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Self-Assembled Film of Carboxylic Acid Substituted Poly(p-Phenylene Vinylene) Derivative and its Luminescence Properties

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Self-Assembled Film of Carboxylic Acid Substituted Poly(p-Phenylene Vinylene) Derivative and its Luminescence Properties

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Carboxylic acid group pendent poly(p-phenylene vinylene) was synthesized and its layer-by-layer film with poly(ethylene imine) was fabricated by means of self assembly technique. The photoluminscence efficiency of the PPV-COOH in solution increases as increasing pH and the size of counter cation. The photoluminescent spectrum of the self-assembled PPV-COOH film is red shifted by ca. 10 nm compared to that of the casted film.

Keywords: luminescence; self assembly; PPV

INTRODUCTION

The ionically charged polymers can be utilized to construct a self-organized layer-by-layer nanostructure, which is a very convenient technique to build a molecular electronic devices[1-3]. It is also an important subject to learn how to incorporate functional polymers such as semiconducting conjugated polymers into the nanostructure.

It has been reported that sulfonium salt of PPV precursor and poly(styrenesulfonic acid) were successfully used to build the layer-by-layer films[4,5]. But the deterioration of the layer structure and/or degradation of polymer can not be avoidable since thermal elimination process is necessary

to convert the precursor into the conjugated form of PPV.

In this paper, carboxylic acid group pendent PPV (PPV-COOH) was synthesized, and the layer-by-layer deposited film with poly(ethylene imine) was prepared by means of the self assembly technique.

EXPERIMENTAL

The synthetic route of PPV-COOH is shown in Fig. 1. Details on the synthesis of the monomers and PPV-COOH polymers will be reported elsewhere. The self-assembled films were prepared by ionic interactions between negatively charged PPV-COOH and positively charged ITO or Si surface which was modified with aminopropyl trimethoxy silane. Multilayer films were fabricated by sequential dipping of the substrate in poly(ethylene imine) and PPV-COOH solutions. The films were carefully washed with water and dried for further study.

UV-Visible and luminescence spectra of the PPV-COOH were obtained by using Guided Wave Model 260 spectrophotometer and ISA FluoroMax-2 spectrofluorophotometer, respectively.

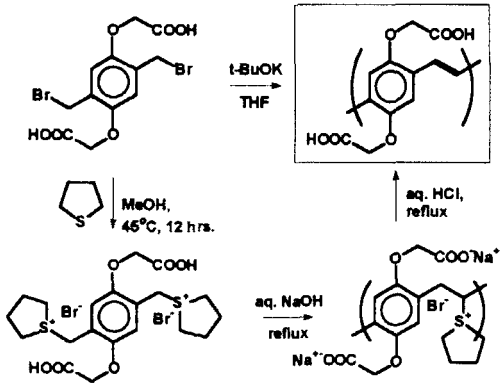

FIGURE 1 Synthesis of the PPV-COOH.

RESULTS AND DISCUSSION

The resulting PPV-COOH is soluble in water in the presence of base such as ammonium hydroxide, triethylamine, etc. The PPV-COOH complex with longer alkyl chain amine is also soluble even in toluene.

The polymer in solution is highly luminescent and the emission maximum is shown at ca. 550 nm. The photoluminescence spectrum strongly depends on the counter cations and pH of the solution (see Fig. 2). As the size of counter cation increases, the emission intensity increases, and the peak wavelength shifts to the shorter wavelength. Similarly, the emission intensity increases as increasing pH of the solution. The caboxylic group in this polymer may induce the interchain and/or intrachain hydrogen bonding. Since the interchain and/or intrachain hydrogen bonding may decrease in basic or in large cationic solution, the probability of the excimer formation may be reduced[6].

Characteristic absorption spectra of the multilayer self-assembled film are shown in Figure 3 a). The UV-Visible spectra of the self-assembled multilayer film are essentially same as that of the casted film. Linear increase of absorbance as a function of the number of bilayers means that

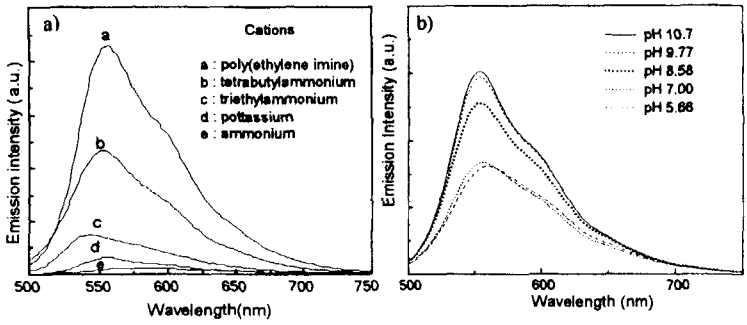

FIGURE 2 Photoluminescence spectra of PPV-COOH in aqueous solution depending on the a) counter cations and b) pH.

the thickness of the deposited bilayer film by the self-assembled technique is fairly uniform. The thickness of a bilayer is measured to be ca. 4.00 nm by means of ellipsometer.

Photoluminescence spectra of the self-assembled multilayer film and the cast film are shown in Fig. 3 b). The photoluminescence spectrum of the self-assembled film is red shifted by ca. 10 nm compared to that of the casted film.

In summary, the self-assembled mutilayer film of the carboxylate substituted PPV and poly(ethylene imine) is successfully fabricated by direct ionic interaction.

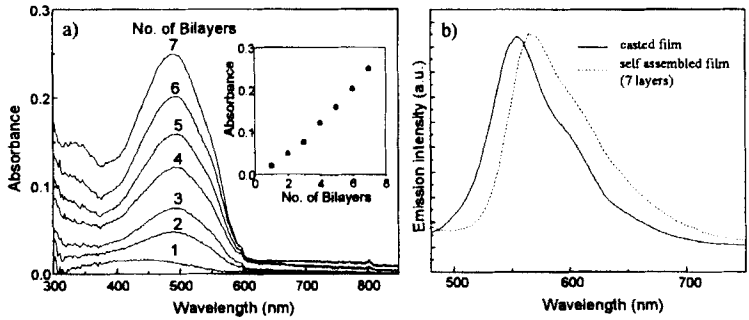

FIGURE 3 Absorbance changes as a function of number of bilayers (a) and photoluminescence spectra of the cast film and self assembled film (b).

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