

# Large Enhancements in Optoelectronic Efficiencies of Nano-plastically Stressed Conjugated Polymer Strands

Kuang-Po. Tung,<sup>†</sup> Chein-Chung Chen,<sup>†</sup> Peiwei Lee,<sup>†</sup> Yi-Wei Liu,<sup>‡</sup> Tzay-Ming Hong,<sup>‡</sup> Kuo Chu Hwang,<sup>§</sup> Jui Hung Hsu,<sup>⊥</sup> Jonathan David White,<sup>¶</sup> and Arnold Chang–Mou Yang<sup>†,\*</sup>

<sup>†</sup>Department of Materials Science and Engineering, <sup>‡</sup>Department of Physics, <sup>§</sup>Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan,

<sup>⊥</sup>Department of Materials and Opto-electronics Science, National Sun-Yat-Sen University, Kaohsiung 804, Taiwan, and <sup>¶</sup>Department of Optoelectronics, Yuan Ze University, Taoyuan 320, Taiwan

Conjugated polymers (CPs) have gained considerable interest owing to their unique optoelectronic properties, low cost, and ease of processing that promise an important role in future lighting, photovoltaics, and microelectronics.<sup>1,2</sup> With the  $\pi$ -orbitals extending along the backbone, they harvest photons to generate electron–hole pairs<sup>3–18</sup> that are known to interact strongly with chain vibrations (electron–phonon interaction)<sup>11–18</sup> to result in self-trapping<sup>3,17,18</sup> and retarded charge recombination. With the carrier mobility significantly reduced,<sup>3,6–10,19,20</sup> nonradiative pathways may dissipate up to well above 90% of the total absorbed energy.<sup>4,6,8</sup> Low quantum yields have long been the major hurdle for viable polymer devices.

The driving force of the electron–phonon interactions may be linked to the elevated local steric interactions (Coulomb energies) introduced amid the freshly formed excited states and the surrounding backgrounds.<sup>5,12,14,15</sup> In abating the energy increase, the excited states, extending across several monomer units,<sup>5,8,11,12,14–16</sup> may interact with chain vibrations to accumulate local molecular deformations with which the excited species were immobile for phase-conserving intrachain migration.<sup>3</sup> Flexible chains are a prerequisite for this type of interactions, as in the case of ordinary stress-free linear polymers. However, if the molecules are stretched such that the required local chain motions, such as rotations, are hindered, the Franck–Condon type interactions would be restricted and drastic enhancements of optoelectronic efficiencies may emerge as a result.

In fact, stretching CPs into large strains with negligible relaxations can be done by blending them into an optically inert glassy

**ABSTRACT** The photoluminescence (PL) of well dispersed molecules of a conjugated polymer, poly[2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylene-vinylene] (MEH-PPV), in an optically inert matrix manifested dramatic increases when the individual molecular strands were fully stretched. The PL increase rose with stretching and may reach several folds when the mechanical strain of the matrix polymer went beyond 550%. Strong polarization effects indicate that stretching individual polymer chains was responsible for the PL enhancement. This effect was attributed to suppression of electron–phonon interactions in the stress-rigidified polymer chain segments and may be useful for efficiency-enhanced polymer-based optoelectronic devices.

**KEYWORDS:** conjugated polymers · photoluminescence · optoelectronic efficiency · stress effects · electron–phonon interactions · molecular constraints

polymer matrix and stretched into local deformation zones (LDZs),<sup>21,22</sup> where the local strains vary from 60% to more than 500% as predetermined by the matrix chain entanglement density.<sup>22–29</sup> When in dilute concentrations, the dispersed CPs would likely deform congruently with the matrix and large stresses can be applied effectively to the backbones of the dispersed CP. Using this method, we have successfully unveiled the effect of mechanical stretching that gave rise to dramatic enhancements in PL efficiencies. This important property can be further exploited for applications in polymer optoelectronic devices.

