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ONE PHOTON AND TWO PHOTON SPECTROSCOPY IN POLYMER OPTICAL FIBERS DOPED WITH A CONJUGATED POLYMER

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Abstract: In this work, we have compared the characteristics of the spectral emission of plastic optical fibers (POFs) doped with the conjugated polymer poly(9,9 dioctylfluorene)-alt-benzothiadiazole (F8BT), under one- and two-photon excitation. Measurements include evolutions of the fluorescence spectra with excitation wavelength and propagation distance, together with an analysis of the emission photostability.

Key words: Polymer optical fibers, fluorescence, fiber lasers, fiber amplifiers, organic materials.

1. Introduction

In the last years, poly (methyl methacrylate) (PMMA) polymer optical fibers (POFs) have raised a great interest in applications such as short-haul communications links, sensing applications and, by using active dopants, also in the field of fiber lasers and amplifiers in the visible region [1],[2]. POFs have the advantages of being robust, of having large core diameters and high numerical apertures, and of presenting lower manufacturing temperatures as compared to glass fibers. At such temperatures, the core of POFs can be manufactured embedding a wide variety of active materials. Organic dyes and conjugated polymers can be easily embedded in the core of POFs to obtain high gains in particularly short fiber lengths, due to their large absorption and emission cross sections [3]. Moreover, the conjugated polymers are good candidates for optical switching, due to their fast electronic transitions [4],[5]. One of the advantages of using organic dyes and conjugated polymers embedded in the solid PMMA material is the higher two-photon absorption cross-section that can be obtained as compared to using these dopants embedded in solutions [6].

There are upconversion pumping schemes in which two or more pump photons are used to transfer a dopant molecule to the high-energy band. This type of process was first predicted by Göppert-Mayer [7] in 1931 and was demonstrated experimentally in 1961 by Kaiser and Garret [8] in a $CaF_2:Eu^{2+}$ sample. Since then, two-photon-pumping schemes have been used to generate coherent radiation. Moreover, two-photon pumped stimulated emission and lasing have been shown in a variety of gain media, such as semiconductor crystals [9], organic dyes in solution [10], solid matrices [11] and polymer fibers [12]. Being a nonlinear process, the probability of two-photon absorption is much smaller than that of one-photon absorption. Therefore, in order to obtain high upconversion efficiencies, the dopant molecule should have a large two-photon absorption cross section and we should employ a device structure that facilitates efficient interaction between pump light and gain medium. Moreover, when the goal is to employ the waveguide as a laser, if we use a waveguide structure, such as a POF, to achieve upconversion by two-photon absorption, there exits a much longer effective gain length and the optical confinement is stronger, which allows higher light intensities. Despite these advantages, few works can be found in the literature about upconverted lasing in a polymer fiber configuration [12]-[14].

In this work we analyze the emission features of PMMA POFs doped with conjugated polymers using both one-photon (OP) and two-photon (TP) excitation schemes. Specifically, the emitted fluorescence spectrum as a function of the excitation wavelength and of the propagation distance are studied in both cases. We also analyze the evolution of the emitted fluorescence characteristics when doped POFs are exposed to laser excitation, in order to gain insight into their photostability properties.

2. Experimental set-up

Measurements have been carried out using a PMMA step-index POF doped with the conjugated polymer poly(9,9 dioctylfluorene)-alt-benzothiadiazole (F8BT). The dopant concentration in the fiber core is 0.003 wt% and the cladding material is not doped. The fiber diameter is 1 mm, the core diameter being 980 μm and the cladding thickness being 10 μm. The doped fiber was produced by the POF manufacturer Luceat S.p.A (Italy)

using an adapted preform-drawing technique, and the manufacture details are described in [15]. The different fiber samples were 30-40 cm long and the fiber ends were carefully polished by hand using polishing papers.

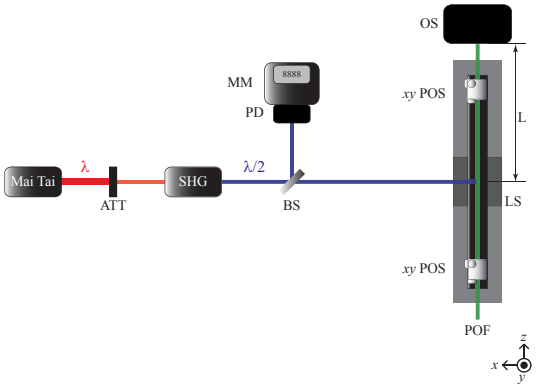

Fig. 1: Experimental set-up employed to measure the emission spectra obtained from doped POFs. Legend: ATT: variable Attenuator; SHG: Inspire Blue Second Harmonic Generator; BS: Beam Splitter; PD: Photodetector; MM: Multimeter; LS: Linear Stage; xy POS: xy micropositioner; OS: Optical Spectrometer.

