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ENHANCING THE PHOTOLUMINESCENCE OF POLYFLUORENE-BASED THIN FILMS VIA ILLUMINATION

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ABSTRACT. We show in this work that exposing thin films of conjugated poly[9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl] to light under nitrogen atmosphere led to an increase of their emission up to 2.2 folds. This enhancement was due to the appearance of structural changes in the glassy and β-phase conformations induced upon thin film illumination, as revealed by the Franck-Condon analysis of the photoluminescence spectra. Interestingly, the photoluminescence of thin films remained at the enhanced value for 75 days after stopping the illumination, most probably due to the permanent structural changes induced upon illumination.

Keywords: *conjugated polymers, illumination, photoluminescence, β-phase conformations.*

INTRODUCTION

Due to the evident structure-property relationship existent in conjugated polymeric materials [1–7], the scientific community is continuously looking for novel processing methods to manipulate, control and tune the microstructure of conjugated materials, with the aim to improve their optoelectronic properties and consequently, the functionality of potential organic devices. Detailed information on various processing methods prominently adopted by scientists are well described in the literature [8–10]. One of such processing tools appears to be the exposure to light [11–16]. Scientific reports have shown that illumination of conjugated polymers with white light in controlled nitrogen atmosphere influenced the behavior of an

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ensemble of conjugated molecules, *i.e.*, their mechanical properties such as viscosity [11]. Several other experiments have shown that conjugated materials such as poly(3-hexylthiophene-2,5-diyl) (P3HT) and the poly[2-methoxy-5-((2′-ethylhexyl)oxy)-1,4-phenylenvinylene] (MEH-PPV) chains suffered conformational changes in solutions and adopted more coiled-like conformation when illuminated [14,15]. Similar behavior was observed in thin films [16]. Moreover, structural changes of MEH-PPV in thin films were reported along with an increase in photoluminescence (PL) upon illumination in nitrogen [12,13]. The enhancement of the PL properties in thin films was tentatively attributed to structural changes induced by photoexcitations.

In this work, we study the alteration of PL properties of conjugated poly[9,9-bis(2-ethylhexyl)-9*H*-fluorene-2,7-diyl] (PFO) films upon illumination. Our aim is to find out how different type of light used in the illumination process impacts the PL enhancement in such polymer films and to reveal the best experimental conditions under which the PL enhancement is maximized and, eventually, remains stable for long periods of time. Such information might then be useful in the design of future energy devices, including light-emitting diodes.

EXPERIMENTAL

PFO of a weight-average molecular weight M_w = 13.2 kg/mol, number-average molecular weight M_n= 6.8 kg/mol and polydispersity $Đ$ = 1.94, was purchased from Sigma-Aldrich. Thin films of PFO (127±5 nm in thickness) were prepared by spin casting at 2000 rpm from a toluene solution. For all films, regular microscopy cover glass, previously cleaned in UV-ozone for 20 minutes, was used as substrate.

Absorption spectra of thin films were acquired using a V-530 UV-VIS spectrophotometer from Jasco (spectral range of 190-1100 nm). PL spectra were collected using an FP-6500 Spectrofluorometer from Jasco (excitation wavelength range of 220-750 nm). All PL spectra were recorded using an excitation wavelength of 375 nm. Illumination of all films was always performed both at controlled temperature and in nitrogen atmosphere inside a Linkam hot stage (model THMS 600 that was equipped with a precise temperature controller in the range of -196°C to 600 °C and which could be continuously flashed with nitrogen flow).

Different LED sources from Thorlabs were used to illuminate the PFO films: SOLIS-1A/M (white cold), SOLIS-365A/M, SOLIS-385A/M, SOLIS-445B/M, SOLIS-525A/M and SOLIS-623A/M. The sources were operated using a ThorlabsDC2200 (1 Channel) LED driver, the latter being also used to precisely control the power of LEDs. Illumination of PFO films at 30°C for 45 minutes was done using a white xenon lamp (powered by 50 W and equipped with a UV filter).

RESULTS AND DISCUSSION

Figure 1a depicts the large increase of the PL intensity of PFO films upon their illumination with white light at a constant temperature of 30 °C in nitrogen atmosphere. The longer the films were illuminated, the higher their PL intensity became. Nonetheless, illuminating PFO films beyond 2 hours did not lead to any further increase in PL intensity. To exclude possible alterations of PL due to contaminations with oxygen [17], control experiments, using films prepared from solutions nitrogen-bubbled in anhydrous toluene, were performed inside a nitrogen-flooded glove box (with oxygen content < 10 ppm [18]). Results shown in Figure 1b proved that, even under such circumstances, the PFO film still exhibited a clear PL enhancement when exposed to light.