## RESULTS AND DISCUSSIONS

The experiment was conducted by stretching poly[2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylene-vinylene] (MEH-PPV) dispersed in polystyrene (PS) or poly(2,6-dimethyl-1,4-diphenylene oxide) (PPO), both optically inert. The choice of PPO as a matrix candidate was based on the consideration that it was fully miscible with PS, thus offering a similar level of MEH-PPV dispersion prerequisite for fair comparisons between the data based on these

\* Address correspondence to acyang@mse.nthu.edu.tw.

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two types of polymers. The MEH-PPV weight fractions ( $c$ ) ranged from 0.1 to 10.0 wt %. The thin film samples containing MEH-PPV molecules developed local deformation zones (LDZs) upon stretching beyond a critical total strain of  $\sim 0.5\%$  (Figure 1b,c). The local strain ( $\varepsilon$ ) in the LDZs is approximately equal to  $(l_e/d_e - 1)$  where  $l_e$  is the average molecular contour length and  $d_e$  is the distance between adjacent entanglements.<sup>22</sup> For a typical PS,  $\varepsilon$  in the LDZs is around 300%, but one can increase it by adding low molecular weight diluents to the polymer.<sup>22–29</sup> For PPO, the  $\varepsilon$  in the LDZs is around 60% due to the tighter chain entanglement structure.<sup>22,23,27</sup> The local strain outside the LDZs in the film remains equal to the critical strain,  $\sim 0.5\%$  for PS or  $\sim 1\%$  for PPO.<sup>22</sup> In the stretched samples that contained MEH-PPV, the distribution of the LDZs and the microstructure of the stretched materials were virtually identical to that of the matrix polymers and independent of  $c$  (Figure 1b,c). However, the surface depression of the LDZs determined from AFM was found to decrease modestly with  $c$  (not shown), indicating that MEH-PPV participated to the local deformation. In the concentrated films ( $c \geq 5.0$  wt %), tiny aggregates of MEH-PPV (diameter  $< 0.1 \mu\text{m}$ ) were present even in the LDZs (Figure 1f). It indicates the poor dispersion of MEH-PPV in these samples and that the local deformation of the matrix was not able to break them. Nevertheless, for  $c \leq 1$  wt %, the dispersion of MEH-PPV appeared to be good under the electron microscope.

The PL spectra of the samples without stretching (total applied strain ( $e$ ) = 0% in Figure 2a–d,) manifested a prominent intrachain emission at  $\sim 550$  nm that blue-shifted relative to that at  $\sim 565$  nm of the pristine MEH-PPV ( $c = 100$  wt %) due to the dilution of the MEH-PPV molecules.<sup>20,30</sup> For dilute samples ( $c \leq 1$  wt %), the intermolecular emission was barely visible as a shoulder at  $\sim 600$  nm.<sup>9,10,19</sup> For concentrated samples ( $c \geq 5.0$  wt %), the intermolecular emission was strong with intensities comparable to the intramolecular emissions. The PL features below 500 nm were artifacts from background and neglected. The intensity of the intrachain emission increased with  $c$ . However, when normalized with  $c$ , it decreased significantly as the MEH-PPV concentration increased (not shown), indicating the strong effect of intermolecular energy dissipation pathways.<sup>6–10</sup>

Upon stretching, considerable PL enhancement was observed in the dilute samples ( $c \leq 1$  wt %). The PL intensities increased with the total applied strain  $e$  (Figure 2a,b), consistent with population increase of the stretched MEH-PPV molecules. The shape of the PL spectra, however, was largely unchanged. Under a fluorescence microscope, the LDZs appeared bright against the dark background. In contrast, no enhancement was observed in the concentrated samples ( $c \geq 5.0$  wt %) where the deformations gave rise to only small variations of the emissions spectra (Figure 2c,d).

Recalling the MEH-PPV aggregates prevalent in the TEM micrograph of the LDZs (Figure 1f), the micronecking process of the PS matrix during stretching<sup>22–29</sup> was obviously incapable to break down these aggregates to stretch the MEH-PPV chains therein. Hence no deformation-induced effect was observed in these concentrated samples. In contrast, no MEH-PPV aggregates were observed in LDZs of the dilute samples (Figure 1e). Other than the presence of the CP aggregates, the LDZs in all samples (Figure 1d–f) appeared to have very similar structure under TEM. Furthermore, for all samples including the dilute and concentrated, the PL excitation spectra (PLE) that illustrated the absorption behavior remained unchanged with the deformation (Figure 3a).

