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Research paper Light induced fluorescence enhancement in MEH-PPV thin films

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HIGHLIGHTS

- Light processing can enhance Photoluminescence (PL) from MEH-PPV by 400%.
- PL continues to increase for 16 h after light processing discontinued.
- Enhanced PL remains stable for over 100 days at 23 C in Nitrogen.
- Below $1 \,\mu W/\mu m^2$, no enhancement, only photobleaching, was observed.
- Enhanced PL likely due to reduced interchain energy transfer to non-radiative recombination sites.

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ABSTRACT

Laser treatment of MEH-PPV films increased photoluminescence (PL) by up to 400% in nitrogen. Maximum enhancement was observed with irradiances between 20 and 70 μ W/ μ m², and a total fluence of ~700 μ J/ μ m². (Below ~1 μ W/ μ m² only photobleaching was observed). PL continued to increase for 16 h after treatment ended suggesting that the morphology continued to evolve in the absence of light. After 1 day, emission remained unchanged suggesting the new morphology is stable at room temperature. We believe this increased PL efficiency in primarily the result of reduced efficiency of trap-assisted recombination due to decreased interchain energy transfer.

1. Introduction

Light: its presence or absence during material processing affects the resulting material – sometimes in totally unexpected ways. Kaneko et. al., demonstrated numerically that superconductivity can be photo-induced in a Mott Insulator [1]. Alberi and Scarpulla showed theoretically that light can be used to suppress defect populations in semiconductors [2]. For conjugated polymers, emission properties can be altered in many ways such as by controlling solvent vapour, solvent quality, pressure, space, mechanical stretching, dewetting, or blending with other polymers [3]. Of particular interest for this paper are modifications to photoluminescence (PL) caused by light exposure.

The most well known effect of light on conjugated polymers is photobleaching or photo-oxidation [4]. In this process, involving both light and oxygen that has diffused into the polymer film, a small proportion of individual chromophores in a polymer after being excited into a singlet excited state decay non-radiatively into the long lifetime triplet state. Nearby oxygen (triplet state) molecules then react with these triplet state excitons leading to bond breakage and thus decreased photoluminescence emission. This is accompanied by a spectral blue shift due to the preferential quenching of lower energy chromophores as they spend more time in the excited state due to energy transfer from higher energy chromophores.[5]

Recent work has shown that light may also affect the conjugated polymers in additional ways that are unexpected. For example, Mark Dadmun found that illumination of conjugated polymers in solution with white light alters both their conformation and thermodynamics, resulting in significant decreases in both Kuhn length (b) and radius of gyration (Rg). [6] In later work they demonstrated (1) the poorer the solvent, the stronger the effect [7] and (2) the more photons absorbed, the stronger the effect [8]. Reiter's group examined the dewetting behavior of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)/polystyrene (PS) blend films. They found that the dewetting rate dramatically slowed down when exposed to white light compared to when the films dewetted in the dark.[9]

In related studies, the same group treated thin (t \sim 20–60 nm) films with white light in N₂. In contrast to expectations, they observed not a gradual decay in PL due to photobleaching, but rather an increase in PL emission of up to 40% for blend films MEH-PPV/PS (5%/95%) after an hour's excitation. [10] (A smaller increase was observed for pure MEH-

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PPV (t ~20 nm) films.) They attributed the increase to a planarization of the MEH-PPV chain upon exposure to light due to the formation of excitons on the chain (a condition that has been shown to alter photophysical properties in pyridine-based luminescent polymers [11]) This was supported by simulations which demonstrate that the exciton formation can force a planarization of poly(phenylenevinylene) (PPV) chains (in the excited state relative to the ground state), thus increasing chain rigidity and stiffness due to the delocalization of the exciton over several monomer units [12].