To quantify the enhancement of PL upon illumination, we have extracted the I_{PL}/I_{ref} ratio for various illumination times. Here, I_{PL} is the PL intensity of the total area under the peak measured for each illuminated film. Instead, I_{ref} is the PL area peak intensity corresponding to a nonilluminated reference film. Figure 1c shows the evolution of this ratio with the illumination time. The PL intensity increased by 1.5 folds in less than 15 minutes of illumination and kept increasing up to 2 folds after 2 hours of illumination. Indeed, beyond this time no further increase in PL was observed. In order to exclude a possibly PL alteration due to the incomplete solvent evaporation upon spin casting, we have monitored the PL of other reference PFO films that were prepared under same conditions, but kept for specific times in dark (no light was allowed to shine on these films). The evolution of the I_{PL}/I_{ref} ratio of these films, as depicted in Figure 1c by the square symbols, showed that there was only a weak (several %) variation of the PL intensity that could be attributed to solvent traces remaining in PFO films. Therefore, our results clearly showed that illuminating PFO films with white light induced large enhancement in their PL intensity.

We have repeated all the experiments described above once more, but this time we kept the PFO films at 70 °C (Figure 1d). In this case, the PL intensity doubled in less than 5 minutes of film illumination and further increased to a maximum of 2.2 folds after 12 minutes of illumination. Instead, the illumination of PFO films for times longer than 40 minutes led to a decrease of the PL intensity. Again, almost no PL alteration attributed to solvent traces was detected for the control samples kept in dark. Furthermore, by fixing the illumination time to 30 minutes, we have varied the film temperature at which illumination was performed. The obtained results, shown in Figure 1e, revealed a clear dependence of the PL increase with respect to the film temperature and the best PL enhancement happened at 70 °C. Above 70 °C, the PL decreased, probably due to an increased mobility of PFO molecules (PL also