The stress-induced enhancement in the dilute samples rose further when the PS blends (b-PSs), of PS2M and a low molecular weight PS diluent, were used for the matrices (Figure 2e). In these samples, the local strain  $\varepsilon$  in the LDZs increased with the diluent fraction  $(1 - \chi)$  and eventually reached 530% at  $(1 - \chi) = 0.5$ .<sup>25</sup> Conversely, when the molecular stretching in the LDZs was reduced to  $\varepsilon \approx 60\%$  in the PPO matrix, the PL enhancement diminished<sup>22,23</sup> (Figure 2f). Still, when the formation of LDZs was switched off and only uniform deformation took place ( $\varepsilon = e$ ) in the matrix of the fully plasticized PS (p-PS), the PL manifested no increases for all strains up to  $e \approx 25\%$  when the supporting copper grids broke (not shown).

All these experiments illustrated that the PL enhancement arose from the stretched MEH-PPV molecules within the deformation zones. The MEH-PPV in the film regions outside the LDZs where the molecular stretching was limited to a very small local strain  $\varepsilon \approx 1\%$  did not contribute to the PL enhancement. The PL enhancement arising from stretching in the LDZs was strongly dependent on the level of molecular stresses operative in the CP chains manifested by the local strain  $\varepsilon$  of the LDZs. It increased with  $\varepsilon$  and diminished as  $\varepsilon$  became smaller than a threshold of around  $\varepsilon = 60\%$ . This stretching effect was operative only in the dilute samples where the MEH-PPV molecules were well dispersed. In the concentrated samples where the MEH-PPV molecules aggregated prevalently, the molecular stretching induced by the plastic flows of the matrix PS had yielded no effects.

The effect of stretching in the dilute samples was further examined by using a focused laser beam (spot size  $\approx 3 \mu\text{m}$ ) with a detector positioned off-axially to probe the local regions of the stretched samples using three different excitation wavelengths (405, 488, 532 nm) in polarized conditions. The intrachain emission was found significantly enhanced in the LDZ regions as compared to that in the film outside the LDZs. The enhancement was the largest, to several folds of that without deformations, when both the laser polarization and the emission detection were aligned parallel to the stretching ( $V-v$ , in Figure 3b).

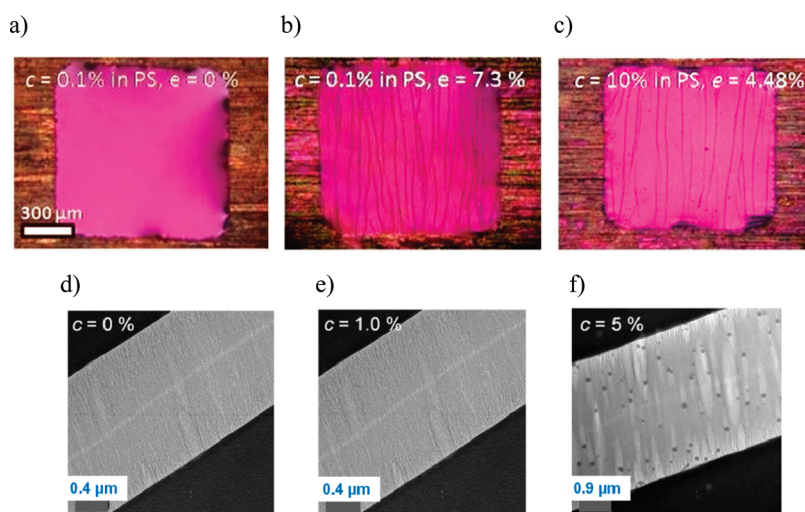


Figure 1. Optical micrographs of (a) a typical thin film sample ( $c = 0.1\%$  in PS2M) before stretching, and (b,c) stretched samples where the local deformation zones (LDZs) grew perpendicular to the drawing direction (horizontal). TEM micrographs of the LDZs in (d) the neat PS2M film ( $c = 0$ ), (e)  $c = 1.0\%$  in PS2M, and (f)  $c = 5.0\%$  in PS2M.