Concurrently, Lewis Rothburg's group has also investigated enhanced PL due to light in a variety of films ranging from single isolated MEH-PPV polymers embedded in a PS matrix to neat films. [13] However, the signature and underlying mechanism of the PL enhancement in Rothberg's work is totally different. Their technique is based on a model of MEH-PPV consisting of two basic types of chromophores that they characterize as "isolated" vs "aggregated". (Other groups characterize these two types of emitting species as "blue" vs "red" chromophores [14] (spectroscopy based classification), or with a view towards over all polymer conformation "extended" vs "tightlyfolded" [15] or "extended" vs "core" regions [16]) Aggregated chromophores have lower emissive yields but are favored by energy migration. Rothberg preferentially photobleached aggregated chromophores with $\lambda \sim 590 \text{ nm}$ light, blocking energy transfer to them, resulting in substantially improved fluorescence quantum yield as absorption and emission became concentrated in the "isolated" or "blue" chromophores. Unfortunately this deliberate photo-oxidation strategy does not increase photoluminescence yields in neat films as one would wish for OLED improvement.[13]

In summary, two methods of light processing have been shown to increase PL from MEH-PPV. The first method involving white light processing in N₂ of thin (20 nm) thick films and the second involving selective photobleaching of "aggregrated" chromophores under ambient conditions. In our work, we expose neat drop-cast films of MEH-PPV, such as are applicable for OLEDs, to light at their absorption maximum. All processing was done in N2 rich (oxygen poor) environment in order to minimize photobleaching. The use of thicker films allows us to slow the diffusion of oxygen molecules into the thin film, as well as to avoid interfaces effects (which can have a significant influence on the photophysics for films < 50 nm in thickness [17–19]. Drexhage showed that dielectric interface effects (related to molecular orientation at the interface) can change the measured lifetime by a factor of three [20] for films of thicknesses < 20 nm.) Drop casting also minimizes orientation effects seen in spin casting and the longer drying time suggests that the structure is closer to equilibrium. Using a laser confocal setup with lasers exciting the sample near the peak of the absorption spectra enables us to (1) vary the processing irradiance by over five orders of magnitude (90 W/m^2 to 0.2 MW/m^2), (2) collect PL from the same position in the sample, and (3) observe changes in PL emission concurrently with photo-processing. We observed up to a 400% increase in emission after photo-processing under optimal conditions. This was accompanied by changes in PL spectrum, and small changes in the magnitude of absorption. These changes were stable over time at room temperature.

2. Experimental section

MEH-PPV ($M_w = 369 \text{ K}$, $\delta = 6.26$, Aldrich Scientific)was dissolved in room temperature chlorobenzene at the concentration of 5 mg/cm³. N₂ was continually bubbled through the solution to reduce the concentration of residual oxygen. After passing through a 100 nm filter, the MEH-PPV solution was drop cast onto cleaned indium tin oxide coated glass to form ~4 µm thick films (Time of flight data was previously published [34]). After drying for 24 h at room temperature in an inert environment, films were placed in a high vacuum chamber for a further 12 h to remove any residual solvent. All processing was conducted under low-light conditions and samples stored for a considerable time in a dark N₂ rich environment to allow the films to adopt an equilibrium morphology.

Photo-processing was performed using our home built inverted vacuum confocal microscope. After purging, the chamber was filled with N₂ to slightly above atmospheric pressure and photo-processing commenced. Films were excited near the peak of their absorption curves using either continuous wave ($\lambda = 488$ nm), short pulse ($\lambda = 466$ nm, picosecond pulses at 10 MHz repetition) or ON/OFF excitation. Excitation light was focused (60x, NA = 0.85 objective lens (Nikon)) through a cover glass into the MEH-PPV film using to obtain ~1 µm² spot sizes (not tightly focused). Irradiance was varied over 5 orders of magnitude. Processing of areas larger than the confocal spot size (10 µm × 10 µm squares) was accomplished by slowly scanning the sample (peizo-electric stage (Physic Instruments)).