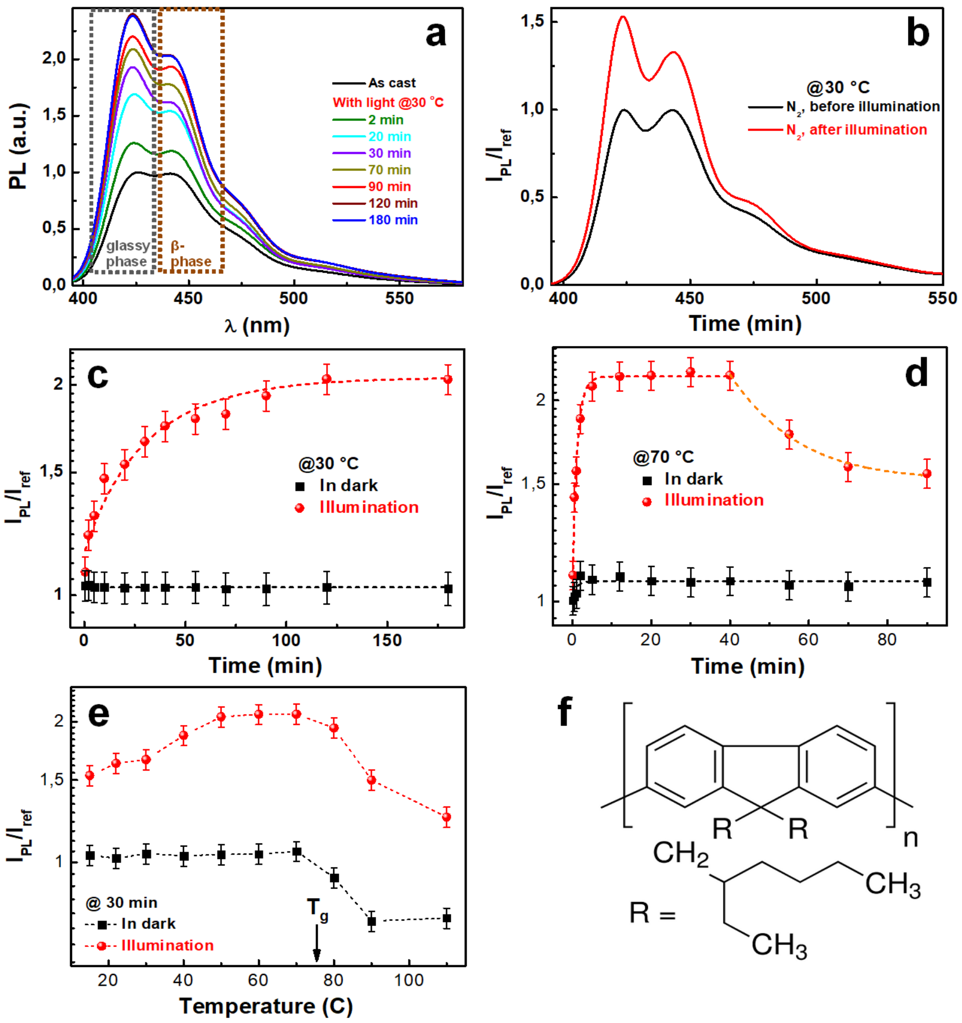

Figure 1. (a) PL spectra of PFO films before and after illumination at 30 °C for various times. Spectral components of the glassy and β-phases are indicated by the dotted rectangular shapes. (b) Normalized PL spectra of a PFO film before and after its illumination at 30 °C for 45 minutes inside a glove box filled with nitrogen. This PFO film was obtained from a solution that was prepared using anhydrous toluene and that was then bubbled with nitrogen before further use. (c-d) PL enhancement of PFO films illuminated at 30 °C (c) and at 70 °C (d) as a function of illumination time. Dashed black and red lines in (c) and (d) are fits of single exponential growth functions, while the dashed orange line in (d) was fitted using a single exponential decay function. (e) PL enhancement of PFO films illuminated for 30 minutes at various temperatures. Square symbols show the PL changes taking place in the reference films kept in dark. Illumination of films was performed in nitrogen atmosphere and using a white cold LED source with an output power of ~252 mW. The black arrow indicates the expected T_g for PFO films (f) Chemical structure of PFO system.

decreased for the reference films kept in dark) caused by the transition to a less glassy state, as the glass transition temperature T_g was estimated to be around 70-75 °C for PFO films. Our flash differential scanning calorimetry measurements in bulk revealed a T_g of about 84 °C for this PFO system (see its chemical structure in Figure 1f). Nonetheless, it is well-known that, for a specific polymer, the T_g in thin films is lower than the T_g in the bulk [19–23]. Thus, above 70 °C the effect of illumination might have been diminished by other conformational changes induced thermally [24,25]. For the lower film temperatures, the PL amplification was smaller too but, according to Figure 1c, this PL amplification, that corresponded to only 30 minutes of illumination, did not reach yet the maximum of PL enhancement observed for longer illumination times (*i.e.*, 2 hours).

The photophysical properties of PFO are known to strongly depend on the film microstructure [26,27]. Therefore, one possibility is to link the PL enhancement upon illumination to conformational changes, especially when knowing that thin PFO films generally display the coexistence of two phases. In the glassy phase, PFO molecules adopt a range of disordered wormlike conformations characterized by a broad distribution of intermonomer torsion angles [28,29]. Instead, in the β-phase, PFO molecules adopt an extended coplanar geometry with a torsion angle of 165°-180° between the adjacent fluorene units [28–33]. In order to follow the possible changes of the glassy and β-phases in PFO films during illumination, we have performed a Franck-Condon analysis (FCA; details on FCA are described elsewhere [34]) on the PL spectra shown in Figure 1a. For that, two molecular species corresponding to the glassy phase and the β-phase conformations, that exist in an intermediary state (*i.e.*, within the PL spectrum recorded after 90 minutes of illumination), were separated and scaled appropriately to all the other PL spectra recorded at different illumination times. For instance, Figure 2a and Figure 2b display the separation and scaling of glassy and β-phase contributions to PL spectra of Figure 1a recorded at 0 and 180 minutes of illumination. Furthermore, the data points of Figure 1c (red spherical symbols) were normalized to 100% at the time corresponding to 0 minutes of illumination and were then fitted using a single exponential growth function. The glassy and β-phase spectra for all illumination times were further integrated and their fraction on the total integrated PL intensity was calculated (Figure 2c). Fits through the spectra (as a guide to the eye) were done using single exponential growth functions. Note that the parameters that we have used in the FCA, including Huang-Rhys parameters, are comparable to the parameters reported in the literature [35]. The obtained results have shown that, while the fraction of glassy phase was increasing from about 88% to 94%, the fraction of β-phase was decreasing from around 11% to about 5% when increasing the illumination time from 0 to 180 minutes (Figure 2c). Thus, these results clearly proved that illumination was reducing the amount of β-phase in thin films of conjugated PFO. This observation was further sustained by the fact that the PL ratio between the 422 nm and 442 nm peaks increased upon illumination (this information can be seen when performing the normalization to 422 nm peak of all PL spectra presented in Figure 1a; *not shown*), indicating the appearance of a more disordered, possibly less planarized phase [36].

