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Optical gain characteristics of β -phase poly(9,9-dioctylfluorene)*

G Ryu, R Xia and D D C Bradley

EXSS Group, Blakett Laboratory, Imperial College London, Prince Consort Road, London SW7 2AZ, UK

E-mail: D.Bradley@imperial.ac.uk

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Abstract

We report an investigation of the effect of morphology on the gain properties of poly(9,9-dioctylfluorene) (PFO). The PFO β -phase morphology has previously been reported to be detrimental to lasing threshold, a conclusion at odds, however, with pump–probe measurements on PFO/poly(methylmethacrylate) blend films that show enhanced stimulated emission characteristics for β -phase chains. In order to understand these conflicting indications, we have undertaken a detailed study of the gain properties for spin-coated PFO films, including samples in which the fraction of β -phase chains is deliberately enhanced by post-deposition exposure to toluene vapour. We find that the amplified spontaneous emission (ASE) threshold (390 nm pump, 10 ns pulses, 10 Hz repetition rate) is of order 80 nJ/pulse, independent of the presence of a significant β -phase component. Surface emitting distributed feedback lasers comprising polymer-coated second-order gratings etched into silica substrates are also insensitive to the β -phase morphology: lasing threshold energies are equivalent so long as the structures are tuned to the correct peak gain wavelength for each film morphology. This occurs at the 0–1 vibronic peak in the corresponding photoluminescence emission spectra, namely 465 nm for films *with* and 450 nm for films *without* a significant β -phase component. We can thus conclude that whilst the introduction of β -phase chains leads to new lasing wavelengths (some 15 nm red shifted from those for films without β -phase chains) it is not obviously detrimental to lasing performance. An additional effect does occur, however, when the pump beam energy is increased by one to two orders of magnitude above the ASE threshold energy: the ASE peak position for the β -phase films then migrates from 465 to 450 nm. This phenomenon is irreversible and appears to be the result of exciton quenching on β -phase chains due to the photo-oxidative formation of fluorenone moieties.

* Based on a presentation at the 2006 International Conference on Synthetic Metals, Dublin, Ireland.

Poly(9,9-dioctylfluorene) (PFO) has proven to be an interesting material with which to explore the sensitivity of conjugated polymer electronic properties to variations in physical structure [1–11]. Film samples can be prepared with distinct morphologies via controlled deposition conditions and subsequent thermal and/or vapour treatments, also making use of the fact that PFO is a thermotropic liquid crystal that can be aligned and/or crystallized [1–6]. One can obtain different types of glassy films via spin coating from good solvents and by rapid quenching from the nematic or isotropic melt. Annealing such glassy films or slowly cooling samples from the nematic or isotropic melt leads to crystalline films. Orientation can be achieved on an alignment layer by annealing in the nematic phase and the oriented films can then be quenched or crystallized on fast or slow cooling, respectively. Oriented films are of interest for polarized light emission [8], for enhanced charge carrier transport [9] and as a means to enhance gain properties [10] via control over absorption and propagation [11]. A specific extended rigid chain conformation can be obtained in glassy film samples by choice of spin-coating solvent and deposition conditions, by thermal cycling to low temperatures, and by post-deposition exposure to solvent, typically toluene, vapour [1, 2]. Films that possess a significant fraction of chains with this conformation are termed β -phase samples and they possess characteristically red-shifted absorption and photoluminescence (PL) spectra with well-resolved vibronic features [1, 2]. The β -phase samples have a number of interesting photophysical properties and have for instance been investigated as systems well suited to the detailed study of energy transfer processes [1, 2, 5–7].