Samples were observed in epifluorescence mode using the same inverted vacuum confocal microscope allowing photo-processing to be paused at different points for lifetime, spectrum and intensity measurements to be completed. For confocal PL imaging, the sample was slowly scanned making use of the piezo-electric stage on which it is mounted. For lifetime measurements, 5 ps (FWHM), $\lambda_{\text{excite}} = 466 \text{ nm}$ (FWHM = 6 nm) pulses at 10 Mhz (PicoQuant, PDL 800-B laser driver with PicoQuant LDH-P-C-470 laser head) were used. Maximum excitation power on the sample was $\sim 6 \text{ kW/cm}^2$ (80 nJ/cm²) to ensure that non-linear effects such as exciton-exciton annihalation (EEA) were minimal [21]. The optical fiber collecting the light was directed to an SPCM avalanche photodiode (Perkin-Elmer) connected to a time-correlated single-photon counting card (SPC 630, Becker & Hickl). The instrument response function (IRF) was deconvoluted out of the measurements and the lifetime data was fit using SPCimage (Becker & Hickl). For μ -PL spectral measurements, the output optical fiber was directed to a spectrometer (BWTEK BRC111A). After all laser processing and other characterization work was completed in the N2 environment, the sample was removed from the chamber, u-RS spectra were recorded under ambient conditions using a WiTec alpha 300R confocal Raman microscope equipped with charge coupled device (CCD) with excitation provided by a He – Ne laser ($\lambda = 632.8$ nm).

3. Results

Fig. 1 presents time traces of the intensity of PL emitted from the MEH-PPV thin film taken during photo processing at a variety of irradiances. (Note time is log scale). At low power excitation $(0.5 \,\mu W/\mu m^2)$, black curve), the PL emitted by the sample decays exponentially as is expected for photobleaching. At the highest irradiance shown $(50 \,\mu W/\mu m^2)$, blue curve) the emitted PL first increases dramatically during the



Fig. 1. PL time traces of MEH-PPV films at selected irradiances. The average lifetime is shown at selected points. Time traces showing enhancement were recorded in a N_2 environment.

first 10 s of irradiation, and then from 40 to 100 s drops down to 70% of the initial emission intensity. At $5 \mu W/\mu m^2$ (red curve), an order of magnitude lower irradiance, the intensity increases for the first 50 and then gradually falls off at a much slower rate than at the highest power. At excitation close to threshold, $2 \mu W/\mu m^2$ (green curve), there is almost no increase in emission for 100 s, followed by a slow increase in emission over the next 8 min when it reaches a maximum before starting a slow decay. The threshold behavior suggests that there are two competing types of processes going on simultaneously: one type leading to enhanced emission and another (photo-oxidation) leading to decreased emission (the wavelength we are using, unlike that of Rothburg et al. [13], will not preferentially quench "aggregated" chromophores). Photo-oxidation, as the name implies, requires both light and oxygen. When the film is first exposed to light, triplet state chromophores react with nearby triplet oxygen resulting in an initial steep drop in intensity. If the concentration of dissolved oxygen is extremely low (one defect can kill emission from 400 repeat units [4], and can affect excitons within the order of a 40 nm radius [22]), oxygen will soon be exhausted. The rate of photobleaching will slow down as it is then limited by the rate of diffusion of new oxygen into the film. Evidence for this is that the survival time trace of PL emission is usually fit by a double or triple exponential decay [17]. Well above threshold, the strength of the enhancement mechanism completely overpowers photooxidation. Slightly above threshold, the rate of photo-enhancement balances the rate of photo-oxidation initially. However, once the supply of unreacted oxygen dries up, photo-bleaching slows down and there is a slow increase in PL emission. As oxygen slowly diffuses into the film, the emission of all films start to decrease due to photo-oxidation.

Superimposed on the time trace are our results for the fluorescence lifetime. The lifetime continuously increased as a function of excitation time. Starting at $\tau_{dark} \sim 0.35$ ns for the as-cast film, to $\tau_{maxPL} \sim 0.38$ ns at maximum emission to $\tau_{bleach} \sim 0.47$ ns at 70% photo-bleaching. The bulk of this change occurred after the emission intensity had started to decrease. We note that this is in contrast to the work of Botiz et al. [10] who observed a decrease in lifetime for their spin-cast films from $\tau_{dark} \sim 0.67$ ns to $\tau_{maxPL} \sim 0.35$ ns at maximum enhancement of 40%. This absence of a shortening lifetime suggests that a different mechanism of light enhancement is present in our case and will be discussed later in the text.