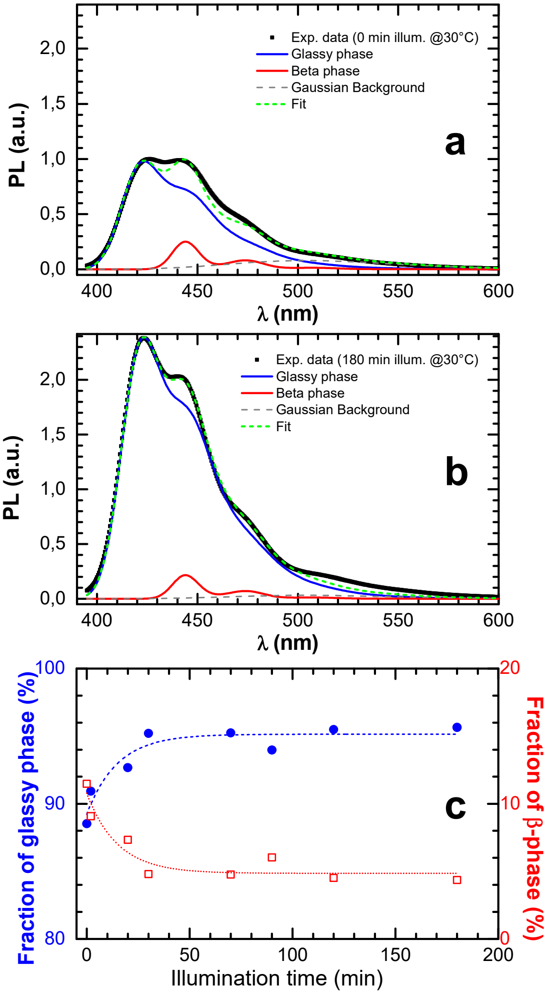

Figure 2. (a-b) Separation and scaling of glassy and β-phase contributions to all the other PL spectra of Figure 1a recorded at 0 and 180 minutes of illumination. (c) Evolution of the glassy and β-phase fractions in PFO films during illumination as deduced from the FCA using data of Figure 1a and Figure 1c. Dotted fits through the spectra were done with a single exponential growth fit $y=y_0+A_1\cdot\exp(x/t_1)$ for the glassy phase (with $y_0=95\%$, $A_1=-5.9\%$ and $t_1=-14.8$ *min*) and with another single exponential decay fit $y=y_0+A_1\cdot\exp(-x/t_1)$ for the β-phase (with $y_0=4.9\%$, $A_1=-5.9\%$ and $t_1=-14.8$ *min*).

According to the literature, the amount of polymer chains planarized in β-phase conformation determines the PL efficiency [37]. Therefore, we expected a PL alteration to take place upon illumination. While the mechanism by which illumination reduces the β-phase is not clearly understood, the enhancement of PL associated with the reduction of β-phase could be tentatively explained assuming the behavior of the geminate pairs (*i.e.*, charge transfer states) formed from excitons in the β-phase. For instance, the absorption spectra display only weak changes in absorption when PFO films are illuminated, with no visible evidence of the existence of the absorption peak expected to be located around 435-440 nm (*not shown*) and corresponding to the β-phase [34,35,38,39]. This means that there is only a very small amount of β-phase in the PFO films, but with rather efficient energy transfer to it [35,40]. These β-phase sites quench the emission most probably due to the fact that the excitons in the β-phase tend to form geminate pairs rather than to emit light [41]. Therefore, the emission from neat β-phase should be less than emission from the neat glassy phase. Nonetheless, when PFO films are being illuminated and consequently the amount of β-phase is reduced, there is less quenching of the emission and the overall PL efficiency increases. This observation is in line with other results reported in the literature and indicating both that PFO films with lower β-phase fraction exhibit higher PL quantum efficiency [42] and that simple white light exposure sharply retards the growth of conjugated polymer microstructures [15]. Finally, note that although there are many examples in the literature where illumination may alter or keep stable the optoelectronic properties of conjugated polymers [17,43–46], yet the enhancement of PL via illumination might be, to the best of our knowledge, the only example where light has exhibited a beneficial impact on such a material.

