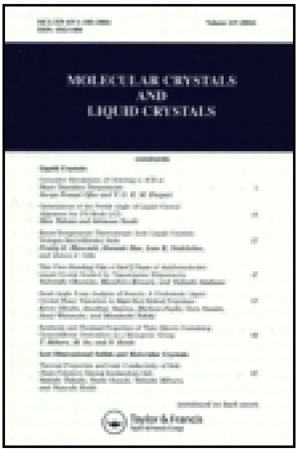

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Emission of Circularly Polarised Light in Highly Oriented Poly(*p*-Phenylene Vinylene) Langmuir-Blodgett Films

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Langmuir-Blodgett (LB) films of poly(*p*-phenylene vinylene) (PPV) were prepared using an amphiphilic precursor. These LB-PPV films are highly ordered along the dipping direction as demonstrated by linear dichroism experiments using linearly polarized optical absorption. The dichroic ratio between the intensity of the emitted light parallel and perpendicular to the dipping direction is *ca.* 3.6. In addition, the LB films displayed circular polarization with a dissymmetry factor, g_e, varying from 0.6 to –0.2 after increasing the sample temperature from 36 to 300 K.

Keywords: poly(*p*-phenylene vinylene), Langmuir-Blodgett films.

INTRODUCTION

The significant progress in the synthesis and processibility of conjugated polymer such as poly(*p*-phenylene vinylene) (PPV) has been employed to produce efficient light-emitting devices [1,2]. However, for a more conventional fabrication of devices, the structural disorder is a relevant limitation for their wide applicability [3]. In particular, stretched PPV films have shown higher external quantum efficiency and preferential polarized light emission as compared with isotropic films [3-5]. From this point of view, the Langmuir-Blodgett (LB) is a promissory technique to produce ultrathin films with a high degree of order, controllable thickness and a low number of defects [6]. In the present work, we demonstrate that LB-PPV films are highly anisotropic and present both linear and circular polarized luminescence. The asymmetry factor between the left and right circular polarizations is dependent on the temperature.

EXPERIMENTAL DETAILS

Langmuir monolayers of PTHT-DBSA were transferred onto glass and quartz substrates at a vertical speed of 2-4 mm/min. The transfer was carried out at a fixed monolayer pressure of 25 nN/m, with a barrier speed of 5 mm/min [1]. PTHT-DBSA films with 40 monolayers (40 ML) were converted to PPV at 230 °C for 2 hours. Converted LB-PPV films were characterized by UV-Vis and photoluminescence spectroscopy. For the photoluminescence experiments, the samples were excited by the 458 nm line of an Ar^+-laser with an average excitation density of about 5 mW/cm^2. A photomultiplier mounted on a 0.5 m monochromator was used for detection in the lock-in mode. The samples were analyzed in a closed-cycle cryostat that allows one to use temperatures from 30 to 300 K. Absorption measurements were carried out in a spectrophotometer Hitachi U-2001 equipped with a closed-cycle cryostat at 36 K.

RESULTS

Figure 1(a) shows the optical absorbance and photoluminescence (PL) spectra in UV-Vis region for a 40 ML LB-PPV film (continuous line) and a conventional Cast-PPV film at 36 K (open circles). When compared with the Cast-PPV film, one observes that the absorption spectrum of the LB film is shifted towards lower wavelengths and present well resolved vibronic structures. This indicates that LB films present a higher conjugation degree and lower intra and/or inter-chain interactions when compared with the Cast film. These properties are also reflected in the emission spectrum in Fig. 1(a), which shows a sharp and resolved vibronic progression, indicating that a high degree of chain alignment can be achieved through the LB technique.

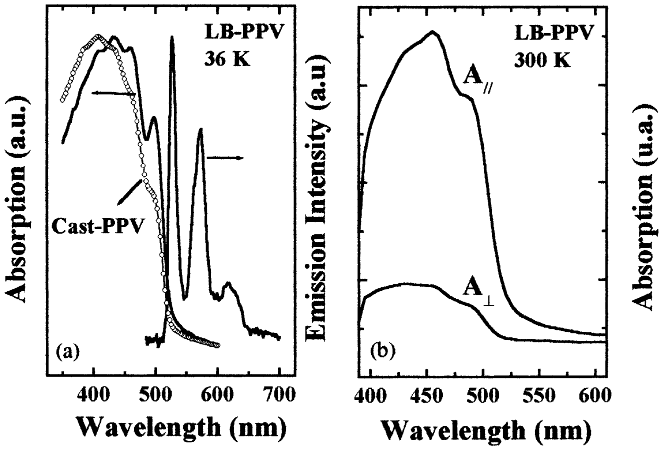

FIGURE 1. (a) Absorption and PL spectra at a low temperature (30K). The absorption spectrum of Cast-PPV film is also presented for the sake of comparison (open circles). (b) Linear polarized absorption measurements at 300 K ($A_{//}$ - parallel and $A_{\perp}$ - perpendicular to the dipping direction, respectively).

