

# Role of doping concentration on the competition between amplified spontaneous emission and nonradiative energy transfer in blends of conjugated polymers

A. Camposeo,\* E. Mele, L. Persano, D. Pisignano, and R. Cingolani

*National Nanotechnology Laboratory of CNR-INFM, Distretto Tecnologico ISUFI, Università di Lecce, via Arnesano, I-73100 Lecce, Italy*

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We investigated the amplified spontaneous emission (ASE) of a blend of light emitting conjugated polymers. The effects related to the acceptor/donor polymer relative concentration on both cw photoluminescence and ASE were investigated experimentally and interpreted by a quantitative model describing ASE in presence of fast non radiative energy transfer processes. The range of acceptor concentrations where ASE does not occur is experimental determined, whereas outside such interval ASE is observed from the donor or from the acceptor polymer. In particular, the blend with 10% acceptor molecules shows ASE-induced line narrowing for excitation fluences larger than  $100 \mu\text{J cm}^{-2}$ , with a maximum optical gain coefficient of  $8 \text{ cm}^{-1}$  and a loss coefficient as low as  $0.3 \text{ cm}^{-1}$ . These optical and gain properties make the investigated conjugated polymer blend an appealing material as active layer for laser devices.

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## I. INTRODUCTION

Polymer and hybrid blend systems have become increasingly attractive for a large number of applications, including photonics,<sup>1</sup> biotechnology,<sup>2</sup> and optoelectronics.<sup>3,4</sup> In particular, blending different polymers or inorganic particles<sup>5</sup> represents a strategic route to improve the performance of a material, allowing the realization of novel composite systems inheriting and enhancing the performance of the original components. By this way, solar cells with high power conversion and external quantum efficiencies have been obtained,<sup>6</sup> using blends of hole- and electron-accepting conjugated polymers with differing ionization potentials and electron affinities. Following the same principle, high efficiency organic light-emitting diodes (OLEDs) have been fabricated.<sup>7,8</sup> Blends of different materials can be effectively used to tailor the spectral properties of the resulting composite both at macroscopic<sup>9</sup> and microscopic<sup>10,11</sup> scale, enabling for example the realization of white light-emitting OLEDs.<sup>12,13</sup> In these blends, energy transfer by dipole-dipole coupling (Förster transfer<sup>14,15</sup>) occurs, provided the emission spectrum of the donor component overlaps with the absorption spectrum of the acceptor, and the dipoles are sufficiently close to each other. This kind of blends offers color tunability through changes in either the type or the concentration of the acceptor, thereby permitting the realization of color displays based on common donor polymers.<sup>16,17</sup> Most of the above results have been accomplished by evaporation of low-molar-mass compounds,<sup>18,19</sup> whereas very few works explored soluble active conjugated polymeric blends<sup>20,21</sup> and their gain properties, and especially the effects of the acceptor/donor relative content on the gain of the resulting blend system.

Optical gain in thin films of conjugated polymers has been evidenced in a variety of compounds by spectral line narrowing above threshold. This process, observed in films thick enough to support waveguided modes,<sup>22</sup> has been assigned to amplified spontaneous emission (ASE).<sup>23–25</sup> ASE

and lasing have also been reported in blends of organic molecules.<sup>21,26</sup> In particular, Sheridan *et al.* observed a sudden shift of the ASE wavelength from the donor to the acceptor one upon increasing the acceptor concentration in the blend. This was attributed to the competition between stimulated emission and nonradiative energy Förster transfer, although a full investigation of the possibility of tuning the gain properties of blends of conjugated polymers is still lacking. The interest for this kind of composite materials relies on the significantly lower loss coefficient, that can be achieved by blending two different organics. In fact, the overall resulting absorption and emission are spectrally separated and, consequently, self-absorption, which is one of the main contribution to the internal losses, remarkably reduced. We thus believe that a better understanding of the emission and gain properties of conjugated polymer blends, and especially of the role played by the acceptor concentration on the spectral and gain properties of the blend is quite relevant at the moment.

In this work, the effects of acceptor/donor relative concentration on the photoluminescence (PL) and on the ASE of blends of conjugated polymers are investigated experimentally and interpreted by a model. This analysis accounts for the influence of the acceptor content on the competition between nonradiative energy transfer and stimulated emission and it allows us to predict the gain properties of the polymer blend. In our prototype polymer blends, the ASE occurs at 445 nm (donor wavelength) and 515 nm (acceptor wavelength), with a gain coefficient of  $8 \text{ cm}^{-1}$  and a loss coefficient as low as  $0.3 \text{ cm}^{-1}$ .