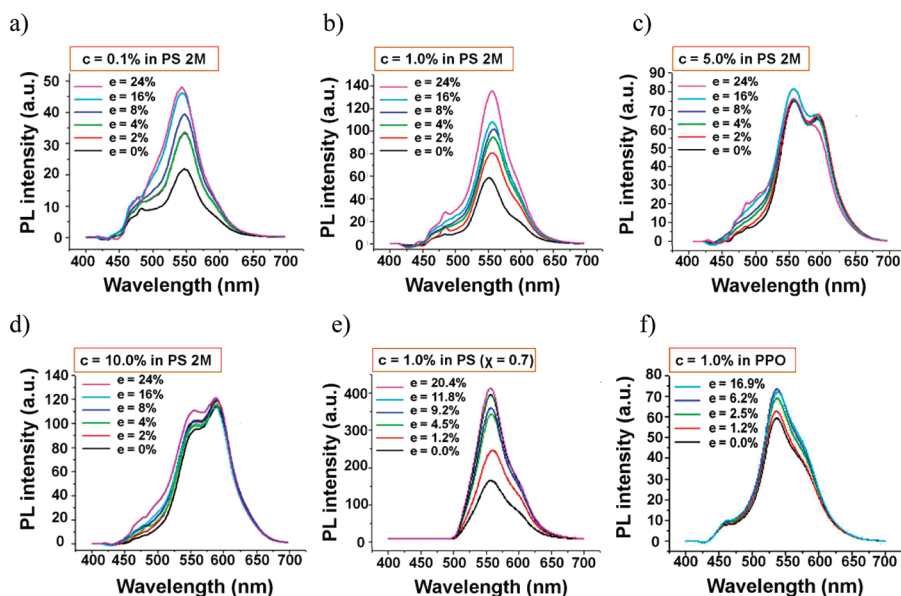


Figure 2. PL spectra as a function of the total applied strain  $e$  for (a)  $c = 0.1\%$  in PS2M, (b)  $c = 1.0\%$  in PS2M, (c)  $c = 5.0\%$  in PS2M, (d)  $c = 10.0\%$  in PS2M, (e)  $c = 1.0\%$  in the PS blend ( $\chi = 0.7$ ), (f)  $c = 1$  wt % in PPO.

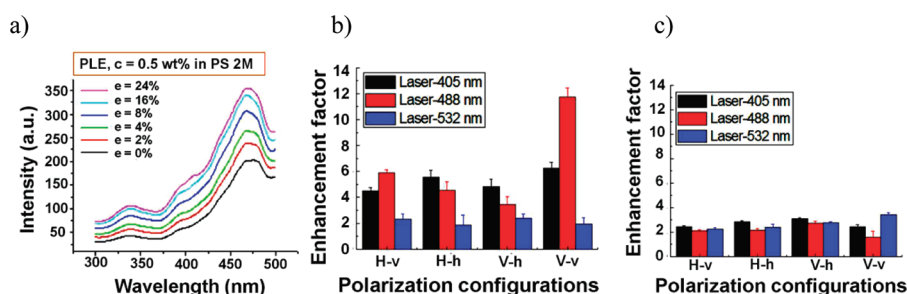
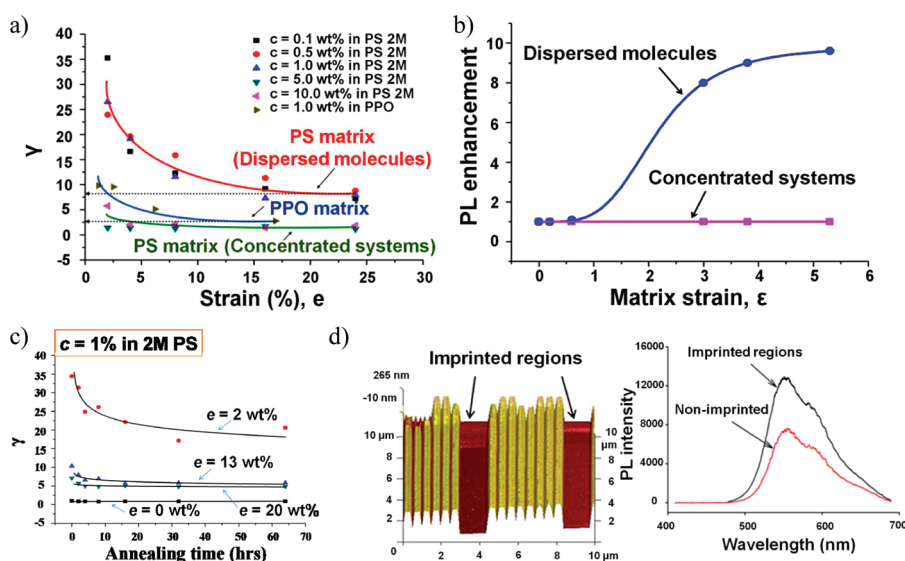