The preferential orientation of molecules can be studied by linear polarization measurements. Figure 1(b) displays polarized absorption measurements in the energy range near the band-edge for two polarizations of the incident light: parallel ($A_{||}$) and perpendicular ($A_{\perp}$) to the dipping direction. The dichroic ratio d=$A_{\perp}/A_{||}$ (perpendicular andINCORPORER parallel to the dipping direction, respectively) obtained from the polarized spectra was of 3.6 between the two values of maximum absorbance for the π-π^* band. This result indicates a strong molecular anisotropy in the LB films.

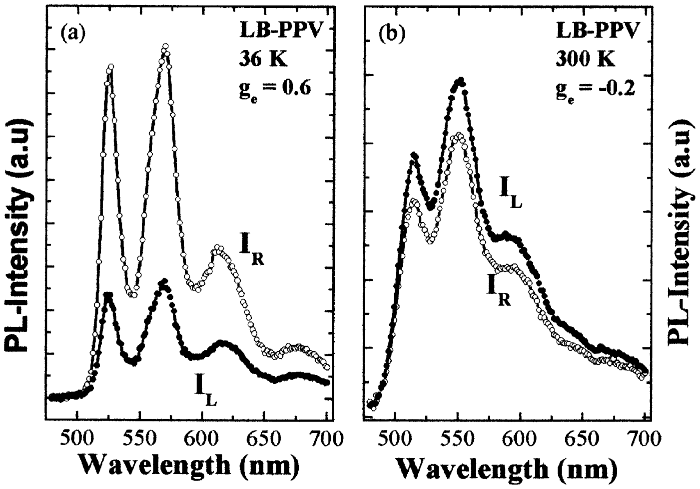

FIGURE 2. Circularly polarized photoluminescence at 36 K (a) and 300K for a 40 ML LB PPV film. The I_L (close circles) and I_R (open circles) are left and right components, respectively.

The emissions of the LB-PPV films present a circular polarization with large asymmetry at low temperatures, following linearly polarized excitation. Details of the optical set-up used for collecting the circular components of luminescence are described in reference [7]. The right- (I_R) and left-handed (I_L) intensity components of the circularly polarized light are shown in Figure 2(a) and (b), which correspond to measurements at 36 and 300 K, respectively. It is important to note the inversion in the PL intensity for the left and right components when temperature changes from 36 K (Figure 2(a)) to 300 K. The dissymmetry factor, $g_e=2(I_L - I_R)/(I_L + I_R)$ is dependent on the sample orientation and temperature. While the intensity in the whole spectra decreases with increasing temperature, as a result of thermal activation of competitive nonradiative processes, the dissymmetry factor g_e shows a linear decrease when temperature is increased, but the g_e inverts the signal at around 250 K for two excitation orientations [7]. At a low temperature (36 K), the value of g_e is 0.6, and at room temperature (300 K) g_e is –0.2.

CONCLUSIONS

Langmuir-Blodgett films of a poly(*p*-phenylene vinylene) (PPV) precursor were prepared using an amphiphilic precursor, where the counter-ion chloride was partially exchanged by a long chain dodecylbenzenesulfonate (DBS) ion [8]. These LB-PPV films are strongly ordered along the dipping direction as demonstrated by linear dichroism experiments using linearly polarized optical absorption and emission [1]. The results presented here have several implications on optical information processing, display and storage media, which use a conjugated polymer as the emitting layer. Although the linear polarization has reached a more advanced stage of research and development than circular polarization, circularly polarized light is still an alternative remaining field to be explored. The anisotropic properties are within our expectations for the layer-by-layer LB process which produces a strong molecular alignment along the dipping direction. Therefore, the circularly polarized luminescence can be related to a birefringence effects related to the molecular order in the LB-PPV films.

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