In the present paper we report an investigation of the effect that the β -phase morphology has on the gain properties of PFO films. It has previously been argued that the presence of β -phase chains is detrimental to lasing, resulting in an enhanced threshold [12]. This conclusion is at odds, however, with ultrafast pump–probe measurements on PFO/poly(methylmethacrylate) blend films that showed superior stimulated emission characteristics in spatial regions where the PL emission was dominated by the β -phase chain contribution [13]. In particular, the optical gain (measured as a differential change in transmission) was an order of magnitude larger and it mapped across the full PL spectrum, rather than being cut off at longer wavelengths by absorptive losses. It is also at odds with reports [14, 15] on novel copolymer gain systems for which the incorporation of a small fraction of longer wavelength emission chromophores (namely dialkoxy-*p*-phenylenevinylene or benzothiadiazole), to which efficient Förster transfer can occur, leads to reduced lasing thresholds. The PFO β -phase samples are equivalent ‘self-doped’ systems wherein a fraction of polymer chains with the extended β -phase conformation (smaller HOMO–LUMO optical gap) is intimately dispersed in a glassy matrix of chains with a larger energy gap. The result is that excitons photogenerated on the glassy PFO matrix chains rapidly and efficiently transfer to the lower energy β -phase chains, such that introducing even a small fraction of β -phase chains leads to a PL emission very much dominated by the red-shifted β -phase spectrum [1, 2]. This is illustrated in figure 1, which shows the room temperature absorption and photoluminescence spectra of an as-spin-coated film (upper panel) and of a film with a significant β -phase component (lower panel). The β -phase sample shows an additional absorption peak at 433 nm (as well as other less dramatic absorption changes) and a PL spectrum with well-resolved vibronic peaks (0–0: 438 nm; 0–1: 465 nm; 0–2: 497 nm) that are shifted some 15 nm to the red of those in the glassy film (0–0: 423 nm; 0–1: 450 nm). There is also a relatively small Stokes’ shift between the lowest energy absorption (433 nm) and highest energy PL (438 nm) peaks and the relative weighting of the PL vibronic structures indicates a small Huang–Rhys parameter. All of these characteristics agree with the original assignment that the β -phase comprises a well-ordered, extended, rigid chain conformation, characterized by an enhanced effective conjugation length [1, 2], a conclusion also supported by subsequent

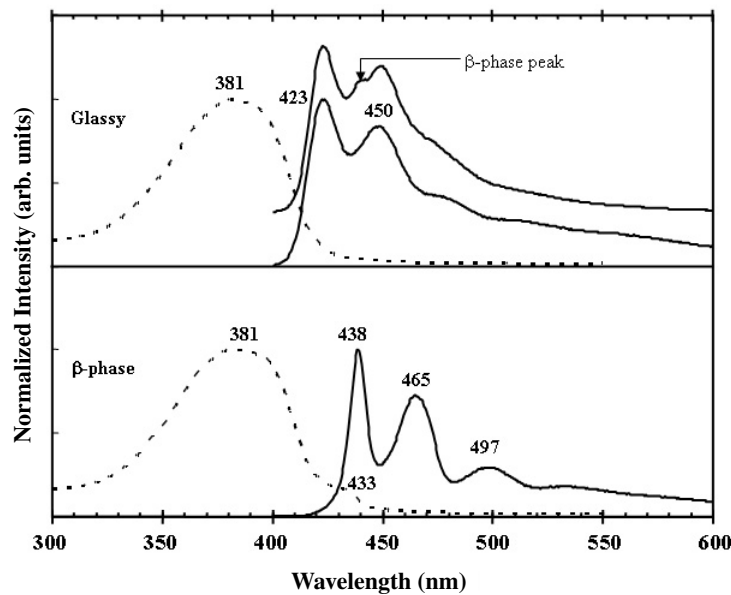


Figure 1. Absorption (dashed line) and photoluminescence (solid line, $\lambda_{\text{ex}} = 350$ nm) spectra of glassy-phase (upper panel) and β -phase (lower panel) PFO films. The vertically displaced photoluminescence spectrum in the upper panel is typical for films that contain a small fraction of β -phase chains.

studies [6]. Sometimes in heterogeneous samples (with spatial regions that do and do not have a significant β -phase component) [7], it is possible to see spectra that are a superposition of the glassy-phase and β -phase spectra since the heterogeneity precludes uniform energy transfer. In these circumstances the spectra typically vary from region to region across the sample.