Figure 3. a) The typical PLE spectrum versus the total applied strain  $e$  in  $c = 0.5\%$  in PS2M, b,c) the enhancement factors of the PL emissions from the LDZs to those from regions outside the LDZs (area integration) determined by microscopic laser probing for the intrachain emission (b) and interchain emission (c).

The conjugated polymer chains in the LDZs were taken to be oriented along with the matrix polymer chains.

Since the matrix polymer chains in the LDZs were aligned to the stretching direction, as shown for



**Figure 4.** (a) The apparent enhancement factor  $\gamma$  vs  $e$  for various  $c$ 's and matrices, (b) the extrapolated PL enhancement factor vs the matrix strain  $\epsilon$ , (c) The decrease of PL enhancement by stress relaxation *via* physical aging (90 °C in N<sub>2</sub>), (d) (Left) nanoimprinted film of concentrated MEH-PPV in PS2M (25 wt %), and (right) the confocal micro-PL spectra of the imprinted and nonimprinted regions.

example, by selected area electron diffraction patterns within the LDZs,<sup>22,31</sup> it thus indicates that the PL enhancement was the largest along the chain stretching direction. In contrast, the interchain emission from the LDZs demonstrated no significant emission increases compared to the outside film. The polarization behavior dwindled as the excitation wavelength shifted away from the optimized absorption peak of 488 nm (Figure 3a) to higher (405 nm) or lower (532 nm) photon energies. (Figures 3b,c).

The magnitude of the PL enhancement was estimated quantitatively by normalizing the intrachain emission intensities (at  $\sim 550$  nm) determined by the PL spectrometer to the LDZ fraction ( $\phi_{\text{LDZ}}$ ) in the stretched samples. The LDZ fraction ( $\phi_{\text{LDZ}}$ ) is readily shown to be  $(e - e_c)$  for area estimates. An apparent enhancement factor  $\gamma$  is defined as  $\gamma \equiv I_{\text{LDZ}}/I_b$  where  $I_{\text{LDZ}}$  and  $I_b$  represent the PL emission intensities per unit area from LDZ and the bulk film outside the LDZs, respectively. The enhancement factor  $\gamma$  can be shown to be  $\gamma = (I_t/I_b - 1 + \phi_{\text{LDZ}})/\phi_{\text{LDZ}}$  since the total PL intensity ( $I_t$ ) was approximately a linear sum  $I_t = I_{\text{LDZ}} + I_b(1 - \phi_{\text{LDZ}})$ . A light extraction effect from the LDZ edges also contributed to  $\gamma$ , which, however, can be removed by extrapolating  $\gamma$  to large  $e$  values (Figure 4a) where the LDZ population had saturated and the extraction effect became less important compared to the stretch-induced enhancements.<sup>28,29</sup> This approach was verified by detailed calculations of  $\gamma$  values for each strain increment ( $e_i, e_{i+1}$ ). The PL enhancement was found to be independent of  $c$  in the dilute regime (Figure 4a) and increased with  $\epsilon$  for  $\epsilon \geq 60\%$ , reaching  $\sim 8$ -fold at  $\epsilon = 300\%$ , and finally leveling off to  $\sim 10$ -fold for  $\epsilon \geq 550\%$  (Figure 4b). The magnitudes of the

enhancement were comparable to that manifested by the micro-PL behavior shown in Figure 3b.

