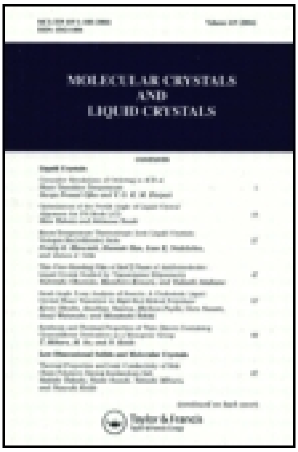

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Spectral Redistribution of Waveguided Emission in BEH-PPV Films

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We report on spectral redistribution of the photoluminescence (PL) emission from the edge of thin-film planar waveguides of the conjugated polymer BEH-PPV [Poly(2,5-bis(2'-ethyl-hexyl)-1,4-phenylenevinylene] induced by self-absorption in the polymer film. The PL spectra present drastic changes and displace to longer wavelengths with increasing self-absorption. We observe an enhancement of the absolute PL intensity at longer wavelengths, which was interpreted as due to re-emission of self-absorbed photons. The significant efficiency for the PL re-emission suggests the use of self-absorption as a mechanism for tuning the emission into the near infrared.

Keywords BEH-PPV; Photoluminescence; Self-absorption; Thin-film waveguides; Spectral redistribution; Conjugated Polymers.

INTRODUCTION

Conjugated polymers have attracted considerable attention because of their potential applications as organic light emitting diodes [1], solar cells [2] and displays [3]. Conjugated polymers could also be used as solid state laser materials. Lasing in thin films of conjugated polymers incorporated in distributed feedback (DFB) [4,5] and micro-cavity [6,7] structures have been recently reported. Broad-range emission wavelength tunability has not yet been achieved in a single polymer film, but is a desirable property in electro-optical device applications. Here we investigate the effect of self-absorption in conjugated polymer thin-film waveguides. It leads to a spectral redistribution, with a shift of PL emission towards longer wavelengths with a relatively low loss in PL efficiency. This could perhaps be useful for extending the PL emission into the near infrared.

SAMPLE AND EXPERIMENTAL DETAILS

Thin-film planar waveguides were fabricated by spin casting BEH-PPV at 2000 rpm from 10.5 mg/ml xylene solution onto SiO_2/ Si wafers. The wafers were primed with hexamethyldisilane prior to the BEH-PPV deposition in order to promote its spreading. To avoid any possible non-uniformity near the edges, the silicon substrates were cleaved before the optical measurements.

During all measurements the sample was maintained under vacuum inside a cryostat to avoid any photo-oxidation effect. The excitation source was a CW argon-ion laser emitting at 488 nm, which is near the absorption maximum of BEH-PPV. A cylindrical lens was used to shape the laser beam into a stripe with a width of ~ 620 μm. The length of the stripe was controlled by an adjustable slit. The pump beam was normally incident on the sample with intensities lower than 20 mW/cm^2. The PL emission was collected from the cleaved edge, focused into a 0.75 m monochromator, and detected by a photomultiplier.

RESULTS AND DISCUSSIONS

Room temperature PL spectra for various distances *X* of the laser stripe from the sample edge are shown in Figure 1a.

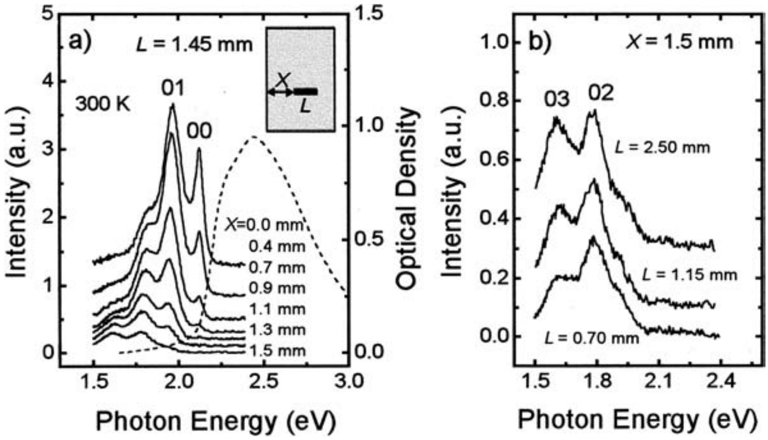

FIGURE 1 a) Room temperature PL spectra from the edge for various *X*. The dashed curve is the BEH-PPV absorption spectrum. The inset shows a frontal view of the film with the black rectangle representing the excitation region of length *L* at normal incidence. b) PL spectra at *X* = 1.5 mm for different excitation lengths *L*.