The set-up employed to measure the fluorescence spectra can be seen in Fig. 1, in which we can see that the side-illumination technique has been used [16]. The light source used to excite the active fibers was a femtosecond laser system (Mai Tai HP, ~100 fs width laser pulses and a repetition rate of 80 MHz) with a frequency doubling unit (Inspire Blue) to be able to excite in the range from 345 nm to 520 nm. By adjusting manually the variable attenuator placed after the laser output, the impinging irradiance could be controlled. The measured doped fiber was held between two *xy* micropositioners standing on a linear stage. These were used to maintain the working area of the fiber completely horizontal and to focus the incident laser beam just on the centre of the fiber side. In most of the measurements, the distance from the incidence beam to the output end of the fiber was constant (16 cm). All the emission spectra obtained from the fiber end were measured by a USB4000 fiber-optic spectrometer with an optical resolution of 1.5 nm of full width at half maximum (FWHM), and the data obtained were corrected for the response of the detection system. A reference signal was obtained using a beam splitter to cancel the irradiance fluctuations of the laser. The emission spectrum was also measured as a function of the propagation distance through the doped fiber, by changing the position of the launching point of the light. An ILS250CC linear stage driven by an ESP300 motion controller was used for this purpose. Our own LabVIEW program was built to automate both the motion controller and the spectrometer, and also to achieve a good synchronization during the measurements. In order to measure two-photon induced fluorescence spectra the frequency-doubling unit was removed from the set-up to be able to excite in the range from 690 nm to 1040 nm, and the laser beam was focused onto the fiber side by using a convergent lens of 7.5 cm of focal length. In addition, in order to remove the pump power that could propagate through the fiber, a 10SWF-800-B short-pass filter (with a cut-on wavelength of 800 nm) was inserted in a filter holder placed between the fiber end and the spectrometer. The holder (Avantes FH-Inline-1") had two quartz collimating lenses and two SMA 905 connectors to facilitate light coupling into the spectrometer.

3. Results and discussion

The measured one-photon and two-photon induced fluorescence spectra can be seen in Fig. 2. The input irradiance for OP induced emission was 0.97 Wcm^{-2} at 400 nm, and that for TP was 6250 Wcm^{-2} at 800 nm. Fig. 2 shows that there are slight differences in the emission spectra depending on the excitation configuration: the two-photon emission spectrum is shifted toward longer wavelengths and there are small changes in the spectral width. Similar behaviors could also be observed in SP35 doped POFs [13],[17].

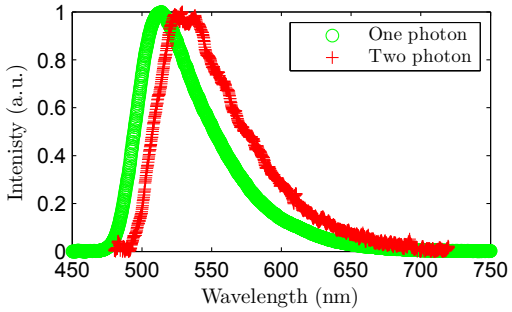

Fig. 2: One-photon (circles) and two-photon (crosses) induced fluorescence spectra for a F8BT-doped POF (L=16 cm). The OP and TP excitation irradiances are 0.97 Wcm^{-2} (at 400 nm) and 6250 Wcm^{-2} (at 800 nm), respectively.

3.1. Dependence on excitation wavelength

We have measured the emission spectrum as a function of the excitation wavelength with constant light propagation distance (16 cm). Since the spectra obtained are not symmetrical (see Fig. 2), their evolution as a function of the excitation wavelength has been studied by using its first and second moments (N_1 and N_2). The first moment represents the average emission wavelength and the square root of the second moment is proportional to the spectral width [18]. Fig. 3 shows the evolution of N_1 and of $N_2^{1/2}$ as the excitation wavelength changes, for both excitation conditions. Note the absence of noticeable spectral changes in both cases, which means that the dopant molecule distribution in the PMMA matrix can be considered to be uniform [18]. On the other hand, there are slight differences in the emission spectra depending on the excitation configuration. For the comparable wavelength range, two-photon emission spectra are shifted 15 nm toward longer wavelengths and they are slightly broader.