The PL enhancement decreased rapidly when the LDZs underwent partial stress relaxation<sup>24</sup> in an aging experiment at 90 °C (Figure 4c). The observed decreases of PL enhancement without significant creep implied the dominant effect of the stress, rather than strain, in the stretch-induced PL enhancement.

The physical origin of the PL enhancement was attributed to suppression of electron–phonon interactions in the stress-rigidified MEH-PPV chains.<sup>3</sup> Following the Franck–Condon vibronic scheme, the segmental motions for accumulating local deformations conducive for self-trapping were more restricted in the stress-rigidified polymer chains. Consequently, dramatic enhancement of quantum efficiencies emerged. In a close analogy to the stretch-induced PL enhancement, single polydiacetylene chains had demonstrated the 1D quantum wires behavior when confined in the monomer crystals.<sup>17,18</sup> Likewise, charge conductivity of polyaniline films was observed to increase more than an order of magnitude when fully stretched.<sup>32</sup> Furthermore, the binding energies of the trapped transient photoexcited polarons in MEH-PPV ranged from  $\sim 0.09$  to 0.22 eV,<sup>10,12,13</sup> comparable to the chain vibration energy ( $\sim 0.2$  eV) determined from photoinduced IR-active vibrations.<sup>12</sup> The absence of spectral changes in convoy with the PL enhancement elucidated the fact that the activation energies of the hereby proposed traps were approximately 1 order of magnitude less than those of photoexcitations. Strain-induced PL enhancements thus in general were not necessarily accompanied with spectral changes.



Furthermore, stretching CP chains may remove some of the chain distortions that create traps for the photoexcited states, thus possibly contributing to the PL enhancement observed here. The resulted increase of conjugation lengths, however, would generally give rise to spectra shifts unless the shortest conjugation lengths are long enough and the exciton lifetimes do not change significantly. Recently, a complete switch-off of exciton quenching along with a huge PL enhancement was observed by stretching *via* dewetting the MEH-PPV chains at a Fermi level-aligned interface on bare silicon.<sup>33–35</sup> It implied that the electron–phonon interactions involved during exciton formation and thus the exciton lifetimes had been altered considerably by the applied molecular stresses. Hence, although potentially important, the magnitude of this contribution from conjugation length enhancement still requires more work to unveil, for example, *via* in-depth investigation of the CP chain conformations and their deformation behavior in thin cast films.

The work unveiled here highlights the stress-induced enhancement of the intrachain emissions. Nonetheless, the interchain interactions are generally crucial in the optoelectronic performance of CPs, hence should be carefully considered in the light of the stretching effect. In general, stretching tends to reduce interchain interactions. This effect, however, had only contributed marginally to the PL enhancement in the dilute CP samples (Figure 3b,c), obviously due to the relatively small fraction of the interchain emission before stretching (Figure 2a,b). On the other hand, stretching may result in new interchain interactions by aligning the MEH-PPV chains, particularly in the concentrated samples if deformations in the molecular scales were effective. Although the concentrated samples may provide important information regarding the stretching effect on the interchain interactions, the mechanical force incurred by the plastic flows of the matrix produced only very limited deformations to most of the MEH-PPV chains, as evident from the intact MEH-PPV aggregates in the LDZs (Figure 1f), rendering the quest impossible. Nevertheless, the herein reported results may serve as new grounds for further exploring the optoelectronic behavior of CPs using alternative methods for stretching, for example, thin film dewetting,<sup>30,33–35</sup> that can

stretch concentrated CPs into large deformations. Owing to the insignificant molecular stresses applied to the individual MEH-PPV chains and the robust nonradiative pathways provided by the interchain interactions, for example, absorptions of the intrachain emissions through excimers and exciplexes,<sup>10</sup> the stress-induced PL enhancement diminished in the concentrated MEH-PPV systems.