## II. NONRADIATIVE ENERGY TRANSFER IN GAIN POLYMERS

By Förster energy transfer we mean the transfer of energy from a donor excited molecule to an acceptor molecule via resonant, near field dipole-dipole interaction. The transfer

rate ( $K_{\text{FT}}$ ) between isolated single molecules at a distance  $R$  is given by<sup>14</sup>

$$K_{\text{FT}} = \frac{1}{\tau} \left( \frac{R_0}{R} \right)^6, \quad (1)$$

where  $\tau$  is the radiative luminescence life-time of the donor and  $R_0$  is the Förster radius, given by

$$R_0^6 = 0.5291 \frac{k^2 \eta_D}{n^4 N_{\text{Av}}} \int_0^\infty f_D(\tilde{\nu}) \varepsilon_A(\tilde{\nu}) \frac{d\tilde{\nu}}{\tilde{\nu}^4}. \quad (2)$$

In the above expression,  $N_{\text{Av}} = 6.022 \times 10^{23}$  is the Avogadro's number,  $\eta_D$  indicates the native luminescence efficiency of the donor,  $n$  is the refractive index of the material,  $f_D$  is the normalized emission spectrum of the donor in the absence of acceptor molecules,  $\varepsilon_A$  is the molar decadic extinction coefficient of the acceptor,  $\tilde{\nu}$  is the frequency wave number, and  $k^2$  is a factor related to the orientation of the donor and the acceptor dipole moments; an average value of  $k^2 = 2/3$  is generally used.<sup>27,28</sup> Other reports concerning the energy transfer in polymer-polymer or polymer-dye blends suggest deviations from the Förster theory, partly due to the fact that the  $R^{-6}$  dependence arises from a dipole-dipole interaction between two isolated molecules.<sup>29</sup> It is well known that by blending two polymers with different molecular weights and chemical structure can lead to phase segregation, with formation of microscale and nanoscale domains, depending on the used solvent, the casting method, the temperature.<sup>30</sup> The presence of these domains affects the transfer rate, because the resulting transfer is not only due to a point-point dipole interactions but also to a point-surface or surface-surface interaction. Different models have been developed, resulting in a  $R^{-2}$ ,  $R^{-3}$ , and  $R^{-4}$  functional dependency of the transfer rate, depending on the considered geometry.<sup>29,31,32</sup>

Furthermore, even for a Förster theory in the case of polymer films, the transfer rate has to be modified in order to take into account the dipole interaction between different molecules distributed over the film volume.<sup>33</sup> Thus, Eq. (1) becomes

$$K_{\text{FT}}^{\text{tot}} = \frac{1}{\tau} \int \left( \frac{R_0}{R} \right)^6 \rho_a \phi dV = \frac{1}{\tau} \frac{R_0^6 \phi}{8a^6}, \quad (3)$$

where the volume integral is evaluated over the sample volume,  $a$  is the acceptor molecular radius,  $\rho_a = 3/(4\pi a^3)$  is the acceptor density, and  $\phi$  stands for the acceptor/donor relative molar concentration, defined as the ratio of the number of acceptor molecules over the number of donor molecules per unit volume. In Fig. 1 we plotted the ratio of the radiative luminescence lifetime ( $\tau$ ) and the Förster transfer characteristic time scale ( $\tau_{\text{FT}} = 1/K_{\text{FT}}$ ) as a function of the doping concentration for the blend studied in this work. The Förster transfer becomes more and more efficient with respect to spontaneous emission upon increasing the number of acceptor molecules. Indeed, the probability of exciton transfer from donor to acceptor molecule, defined as  $P = \frac{K_{\text{FT}}^{\text{tot}}}{K_{\text{FT}}^{\text{tot}} + 1/\tau}$ , can be related to  $R_0$  and  $\phi$  by the expression

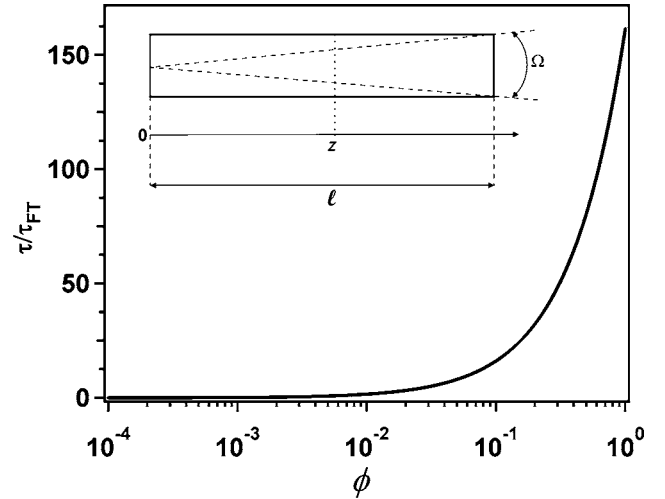


FIG. 1. Ratio of the luminescence lifetime ( $\tau$ ) over the Förster transfer time ( $\tau_{\text{FT}}$ ) as a function of the doping concentration ( $\phi$ ), calculated by Eq. (3). Inset: schematic representation of the amplified spontaneous emission geometry in a slab waveguide.

$$P_{\text{FT}} = \frac{R_0^6 \phi}{8a^6 + R_0^6 \phi}. \quad (4)$$

The above expression allows one to evaluate  $R_0$  by analyzing the probability of exciton transfer as a function of the acceptor/donor relative concentration (see Sec. IV).

