# Photodegradation Effects on the Emission Properties of an Amplifying Poly(9,9-dioctylfluorene) Active Waveguide Operating in Air

M. Anni*

Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, Via per Arnesano, 73100 Lecce, Italy

ABSTRACT: We investigated the effects of photodegradation on the emission properties of a poly(9,9-dioctylfluorene) (PF8) active waveguide operating in air. We demonstrate that the PF8 degradation results in an unexpected wavelength dependent intensity variation, with an intensity enhancement of the PF8 0−0 line, an exponential decrease of the amplified spontaneous emission (ASE) intensity stronger than the one expected due to exciton quenching and a weak intensity quenching in the green emission range. We ascribe these results to the PF8 exciton quenching and keto defect formation due to photodegradation, affecting not only the exciton densities but also the waveguide losses, reducing the intrinsic PF8 self-absorption and increasing the keto defect absorption.
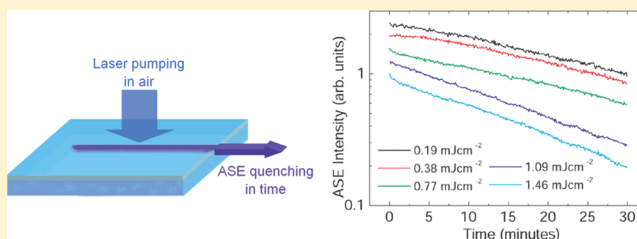
1. INTRODUCTION

Organic conjugated polymers are receiving large attention in the last decades not only for basic science interest but also for their possible device applications. In particular, it has been demonstrated that amplified spontaneous emission (ASE) can be observed in thin films of several classes of luminescent polymers, thus proposing these molecules as potential active materials for light amplifying waveguides and solid state lasers.[1] While the interplay between optical gain, bimolecular recombination, and photoinduced absorption induced by charge injection makes the realization of an electrically pumped organic laser still a big challenge,[2] the development of organic systems showing a low ASE and lasing threshold recently allowed the demonstration of organic optically pumped lasers with compact pump sources, spanning from frequency doubled Nd:YAG pulsed lasers,[3] to UV laser diodes[4] and light emitting diodes.[5] These demonstrators, together with the well-known tunability of the optical gain of several classes of active organic molecules[6,7] and with their easy processing, can allow the realization of compact, low cost, and tunable optically pumped lasers, based on active organic layers in the solid phase.

Despite these perspectives of application to real laser devices of organic active materials, a fundamental aspect related to the laser operation, such as the intensity decrease during operation that determines the device operational lifetime, has been to date investigated in very few experiments. Few papers on the realization and characterization of optically pumped lasers, or amplifying waveguides, included the measurement of the operational lifetime,[8−10] while the origin of the intensity quenching has been to date only related to exciton quenching due to a photodegradation process of the active molecule.[8,11]

In this article, we investigate the photodegradation effects on the spontaneous emission and ASE intensity of a poly(9,9-dioctylfluorene) (PF8) active waveguide operating in air for different pump excitation densities. PF8 can be considered a good prototype active polymer for lasing application as it shows ASE[12,13] and lasing[14] under strong enough optical pumping. Moreover, PF8 is characterized by the formation of fluorescent keto defects,[15] as a result of oxidation, that typically allows to observe emission line shape variations as a result of the molecule degradation.[16]

We show that the observed PF8 photodegradation, resulting in PF8 exciton quenching and in keto defects formation, leads to emission intensity variations in the waveguide unexplainable with exciton quenching only. In particular, we observe that the ASE intensity exponentially decreases during pumping, with the quenching becoming stronger as the pumping excitation density increases, as expected with exciton quenching, but the quenching is stronger than the one due to exciton quenching. Moreover, we find that, despite the exciton quenching, the waveguide emission intensity at the 0−0 PF8 PL resonance increases during pumping and that, despite the formation of a light emitting keto defect at about 530 nm, the waveguide emission in the 470−600 nm spectral range decreases. We show that all these effects can be attributed to the interplay between PF8 exciton quenching and the variation of waveguide losses, due to the reduction of PF8 self-absorption and the increase of keto defects absorption.