In order to study the impact of the type of light, used for the illumination of PFO films, on the PL enhancement, we have replaced the white light with other light sources (*e.g.*, 365 nm, 385 nm, 445 nm, 525 nm and 623 nm). For example, a 2-fold enhancement of PL in PFO films was also observed upon their illumination with light of a wavelength of 385 nm (Figure 3a). In this case, much shorter illumination times of up to only 40 s were sufficient to enhance the PL. Moreover, the general behavior of the I_{PL}/I_{ref} ratio with respect to the illumination time at 30 °C and 70 °C (Figure 3b-c), as well as with respect to the temperature when keeping the illumination time at 40 s (Figure 3d), was like that reported in Figure 1 for the white light.

The enhancement of PL was also significant when utilizing 365 nm and 445 nm light sources (*not shown*). In contrary, when employing light of 525 nm and 623 nm for the illumination of PFO films, the PL enhancement was rather negligible and the maximum PL enhancement depended on the light intensity of each illumination source (*not shown*). Therefore, for a clearer comparison, we have further fixed the output power

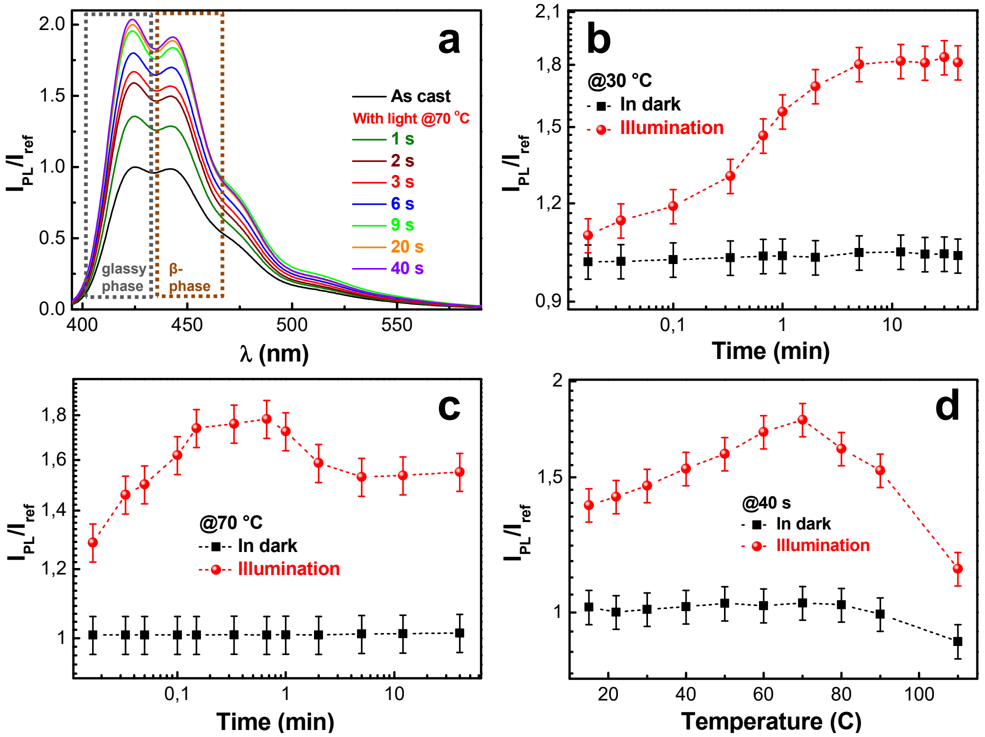

Figure 3. (a) PL spectra of PFO films before and after their illumination at 70 °C for various times. (b-c) PL enhancement of PFO films illuminated at 30 °C (b) and at 70 °C (c) as a function of illumination time. (d) PL enhancement of PFO films illuminated for 40 s while annealed at various temperatures. Square symbols show the PL changes taking place in control PFO films kept in dark. Illumination of films was performed using a 385 nm LED source with an output power of ~ 258 mW. Spectral components of glassy and β-phases are indicated by the dotted rectangular shapes in (a).

of all light sources and measured the corresponding PL enhancements induced in PFO films upon illumination (Figure 4). The most significant enhancement of PL was observed when exciting the glassy phase at 385 nm, as at this wavelength the PFO system absorbs almost 100% of the incoming light (Figure 5a). Furthermore, when illuminating PFO films with light of 445 nm, a significant increase in PL was also noticed, even though the PFO system absorbs at this wavelength only a small fraction of the incoming light (see Figure 5a). This result could be explained by the fact that PFO molecules adopting a β-phase conformation absorb light around 435-440 nm [34,35,38,39].