Let us now consider the gain properties of a conjugated polymer blend. A well established method for analysing the optical gain of conjugated polymers is to characterize the ASE of the polymer film, generated by the optical amplification of the spontaneously emitted radiation within a high gain active slab.<sup>34</sup> The power emitted at one edge of the slab can be derived by integrating over  $z$ , angles and frequencies the following expression (see inset of Fig. 1):<sup>35</sup>

$$\frac{\partial I(\nu, z)}{\partial z} = \sigma NI(\nu, z) + \frac{\Omega(z)}{4\pi} NA(\nu) h\nu. \quad (5)$$

$A(\nu)$  being the spectral rate of spontaneous emission,  $\sigma$  the transition cross section at frequency  $\nu$  and  $\Omega(z)$  is the solid angle subtended by the exit side as seen from an element  $dz$ .

In a conjugated polymer blend, the nonradiative energy transfer from donor to acceptor strongly influences the ASE, and a change in the ASE upon varying the molecular concentrations is expected, due to the competition between the energy transfer from the donor to the acceptor polymer and the stimulated emission from the donor and from the acceptor.<sup>26</sup> In order to quantitatively account for these effects, Eq. (5) has to be modified by including the presence of nonradiative energy transfer processes. We consider the case of a nonradiative Förster transfer faster than the stimulated emission, as supported by experimental observations for high doping concentrations<sup>26</sup> and by the results of Fig. 1. In fact, since the depletion of excited states by ASE ( $\tau_{\text{ASE}}$ ) is known to be faster (from about a factor of 2 to about 10, depending on the molecular system and the used pumping fluence) than spontaneous emission,<sup>36,37</sup> from Fig. 1 our assumption is

valid in the range  $10^{-1} < \phi < 1$ . The assumption of an energy transfer rate faster than stimulated emission allows us to neglect the time dependence of the Förster transfer rate<sup>38</sup> namely, the energy transfer between molecules separated by a distance large compared to  $R_0$ .<sup>39</sup> Thus, we derived two distinct expressions for the donor and acceptor molecules, starting from Eq. (5), by replacing  $N \rightarrow N_{\text{exc}}(1-\phi)(1-P_{\text{FT}})$  for donor molecules and  $N \rightarrow N_{\text{exc}}[\phi+(1-\phi)P_{\text{FT}}]$  for acceptor molecules, and by integrating over  $z$ , angles and frequencies. Assuming an  $\Omega(z) \sim \Omega$  and a nonsaturated gain [ $10^3 < G < 10^4$ ,  $G = \exp(\sigma N l)$ ], the ASE intensity emitted from donor and acceptor molecules results

$$I_D = \eta_D L I_D^s \frac{\Omega}{4} \frac{[e^{g_D l (1-P_{\text{FT}})(1-\phi)-1}]^{3/2}}{[g_D l (1-P_{\text{FT}})(1-\phi) e^{g_D l (1-P_{\text{FT}})(1-\phi)}]^{1/2}}, \quad (6)$$

$$I_A = \eta_A L I_A^s \frac{\Omega}{4} \frac{[e^{g_A l [\phi+(1-\phi)P_{\text{FT}}]-1}]^{3/2}}{[g_A l [\phi+(1-\phi)P_{\text{FT}}] e^{g_A l [\phi+(1-\phi)P_{\text{FT}}]}]^{1/2}}, \quad (7)$$

where  $I_{D,A}^s = (h\nu_{D,A}) / (\sigma_{D,A} \tau)$  is the saturation intensity for the donor and acceptor,  $g_{D,A} = \sigma_{D,A} N_{\text{exc}}$  is the gain coefficient of the donor and acceptor polymer (typical values in the range  $5-80 \text{ cm}^{-1}$ )<sup>40,41</sup> and  $L$  is a coefficient that depends on the lineshape function ( $L = \pi^{-3/2}$  for a Lorentzian line and  $L = \pi^{-1}$  for a Gaussian line). These expressions for the ASE intensity are characterized by a typical exponential-like behavior. Although this trend suggests an inherently thresholdless phenomenon, an experimental threshold is commonly observed,<sup>40,41</sup> which is related to the experimental observation of ASE appearing typically around a few hundreds of  $\mu\text{J cm}^{-2}$  of pumping fluence, corresponding to  $10^{-6} < I/I^s < 10^{-5}$ . We will consider this value of  $I/I^s$  as the threshold value ( $I_{\text{th}}$ ) for the experimental observation of ASE.