2. EXPERIMENTAL SECTION

The PF8 was purchased from the American Dyes Source Inc. (ADS129BE) and used without further purification. The samples, with a thickness of about 300 nm, were prepared by spin coating from a 10^{-4} M solution in toluene at room

temperature, after a solution heating at about 50 °C for few minutes,[17] in order to avoid the formation of the PF8 β-phase.[18−20] A nitrogen laser (337 nm) was used as excitation source, delivering 3 ns pulses with a repetition rate of 10 Hz and a maximum pulse energy of 155 μJ, focused in a 6.6 mm × 100 μm rectangular stripe by a cylindrical lens. The excitation density on the sample has been changed with a variable neutral density filter. The PL was collected from the sample edge, dispersed by a TRIAX 320 monochromator with a 150 ll/mm diffraction grating and detected by a Peltier cooled Si-charge coupled device (CCD). The spectral resolution was about 2 nm. All the measurements have been performed at room temperature in air. The degradation dynamics measurements have been performed by measuring the sample emission spectrum every 5 s for 30 min. The ASE and spontaneous emission intensity variations during operation have been measured for different excitation densities, every time choosing a fresh point on the sample. In order to minimize the effects of eventual sample nonuniformity, the measurements have been performed in sample regions showing comparable initial PL spectra at a reference excitation density above the ASE threshold. The waveguide loss and gain measurements have been performed every 7.5 min during the degradation dynamics measurements by the variable stripe method. The PL maps have been measured with a Nikon D-Eclipse C1 confocal laser microscope, by exciting the PL with a diode laser at 405 nm or an argon laser at 488 nm. The PL maps have been acquired in the 425−475 nm and 510−550 nm ranges, selected by two band-pass dielectric filters. The absorption spectra have been measured with a Cary 50 two beams spectrophotometer.

3. RESULTS

The sample PL spectra (see Figure 1) show the typical emission features of the PF8 glassy phase,[13] with a 0−0 line at
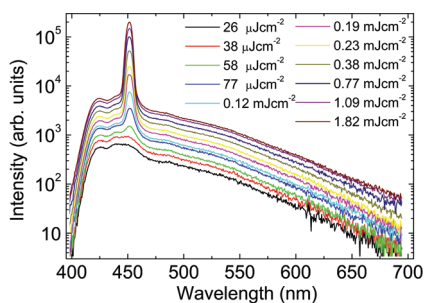

Figure 1. Excitation density dependence of the sample PL spectra.

about 425 nm, followed by vibronic replicas at about 450 and 480 nm. As the excitation density increases, a clear ASE band at about 452 nm appears for excitation density higher than about 45 μJ cm^{-2}.

As first step in the investigation of the laser exposure effects in operational conditions of the amplifying waveguide, we mapped the PL intensity of the sample after 30 min of nitrogen laser exposure for five different excitation densities, starting from 0.19 mJ cm^{-2} (about 4 times larger than the ASE threshold), up to 1.46 mJ cm^{-2} (about 32 times larger than the ASE threshold) (see Figure 2). The PL maps in the 425−475 nm range, excited at 405 nm, clearly show a PL intensity reduction in the region of the stripe irradiated by the nitrogen laser, with a PL intensity decreasing with the increase of exposure excitation density. On the contrary, the PL map in the
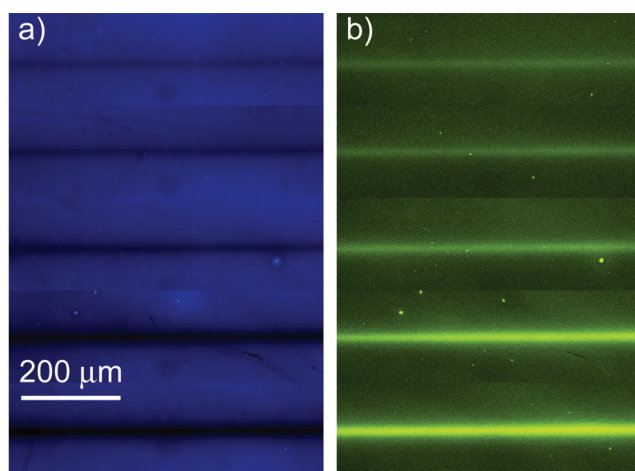

