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Concentration dependence of photoluminescence properties in poly[(2-methoxy,5-octoxy)1,4-phenylenevinylene] thin films

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Abstract

Photoluminescence and selective excitation photoluminescence measurements at room temperature have been performed on poly[(2-methoxy,5-octoxy) 1,4-phenylenevinylene] (MO-PPV) thin films, which are prepared from MO-PPV chloroform solutions of different concentrations. The position of the S0 → S1 absorption peak shows red-shift and broadened relative to that in an MO-PPV solution form due to the solidification effect, while no relative shifts between the absorption spectra of these film samples are observed. A long wavelength emission component near 630 nm has been identified as S2 → S0 vibronic transition through the Gaussian decomposition method and confirmed by below-gap PL and selective-excitation PL experiments. This second vibronic component cannot be observed in the spectra of thick films. The PL efficiency of MO-PPV thin film is also investigated through comparison with that of an MEH-PPV thin film and explained by the side substituent effect.

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Keywords: Photoluminescence; MO-PPV; Excimer; Interchain interaction; Molecular structure

1. Introduction

Conjugated polymers are very attractive for its semiconducting or conducting properties that can be applied in many organic optoelectronic devices, such as light-emitting diodes [1–3], organic lasers [4–6] and organic transistor [7,8]. When the polymer optoelectronic devices are designed, a thin film structure, whose physical thickness is commonly about 100–200 nm, is more important and useful due to its desirable charge transport characteristics in electronic applications with reasonable applied voltage and the advantages

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from resonance effect in microcavity structures [9–11]. For improving the luminescence efficiency in these thin film devices with thickness restriction, an efficient method is that the emission unit number is augmented through the increase of the polymer concentration in solutions. Evidently, the emission properties of such high-concentration thin solid films will be affected by the interchain interactions [12–14], and the optical and electronic properties are expectably different from those in bulk or thick films. Consequently, the investigation on conjugated polymers should be extended to the photoluminescence characteristics in thin film forms for further practical applications. Since most polymer thin films are spin-casted or spin-coated from their solution forms, the solution concentration, the spin speed, the surface morphology of substrates and the thermal treatments will all affect the final film samples and increase the difficulties in the thickness and morphology control. However, efforts in this direction never stop even though these difficulties exist [14–18].

In this paper, attention will be focused on spin-coated thin films from the chloroform solutions of poly[(2-methoxy,5-octoxy)1,4-phenylenevinylene] (MO-PPV) [9,19] with different concentrations and their effect on the luminescence properties. A series of spectral comparisons of these thin films are performed: UV–visible absorption, photoluminescence (PL) spectroscopy as well as photoluminescence excitation (PLE) and selective-excitation PL experiments. Based on experimental results, the underlying trend of PL properties with the increasing concentration is discussed and compared with those in solution and thick film forms.

2. Experiments and curve fitting routine

The molecular structure of MO-PPV is illustrated in Fig. 1, with absorption and PL spectra in its thin film state. Structurally well defined and soluble MO-PPV has been synthesized by a similar process used in MEH-PPV synthesis by Ram et al. [20]. The synthesis procedures of MO-PPV are the same as those of MEH-PPV, except that the preliminary material of halide is n-octyl bromide (27.04 g, 0.14 mol) instead of 2-ethylhexyl bromide used in Ref. [20]. Through this process, the molecular structure and chain length can be effectively controlled. Then MO-PPV is dissolved in chloroform, and thin films can be formed on fused silica slices by the solutions with different concentrations spin-coated at the adjustable speed from 1000 to 4000 rpm. The samples are then dried at room temperature (290 K) in vacuum for 10 h without thermal treatment. The final samples used in this experiment are listed in Table 1 below. The thickness of these samples has been measured with the “Dektak Profiler” from “Veeco”. The thickness fluctuation of every sample given in the list is evaluated by atomic force microscopy. They should be assigned to two factors: the intrinsic surface fluctuation of the substrate and that of the polymer film. In this experiment samples with similar thickness have been chosen in order to emphasize the solution concentration effect on optical performance of thin films. UV–visible absorption spectra have been performed with “UV-3101PC UV-VIS-NIR Spectrophotometer” from “Shimadzu”, and PL spectra, PLE and selective-excitation PL are measured and recorded on “Fluorescence spectrophotometer” from “Hitachi” (Fig. 2).

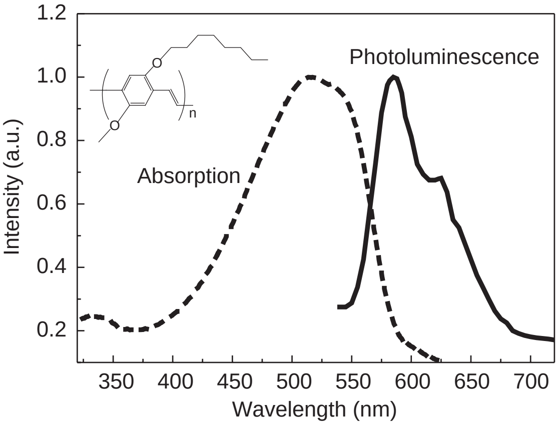

Fig. 1. The illustration of absorption and PL spectra of an MO-PPV film. The upper inset shows the molecular structure of MO-PPV.

To gain more information from measured data, the curve-fitting method is applied in the experiments. Noting that the peaks in PL spectra are