Figure 2 shows the calculated ASE emission intensity (in units of the threshold experimental intensity) of the donor and acceptor polymer as a function of the relative concentration. The used parameters for the donor (PFC) and acceptor (PFV) polymer are reported in Table I. By introducing the concentrations  $\phi_D$  and  $\phi_A$ , defined as the concentration where the ASE emission intensity of the donor (acceptor) equals the threshold intensity value, Fig. 2 shows that below  $\phi_D$  only ASE from the donor can be observed, whereas above  $\phi_A$  only ASE from the acceptor is observed. In the range  $\phi_D < \phi < \phi_A$  no ASE is observed from the blend of conjugated polymers. A similar trend might explain the experimental results of Ref. 26. In particular Sheridan *et al.* observed a sudden change in the position of the ASE spectral peak (from donor to acceptor ASE) upon increasing the acceptor/donor relative concentration, which is consistent with our model, predicting an interval of concentration, delimited by two critical values ( $\phi_D$  and  $\phi_A$ ), for which no ASE emission should occur.

We will show that such simple model describes well our experimental observations, although it is based on a number of assumptions: (i) it does not consider the extension of excitons along the conjugated chain. This effect can significantly change the transfer rate, as observed in a poly(indenofluorene) end-capped with a perylene derivative.<sup>42</sup> (ii)

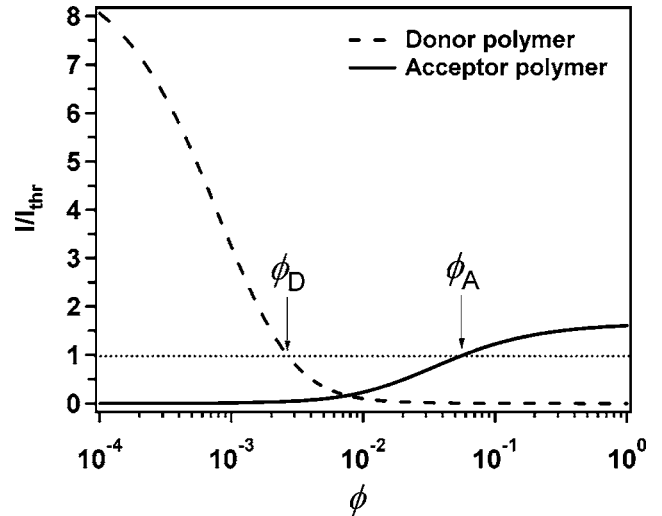


FIG. 2. ASE emission intensity from the donor (dashed line) and the acceptor (continuous line) polymer vs acceptor/donor relative concentration, evaluated according Eqs. (6) and (7). The used parameters are  $N_{\text{exc}} = 2.3 \times 10^{19} \text{ cm}^{-3}$ ,  $l = 0.7 \text{ cm}$ ,  $R_0/a = 3.3$  and  $\Omega/4\pi = 0.5 \times 10^{-6}$ . The dotted horizontal line indicates the threshold intensity.

Exciton migration within the donor polymer is not considered. In fact, it has been demonstrated that the nonradiative energy transfer can be a two step process constituted by (1) diffusion within the donor polymer and (2) transfer to the acceptor one.<sup>43</sup> Such two step process can be more or less efficient than pure non radiative energy transfer, depending on the particular conditions of donor/acceptor relative concentrations.<sup>43</sup> (iii) Finally we have not considered effects related to phase segregation that, as discussed above, can lead to a different distance dependency of the transfer rate [Eq. (1)]. The main effect of a different transfer rate is a shift of the critical concentrations  $\phi_D$  and  $\phi_A$  towards larger or lower values depending on a slower or faster transfer rate, respectively. Comparison with experimental data will unravel the effective contribution of the neglected processes.

### III. EXPERIMENTAL

Films of conjugated polymer blends were obtained by using the poly [(9,9-hexylfluorenyl-2,7-diyl) -alt-co- (9-ethyl-3,6-carbazole)] (PFC) as the donor polymer and the poly[(9,9-dioctylfluorenyl-2,7-diyl) - co-(1,4-diphenylene-vi-

TABLE I. Optical and gain properties of the PFC and PFV polymer.

	PFC	PFV
Transition cross section ( $10^{-19} \text{ cm}^2$ )	4.9 <sup>a</sup>	3.5
Luminescence efficiency ( $\eta$ )	0.75	0.47
Photoluminescence lifetime ( $\tau_{PL}$ , ns)	0.4 <sup>b</sup>	0.25
ASE threshold pumping fluence ( $\mu\text{J cm}^{-2}$ )	200 <sup>a</sup>	100

<sup>a</sup>From Ref. 41.