Figure 2. PL maps of the sample regions exposed to nitrogen laser during the degradation experiments, in order of increasing nitrogen laser excitation density from top to bottom. (a) PL maps in the 425−475 nm range, excited at 405 nm, showing a clear PL quenching in the region exposed to nitrogen laser, increasing with the exposure excitation density. (b) PL maps in the 510−550 nm range, excited at 488 nm, showing a clear PL increase in the region exposed to nitrogen laser, increasing with the exposure excitation density.

510−550 nm region (see Figure 2b), excited at 488 nm (below the PF8 absorption edge), shows a PL enhancement in the nitrogen laser stripe region, increasing with the pump excitation density.

In order to quantitatively investigate this effect, we determined the average emission intensity of a 100 μm wide region (corresponding to the exposed region width) around the quenching or enhancement fluorescence maximum, thus determining the relative variation with respect to the intensity in the unexposed sample regions. Both the blue PL quenching and the green PL enhancement show a linear dependence on the exposure excitation density (see Figure 3), with a maximum
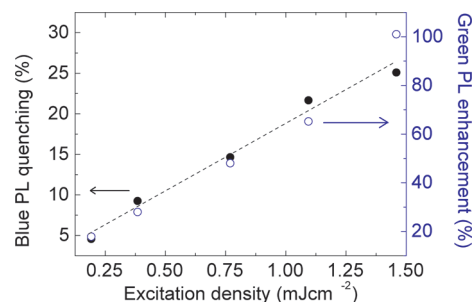

Figure 3. Blue PL relative quenching and green PL relative enhancement in the sample regions exposed to nitrogen laser during the degradation experiments.

blue quenching of about 25% and a maximum green PL enhancement of about 100%, both for an exposure excitation density of 1.46 mJ cm^{-2}.

We also measured the variations of the waveguide PL spectra during pumping at different excitation densities, collecting the PL from the sample edge. These measurements allow us both to determine the whole PL spectra evolution in time, during pumping, and to determine the temporal dynamics of the PL intensity at a fixed wavelength. The time dependence of PL intensity at the ASE peak wavelength shows, at all the

investigated excitation densities, an almost exponential decay becoming faster as the excitation density increases (see Figure 4).
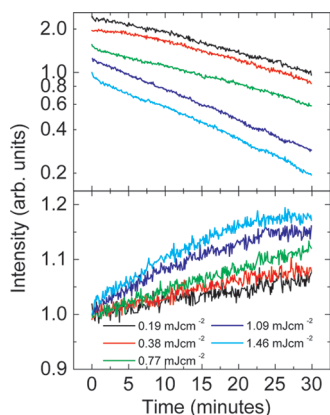

Figure 4. Top: time dependence of the PL intensity at the ASE peak wavelength for five different excitation densities (the data are vertically scaled for clarity). Bottom: time dependence of the PL intensity at the 0−0 line peak wavelength for the same excitation densities (the initial values of the data are normalized to 1).

As the ASE intensity reduction with time is generally taken as a signature of exciton quenching due to the active molecule photodegradation,[8] we also monitored the temporal evolution of the PL intensity at the 0−0 line wavelength (see Figure 4). Quite unexpectedly the PL intensity at the 0−0 line peak wavelength shows an increase in time, becoming stronger as the excitation density increases.

