



On the correlation between morphology and Amplified Spontaneous Emission properties of a polymer: Polymer blend



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ABSTRACT

We investigate the Amplified Spontaneous Emission (ASE) properties of a prototypical host-guest polymer polymer blend, namely poly(9,9-dioctylfluorene) (PF8) and poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) blend, with different concentration ratio. We show that the initial F8BT content increase causes an increase of the F8BT ASE threshold, even leading to ASE suppression for F8BT contents between 25% and 75%. ASE is then recovered upon further increase of the F8BT relative content. We demonstrate that the ASE properties of the PF8:F8BT are dominated by morphology effects, like sub-micrometric phase segregation, determining the net gain of the active waveguides.

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1. Introduction

Since the discovery of electrical conductivity in conjugated polymers [1], the research efforts to develop high performing organic-based optoelectronic devices have been substantial, leading, to date, to full commercialization of various kind of organic optoelectronic devices [2]. With the aim to realize optimal polymeric systems for optoelectronic applications, two general routes are followed. The first is the development of novel polymeric molecules with tailored chemical and electronic properties. The second is to blend two or more known compounds in order to obtain new composites with properties different from the ones typical of each single components [3].

Among the various luminescent systems, the polymer–polymer blends are thus of particular importance due to the easy tunability of the optical and electronic properties of the single components, and in view of possible optoelectronic applications involving biopolymers [4–7]. Generally speaking, when dealing with organic-based optoelectronic devices, the morphology of the organic layers has been identified as one of the primary parameter to be optimized in order to attain the highest performance [8]. This has

been well established in organic solar cells [9], organic light emitting diodes [10] and organic field effect transistor [11,12].

Morphological properties have been also demonstrated to be at the origin of some interesting lasing effects from organic thin films [13]. In this particular field, among the various active material for lasing action, conjugated polymers and oligomers have attracted lot of interest due to: 1) high optical gain; 2) easy processability of the devices starting from solutions in common organic solvents, using scalable and low cost fabrication process such ink-jet printing, roll-to-roll printing, spin-coating; 3) easy tunability of their emission properties simply by changing the nature and/or the position of the substituent groups attached to the core polymer chains [14,15]. In particular the high optical gain – that has been demonstrated in several polymeric and oligomeric thin films [16–20] – can be conveniently exploited in many application like optical data communications [21], gas sensing [22,23], organic lasers [24]. Although, to date, no electrically driven organic laser has been demonstrated [25], elegant and alternative device structures have been suggested to fully exploit the properties of organic lasing materials in an electrically controlled device [26]. The very first step in the development of novel lasing systems is the characterization of the optical gain of the active material.

Optical gain in thin films of polymers is evidenced by a strong line narrowing of the emission spectrum for excitation densities above a threshold value. The origin of the line narrowing has been

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typically attributed to Amplified Spontaneous Emission (ASE) supported by wave-guiding inside the film [27–29]. Since the ASE threshold decreases as the material optical gain increases (*ceteris paribus*), the ASE threshold minimization is a useful way to develop good materials for lasers. In the last years it has been demonstrated that the ASE threshold can be decreased by blending two different species, specifically selected in order to exploit the processes of energy transfer (in particular the Förster Resonant Energy Transfer – FRET) from the excited donor material to the acceptor material with optical gain [30,31]. A necessary prerequisite for energy transfer to occur is the good overlap between the emission band of the donor and the absorption band of the acceptor. As FRET can be very efficient also for small acceptor content in the blend, active blends typically show low ASE threshold due to the combination of high pump laser absorption from the donor, effective acceptor excitation by FRET and low losses due to self absorption and aggregation [32].

To date, the role of donor-to-acceptor concentration has been the subject of few studies focused on ASE from polymer:polymer blends exploiting FRET [30,33]. In particular an improvement of the acceptor ASE with the acceptor content increase, followed by a saturation, has been observed [33], ascribed to a progressive FRET efficiency increase. More recently [34] it has been observed that the eventual acceptor aggregation decreases the ASE effect, dominating over the FRET increase at high enough acceptor content, thus determining the existence of an optimal concentration minimizing the acceptor ASE threshold. Anyway, it is well known that the major part of polymer blends undergo microscopic phase separation that locally changes the FRET efficiency [35] and that can likely add optical loss channels inside the film waveguide, thus potentially affecting the ASE process. Despite this observation, a clear correlation between donor-to-acceptor ratio, blend morphology and ASE is still lacking.