Fig. 2 summarizes the maximum enhancement obtained (left axis, squares) and the time required to reach it (right axis, diamonds) as a



Fig. 2. Maximum Enhancement of PL as a function of irradiance. The value (time) of maximum enhancement is shown by the black squares (blue diamonds). All light processing is done in a N₂. The enhancements are recorded at 0.7 nW excitation power. (inset) μ -PL image of the MEH-PPV film taken near maximum enhancement at different laser processing irradiances. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

function of irradiance. (Note the log scales) Although there was considerable variation between films, the maximum enhancement was found to be ~3.5 times with $50 \,\mu\text{W}/\mu\text{m}^2$ (50 MW/m², sun on earth is ~1 kW/m²). A clear threshold behavior is also seen. Below ~1 μ W/ μ m² $(\sim 1 \text{ MW/m}^2)$, photo-bleaching dominates. There is no photo-enhancement of emission. From 5 to $80 \,\mu\text{W}/\mu\text{m}^2$, PL emission is increases over 300% relative to the pristine film. At irradiances above $80 \,\mu\text{W}/\mu\text{m}^2$ the maximum attainable enhancement drops - perhaps due to another damage mechanism. As seen in the figure, the time to maximum enhancement decreases with increasing power. Interestingly the fluence (F $[J/m^2]$), irradiance multiplied by time, required for maximum enhancement was approximately constant over an order of magnitude (from 20 to $70 \,\mu\text{W/um}^2$) at $\sim 700 \,\mu\text{J/um}^2$. This suggests that in the range of powers in which photo-enhancement occurs, that, once the irradiance is sufficient, this is a cumulative affect based on number of photons – as has been seen for conformation in solution [8]. We tested this hypothesis by comparing the photo-enhancement obtained by continuous excitation (Ar laser), with that obtained using our picosecond pulsed laser and finally by on/off excitation. The maximum enhancement, and the fluence required to reach it was similar in all cases suggesting that the operating mechanism to increase PL is not a coherent effect.

Fig. 3 presents a transmission mode optical (white light) micrograph of the film taken after drawing 100 µm² squares by slowly scanning the focused laser beam. The left image is the composite image recorded by the CMOS RGB sensor. The right 3 images are the components recorded by its blue, green and red sensors. Considering first the RGB image, the bright squares are areas which have been photo-oxidized (the top of the vacuum chamber was removed and the pattern drawn under ambient conditions) while the darker squares were processed in a nitrogen environment. The differences in transmission are seen more clearly in the RBG composite images. Considering first the blue channel (390 nm < $\lambda < 510$ nm, $\lambda_{peak sensitivity} = 450$ nm, Fig. 3(b)), sensitive where MEH-PPV absorbs light but where PL is emitted, one can see in the pristine film, most light is absorbed by the pristine film. In the photooxidized regions, the quenching of fluorescence has been accompanied by a drastic decrease in absorption of light suggesting that the photooxidation of the polymer backbone not only reduces PL emission but also inhibits the ability of the polymer to absorb light (also observed by Orrit's group [23] on a single molecule level). In contrast, squares processed under nitrogen conditions where photo-enhanced emission was observed, appear darker then the pristine film suggesting that photo-processing has increased the absorption of the MEH-PPV film. (A similar result observed by [10].) This suggests that increased absorption may play a role in the PL enhancement with photo-processing. Skipping over the green channel (460 nm < λ < 590 nm, λ_{peak} $_{sensi-}$ $_{tivity}$ = 540 nm, Fig. 3(c)) which is sensitive in the region in which MEH-PPV both absorbs and emits light, consider the red channel (570 nm < λ < 850 nm, $\lambda_{peak sensitivity}$ = 600 nm, (Fig. 3(d))), where MEH-PPV emits PL but only very weakly absorbs. The pristine film is quite transparent. Areas that are photo-processed appear darker (reduced transmission) whether processing was conducted under ambient (photobleaching dominates) or nitrogen (photo-enhancement dominates) conditions. While it would be nice to conclude that the process leading to photo-enhanced emission results in greater absorption of red light, it is more likely that the decreased transmission is due to the photo-bleaching process in both cases.