Given the evidence that the PL intensity temporal dependence is wavelength dependent, we also investigated the difference between the initial and final PL spectra. The typical result (see Figure 5 for the measurements at an excitation
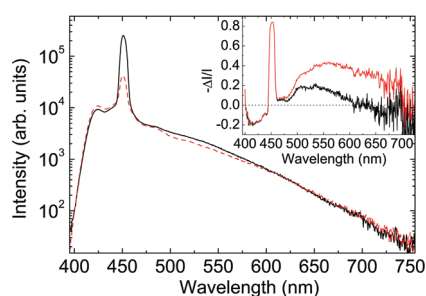

Figure 5. Comparison between the initial (continuous black line) and final (red dashed line) PL spectra at 1.46 mJ cm^{-2}. Inset: relative PL quenching spectrum at 1.46 mJ cm^{-2} (black line) and without the keto defect contribution (red line).

density of 1.46 mJ cm^{-2}) clearly shows the 0−0 line enhancement and the ASE band quenching (up to about 1 order of magnitude). Moreover, a clear weaker PL quenching is also observed in the range between 470 and 600 nm. The PL intensity decrease in time, probed at 525 nm, does not show a strong excitation density dependence (see Figure 6).

4. DISCUSSION

4.1. PL Confocal Mapping. In order to determine the origin of the observed wavelength dependent emission quenching in the waveguides, we started from the analysis of
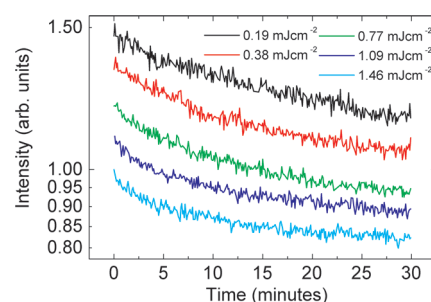

Figure 6. Excitation density dependence of the PL quenching dynamics at 525 nm (the data are vertically scaled for clarity).

the confocal PL mapping results (Figure 2). The evidence of intrinsic PF8 PL reduction in the regions exposed to nitrogen laser, becoming stronger as the exposure excitation density increases, is a typical signature of active molecule photodegradation, resulting in PL quenching. This attribution is confirmed by the observation in the irradiated regions of green fluorescence that, as it can be excited below the PF8 absorption edge, cannot be ascribed to intrinsic PF8 emission. As the green spectral range of confocal measurements coincides with the emission range of keto defects, formed by PF8 photo-oxidation, we can conclude that, for all the investigated nitrogen laser excitation densities, photo-oxidation of the active molecules takes place. The photo-oxidation results in a decrease of the intrinsic PF8 blue emission and in the increase of the keto defect green emission. As the PL intensity is directly proportional to the exciton density, the measured relative PF8 PL quenching and keto defect PL enhancement can be taken as a measure of the relative variation of the corresponding exciton population (both the PF8 and the keto defect PL maps are obtained by directly exciting the corresponding emitting species). For example, at the highest excitation density, the laser exposure for 30 min results in a PF8 exciton quenching of about 25% and in a keto defect density increase of about 100%.

4.2. Photodegradation Effects on the Waveguide PL: Qualitative Analysis. As the investigated samples are light amplifying waveguides, the first result to comment is the ASE intensity reduction during the waveguide operation under pulsed nitrogen laser pumping (Figure 4). Our results clearly show that the ASE intensity exponentially decreases during pumping and that the decay becomes faster as the pump excitation density increases. At a qualitative level, this result is consistent with the previously discussed evidence of PF8 exciton quenching due to photodegradation, as the ASE intensity increases with the exciton density, and thus, it decreases in the presence of exciton quenching. Moreover, as the exciton quenching is found to increase with the excitation density, this results in an increasing ASE quenching, as actually observed.

However, even if in some materials, like MEH-PPV,[11] the lasing intensity decrease during operation has been fully ascribed to the exciton quenching due to photodegradation, our results clearly show that the degradation effects on the waveguide emission properties are more complex and cannot be completely explained by considering PF8 exciton quenching only.

A reduction of the PF8 exciton density should actually lead to a quenching of the intrinsic PF8 spontaneous emission in the same measure for all the PF8 spontaneous emission wave-

lengths, together with a PL intensity increase in the keto defect emission range.