In order to address the conflicting indications in the literature with respect to the expected optical gain performance of β -phase samples, we have undertaken a detailed study for spin-coated PFO films, including samples in which the fraction of β -phase chains is deliberately enhanced by post-deposition vapour exposure [1, 2]. Spin-coated PFO films can often contain a small fraction of β -phase chains, and even when these are not readily detectable in absorption measurements (by the presence of the characteristic 433 nm peak) they can still lead to a discernable contribution to the PL emission: this is illustrated by the vertically displaced PL spectrum in the upper panel of figure 1, where the dominant PL features are those of the glassy phase but where there is also a contribution from the β -phase spectrum, evident here as a subsidiary peak (labelled β -phase peak) on the short wavelength side of the 450 nm 0–1 glassy-phase vibronic peak. The relative concentration of β -phase chains depends very much on the choice of solvent and film processing conditions. With care, β -phase chain formation can be effectively suppressed, yielding pure glassy-phase PFO films that then show no β -phase contribution in their PL emission spectra. Here, PFO films were spin coated (1500–3000 rpm) from toluene solution ($15\text{--}20$ mg ml $^{-1}$) and care was taken to obtain films that did not have any β -phase contribution to their PL emission spectra. For absorption and PL measurements films were prepared with thickness ≈ 100 nm, whilst for ASE and distributed feedback (DFB) laser experiments the thickness was ≈ 150 nm. For both absorption/PL and ASE the films were simply coated onto fused silica (Spectrosil-B) substrates, whilst for lasing experiments, requiring a resonant structure for feedback, silica (thermal-oxide layer) on silicon substrates

etched with 70 nm deep, 50% fill factor, one-dimensional gratings (over a $300 \times 300 \mu\text{m}^2$ area) were used. β -phase film samples were subsequently obtained for both substrate formats using a post-deposition vapour swelling process in which the coated substrates were exposed to toluene vapour at 50 °C for 80 h. We have also noticed that the ASE properties of glassy films show a gradual change if the film is stored at room temperature under normal atmospheric conditions, with an observed steady increase in threshold over time. This process is not fully understood although physical ageing of spin-coated films is a well-known phenomenon for many polymers, involving structural relaxation from the initially frozen-in non-equilibrium structure. This has been taken into account here by measuring the ASE and lasing properties for glassy films that had been first allowed to age for a period of 80 h.

Absorption and PL spectra were measured using a Jasco V-560 spectrophotometer and a FluoroMax-3 spectrofluorimeter, respectively. The excitation wavelength for the PL measurements was 350 nm. A frequency trebled Q -switched Nd:YAG laser pumped optical parametric oscillator was used to deliver 10 ns duration, 10 Hz repetition rate, excitation pulses at 390 nm (close to the main PFO absorption peak) for both ASE and DFB laser experiments. For ASE, the pump beam was focused using a cylindrical lens to form a $400 \mu\text{m} \times 4 \text{ mm}$ stripe on the sample, which was spatially aligned with its long axis orthogonal to and adjacent to the sample edge. The emitted light was collected using a fibre bundle placed in close proximity to the end of the stripe (sample edge) and fed to a grating spectrograph equipped with a charge coupled device (CCD) detector. DFB laser measurements used a $160 \mu\text{m}$ diameter excitation spot spatially aligned with the polymer-coated grating. The pump beam was incident at 45 °C to, and the collection fibre bundle placed normal to, the sample surface. All measurements were performed in air.

As previously reported [10], the ASE peak position can be tuned by varying the polymer film thickness coated on the substrate. For a given polymer film thickness there is a natural *cut-off* wavelength that corresponds to the longest wavelength for which light can be guided within the slab waveguide comprising the polymer film bounded on the top by air and on the bottom by Spectrosil. As a consequence, whilst the ASE peak position in a thick film is simply dictated by the gain spectrum, as the film thickness is reduced the cut-off shifts to shorter and shorter wavelength and forces the ASE peak to shift accordingly. This spectral shift takes one away from the spectral location of maximum gain and consequently the ASE threshold tends to increase. Therefore, in order to avoid any ambiguity in the comparison between glassy-phase and β -phase samples we have deployed a film thickness of 150 nm: this is sufficient to ensure that in both cases the spectral location of the gain maximum coincides with a waveguide supported propagating mode. It is also thin enough to avoid strong competition from higher-order modes.