To gain further insight into the origins for the enhanced emission, we employed optical spectroscopy. Fig. 4 shows the Micro-Photoluminescence (μ -PL) (a) and Micro-Raman (μ -RS) (b) spectrum of the film before, under conditions of enhanced emission and after 70% photo-bleaching. Comparing first the PL spectra, while there islittle change in the shape of the spectra for $\lambda > 595$ nm, for $\lambda < 595$ nm, spectra changes are quite dramatic. In the case of photobleaching, the shorter the wavelength, the greater the relative contribution of light in this region to the total emission. This is primarily the result of



Fig. 3. Transmission mode optical (white light) micrographs of the MEH-PPV film as recorded using a CMOS sensor (a) RGB image, (b) blue channel (c) green channel and (d) red channel. Numbering from top to bottom, squares 1 to 4 were processed under ambient conditions while squares 5 to 8 were processed in the N2 environment, Square 9 was not processed. Each 100 μ m² photoprocessed square was completed by scanning the focused 50 μ W/ μ m², λ = 466 nm laser beam at a

rate of $0.1 \,\mu$ m/s (squares 1 to 4) or $1 \,\mu$ m/s (Squares 5 to 8). Films processed under ambient conditions exhibited reduced PL while enhancement of PL was seen those processed in a N₂ environment. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. μ -PL (a) and μ -RS (b) spectrum of the MEH-PPV thin film before optical processing (black), at enhanced PL (red), and after photobleaching (blue). (inset) Percent of photobleaching(blue) and enhancement(red) as a function of wavelength. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

inefficient quenching of the sources of light in this wavelength region rather than an increase in absolute emission. We note that a nearly identical result was reported in 1997 for P3HT by Holdcroft's group in their foundational work on the interaction of oxygen with their conjugated polymer [22]. In contrast, in areas of enhanced emission, the shorter the wavelength, the lesser the relative contribution of light in this region to the total emission. This is primarily the result of an increased contribution to emission from sources of light in the longer wavelength region rather than a decrease in the absolute value of emission at the shorter wavelengths. This is evident from Fig. 4(inset) which plots the enhancement(photo-bleach) as a function of wavelength. Two things are evident. Firstly a strong wavelength dependence of both processes for $\lambda<595\,nm$ and their relative wavelength independence for $\lambda>595\,nm$. Secondly, the magnitude percentage change in emission is much more pronounced for $\lambda>595\,nm$ than for the shorter wavelengths.

Fig. 4b presents the Raman spectra under the above conditions. There are no significant differences in either the shape or the intensity of the characteristic bands of MEH-PPV, All the spectra display the Raman band frequencies at 1115 cm⁻¹ (mixture of C–C stretching [24] and C-H rocking motion [25]), 1282 cm⁻¹ (C=C stretching band of phenyl group [24]), 1312 cm⁻¹, 1582 cm⁻¹ (C–C symmetric stretch of phenyl group [2425]). Finally the C=C stretching band of vinyl group [25] while appearing at 1631 cm^{-1} in both the pristine and photobleached samples, is shifted $\sim 6 \text{ cm}^{-1}$ towards a shorter wave number in the case of enhancement. According to the literature, the triplet bands around 1582 cm^{-1} (that is at 1625 cm^{-1} and 1547 cm^{-1}) are particularly sensitive to changes in conjugation [24]. Unfortunately the two bands at 1547 cm^{-1} and 1582 cm^{-1} merge so the latter is not accessible. The slight shift of the 1625 cm^{-1} is compatible with the proposal of Botiz that photo-processing causes a slight planarization and hence lengthening of the conjugation [26]. We note; however, that our results here are differ from those of Botiz et al. [26] who observed weak 7.5 cm⁻¹ decrease in Raman shift of all the bands across the spectrum – we have only seen the shift for the weak triplet band at 1625 cm⁻¹. In summary, the Raman spectra suggests that there has been a slight increase in conjugation length – which is supported by the slight red shift of the spectrum.