No one of these effects is actually present in the waveguides (see Table 1):

Table 1. Relative PF8 Exciton Density ($\Delta N/N$), Keto Defect Density ($\Delta K/K$), and Waveguide PL Intensity at the 0−0 Peak (($\Delta I/I)_{0-0}$), at the ASE Peak (($\Delta I/I)_{ASE}$), and at 525 nm (($\Delta I/I)_{525}$) Variations after 30 Minutes of Laser Exposure at All the Investigated Irradiation Excitation Densities

excitation density (mJ cm^{-2})	$\Delta N/N$ (%)	$\Delta K/K$ (%)	$(\Delta I/I)_{0-0}$ (%)	$(\Delta I/I)_{ASE}$ (%)	$(\Delta I/I)_{525}$ (%)
0.19	−4.6	17.8	6.1	−58.4	−20.9
0.38	−9.2	28.1	7.8	−56.7	−21.7
0.77	−14.6	48.0	11.6	−61.5	−22.0
1.09	−21.7	65.2	15.1	−76.7	−18.9
1.46	−25.1	101.0	17.7	−80.5	−17.8

(1) Despite the presence of PF8 exciton quenching up to about 25%, the PF8 spontaneous emission at the 0−0 line peak wavelength is *enhanced* up to 17.7%.

(2) The PF8 PL intensity variations are wavelength dependent, as evidenced by the enhancement of the 0−0 line and the quenching between 470 and 640 nm.

(3) A PL quenching is observed in the range between 470 and 640 nm, despite the relative *increase* of keto defects, up to 101%, emitting in the same range.

These features indicate that the PF8 photodegradation effects on the 0−0 and 525 nm PL intensity in the waveguide are the *opposite* of the ones expected on the basis of the density variation of the emitting species in the active film, thus clearly demonstrating that other effects dominate the waveguide emission intensity, likely affecting also the ASE one.

4.3. Photodegradation Effects on the Waveguide PL: Quantitative Analysis. In order to have a complete understanding of the origin of the observed PL intensity variations of the waveguide, it is useful to recall that, in the employed waveguide collection geometry, the PL intensity is given by

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

where $I_0(\lambda)$ is the PL intensity per stripe length unit at a given λ, L is the length of the excited stripe, and g' is the net gain coefficient given by the difference between the active material gain g and the waveguide losses α, due to scattering outside the waveguide and self-absorption, $g' = g - \alpha$. $I(\lambda)$ is an increasing function of g'; thus, a PL intensity reduction (enhancement) is a signature of a net gain decrease (increase). Remembering that $g = \sigma_g N$, where N is the population inversion density and σ_g is the gain cross-section, a decrease of g' can be caused both by an exciton quenching (reducing g) and by a losses increase $\Delta\alpha = -\Delta g'$ (increasing α).

In order to determine the role of waveguide losses variations on the observed features of the PL intensity variation, we measured, for all the investigated excitation densities, the net gain spectrum of the sample with the variable stripe method every 7.5 min during the degradation measurements, obtaining the data reported in Figure 7. Positive g' (indicating net gain) was observed only in about a 10 nm wide spectral region
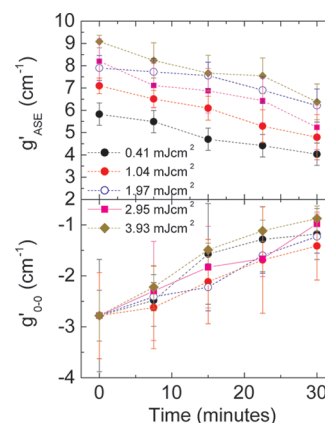

Figure 7. Top: time dependence of the net gain at the ASE peak wavelength for all the investigated excitation densities. Bottom: time dependence of the net gain at the 0−0 peak wavelength for all the investigated excitation densities.

around the ASE peak, corresponding to the ASE band spectral region, while negative g' (indicating dominating waveguide losses) was measured elsewhere. The main results are the following:

(1) At the 0−0 line wavelength, the net gain is negative, indicating that the losses are stronger that the gain. During the waveguide degradation, the net gain progressively becomes less negative, indicating a losses reduction with time, with a total variation up to about 1.8 cm^{-1} for an excitation density of 1.46 mJ cm^{-2}.