We observe that increasing the distance *X* from 0 to 1.5 mm the PL spectrum dramatically changes, with a characteristic shift to lower photon energies E. The intensity of the more dominant 00 and 01 peaks gradually vanish with increasing *X*. Light traveling through the unpumped region of length *X* experiences high losses due to self-absorption in the polymer film. Note that the absorption spectrum in Figure 1a (dashed curve) has a relatively large tail down to the energy region of the 00 and 01 PL peaks. For large values of *X* only the 02 and the 03 PL peaks remain, since they are far from the absorption tail (see Figure 1b). For sake of clarity the spectra in Figure 1a were shifted in intensity. Therefore a direct comparison among them is difficult.

However, it should be stressed that the absolute PL intensity for the 02 and 03 vibronic peaks *increase* with X, becoming ***higher*** than the spectrum at $X = 0$ mm. This cannot be explained only by self-absorption in the polymer waveguide. We suggest that at longer wavelengths and larger values of X the PL enhancement is caused by the re-emission of the radiation absorbed in the unpumped region, leading to a spectral redistribution of the PL. Each time the self-absorption/re-emission process occurs a Stokes shift takes place, shifting the PL emission to longer wavelengths. At long wavelengths, where the self-absorption is small, this results in an effective increase in PL intensity. Since each absorption-emission step has quantum efficiency less than unity, the integrated area of the PL spectrum is reduced with increasing X, but less than if the re-emission process were absent. The integrated area of the PL spectrum at $X = 1.5$ mm is only 5 times less than at $X = 0$ mm, suggesting a significant PL efficiency for the re-emission process.

Figure 1b shows the PL spectra obtained for three representative excitation lengths at a fixed $X = 1.5$ mm. The larger the value of L, the larger the PL enhancement for the peak 03. This result corroborates our re-emission hypothesis. Larger L-values raise the amount of photons emitted toward the unpumped region. For the same distance X, the absorption increases with increasing L (since there is self-absorption in the pumped region as well) and therefore the re-emission effect is enhanced.

In Figure 2 we plot the optical density (OD) of the unpumped region of various lengths X as a function of the photon energy. The inset displays the dependence of the optical density on X for three representative energy values, indicated by the arrows. The OD curves were obtained taking the PL spectra at X = 0 mm as a reference. As expected, the OD increases with X. At lower energies, the OD becomes negative, corresponding to the energy region where the spectral redistribution leads to a higher PL intensity than with X = 0 mm.

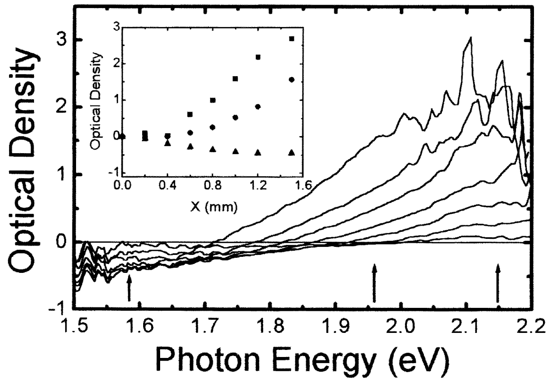

FIGURE 2 Optical density *versus* photon energy for various distances X (0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.5 mm); the inset shows the behavior of OD as a function of X for E = 2.15 eV (squares), 1.96 eV (circles) and 1.58 eV (triangles).

Note in Figure 2 that the energy corresponding to OD = 0 for each curve decreases with increasing X. This can be qualitatively explained by the competition between the absorption (positive OD) and the "gain" (negative OD, due to spectral redistribution) regimes. The competition becomes clearer in the inset of Figure 2, comparing the OD dependence on X for energies corresponding to the absorption, gain, and intermediary regimes. For the curve at 2.15 eV where the absorption dominates, the OD increases linearly for higher X, with a slower increase for X lower than 0.4 mm. At 1.96 eV, larger values of X are needed for the absorption to overcame the spectral redistribution effect. At 1.58 eV the "gain" increases linearly with *X*, as expected, but saturates at higher values of *X* where the absorption becomes significant.

CONCLUSIONS

We observed that controlling the position of the photoexcited region from the sample edge gives us the possibility to have a spectral redistribution of the PL emission due to a self-absorption effect. The significant PL efficiency for the re-emission process makes the self-absorption effect useful as a wavelength tuning mechanism for polymer optoelectronic devices.

Acknowledgments

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References

[1] J H Burroughes, D D C Bradley, A R Brown, R N Marks, K Mackay, R H Friend, P L Burn, A B Holmes, Nature **347**, 539 (1990).
[2] N S Sariciftci, L Smilowitz, A J Heeger, and F Wudl, Science **258**, 1474 (1992).
[3] S Tasch, C Brandstätter, F Meghdadi, G Leising, L Athouel, and G Froyer, Adv. Mater. **9**, 33 (1997).
[4] M D McGehee, M A Díaz-García, F Hide, R Gupta, E Kirk Miller, D Moses, and AJ Heeger, Appl. Phys. Lett. **72**, 1536 (1998).