4. Discussion

In this section we would like to discuss the origin of increased PL. During photo-processing there are competing processes that tend to either decrease or increase PL. The former has been observed by many groups and will not be discussed here while the latter has been reported by 2 groups: Rothberg [13] and Botiz [10], albeit with very different mechanisms being proposed. Availability of oxygen, along with the intensity and wavelength of light appear to be the key factors in determining the dominate mechanism. In Rothberg's work, long wavelength light was used to selectively photo-bleach aggregated chromophores that emit at relatively longer wavelengths with lower quantum efficiency. Photo-bleaching reduces energy migration from the higher efficiency emitting isolated chromophores [26] resulting in a higher efficiency blue shifted PL. It is noteworthy that they were unable to enhance PL with this method in the case of neat films of MEH-PPV most likely due to the existence of multiple energy migration pathways. While clearly the explanation presented by Rothberg is not applicable in our case (The shorter excitation wavelength used in our work excites both isolated and aggregated chromophores, and our emission is red not blue shifted), the idea that photo-processing reduces energy migration we believe is valuable in understanding our results.

Moving on the explanation of Botiz et al. [10], that the increase in PL is due to a planarization of the MEH-PPV chain upon exposure to light due to the formation of excitons. While we did not see a drastic change in lifetime during photo-processing, we have seen spectral red-

shift in the PL accompanied by a shift in the Raman of the C=C stretch mode of the vinyl group. It is possible that previously observed lifetime change was a result of interface effects due to reorientation of the MEH-PPV polymers during photo-processing. Although we accept that planarization is one source of the increased PL, we do not believe it is the dominate source of increased PL in our films.

We believe the dominate effect of photo-processing is to reduce the efficiency of trap assisted non-radiative recombination (oxygen quench sites) by slowing interchain energy migration through changes in the morphology of the thin film. In the following discussion we will make extensive use of the work of G. Scholes on long range energy transfer [27] and that of B Schwartz on how conformation and film morphology influence energy transfer and interchain interactions [28]. Energy transfer is facile in conjugated polymer films with energy migration via molecular resonance energy transfer (RET) taking place in just a few picoseconds. This allows excitations to flow efficiently to low-energy interchain species with lower quantum yield as well as quench sites resulting in reduced PL quantum yield. The 1/r⁶ nature of the Forster mechanism ensures that energy migration is highly dependent on conformation and chain separation/packing. Thus chain conformation and film morphology are key factors in determining the characteristics of PL. Numerous parameters - such as materials (e.g. polymer weight, polydispersity, defect density, solvent), deposition methods (e.g. spincasting, drop casting) and post-processing (e.g. heat annealing, solvent vapor annealing [29], dewetting) - affect the conformation, chain packing and hence interchain energy transfer and quantum yield. We can, however, make a few order of magnitude observations. Firstly the quantum yield in solution of MEH-PPV is around $\eta \sim 65\%$ [30]. When this solution is cast to form an MEH-PPV thin film, the quantum yield of the fresh film drops to $\eta \sim 10\%$ [31]. Over a period of ~ 10 days the quantum yield drops and stabilizes to $\eta \sim 3\%$ [31] most likely due to tighter chain packing. For MEH-PPV embedded in a polystyrene matrix, Orrit's group [23] measured a quantum yield $\eta \sim 10\%$ for commercial MEH-PPV while work done using specially synthesized low defect DOO-PPV suggests that under proper conditions the efficiency of low defect isolated molecules may be up to 65% in a PS matrix [32].