Figure 2 shows ASE (solid line) data for the two film types together with their corresponding PL spectra (dashed line) (note the absence of a β -phase contribution in the PL spectrum of this glassy film). The wavelength at which ASE occurs (sharp peak rapidly increasing with pump pulse energy) coincides in each case with the PL 0–1 vibronic emission peak, consistent with a four level system. For the glassy film the ASE peak is at 452 nm and for the β -phase film it is at 466 nm. As already noted, however, heterogeneous films can show gain narrowing at either or both of these characteristic wavelengths, and gain properties have been reported for each of these situations [10, 12]. Poly(9,9-dioctylfluorene-*co*-9,9-di(4-methoxy)phenylfluorene) (F8DP) differs from PFO only in respect of having methoxy-phenyl (instead of the usual octyl) substituents on every other fluorene unit in the polymer chain. For F8DP the ASE peak always occurs at 452 nm [10], consistent with the fact that the β -phase chain conformation is not observed for this material. One does not therefore need to introduce different aromatic functional groups (e.g. 6,6'-(2,2'-octyloxy-1,1'-binaphthalene) [12]) into the

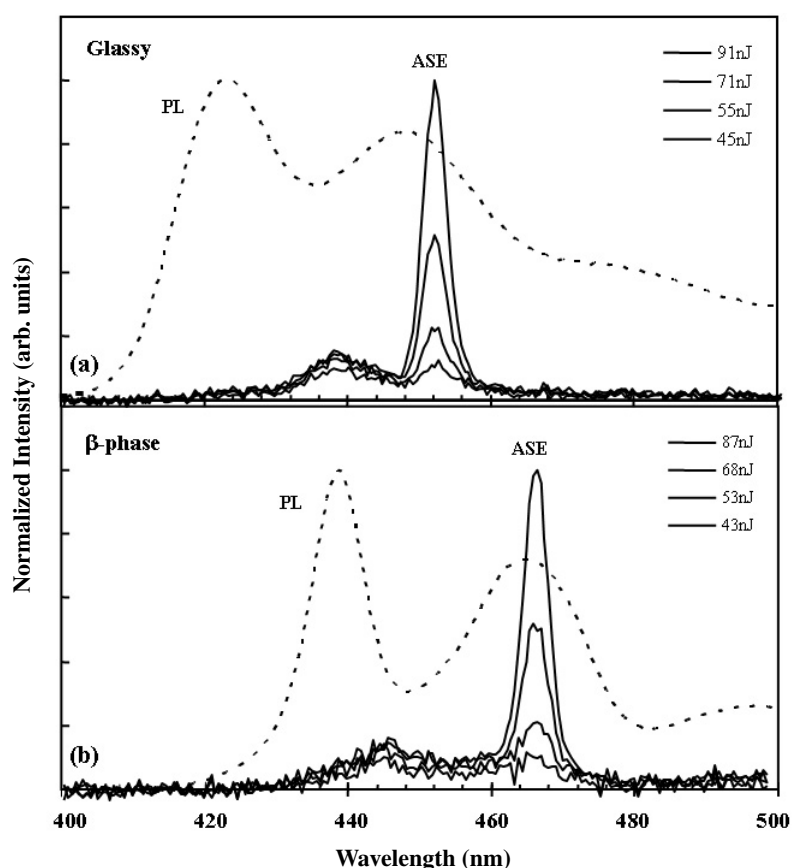


Figure 2. ASE (solid lines) and photoluminescence spectra (dashed lines) for (a) an 80 h aged glassy-phase film and (b) a β -phase film generated by 80 h exposure to 50 °C toluene vapour. The pump energies for the individual ASE spectra are indicated.