Finally, the stretching-induced PL enhancement may be exploited for real applications. For example, a large increase in PL emissions without spectral changes was manifested in nanoimprinted films of concentrated conjugated polymers (Figure 4d).<sup>36</sup> Since such a method of inflicting patterned and controlled molecular deformations is compatible with the fabrication of solar cells and electroluminescence devices, promising prospects due to this stress-induced enhancement for optoelectronic applications are strongly implied.

## CONCLUSIONS

In summary, a large molecular constraint effect due to mechanical stretching was observed that produced large PL enhancement when well-dispersed MEH-PPV molecules were stretched. The stretching-induced PL enhancement increased with the molecular stresses and may reach several folds of that of the nonstretched polymer. Strong polarization effect was observed in the intrachain emission that was enhanced in the molecular stretch direction. On the other hand, little enhancement was observed in the interchain emission that generally remained isotropic. This indicates that the enhancement was arising from the stretching of molecular segments rather than variations in interchain packing. Stress relaxation was found to have a strong and immediate effect on the PL enhancement indicating that the operative stress, rather than strain, was the cause of the deformation-induced enhancement. Along with the PL enhancement, no spectra changes were detected, however. The stretching-induced effect was attributed to restricted segmental rotations of the molecularly constrained polymer chains under large stresses where the electron–phonon interactions were suppressed. The results offer important insights for making efficiency-enhanced polymer-based optoelectronic devices.

## EXPERIMENTAL SECTION

Generally, a high molecular weight PS, PS2M ( $M_w = 2\,000\,000$  g/mol,  $DPI \leq 1.3$ ), was used as the matrix. Nonetheless, for probing the higher strain behavior of the stretching effect, PS matrices of diluted entanglement networks (b-PSs)<sup>25</sup> were employed. Preparation of the b-PSs was done by blending PS2M with a low molecular weight PS ( $M_w = 2\,032$  g/mol,  $DPI \leq 1.06$ ). In addition, for exploring the lower strain behavior, a fully plasticized matrix

(p-PS) was prepared by blending PS2M (of weight fractions  $\chi = 0.55$ ) and a PS oligomer ( $M_w = 760$  g/mol,  $DPI \leq 1.1$ ). The PSs were obtained from the Pressure Chemical Co. while the MEH-PPV ( $M_n = 150\,000$ – $250\,000$  g/mol,  $M_w/M_n \approx 5$ ) and PPO ( $M_w = 244\,000$  g/mol,  $M_w/M_n \approx 3$ ) were purchased from Sigma-Aldrich Chemical Co., all used as received.

Thin film samples (thickness  $\tau \approx 0.5$   $\mu\text{m}$ ) were prepared by spin-casting on a clean silicon wafer from the polymer solution

in a solvent of equal-parts toluene, tetrahydrofuran, and cyclohexanone. Dust and undissolved particles were filtered (0.2  $\mu\text{m}$  pores). The film was subsequently floated off on a water surface and transferred onto a piece of copper grids (Figure 1a) and stretched uniaxially on a strain jig after the solvent treatment for enhanced bonding to the copper grid (Figure 1b,c).<sup>22</sup> The PL spectra were recorded in a PL spectrometer (Perkin-Elmer LS-55) excited at a relatively low wavelength 350 nm for reduced background noises. The data were checked using another PL spectrometer (Horiba-Jobin Yvon FluoroMax-3) via an integrating-sphere method.<sup>4,37</sup> The topography and microstructure of the stretched samples were studied using an atomic force microscope (AFM, Digital Instrumental, Nanoscope IIIa and Dimension 3100) and a transmission electron microscope (TEM, JEOL JEM-2010). A confocal PL microscope (Leica SP2-Confocal) was used to explore the microscopic luminescent properties of the samples.

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