To a first approximation, in RET, $r_o \sim 4$ nm. Within a neat film, a single defect can quench chromophores within the range of up to 40 nm [4,22]. This suggests a total of about 10 jumps by the exciton before quenching. As the efficiency of these processes is strongly affected by the chain separation, even a small change in film morphology that leads to increased chain separation or less efficient chain overlap could have a drastic effect on RET, reducing access to quench sites. Thus, any processing mechanism that can modify film morphology so as to decrease interchain contact could result in a significant drop in quenching efficiency and hence an increase in PL. The absence of a significant change in PL spectrum, in particular the Huang-Rhys factor, suggests that after photoprocessing the emitting species have not changed. Thus we would like to suggest that the dominate affect of photo-processing, just as in blending benzothiadiazole with MEH-PPV [33] is to suppress trap-assisted recombination by interfering with the movement of excitons to traps/quench sites (not by reducing their quantity as in GaAs [2]). (Increased planarization of the MEH-PPV backbone may also reduce trap-assisted recombination efficiency). We note that the lifetime data is consistent with this explanation. Increased lifetime at enhanced emission may reflect a reduced non-radiative decay rate. The further increase in lifetime as photobleaching occurs is consistent with blocking of energy transfer channels (by photo-bleaching) to weakly emissive aggregated sites [17].

Finally we consider the stability morphological changes leading to enhanced emission. Fig. 5 plots the PL intensity (normalized to the unprocessed film's PL intensity) as a function of time after photo-processing ended. Firstly, after 24 h, PL emission is stable for over 100 days. Secondly, during the first 24 h, the PL intensity continues to increase (up to 50%) as the polymer settles into its new equilibrium conformation. There seems to be some slow processes occurring on the



Fig. 5. Stability of PL emission after photo-processing completed. The temperature was maintained at 23 C (inset) μ -PL images of the film taken after photo-processing completed. Bright spots are the locations of photo-processing. The top row was taken at maximum enhancement while for the bottom row excitation was stopped before maximum enhancement obtained.

time frame of hours that act to further inhibit energy transfer to embedded traps or possibly weaker emissive species. (Friend's group in 1995 [31] commented on how PL emitted by MEH-PPV films dropped over a 10 day period before stabilizing)

Reduced energy migration is clearly a two edged sword [28] when it comes to electric devices. Reducing the ability of excitons to diffuse or hop to a defect site results in higher PL quantum yield, but simultaneously limits the mobility of holes and electrons in the thin film resulting in lower carrier mobilities. Nevertheless, we believe that this technique of photo-processing has potential application in device manufacture. As previously mentioned, and discussed by Schwartz [28] there is a fundamental trade-off involved in optimizing the properties of conjugated polymer based LEDs. On the one hand, films with lower average degrees of interchain contact have higher luminescent quantum yields. On the other hand, films with a higher degree of interchain interactions, have much higher carrier mobilities and thus can support higher working currents. Ideally one would like to have a graded morphology that varies continuously from the electrodes to the central recombination zone, I.e, a high rate of interchain energy transfer near the electrodes and a low rate of interchain energy transfer at the central recombination zone. This is exactly what can be done through optical processing by applying focused excitation light directed at the center of the device.

5. Conclusion

A 400% increase in PL emission by photo-processing in a N2 environment at optimal powers $(50 \,\mu W/\mu m^2)$ using wavelengths of light close to the absorption peak of MEH-PPV has been observed. This effect was found to be strongly dependent on excitation irradiance, with no enhancement seen below a critical irradiance $(1 \mu W/\mu m^2)$ and rapidly diminishing returns at higher irradiance (> $80 \mu W/\mu m^2$). From 20 to 70 µW/µm² irradiance, fluence determined the maximum enhancement. Enhancement was accompanied by a red-shift in the PL spectrum suggesting greater planarization of the polymer backbone which was supported by a slight shift in Raman frequency of the C=C stretch mode of the vinyl group. Similar effects were observed using picosecond, gated and continuous wave excitation suggesting that this effect is related to multiple single photon absorption rather than a multiphoton coherent process. Absorption of blue light was found to increase in photoprocessed films. We believe that this increased PL efficiency is primarily the result of a reduced efficiency of trap-assisted recombination due to morphological changes that increase chain

separation resulting in decreased interchain energy transfer. The stability of the enhancement of PL suggests that the changes become locked in at room temperature. We note that enhancement was also seen under ambient conditions (at similar fluence), but was significantly less due to the concurrent and competing effect of photobleaching.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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