chain in order to suppress β -phase formation: changes in substituent groups alone can in fact suffice. Figure 2(a) shows the ASE spectra for the glassy film (80 h aged in normal atmosphere) as a function of increasing pump pulse energy: the ASE peak is already evident at 45 nJ/pulse. Figure 2(b) shows the corresponding data for the (toluene vapour treated) β -phase sample. The spectrum is notably different from that of the glassy film, with the ASE peak red shifted to 466 nm, mapping the red shift of the 0–1 vibronic peak of the PL spectrum. The ASE peak is apparent for pump pulse energies ≥ 43 nJ. The spin-coated film that was subsequently vapour treated to generate this particular β -phase sample had an ASE threshold of 41 nJ/pulse and hence the difference in ASE ‘threshold’ for glassy-phase and β -phase samples is insignificant: any differences are within the sample-to-sample variation that we observe for films made under the same conditions. The conclusion is then that the optical gain properties of the two sample types are very similar. We note also that the ASE peak full width at half maximum (FWHM) line widths ($\Gamma \approx 4$ nm) are the same for both aged glassy-phase and β -phase samples, a further indication that the optical gain is not greatly different.

Most fluorene-based conjugated polymers show a continuous blue shift of the ASE peak position, typically by a few nanometers, as the pump beam energy is increased [10]. This can be explained in terms of the effect that the reducing emission decay time (from of order 500 ps

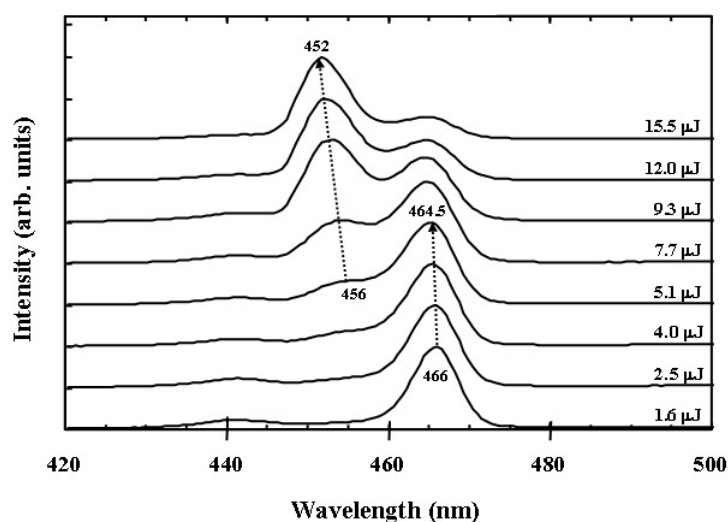


Figure 3. High-energy pump induced ASE peak shifts for a β -phase film. The emission spectra are peak normalized and offset for clarity. The respective pump energies are indicated.

to of order 1 ps) associated with the occurrence of stimulated emission has an energy migration within the inhomogeneously broadened optical density of states [2]. We have observed, however, that a significant fraction of β -phase samples show a more dramatic dependence on pump beam energy (figure 3): a second ASE peak appears and moves to the 452 nm wavelength, characteristic of the glassy phase, whilst the β -phase ASE peak falls away. Initially, the β -phase ASE peak shows a gradual blue shift (≈ 1.5 nm as is typical for many polyfluorenes), accompanied by an increase in FWHM linewidth from 4 to 7 nm. A short wavelength shoulder then appears (first evident at 456 nm in the ≈ 5 μ J/pulse spectrum), gradually strengthens and shifts to 452 nm. This phenomenon is irreversible with no recovery of the β -phase ASE peak strength after resting the sample for extended periods.