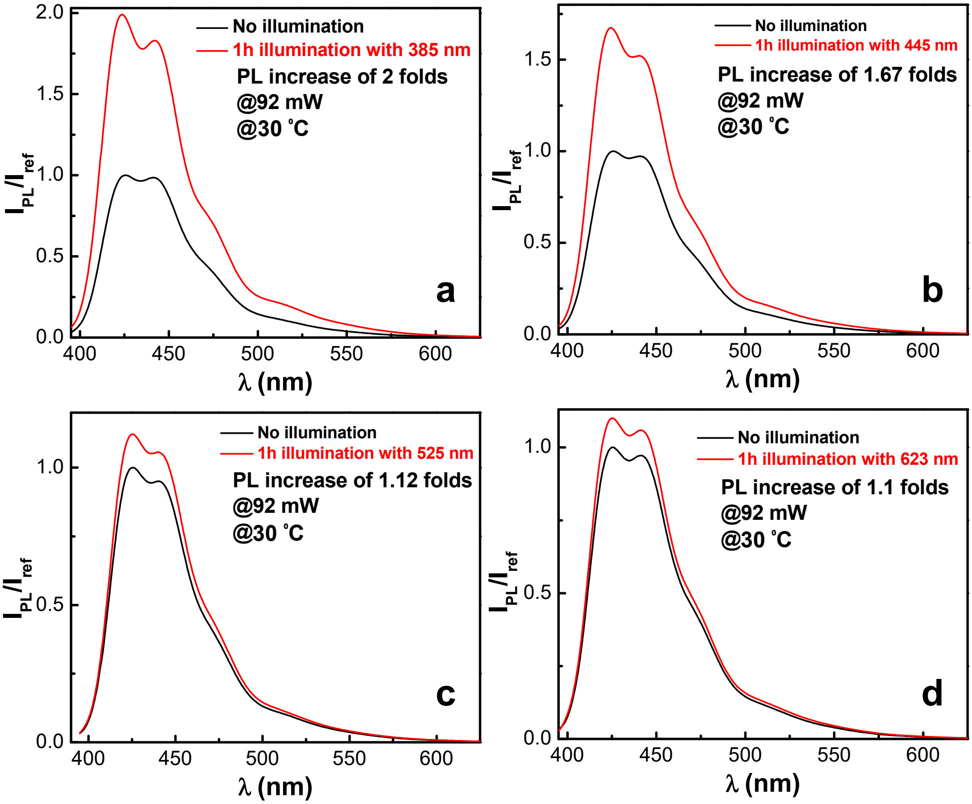

Figure 4. PL spectra of PFO films before and after their illumination at 30 °C for 1 hour, by employing 385 nm (a), 445 nm (b), 525 nm (c) and 623 nm (d) LED sources. All these sources worked at an output power of 92 mW.

In order to see how useful the PL enhancement would be for practical applications, we have broken an as spin cast PFO film in two pieces. One piece was simply monitored in dark in nitrogen atmosphere, as a control sample. The other piece was monitored during illumination for 90 minutes in nitrogen. Then, the illumination of the PFO film was stopped and the film was placed in dark in nitrogen atmosphere. We have then periodically measured the PL spectra of both films. The obtained results, summarized in Figure 5b, showed that the PL enhancement remained stable for 75 days, period after which the experiment was stopped. This was most probably due to the permanent and irreversible reduction of the β-phase induced by the illumination. Such irreversibility of the PL enhancement shows good potential for the future design of organic light emitting diodes.

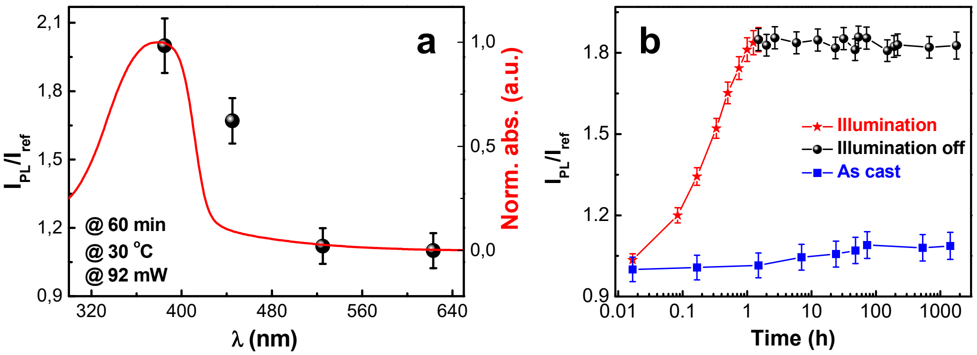

Figure 5. (a) Normalized absorption spectrum (line) of an as spin-cast PFO thin film acquired at 30 °C with the corresponding PL enhancement (symbols) obtained upon the illumination of its analogues using light of a specific wavelength. (b) PL enhancement measured using the total area under the peak for: a spin cast reference PFO film kept in dark (square symbols), a PFO film illuminated with white light (~ 200 mW) for various times (star symbols) and same film monitored in dark after the illumination was stopped (spherical symbols). All films were kept at 30 °C in nitrogen atmosphere.