(2) At the ASE peak wavelength, the net gain is positive and increasing with the excitation density and, during the waveguide degradation, it shows an almost linear decrease with the operation time. This indicates that each laser pulse induces a similar active material damaging, increasing with the laser excitation density. Moreover, this result, considering the almost exponential ASE intensity dependence on g', is consistent with the observed almost exponential ASE intensity decrease with the waveguide operation time.

(3) At 525 nm, the net gain values (not reported) are of about −1 cm^{-1} with a comparable error bar and thus do not allow any meaningful data analysis.

In order to quantitatively determine to which extent the observed intensity variations can be ascribed to the PF8 exciton quenching induced g decrease or to a photodegradation induced losses variations, we also estimated the relative PL quenching at various wavelengths defined as

$$-\frac{\Delta I(\lambda)}{I(\lambda)} = \frac{I^i(\lambda) - I^f(\lambda)}{I^i(\lambda)} \tag{2}$$

where $I^i(\lambda)$ and $I^f(\lambda)$ are the initial and final PL intensity values at wavelength λ, respectively. Substituting the PL intensity of eq 1 in eq 2, we find

$$-\frac{\Delta I(\lambda)}{I(\lambda)} \approx 1 - \frac{g'^i}{g'^i + \Delta g'} \times \frac{(e^{g'^i + \Delta g'(\lambda)L} - 1)}{(e^{g'^i(\lambda)L} - 1)} \tag{3}$$

The simulated relative PL quenching is an increasing function of the initial value of g', for a given $\Delta g'$, and of $\Delta g'$, for a given initial g' (see Figure 8).
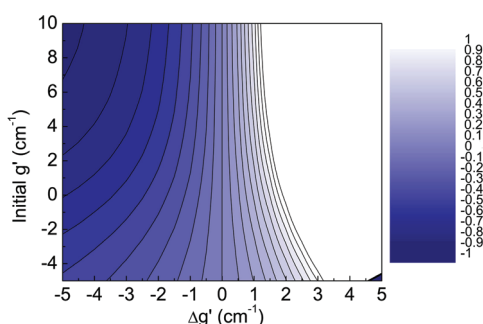
Figure 8. Simulation of the relative PL quenching dependence on the initial value of the net gain g' and on the net gain variation $\Delta g'$.

The simultaneous knowledge of the initial gain values, of the gain variation with time, of the photodegradation induced exciton quenching, and of the experimental relative PL variations allows us to quantitatively compare the experimental data with the prediction based on eq 3 obtaining the following conclusions:

(1) At the 0−0 wavelength, the observed intensity enhancement of the 0−0 line can be explained by the interplay between PF8 exciton quenching (reducing the PL intensity) and the observed losses reduction (increasing the PL intensity). With reference to the data at the highest excitation density, less affected by the error bar of the net gain values, we observe that a losses decrease of about 1.8 cm^{-1} should lead to a PL intensity enhancement of about 45% (using eq 3), which, together with the exciton quenching of about 25%, results in a PL enhancement of about 20%, which is consistent with the observed enhancement of about 18%. The observed losses decrease with time is consistent with a self-absorption reduction, due to the photodegradation of the active molecules, as observed in MeH-PPV.[11]

(2) The observed ASE quenching is quantitatively explained by the net gain reduction, as evident from the comparison between the quenching predicted from eq 3 by using the experimental initial and final values of g' and the ones observed from the ASE intensity decay in time (see Table 2). However, the net gain quenching at