<sup>b</sup>From Ref. 5.

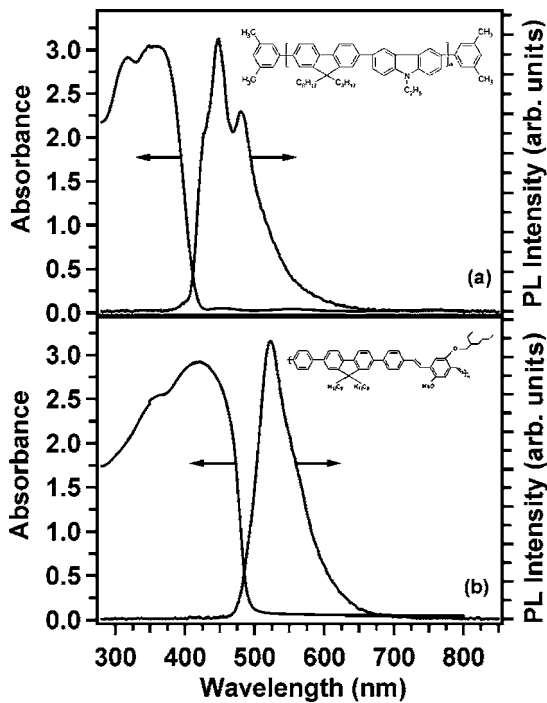


FIG. 3. Absorption (left axis) and PL (right axis) spectra of the PFC (a) and PFV (b) used in the present experiment. The excitation wavelength for the PL spectra was 325 nm. The chemical structures of the polymers are shown in the insets.

nylene-2-methoxy-5-2-ethylhexyloxy-benzene)] (PFV) as the acceptor polymer, both from American Dye Source Inc. The absorption and PL spectra of the donor and acceptor component are shown in Figs. 3(a) and 3(b), respectively (molecular structures of PFC and PFV also displayed in the insets). The overlap between the emission spectra of PFC and the absorption of the PFV provides a quite large Förster radius  $R_0=7$  nm, calculated by using Eq. (2), ensuring efficient nonradiative energy transfer between the donor and the acceptor polymer.

PFC/PFV blends were cast by spin coating from  $4.3 \times 10^{-4}$  M dichloromethane solutions on Corning glass substrates, with acceptor/donor relative concentration varying from  $10^{-4}$  (1:10000) to 1 (1:1). Neat films were obtained by spin-coating at 1500 rpm. The UV-vis absorption spectra of the blends were measured with a Cary 5000 spectrophotometer (Varian Inc.). The PL properties of the blends were analysed by exciting the samples both by a cw and by a pulsed laser source. The cw PL spectra were measured by exciting the samples by a He-Cd laser ( $\lambda=325$  nm) and collecting by a monochromator with a fiber-coupled charge coupled device (CCD). The ASE spectra of the blends were obtained by exciting the polymer slab waveguide by the third harmonic ( $\lambda=355$  nm) of a 3 ns  $Q$ -switched Nd:YAG laser (Spectra-Physics). The pump beam was focused on the sample by a cylindrical lens providing a rectangular excitation stripe of variable length (up to 1 cm). The sample emission was collected from the sample edge, dispersed by a monochromator, and detected by a silicon CCD. In order to inhibit photo-oxidation, all measurements were carried out under vacuum ( $10^{-6}$  mbar).

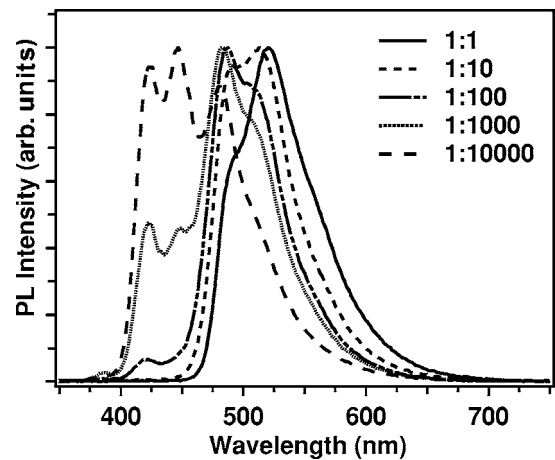


FIG. 4. PL spectra of the polymer blends as a function of the acceptor/donor relative concentration. Spectra were obtained by exciting at a wavelength of 325 nm.