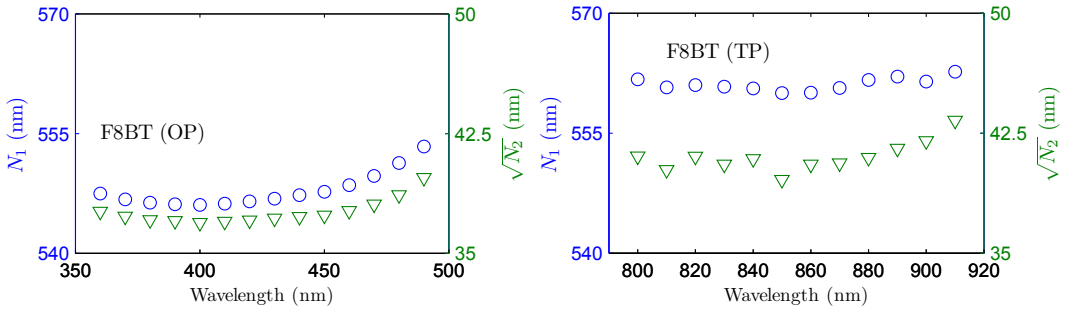

Fig. 3: Evolution of N_1 (circles) and $N_2^{1/2}$ (inverted triangles) as a function of the excitation wavelength from F8BT-doped POFs, and a light propagation distance of 16 cm. The excitation irradiance is 0.97 Wcm^{-2} in the one-photon excitation condition (left) and 6250 Wcm^{-2} in the two-photon excitation (right) condition.

3.2. Dependence on propagation distance

The evolution of the emission spectra as a function of the light propagation distance z has been analyzed when exciting at 400 nm and at 800 nm for both OP and TP excitation configurations, respectively. When the excitation point is moved farther from the detector, the amount of measured emitted intensity is reduced, and both the emission peak and the first moment are shifted towards longer wavelengths. It is known that these red shifts are directly related to the overlap between the absorption and the emission spectra. As can be seen in Fig. 4, in both cases there is a nearly linear red shift of the first moment when the light propagation distance is increased. Moreover, it is worth mentioning that, although two-photon emission spectra are red shifted 17 nm with respect to one-photon emissions, the slopes in both cases are the same, i.e. 0.049 nm/mm. Regarding the spectral width, we can see that there are not variations with the propagation distance or the excitation method. This analysis can be very important in order to know the tunable range of wavelengths in the design of POF lasers or amplifiers.

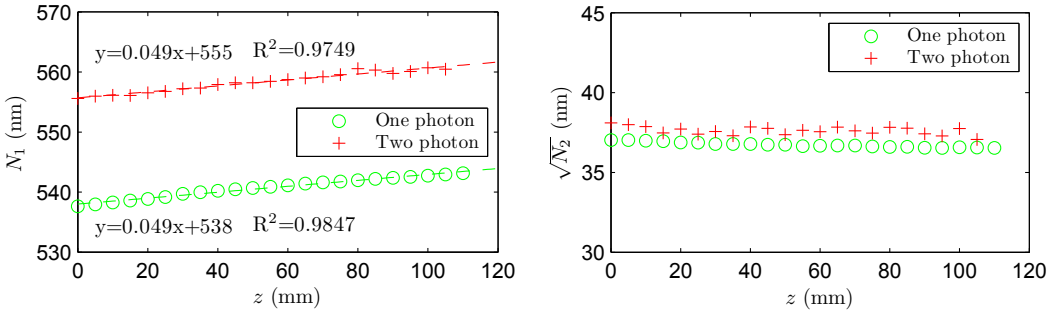

Fig. 4: Evolution of N_1 (left) and $N_2^{1/2}$ (right) of the emission spectra as a function of the propagation distance from F8BT-doped POFs. The excitation irradiance is 0.97 Wcm^{-2} (at 400 nm) in the one-photon excitation (circles) and 6250 Wcm^{-2} (at 800 nm) in the two-photon excitation (crosses). The point of the fiber closest to the detector has been normalized to zero. The linear fittings are shown as dashed lines.

Assuming that the illuminated fiber portion is a homogeneous light source (plane-wave source) and exciting with low irradiances, the output light measured at the fiber end at wavelength λ after propagating a distance z can be expressed by [16]:

$$I(z,\lambda) = I_0(\lambda)\exp\left[-\alpha(\lambda)z\right] \tag{1}$$

where $I_0(\lambda)$ is the intensity spectrum at $z = 0$ and $\alpha(\lambda)$ is the linear attenuation coefficient. This expression fits properly for the range of wavelengths in the tail of the absorption spectrum of the dopant, i.e. close to or inside the overlap between the absorption and emission spectra. Out of this range, the expression does not fit properly due to reabsorption and reemission effects. For both excitation techniques considered, we have obtained the linear attenuation coefficients in the appropriate spectral ranges by fitting the decays in the transmitted intensity with z to (1). The calculated coefficients are shown in Fig. 5. Note that there are differences in the value of $\alpha(\lambda)$ depending on the excitation setup. On the one hand, this could be related to the employed plane-wave source model in (1). In the two-photon excitation case, the laser beam was focused onto the fiber side by using a convergent lens, and, consequently, the light intensity after propagating a distance z would be better estimated by the point-source model. On the other hand, as in the case of other nonlinear optical processes, experimental uncertainties in two-photon absorption are around 10% [17].