CONCLUSIONS

We have demonstrated an increase in PL intensity of about 2.2 folds for thin PFO films upon their illumination, in controlled atmosphere, with light of various wavelength and power. The PL enhancement was attributed to the changes in the glassy and β-phase fractions upon illumination and was proven to be stable for many tens of days. Our results showed that PL was increasing to a maximum with the decreasing of the β-phase fraction from around 11% to about 5%, as revealed by the FCA. Moreover, the PL enhancement was shown to depend on the temperature of PFO films. For temperatures below the T_g, a continuous increase in PL intensity with the time of illumination was measured. For temperatures around the T_g, we found an optimal illumination time at which the PL intensity was generally reaching its maximum value. At temperatures higher than T_g, the enhancement of PL was decreasing, most probably due to an increased mobility of PFO molecules caused by the transition to a less glassy state.

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REFERENCES

1. E. Collini and G.D. Scholes, *Science*, **323**, 369–373 (2009).
2. S. Wang, M. Kappl, I. Liebewirth, M. Müller, K. Kirchhoff, W. Pisula, and K. Müllen, *Adv. Mater.*, **24**, 417–420 (2012).
3. B. Ma, B.J. Kim, L. Deng, D.A. Poulsen, M.E. Thompson, and J.M.J. Fréchet, *Macromolecules*, **40**, 8156–8161 (2007).
4. E.D. Como, N.J. Borys, P. Strohriegl, M.J. Walter, and J.M. Lupton, *J. Am. Chem. Soc.*, **133**, 3690–3692 (2011).
5. J.C. Bolinger, M.C. Traub, T. Adachi, and P.F. Barbara, *Science*, **331**, 565–567 (2011).
6. L. Brambilla, M. Tommasini, I. Botiz, K. Rahimi, J.O. Agumba, N. Stingelin, and G. Zerbi, *Macromolecules*, **47**, 6730–6739 (2014).
7. F. Dubin, R. Melet, T. Barisien, R. Grousson, L. Legrand, M. Schott, and V. Voliotis, *Nat. Phys.*, **2**, 32–35 (2006).
8. R.A. Segalman, B. McCulloch, S. Kirmayer, and J.J. Urban, *Macromolecules*, **42**, 9205–9216 (2009).
9. I. Botiz, *J. Mater. Chem. C*, **11**, 364–405 (2023).
10. I. Botiz, S. Astilean, and N. Stingelin, *Polym. Int.*, **65**, 157–163 (2016).
11. I. Botiz, P. Freyberg, N. Stingelin, A.C.M. Yang, and G. Reiter, *Macromolecules*, **46**, 2352–2356 (2013).
12. I. Botiz, P. Freyberg, C. Leordean, A.-M. Gabudean, S. Astilean, A.C.-M. Yang, and N. Stingelin, *ACS Appl. Mater. Interfaces*, **6**, 4974–4979 (2014).
13. I. Botiz, P. Freyberg, C. Leordean, A.-M. Gabudean, S. Astilean, A.C.-M. Yang, and N. Stingelin, *Synth. Met.*, **199**, 33–36 (2015).
14. B. Morgan and M.D. Dadmun, *Eur. Polym. J.*, **89**, 272–280 (2017).
15. B. Morgan and M.D. Dadmun, *Polymer*, **108**, 313–321 (2017).
16. X.L. Ho and J.D. White, *Chem. Phys. Lett.*, **735**, 136753 (2019).
17. V. Bliznyuk, S. Carter, J. Scott, G. Klärner, R. Miller, and D. Miller, *Macromolecules*, **32**, 361–369 (1999).
18. M. Stoessel, G. Wittmann, J. Staudigel, F. Steuber, J. Blässing, W. Roth, H. Klausmann, W. Rogler, J. Simmerer, and A. Winnacker, *J. Appl. Phys.*, **87**, 4467–4475 (2000).
19. S. Napolitano, E. Glynos, and N.B. Tito, *Rep. Prog. Phys.*, **80**, 036602 (2017).
20. J.L. Keddie, R.A. Jones, and R.A. Cory, *Europhys. Lett.*, **27**, 59–64 (1994).
21. M. Chowdhury and R. Priestley, *Proc. Natl. Acad. Sci. USA*, doi/10.1073/pnas.1704886114 (2017).
22. D. Long and F. Lequeux, *Eur. Phys. J. E*, **4**, 371–387 (2001).
23. J.A. Forrest and K. Dalnoki-Veress, *Adv. Colloid Interface Sci.*, **94**, 167–195 (2001).
24. K.-P. Tung, C.-C. Chen, P. Lee, Y.-W. Liu, T.-M. Hong, K.C. Hwang, J.H. Hsu, J.D. White, and A.C.-M. Yang, *ACS Nano*, **5**, 7296–7302 (2011).

