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Polarized Photoluminescence from Oriented Films based on Blends of Polyethylene and Conjugated Polymers

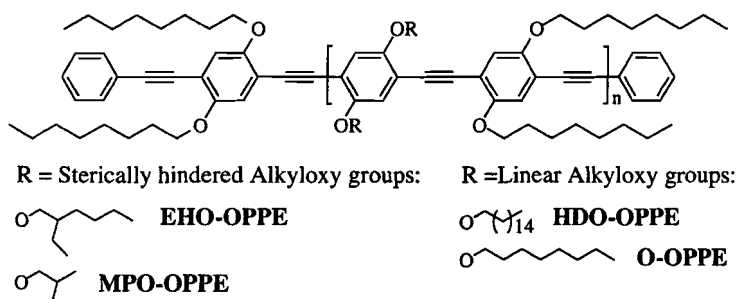
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Introduction

There has been a considerable interest in the electronic properties of conjugated polymers, since these materials combine the processability and outstanding mechanical properties of polymers with the exceptional electronic and photophysical properties of organic semiconductors [1]. Recently much research has been focused on the photoluminescence (PL) and electroluminescence (EL) properties of conjugated polymers, because of the potential application of these materials as emitting layer in EL devices [2,3].

One of us (C.W.) recently reported the synthesis of a series of poly(2,5-dialkoxy-*p*-phenyleneethynylene)s (PPEs, Scheme 1) and investigations of their photophysical properties [4-6]. In solution, PL quantum efficiencies close to unity were measured. The solid-state PL efficiency was found to be highly depending on the morphology of the films, which can be controlled by the choice of the side chains. High PL efficiencies were observed for amorphous samples, while in semicrystalline films, stronger electronic interactions led to significantly lower PL quantum yields.



Scheme 1: Poly(2,5-dialkoxy-*p*-phenyleneethynylene)s under investigation

With the objective to design devices, which efficiently emit light in a highly anisotropic, i.e. polarized, fashion, we now report the preparation of blends of poly(2,5-dioctyloxy-*p*-phenyleneethynylene) (O-OPPE, see Scheme 1) and ultra-high-molecular-weight polyethylene (UHMW-PE). Solution-casting followed by tensile deformation [7] was employed in order to prepare highly oriented films. This processing scheme has been successfully used in the past for the preparation of oriented polymer/dye polarizers [8,9], as well as for the design of polarized-light emitting films based on blends of UHMW-PE and poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) [10].

Experimental

O-OPPE (DP \approx 25) used in this work was prepared according to the procedure published before [4]. UHMW-PE (Hostalen Gur 412) was obtained from Hoechst. O-OPPE (5-100 mg) and UHMW-PE (0.5 g) were dissolved in xylene (50 mL) at 130 °C, after degassing the mixture in vacuum at 25 °C for 30 min. Thin films were prepared by casting the solution into aluminium trays. The gels were dried under ambient conditions for 24 h. The solution-cast, dried films were manually drawn at 120 °C on a thermostatically controlled hot shoe. Polarized UV-VIS spectra were obtained on a Perkin Elmer Lambda 900, fitted with motor driver Glan-Thomson polarizers. PL spectra were recorded on a SPEX Fluorolog 2 (Model F212 I), using unpolarized light (430 nm) for excitation, and a Glan-Thomson polarizer on the detector side.

Results and Discussion

Films of blends containing 1% w/w of O-OPPE in UHMW-PE were prepared as described above. The solution-cast films were drawn to a draw ratio of about 25. This process was by no means optimized, and thus, the data presented here are of preliminary character. Absorption and emission spectra are shown in Figures 3 - 5 for a pristine and a drawn film of the blend. For the purpose of comparison, the spectra for O-OPPE in solution, and an amorphous film of pure O-OPPE are also shown in Figures 1 and 2. The comparison of the different spectra allows several conclusions.

Most noteworthy, highly polarized absorption and emission are observed for the drawn film. Based on the emission spectra, a dichroic ratio of 13 was determined. Thus, already at modest draw ratios and a relatively low degree of orientation, highly polarized emission can be obtained with the processing scheme employed.

The PL spectrum of the undrawn blend (Figure 3) is relatively broad and only poorly resolved; the emission is comparable to the one of a pure film of the conjugated polymer (Figure 2). In contrast, the emission spectrum for the drawn blend (Figure 5) is fairly narrow, shows well resolved vibronic features, and matches the spectra of the pure O-OPPE in solution. This behaviour suggests different morphologies for the pristine and the drawn blends: In pristine blends, a phase separation between O-OPPE and UHMW-PE seems to occur, and consequently the photophysical properties are similar to those of pure O-OPPE. In drawn films, however, O-OPPE behaves as if it was molecularly dispersed or dissolved in a hydrocarbon matrix and therefore the photophysical properties are comparable to a dilute solution of the conjugated polymer. Detailed investigations on the structure of undrawn and drawn films are currently in progress.