#### IV. RESULTS AND DISCUSSION

The cw PL spectra of PFV/PFC blends with different relative concentrations are shown in Fig. 4. As the number of acceptor molecules increases, the PL spectrum redshifts and the emission intensity from the PFV increases due to the Förster transfer mechanism. In order to assess in depth that a nonradiative Förster transfer process occurs, we have extracted the probability of nonradiative transfer  $P_{FT}$ , by analyzing the donor and acceptor component of the PL spectra. Once the PL efficiencies of the PFV and PFC polymers are known (see Table I), the dependence of  $P_{FT}$  on the acceptor/donor relative concentration ( $\phi$ ) can be obtained by the spectra of Fig. 4. The results of this analysis are reported in Fig. 5, where we also display the absorbance of the PFV molecules derived from absorption measurements on the polymer blends films. The occurrence of a nonradiative Förster transfer is evident from the comparison of data reported in

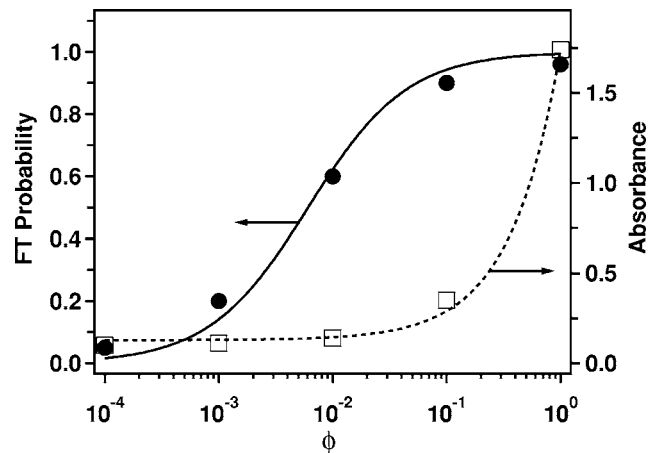


FIG. 5. Full circles: Förster transfer probability as a function of the acceptor/donor relative content, derived by PL measurements. The continuous line is a fit to the data with Eq. (4). The PFV absorbance as a function of  $\phi$  is also displayed for reference (open squares). Dotted curve: linear fit to the PFV absorbance data.



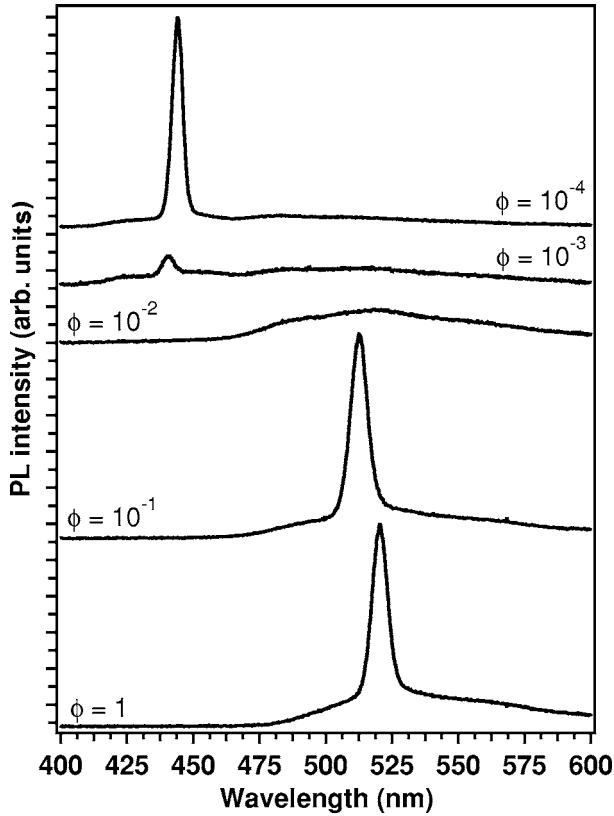


FIG. 6. ASE emission of the polymer blends as a function of the acceptor/donor ratio. The spectra for different acceptor/donor relative concentrations have been displaced vertically for clarity (from top to bottom  $\phi=10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$ , 1). Excitation fluence  $1 \text{ mJ cm}^{-2}$ .

Fig. 5, as the emission has a nonlinear trend, which is instead observed on the absorption data of the acceptor PFV polymer. While the PFV absorption increases linearly with the increase of the acceptor molecule content, the emission has the nonlinear trend characteristic of a non radiative energy transfer mechanism [Eq. (4)]. Furthermore by fitting the data with Eq. (4), the Förster radius can be derived. We find that  $R_0/a=3.3$ ,  $a$  being the molecular radius of the acceptor polymer, that we have estimated to be in the range 0.4–4 nm by evaluating the density  $\rho_a$  through linear absorption measurements at different concentrations and assuming hard spheres polymer molecules with radius  $a$ . Thus the Förster radius estimated by PL measurements lies in the interval 1.3–13 nm, in agreement with the value calculated by the donor emission and acceptor absorption spectral overlapping integral [Eq. (2)].

