Investigation of the local composition and morphology effects on the Amplified Spontaneous Emission properties of polymer-polymer blends

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Since the discovery of electrical conductivity in conjugated polymers, 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 [1]. 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 properly blend two or more known materials in order to obtain new composites with properties different from the ones typical of each single components [2].

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 [3].

Concerning the optimization of high gain organic active materials for lasers application it has been demonstrated that lasing 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 an excited donor material to an acceptor material with optical gain [5,6]. A necessary prerequisite for FRET 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 lasing 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 [7].

On the other side it is well known that the major part of polymer blends undergo microscopic phase separation that locally changes the FRET efficiency [8] and that can likely add optical loss channels inside the film waveguide, thus potentially affecting the gain process.

Rather surprisingly the understanding of the morphology role on the final gain properties of organic active layers for lasers is extremely limited. During 2015 we thus investigated the role on the optical gain of the local inhomogeneity of the film composition and morphology of two polymer-polymer blends with the spectral properties allowing efficient FRET. The experiments are based on the quantitative measurement of the gain of the films by measuring both the excitation density dependence of the Amplified Spontaneous Emission (ASE) in the films and the gain spectra. Two complementary experiments have been performed by systematically varying:

- 1. the solvent used for the deposition at fixed composition;
- 2. the active blend donor acceptor relative composition at fixed deposition conditions.

The full results of the first experiment have been published in the Journal of Physical Chemistry C **119**, p. 21620 (2015) [3].

The second experiment has been performed in collaboration with the Lecce Unit of CNR-IMM (Mauro Lomascolo and Arianna Cretí), all the results have been published in Organic Electronics **29**, p. 44 (2016) [9].

In the first experiment we investigated the morphology dependence of the ASE of blend between poly(9,9-dioctylfluorene-coa benzothiadiazole) (F8BT) and regio regular Poly(3-hexylthiophene) (rrP3HT). This system show ASE around 650 nm, and it is thus an interesting candidate as active material in optical amplifier for polymeric optical fibers telecommunication. The active films have been deposited by spin coating, starting from blends with identical relative composition, and realizing films with the same thickness. The morphology has been changed by acting on the solvent used for the molecule dissolution (chloroform, toluene, xylene and chlorobenzene).

We show that nominally identical layers have extremely different ASE properties, with a relative difference of ASE threshold up to 6 times between the worst film (from xylene) and the best



Figure 1. 300 μ m × 300 μ m map of the phot luminescence of the sample from chloroform (ϵ toluene (b) and xylene (c). The first map show the overlap between the green F8BT emission at the red rrP3HT one, while only the rrP3HT ma is reported in frame b and c.



Figure 2. 15 μ m × 15 μ m map of the photoluminescence of the PFO-F8BT sample with 75% of F8BT. The green is the intensity of F8BT photoluminescence, while the blue is the PFO one.



Figure 3. 300 μ m × 300 μ m map of the F8BT photoluminescence in the PFO-F8BT sample with 90% of F8BT.

one (from toluene). Confocal laser spectroscopy maps allowed us to correlate the measured ASE threshold, the gain and loss values of the waveguide to the local morphology and composition of the four samples. The strong variation of the local photoluminescence properties of the different samples is evident in Fig.1. The best sample, realized from toluene, show uniform intensity of the rrP3HT, indicating uniform composition and uniform FRET, resulting in high gain due to optimized FRET, and low losses due to lack of defects scattering. The sample realized from chloroform (ASE threshold about 2.5 higher than toluene) clearly shows thickness non uniformity, increasing the scattering propagation losses and non uniform mixing of the two materials, decreasing the optical gain. Finally the worst sample (from xylene) shows several islands of crystalline rrP3HT (dark in the map), leading to low gain.

In the second experiment we investigated the ASE properties of poly(9,9-dioctylfluorene) (PF8) and poly(9,9-dioctylfluorene-cobenzothiadiazole) (F8BT) blends, 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 not determined by the FRET efficiency (as typically assumed under the hypothesis of uniform mixing), but they are dominated by morphology effects, like submicrometric phase segregation, determining the net gain of the active waveguides.

For example a blend with 25% of PFO and 75% of F8BT does not show any ASE, despite the high intrinsic gain of F8BT and its high content. The confocal photoluminescence maps (see Fig. 2) clearly show that the film is strongly non uniform, with the presence of several F8BT island with a lateral size of about 500 nm, evidencing the phase separation between the PFO and the F8BT. In this condition the FRET efficiency is strongly limited by the poor mixing, thus leading to non optimal gain, and the light suffers strong scattering during propagation in the waveguide, resulting in strong losses.

On the contrary at F8BT contents below 10% and above 90% uniform F8BT intensity is observed, evidencing uniform mixing of the two materials and absernce of morphology irregularities, leading to both high gain and low losses.

Overall these experiments allowed to evidence the importance of the microscopic composition and morphology of the active film on its macroscopic optical gain, clearly demonstrating that the realization of an efficient active layer cannot be in general based on any assumption on the uniformity of its properties.

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