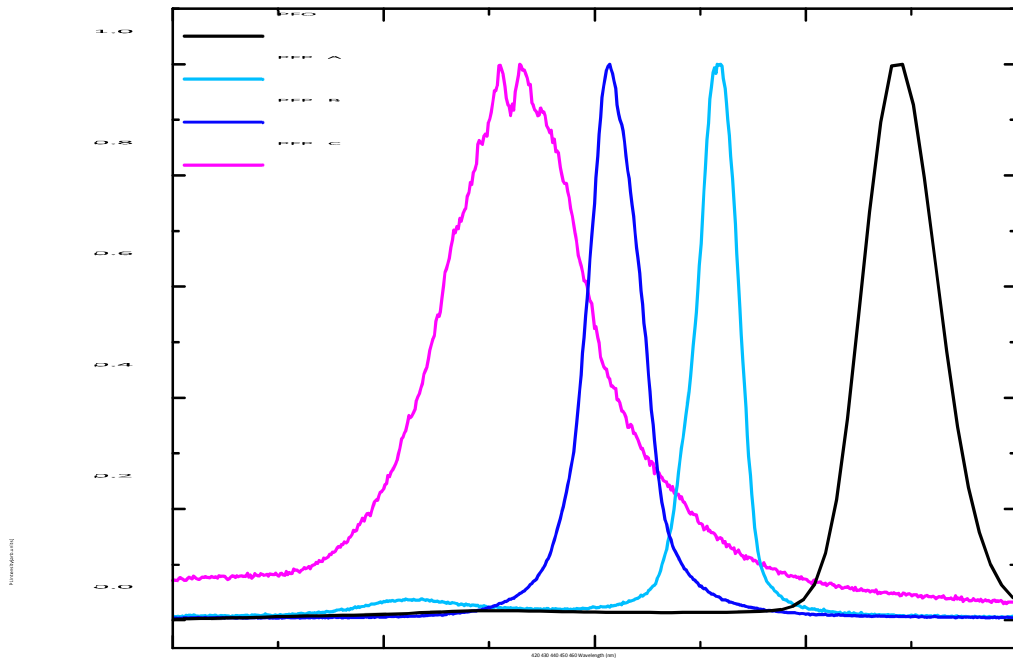
Figure 3: PL spectra above the ASE threshold of the investigated samples. The progressive blue-shift of the ASE band as the PFP film thickness decreases is evident. The black line is the PFO spectrum, evidencing the blue-shift of the PFP ASE with respect to the PFO one.

$$I(\lambda, g', l) = \frac{I_0(\lambda)}{g'(\lambda)}(e^{g'(\lambda)l} - 1) \tag{1}$$

where I_0 is the emission intensity per unit length, g' is the waveguide net gain, and l the stripe length.

The best fit peak gain is 26.4±0.8 cm^{-1} for PFP and 37±2 cm^{-1} for PFO. In order to quantitatively compare the two materials we remember that the net gain g' is the difference between the gain g and the waveguide losses α. Moreover the gain coefficient can be expressed as $g = \sigma N$, where σ is the gain cross section and N the volume density of population inversion. As in our experiment the pump pulse is much longer than the typical ASE lifetime in conjugated polymers, the measurements are performed in quasi steady state, thus $N = D\tau/h\nu d$, where D is the pump laser excitation density, d the sample thickness, $h\nu$ the pump photons energy, and τ the lifetime of the emitting state. Thus the sample net gain linearly increases with the excitation density (far from gain saturation), whit a slope proportional to $\sigma\tau$. As the used excitation density are below the typical values to observe gain saturation [22] we assumed a linear dependence of g on D, and we determined the slope also considering that at the ASE threshold the gain compensates the losses, thus $g'=0$ (see Fig. 4). A slope of about 128 cm/mJ was obtained for PFP, and of about 59 cm/mJ in PFO. Thus PFP shows a $\sigma\tau$ value about 2.2 times higher than the PFO one, evidencing the possibility to obtain a much larger net gain at a given common excitation density or, equivalently, the same net gain value at much lower excitation density. Finally by looking at the extrapolated value

of g' at D=0 we can estimate a loss value in PFP of about 3 cm^{-1}, that is smaller than the PFO one of about 4 cm^{-1}.
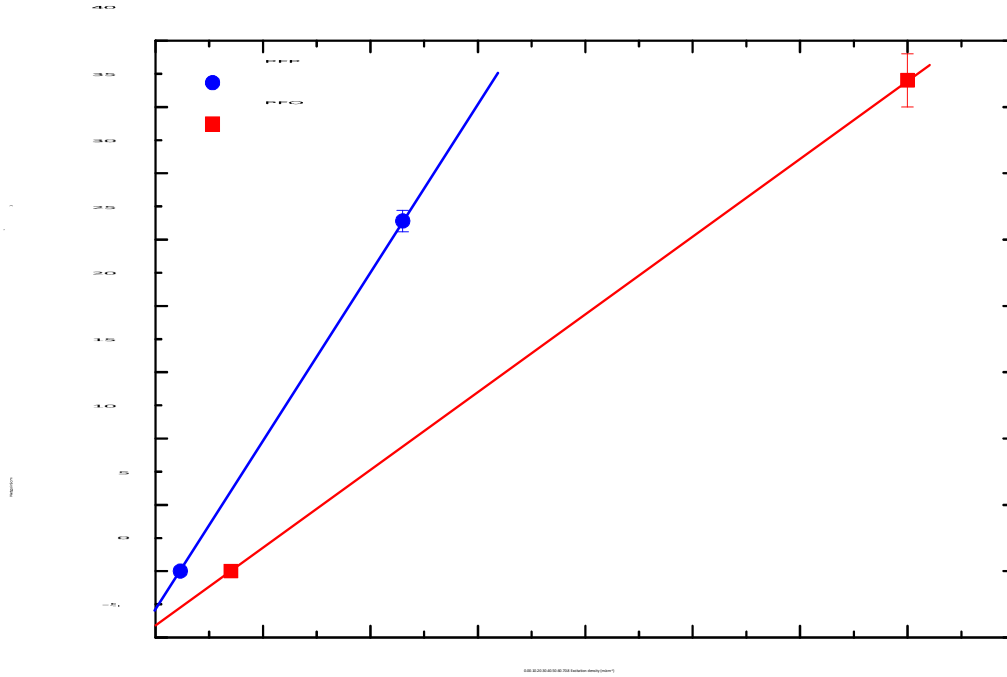

Figure 4: Excitation density dependence of the net gain in PFP and PFO. The lines are the best fit curves with a linear function.

4. Conclusions

In conclusion we have demonstrated thanks to the introduction of a phenylene moiety between two fluorene units in PFP allows to simultaneously obtain efficient ASE at lower wavelength with respect to the well known PFO, with lower ASE threshold and higher net optical gain.

These properties make PFP an interesting material for applications that require stimulated emission in the blue region of the visible spectra.

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