The gain properties of the polymeric blends were investigated by the characterization of the ASE, upon excitation by a high energy UV pulse. The PL spectra of the different investigated blends, when pumped by the pulsed source, are displayed in Fig. 6. For low acceptor concentration ( $\phi \leq 10^{-3}$ ), ASE was observed from the donor polymer. We did not observe any ASE emission for  $\phi=10^{-2}$ , although the pumping fluence has been increased up to the threshold for ablation of the organic blend from the substrate ( $20 \text{ mJ cm}^{-2}$ ). ASE from the acceptor polymer was observed

for  $\phi \geq 10^{-1}$ . These experimental results are fully consistent with the results shown in Fig. 2. In fact, our model predicts the existence of two critical values ( $\phi_D, \phi_A$ ) of the relative concentration, that for the conjugated polymers used in this work as donor and acceptor are calculated to be  $\phi_D=3 \times 10^{-3}$ ,  $\phi_A=6 \times 10^{-2}$ , respectively (see Fig. 2). In the range of concentrations  $3 \times 10^{-3} < \phi < 6 \times 10^{-2}$  the ASE intensity (both from the donor and the acceptor) is below threshold and the amplified emission is not experimentally observed. At higher concentrations ( $\phi > \phi_A=6 \times 10^{-2}$ ), the energy transfer rate to the acceptor is larger than the stimulated emission rate of the donor. The excitation is then transferred to the acceptor polymer, before ASE from the donor is produced. Therefore, for blends with high concentrations of PFV polymer, the ASE peak is observed at the same wavelength of the pure PFV polymer (515 nm). In the range of concentration values  $\phi < \phi_D=3 \times 10^{-3}$  the model predicts ASE emission only from the donor polymer, as it is also observed experimentally (Fig. 6). In this range the assumption  $\tau_{FT} \ll \tau_{ASE}$  is not valid, namely the Förster energy transfer is slower than typical emission decay times (Fig. 1). However, the results obtained by Eqs. (6) and (7) shown in Fig. 2 are still in agreement with the experimental observation of a lower critical concentration for ASE ( $\phi_D$ ). Indeed, in this range of relative concentrations one has  $P_{FT} \ll 1$ , hence, one is able to recover from Eq. (6) the native equation for ASE output intensity,<sup>35</sup> with the excitation mainly localized at the donor molecules. This leads to stimulated emission and spontaneous emission amplification mainly from the PFC donor polymer. The accordance found between the experimental observation and the model described in Sec. II, confirms the validity of the Förster theory for the polymer blends we analyzed.

To assess the performances of the system as lasing medium, we have characterized the gain properties of the 1:10 blend (which is the blend exhibiting ASE at the PFV wavelength with the lower content of acceptor molecules). This is expected to be characterized by a low loss coefficient, a key property in view of possible exploitation of such blend as active layer in laser devices. The ASE for the 1:10 blend becomes evident for fluences above  $100 \mu\text{J cm}^{-2}$ , when a peak at 515 nm becomes more and more intense and narrow as shown in Fig. 7. This peak is produced by the ASE emission assisted by the waveguiding effect due to the different refractive indexes of substrate, gain medium and vacuum, respectively. The width of the peak decreases upon increasing pumping fluence, down to 8 nm.

The gain coefficient of the blend was measured by the variable stripe method, which has been widely used to characterize the optical gain in both organic slabs<sup>25</sup> and bulk inorganic semiconductors.<sup>44</sup> The sample was optically excited with a stripe-shaped beam, and the light intensity, emitted from the photopumped region, was measured as a function of the stripe length ( $l$ ). The gain coefficient spectrum  $g(\lambda)$  is obtained by fitting the emission intensity to the well known expression  $I=I_0(e^{g(\lambda)l}-1)$ . The obtained gain coefficient spectrum is shown in Fig. 8. The blend has a maximum value of about  $8 \text{ cm}^{-1}$  at 515 nm, a value comparable to those measured for the PFC ( $8 \text{ cm}^{-1}$ ) (Ref. 41) and PFV polymer ( $7.6 \text{ cm}^{-1}$ ).

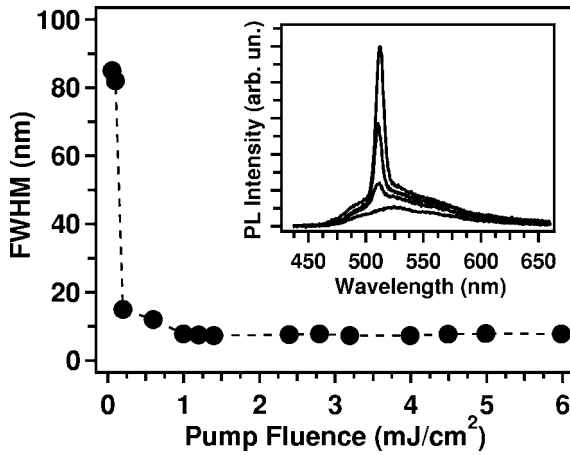


FIG. 7. ASE emission and spectral FWHM as a function of the pumping fluence. Data are obtained for the 1:10 blend. Inset: emission spectra; from bottom to top: 0.1, 0.5, 1, 4.5  $\text{mJ cm}^{-2}$ .