Regions of the film in which irreversible changes in ASE properties have occurred are evident when viewed under UV light: a stripe shaped mark is seen, consistent with a localized change in emission character. Spatially resolved Raman, absorption, and PL measurements were used to further study the nature of these changes. There were no obvious differences in the Raman spectra (not shown) recorded for pump beam exposed and unexposed regions. Figure 4 records how the absorption, PL and ASE spectra differ in the two regions. The spectra of the unexposed region (figure 4(a) inset, absorption (dashed line); figure 4(b) PL (solid line with vibronic peaks) and spectrally narrowed ASE at 1 μ J (dashed line) and 3 μ J (bold solid line) pump energy) are, unsurprisingly, essentially the same as those of the typical β -phase film shown in figure 1. The spectra of the exposed region show significant changes. The intensity of the 433 nm absorption peak (figure 4(a) inset, solid line) is noticeably decreased, suggesting a loss of β -phase chains. There is a concomitant overall reduction in PL intensity: the PL spectra in figures 4(a) and (b) were measured under identical conditions and are normalized to the 0–1 β -phase vibronic peak of the unexposed region. In addition, there is an apparent reappearance of PL spectral features characteristic of the glassy phase. Particularly clear in this regard is the observation (figure 4(a)) of the glassy-phase 0–0 vibronic peak at 423 nm. ASE measurements on the unexposed region (figure 4(b)) show the usual β -phase ASE behaviour (peak at 0–1 vibronic peak of the β -phase PL spectrum) but the high-energy pump beam

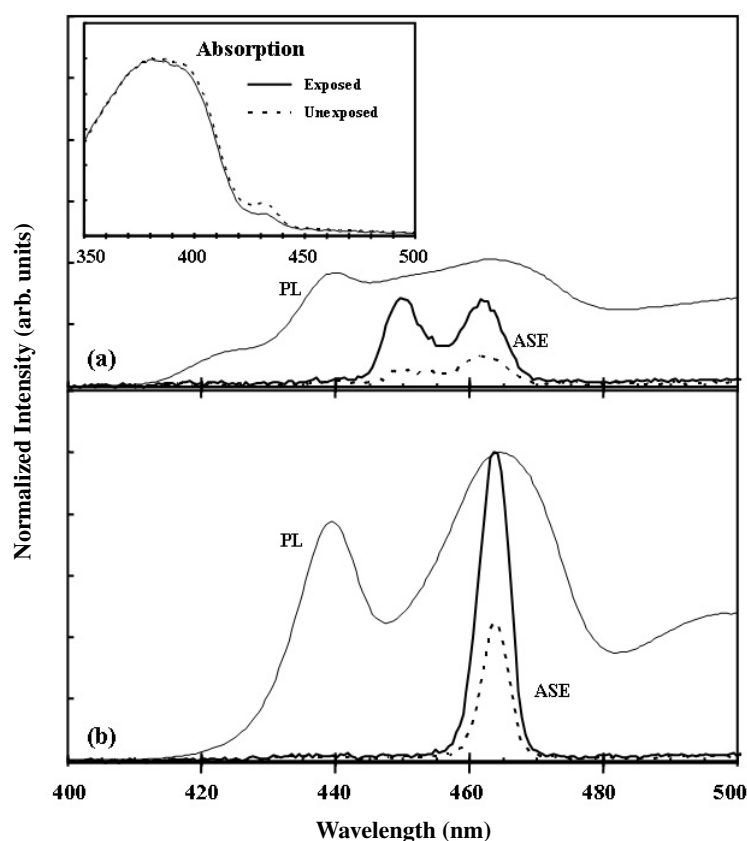


Figure 4. Spatially resolved absorption, PL and ASE spectra for a β -phase PFO film subjected to high pulse energy stripe excitation. PL (solid line) and ASE (dashed line ($1 \mu\text{J}/\text{pulse}$) and bold solid line ($3 \mu\text{J}/\text{pulse}$)) spectra are shown for (a) the modified stripe region and (b) a previously unexposed region. The corresponding absorption spectra are shown in the inset to (a). The PL spectra are normalized relative to the 0–1 peak of the unexposed region and the ASE spectra are normalized to the $3 \mu\text{J}$ pump energy ASE peak of the unexposed region.

exposed region shows instead two peaks (characteristic of both the glassy phase and the β -phase) with the shorter wavelength peak initially weaker but increasing more rapidly with pump energy. Furthermore, the overall stimulated emission intensity is reduced for the exposed region. Note that the ASE spectra in figure 4 are peak normalized to the unexposed ASE emission intensity at $3 \mu\text{J}$ pump energy (figure 4(b) solid line).