In this paper we investigate the ASE properties of poly(9,9-dioctylfluorene) (PF8):poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) blends [36] with different concentration ratios, chosen as prototypical host:guest polymer:polymer blend [37]. The PF8 photoluminescence (PL) [38] overlap with the F8BT absorption spectrum, thus fulfilling the necessary prerequisite for a good FRET to occur. We have correlated the optical gain properties of the blends with the blends morphology by Laser Scanning Microscopy. We show that the concentration ratio and the energy transfer process alone can not fully describe the ASE behavior of the blends as previously reported [33]. We show that the PF8:F8BT phase segregation between the species has a deep impact on the ASE properties even in blends whose concentration ratio should be optimal from an energetic point of view, where we find a total suppression of any ASE effect. These results can be generalized to several polymer blend systems due to the generic phase segregation behavior of such systems, extending our results in contiguous fields like high performance organic-base LEDs and Light Emitting FETs.

2. Experimental

Individual PF8 and F8BT toluene solutions (15 mg/ml each) have been prepared and stirred overnight. PF8 solutions have been initially heated at about 70 °C for 5 min during stirring in order to avoid the formation of the PF8 beta phase [39] in the final samples. The F8BT relative content in the blend has been varied from 5% to 100% by mixing the appropriate content of the initial single solutions using LLG micro-pipettes. Eight samples with different F8BT relative contents have been investigated, named X-F8BT (where the X value indicates the F8BT percentage in the blend). The films have been prepared by spin coating the solutions on toluene-cleaned

ultrathin microscopy cover glass slides (from Bresser, certified thickness of 130–170 μm) in air and at room temperature. The film thicknesses have been measured by a Dektat Alpha Step Profilometer; the obtained thickness values are reported in Table S1 in the Supporting Information. All the measured thicknesses are above the waveguide cut-off.

Room temperature Time-Resolved Photo-Luminescence (TR-PL) has been excited by the 400 nm line delivered by a solid state pulsed laser (mod. PLP-10, Hamamatsu), which provides a pulse of about 58 ps at repetition rate of 1 MHz. The max peak power was of about 70 mW. The PL has been dispersed by an iHR320 (focal length of 0.32 m) Horiba monochromator equipped with a Peltier cooled Hamamatsu (Head-on mod R943-02), operating in single photon counting. The spectral resolution was about 4.8 nm for TR-PL experiments. Time-Correlated Single Photon Counting (TCSPC) technique has been used to record TR-PL in the spectral visible range by using an Edinburgh Instruments TCC900 TCSPC electronics card.

ASE has been measured in a different experimental set-up, exciting the samples with the 337 nm emission from a Nitrogen 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 6 mm. Only the central region of the pump beam has been selected with a variable slit thus obtaining an homogeneous excitation density. The sample emission has been collected from the sample edge using an optical fiber connected to a SM442 Preconfigured CCD spectrometer. The spectral resolution was about 0.6 nm. ASE measurements have been performed at room temperature in a vacuum chamber (about 10^{-3} mbar) in order to avoid photo-oxidation at high excitation densities. The samples have been morphologically characterized by Confocal Laser Scanning Microscopy with a Nikon Eclipse C1 inverted confocal microscope using a 60X DIC Plan Apochromat oil-immersed objective (N.A. 1.4). The samples have been excited by both the 405 nm line of a diode laser and the 488 nm line of an argon laser, and the PL signal has been detected by a couple of photo-multipliers (PMTs). The signal was detected simultaneously at 450 ± 20 nm and at 605 ± 30 nm using bandpass filters, in order to map the PL of PF8 and F8BT, respectively.

3. Results and discussion

The absorption spectra and the photoluminescence spectra of all of the samples are reported in Fig. S1 and in Fig. S2 in the S. I. The absorption main peaks of both the species are evident in the blends, while the PL is clearly dominated by the F8BT emission, suggesting efficient FRET in the blends.

3.1. Concentration dependence of the Amplified Spontaneous Emission

Fig. 1 reports the first 5 photoluminescence spectra as a function of the excitation density from the 5-F8BT sample in a semi-log scale. For excitation densities lower than 0.028 mJ cm^{-2} the spectra resembles the traditional photoluminescence from the acceptor F8BT. As the excitation density increases over 0.040 mJ cm^{-2} a clear line narrowing peaked at about 540 nm appears, attributed to waveguide assisted ASE [29]. The FRET mechanism between the PF8 donor to the F8BT acceptor is clearly evident even for such a low acceptor content in the blend. Indeed the emission is almost completely from the F8BT phase (a low residual PF8 emission is detected peaked around 435 nm, see Fig. S2 in the Supporting Information, that is a signature of a non complete FRET from the donor phase to the acceptor phase [33]).

In order to determine the ASE threshold, we have considered the

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