Table 2. Initial Net Gain at the ASE Peak g^i, Final Net Gain Variation $\Delta g'$, Expected Net Gain Variation in Presence of Exciton Quenching Only $\Delta g'^q$, and Relative ASE Quenching Estimated from the Experimental g^i and $\Delta g'$ Values

excitation density (mJ cm^{-2})	g^i (cm^{-1})	$\Delta g'$ (cm^{-1})	$\Delta g'^q$ (cm^{-1})	$(\Delta I/I)_{ASE}^{th}$ (%)
0.19	5.8 ± 0.5	−1.8	−0.42	−57 ± 5
0.38	7.1 ± 0.5	−2.3	−0.98	−68 ± 5
0.77	7.9 ± 0.4	−1.7	−1.67	−60 ± 5
1.09	8.2 ± 0.4	−3.0	−2.53	−79 ± 5
1.46	8.4 ± 0.5	−2.7	−2.99	−77 ± 5

the lowest excitation densities is clearly higher that the one due to exciton quenching $\Delta g'^q$, estimated from the experimental exciton quenching values and by using the experimental loss value of 3.5 cm^{-1}. This suggests that, at the ASE wavelength, the photo-oxidation also results in a waveguide loss increase (see Table 2) of the order of 1 cm^{-1}.

(3) At the keto defect peak emission wavelength, the progressive PL quenching is due to the interplay between the keto defect density increase (increasing the PL intensity) and a dominating loss increase (decreasing the PL intensity). In order to quantify and to attribute such loss increase, we recalculated the relative PL quenching $-(\Delta I/I)_{525}$ by subtracting the contribution of keto defect emission[21] (see the inset of Figure 5), obtaining a maximum value of about 45% at $\lambda \approx 560$ nm for an excitation density of 1.46 mJ cm^{-2}. Starting from eq 3, we estimate that, in order to have an intensity decrease of 45% starting from a loss value of 1 cm^{-1}, a loss increase of 2.5 cm^{-1} would be necessary, that we ascribed to increased waveguide self-absorption due to keto defect absorption.[22] This attribution is confirmed by the sample absorbance spectra (see Figure 9) that show a weak
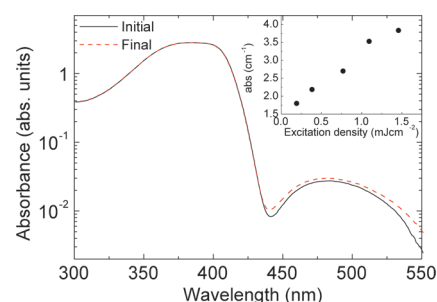

Figure 9. Initial (continuous black line) and final (dashed red line) absorbance of the sample aged at an excitation density of 0.19 mJ cm^{-2}. Inset: absorption increase at 481 nm as a function of the nitrogen laser excitation density.

absorption band, peaked at 481 nm, with a line width of about 80 nm, and a maximum value about 2 orders of magnitude weaker than the PF8 one. After laser exposure, the intensity of this absorption band linearly increases as a function of the exposure excitation density, with an increase intensity of few cm^{-1}, consistent with the values estimated from the PL quenching analysis. Finally, the keto defects absorption values at the ASE peak wavelength are consistent with the observed losses increase of about 1 cm^{-1} in the ASE range.

5. CONCLUSIONS

In conclusion, we investigated the intensity quenching dynamics of the ASE and of the spontaneous emission in a poly(9,9-dioctylfluorene) active waveguides operating in air. We demonstrate that the PF8 photodegradation, leading to PF8 exciton quenching and to keto defects formation, results in waveguide PL intensity variations strongly different from the one expected by considering only the exciton population variations because of the relevant contribution of the waveguide losses variations due to the active material self-absorption.

■ AUTHOR INFORMATION

Notes
The authors declare no competing financial interest.

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(21) For a wavelength larger than 620 nm, the PL intensity actually increases. As in this range self-absorption of the PF8 can be excluded, this feature can be ascribed to keto defects emission. We then recalculated the relative PL quenching $-(\Delta I/I)_{525}$ by subtracting from the final PL spectra the keto defect spectrum,[16] properly scaled in order to have $-(\Delta I/I)_{525} = 0$ at 700 nm.
(22) As the PL intensity variation is found to be irreversible on the time scale of more than 10 min at all the investigated excitation densities, it cannot be due to photoinduced absorptions, like polaron absorption,[23,24] taking place in the same spectral region.
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