Interpreting the observed loss of absorption as the result of photooxidation, we can propose an explanation for the changes that are seen in ASE behaviour. The overall decrease in PL emission is consistent with the oxidative formation of fluorenone defects that are known to efficiently quench luminescence [16]. That the absorption loss is spectrally characteristic of β -phase chains indicates selective oxidation. More detailed studies are needed to fully understand this effect. We note, however, that β -phase chains have been reported to have a larger photogenerated charge yield than glassy chains [2, 5] and also that PFO reduction (i.e. accepting an electron) promotes fluorenone defect formation [17]. This offers a possible reason for the preferential quenching of β -phase absorption and a concomitant reduction in energy transfer from the glassy-phase chains. The reduced energy transfer could then allow

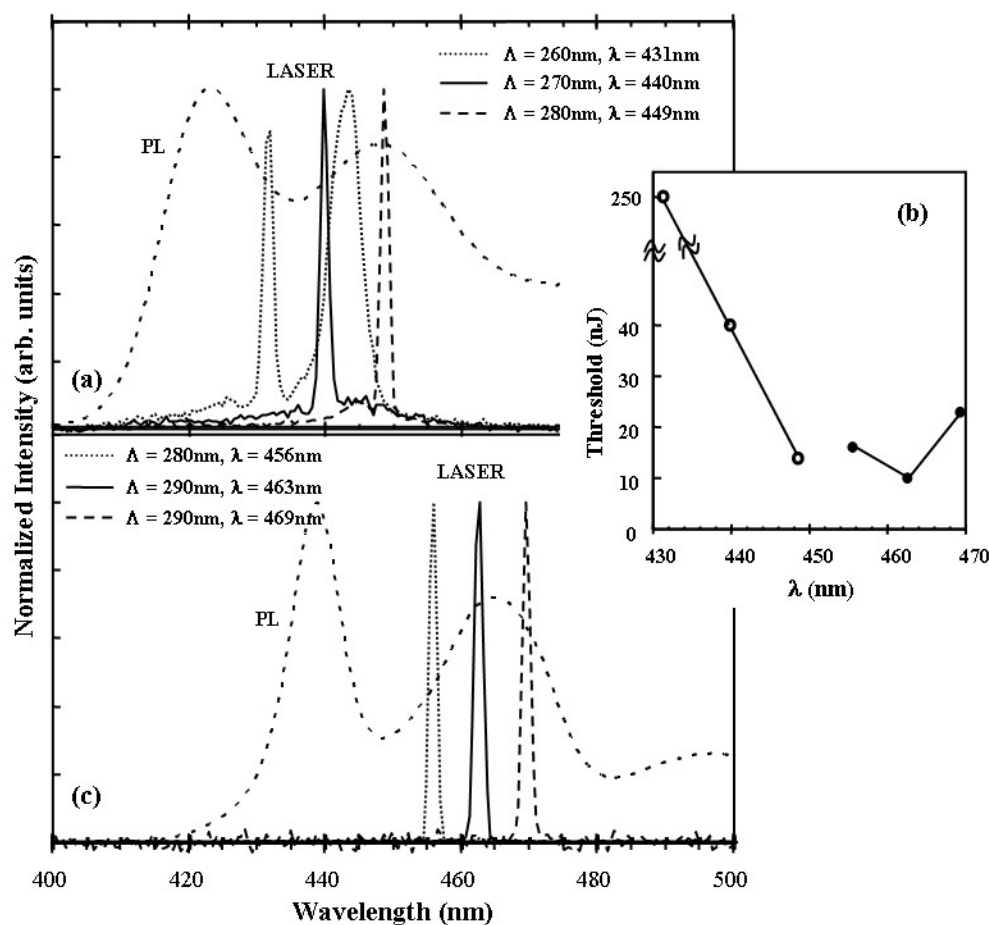


Figure 5. Second-order DFB laser and PL emission spectra of (a) glassy-phase and (c) β -phase PFO samples. The grating periods used ($\Lambda = 260, 270, 280$ or 290 nm) and the corresponding lasing wavelengths ($\lambda = 431, 440, 449, 456, 463$ and 469 nm) are indicated. The wavelength dependence of the lasing threshold energy is shown in (b) for both glassy-phase (open circles) and β -phase (filled circles) samples. The lowest thresholds are clearly obtained when the lasing wavelength coincides with the 0–1 vibronic peak of the relevant PL spectrum. Please note the discontinuity in the ordinate scale for the shortest wavelength laser ($\lambda_{\text{Laser}} = 431\text{ nm}$) which has a much larger threshold and for which there is a competing ASE peak at 443 nm (with broader linewidth than the lasing peaks). The minimum threshold energies for lasing were of order 10 nJ/pulse in both sample types.