Finally, it has to be pointed out that an important property of a conjugated material as active layer in a light amplifier is represented by the loss coefficient, that (together with the gain one) determines the performance of an active laser medium. The losses of our blend waveguide were determined by fixing the excitation length ( $l=7$  mm), and by moving the pump stripe away from the emission edge of the sample, thus increasing the length ( $x$ ) of the unpumped region.<sup>25</sup> The output intensity at the ASE peak wavelength decreases according to an exponential law:  $I=I_0e^{-\alpha x}$ ,  $\alpha$  being the loss coefficient. The measured loss coefficient of the PFC/PFV 1:10 blend waveguide was  $0.3 \text{ cm}^{-1}$ , which is one order of magnitude lower than the value found in PFC slabs<sup>41</sup> and than those reported for poly(9,9-dioctylfluorene) waveguides ( $3 \text{ cm}^{-1}$ ) (Ref. 40) and in blends of poly(p-phenylene vinylene) derivatives ( $2.5 \text{ cm}^{-1}$ ).<sup>21</sup> The loss coefficient from the PFV/PFC blend is two order of magnitude lower than those measured for poly-[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] films ( $44 \text{ cm}^{-1}$ ) (Ref. 25) and two times smaller than that found for a blend of a soluble derivative of polyphenylene vinylene in 2-(4-biphenyl)-5-(4-t-butylphenyl)-1,3,4-oxadiazole ( $0.6 \text{ cm}^{-1}$ ).<sup>18</sup>

## V. SUMMARY

In summary, we have analysed PL and amplified spontaneous emission of a blend of conjugated polymers. A de-

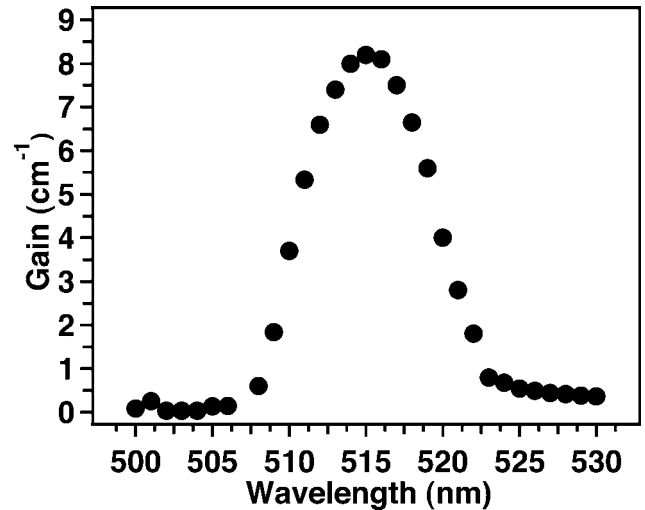


FIG. 8. Spectral dependence of the optical gain. Excitation fluence:  $3 \text{ mJ cm}^{-2}$ .

tailed analysis of the PL emission as a function of different doping concentration both by cw and pulsed UV irradiation evidenced that the relative acceptor/donor concentration strongly affects the nonradiative Förster transfer (characterized by a typical Förster radius  $R_0=7$  nm) and the ASE emission and gain properties of the material composite. In particular, our experimental results were interpreted by a model that predicts the existence of two critical relative concentrations ( $\phi_D=3 \times 10^{-3}$ ,  $\phi_A=6 \times 10^{-2}$ ): between these critical concentrations, ASE emission from the blend is completely suppressed. For  $\phi < \phi_D$  ASE emission occurs by the donor polymer, whereas for  $\phi < \phi_A$  only ASE from the acceptor polymer is observed. A more quantitative model describing the ASE in presence of a nonradiative energy transfer process would include the time dependence of the transfer rate, and effects related to exciton migration within the donor polymer, exciton extension along the conjugated chain and phase segregation. The characterization of the gain properties of the conjugated polymer blend with 1:10 of acceptor to donor content provides a gain coefficient of  $8 \text{ cm}^{-1}$ , which is comparable with the donor and acceptor gain coefficient and a record loss coefficient of  $0.3 \text{ cm}^{-1}$ , that makes the studied conjugated polymer blend very attractive as active layer of laser resonators. Furthermore, the energy transfer efficiency can be further enhanced by microcavity effects,<sup>45,46</sup> thus providing the possibility of using an even smaller doping concentration, still achieving an effective nonradiative coupling.

\*Corresponding author: andrea.camposeo@unile.it

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