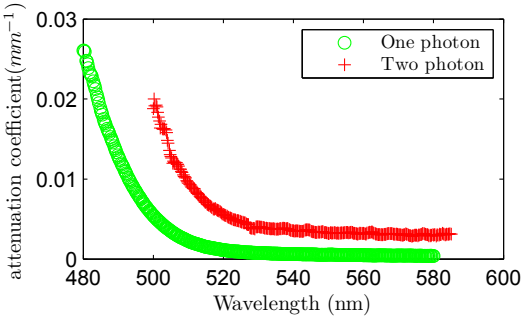

Fig. 5: Linear attenuation coefficients for a F8BT-doped POF excited using one-photon (circles) and two-photon (crosses) absorption techniques. The excitation irradiances are 0.97 Wcm^{-2} (at 400 nm) and 6250 Wcm^{-2} (at 800 nm), respectively.

3.3. Photostability

In order to characterize the photostability of both excitation conditions, firstly we have exposed the F8BT-doped fibers for 60 minutes (see Fig. 6(left)). The excitation irradiance was 0.97 Wcm^{-2} (at 400 nm) in OP excitation condition and 6250 Wcm^{-2} (at 800 nm) in TP excitation condition. After a rest interval in which the samples were in darkness and at room temperature for 24 hours, the fibers were exposed again for another 60 minutes under the same conditions (see Fig. 6(right)). In the first measurements, the doped fibers had never been exposed to laser light, so there was no previous degradation that could affect the results. In the second measurements, light was launched at exactly the same point of the fiber. For the sake of comparison, we have normalized the fluorescence intensities to 100% at the start of the first measurements.

As can be noted in Fig. 6(left), the photostability of the F8BT-doped fiber is better using OP absorption technique. After 60 minutes of exposition at 80 MHz (equivalent to $2.88 \cdot 10^{11}$ laser shots), the fluorescence

capacity is reduced by 25%. According to the definition of lifetime given in [19], which is the time elapsed before the fluorescence intensity is reduced by half, the sample excited by OP technique has not reached its lifetime value yet. In the case of the sample excited by TP absorption technique, its fluorescence capacity is affected much more, maintaining only 14% of its initial intensity after the same period. Besides, its lifetime is only of around 100 s ($8 \cdot 10^9$ laser shots). The worse photostability could be related to the much higher excitation irradiances necessary to obtain TP induced fluorescence emission. After 24 hours of rest in darkness, there is a partial recovery in the fluorescence capacity in both cases. Fig. 6(right) shows that the emissions are initially 7% and 12% higher than at the last point of the first excitation period for OP and for TP absorption techniques, respectively.

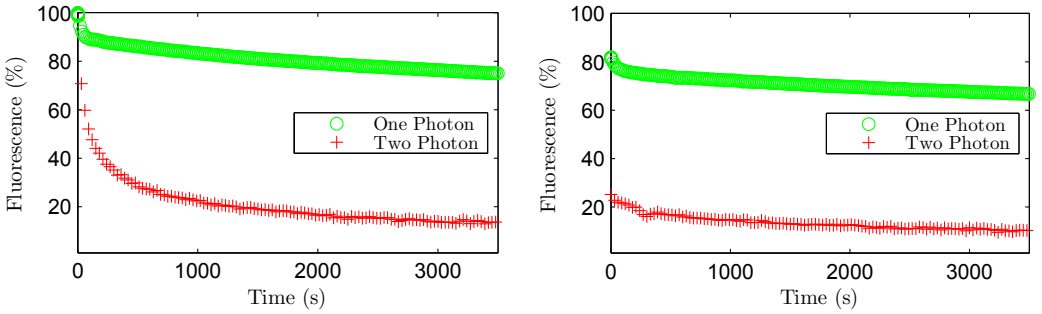

Fig. 6: One-photon (circles) and two-photon (crosses) induced fluorescence as a function of the excitation time. The excitation irradiance is 0.97 Wcm^{-2} (at 400 nm) and 6250 Wcm^{-2} (at 800 nm), respectively, and the light propagation distance is 16 cm. Fibers excited for up to 60 minutes in (a) and re-excited for another 60 minutes after a rest in (b).

4. Conclusions

The optical properties of the F8BT conjugated polymer embedded in PMMA POFs have been characterized by using one-photon and two-photon absorption techniques. We have proved that there are slight differences in the emission spectra depending on the excitation configuration. We have also measured the variation of the emission spectra as a function of the light propagation distance through the doped fibers with the same slopes depending on the excitation technique. The longer the propagation distance is, the more red shifted the emission spectrum is, with the same variation for both excitation set-ups. The optical losses for the doped fiber have also been calculated, for both excitation techniques. Finally, we have analyzed the photostability of the F8BT-doped fiber using both excitation techniques.

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