25. P.W. Lee, W.-C. Li, B.-J. Chen, C.-W. Yang, C.-C. Chang, I. Botiz, G. Reiter, Y.T. Chen, T.L. Lin, J. Tang, J.-H. Jou, and A.C.-M. Yang, *ACS Nano*, **7**, 6658–6666 (2013).
26. U. Scherf and E.J. List, *Adv. Mater.*, **14**, 477–487 (2002).
27. D. Neher, *Macromol. Rapid Commun.*, **22**, 1365–1385 (2001).
28. A. Perevedentsev, N. Chander, J. Kim, and D.D. Bradley, *J. Polym. Sci. Part B: Polym. Phys.*, **54**, 1995–2006 (2016).
29. W. Chunwaschirasiri, B. Tanto, D. Huber, and M. Winokur, *Phys. Rev. Lett.*, **94**, 107402 (2005).
30. M. Grell, D. Bradley, X. Long, T. Chamberlain, M. Inbasekaran, E. Woo, and M. Soliman, *Acta Polym.*, **49**, 439–444 (1998).
31. C. Liu, Q. Wang, H. Tian, J. Liu, Y. Geng, and D. Yan, *Macromolecules*, **46**, 3025–3030 (2013).
32. A. Perevedentsev, P.N. Stavrinou, D.D.C. Bradley, and P. Smith, *J. Polym. Sci. Part B: Polym. Phys.*, **53**, 1481–1491 (2015).
33. X. Li, Z. Bai, B. Liu, T. Li, and D. Lu, *J. Phys. Chem. C*, **121**, 14443–14450 (2017).
34. A.L.T. Khan, M.J. Banach, and A. Köhler, *Synth. Met.*, **139**, 905–907 (2003).
35. A.L.T. Khan, P. Sreearunothai, L.M. Herz, M.J. Banach, and A. Köhler, *Phys. Rev. B*, **69**, 085201 (2004).
36. I. Botiz, M.-A. Codescu, C. Farcau, C. Leordean, S. Astilean, C. Silva, and N. Stingelin, *J. Mater. Chem. C*, **5**, 2513–2518 (2017).
37. M. Ariu, D. Lidzey, M. Sims, A. Cadby, P. Lane, and D. Bradley, *J. Phys.: Condens. Matter*, **14**, 9975 (2002).
38. A. Cadby, P. Lane, H. Mellor, S. Martin, M. Grell, C. Giebeler, D. Bradley, M. Wohlgenannt, C. An, and Z. Vardeny, *Phys. Rev. B*, **62**, 15604 (2000).
39. C. Rothe, S. King, F. Dias, and A. Monkman, *Phys. Rev. B*, **70**, 195213 (2004).
40. M. Ariu, M. Sims, M. Rahn, J. Hill, A. Fox, D. Lidzey, M. Oda, J. Cabanillas-Gonzalez, and D. Bradley, *Phys. Rev. B*, **67**, 195333 (2003).
41. C. Yang, Z. Vardeny, A. Köhler, M. Wohlgenannt, M.K. Al-Suti, and M.S. Khan, *Phys. Rev. B*, **70**, 241202 (2004).
42. Q. Zhang, L. Chi, G. Hai, Y. Fang, X. Li, R. Xia, W. Huang, and E. Gu, *Molecules*, **22**, 315 (2017).
43. T. Tromholt, M.V. Madsen, J.E. Carle, M. Helgesen, and F.C. Krebs, *J. Mater. Chem.*, **22**, 7592–7601 (2012).
44. S. Alem, S. Wakim, J. Lu, G. Robertson, J. Ding, and Y. Tao, *ACS Appl. Mater. Interfaces*, **4**, 2993–2998 (2012).
45. A. Rivaton, S. Chambon, M. Manceau, J.-L. Gardette, N. Lemaître, and S. Guillerez, *Polymer Degradation and Stability*, **95**, 278–284 (2010).
46. M. Jørgensen, K. Norrman, and F.C. Krebs, *Sol. Energy Mater. Sol. Cells*, **92**, 686–714 (2008).