ASE to occur within the glassy-phase component of the film, leading to the appearance of the 452 nm peak. The homogeneity, or otherwise, of this effect remains to be determined.

The last stage of our investigation was to measure the properties of surface emitting second-order DFB lasers, comprising PFO films spin coated on one-dimensional gratings etched into silica on silicon substrates. To find the minimum threshold pump energy it is important to select an appropriate combination of polymer film thickness and grating period. Gratings with periods $\Lambda = 260, 270, 280,$ and 290 nm were studied. Calculations of the expected mode confinement (using the measured refractive index dispersion for PFO [18] and the known properties of silica) indicated that films of less than 100 nm thickness would not be suitable. PFO film thicknesses of $140\text{--}150\text{ nm}$ were therefore used. Figure 5(a)

shows the glassy-phase PFO lasing spectra together with the corresponding PL spectrum. The lasing threshold energies are plotted (as open circles) as a function of wavelength in figure 5(b) and are seen to decrease as the lasing wavelength approaches the PL spectrum 0–1 vibronic peak at 450 nm (maximum gain position). A minimum value of 12 nJ/pulse was found for $\lambda_{\text{laser}} = 449$ nm ($\Lambda = 280$ nm grating). Going beyond the 0–1 vibronic peak wavelength caused the lasing threshold to increase rapidly again (not shown) due to the onset of photoinduced absorption at wavelengths beyond ≈ 470 nm [13]. Figure 5(c) shows the corresponding data for β -phase samples (prepared as described above by prolonged vapour exposure after deposition of the PFO films onto the various grating substrates). The minimum lasing threshold (see figure 5(b)) of 10 nJ/pulse was found for $\lambda_{\text{laser}} = 463$ nm ($\Lambda = 290$ nm grating), again close to the PL 0–1 vibronic peak in the β -phase film. The two film types (glassy phase and β -phase) thus show remarkably consistent threshold energies provided that lasing is adjusted to coincide with their respective PL 0–1 vibronic peaks. The lasing peak FWHM linewidths (1.3 nm) were also consistent for the two samples. It is clear from these experiments that there is no degradation of performance for the β -phase PFO samples in comparison to standard glassy films. Readers should note the discontinuity in the ordinate scale (figure 5(b)) for the shortest wavelength laser ($\lambda_{\text{laser}} = 431$ nm) which has a much larger threshold (250 nJ/pulse) and for which there is, simultaneously, a competing ASE peak at 443 nm (with broader linewidth than the lasing peaks).

Conclusion

We have presented the results of a detailed study of the ASE and second-order grating DFB laser characteristics for glassy-phase and β -phase PFO films. The threshold energies and peak line widths for both film types lie within experimental error of each other. The ASE threshold energies and peak line widths are of order 45 nJ/pulse and 4 nm whilst for the second-order DFB lasers they are of order 10 nJ/pulse and 1.3 nm. Our results are thus inconsistent with earlier reports of poor optical gain for β -phase relative to glassy-phase PFO samples. Under high-energy (i.e. one to two orders of magnitude higher than threshold) pumping in air, the β -phase films do, however, show an irreversible change in ASE properties. A 452 nm ASE peak (characteristic of the glassy phase) appears and then grows at the expense of the original 466 nm β -phase peak, with also an overall reduction in stimulated emission intensity. This effect can be attributed to exciton quenching on β -phase chains due to the photo-oxidative formation of fluorenone moieties thereon, and might well explain the literature inconsistency.

Acknowledgments

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