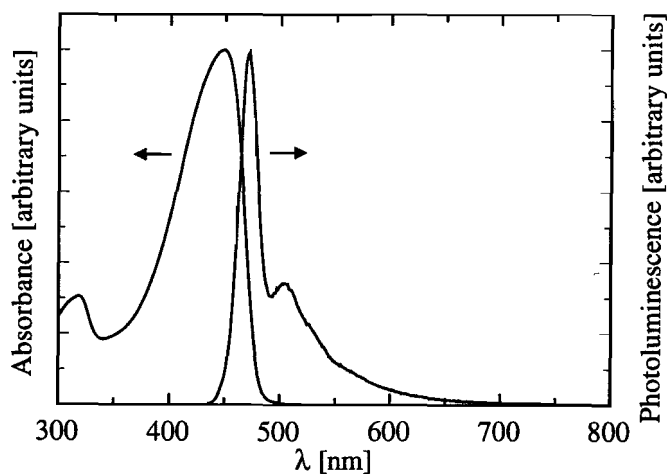


Figure 1: Absorption and emission spectra of O-OPPE in CHCl_3

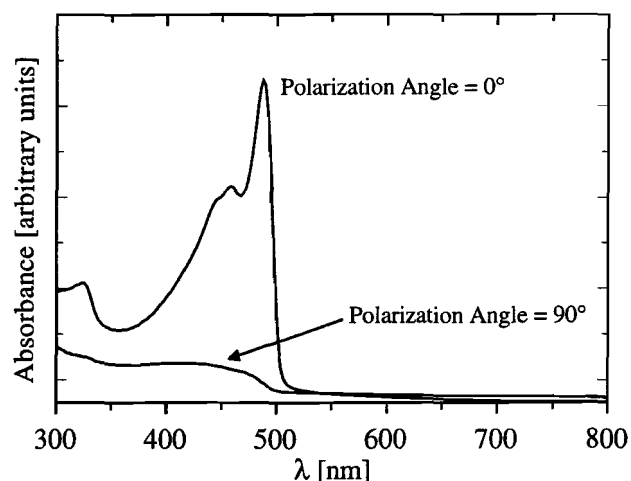


Figure 4: Absorption spectra of a drawn film of O-OPPE/UHMW-PE blend for light polarized parallel (0°) and perpendicular to the drawing direction (90°)

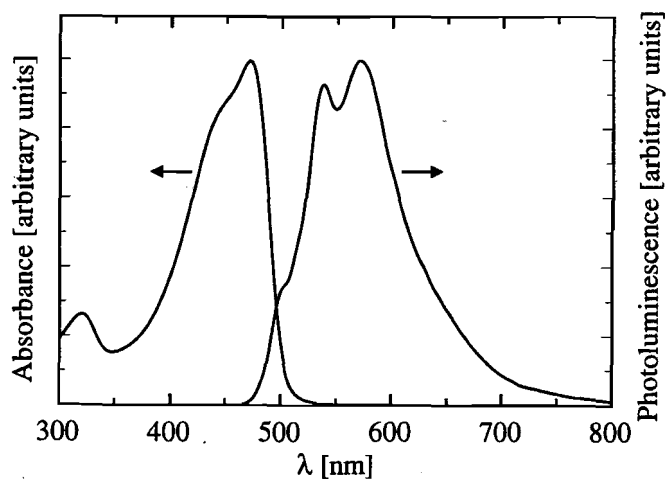


Figure 2: Absorption and emission spectra of a film of pure O-OPPE

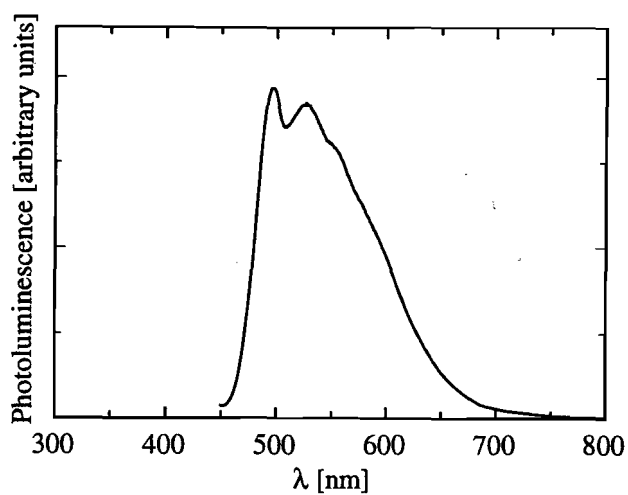


Figure 3: Emission spectrum of an undrawn film of O-OPPE/UHMW-PE blend

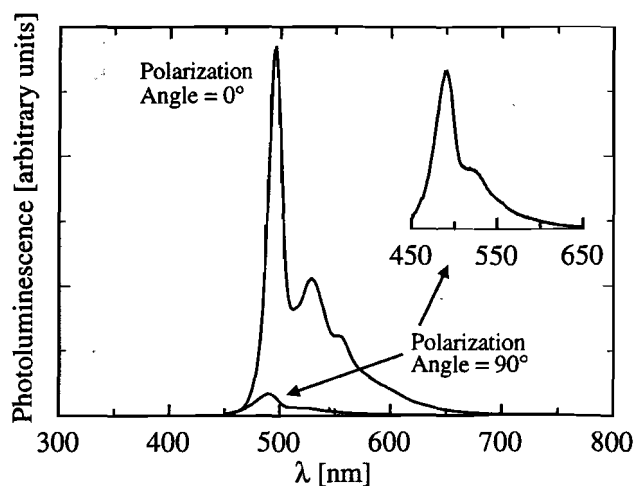


Figure 5: Emission spectra of a drawn film of O-OPPE/UHMW-PE blend for light polarized parallel (0°) and perpendicular to the drawing direction (90°). Inset: magnification of the spectrum for 90° .

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