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# Change in the quantum efficiency due to relative thickness variation of hole transport and emitting layers in a self-assembled device

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## Abstract

Using (Poly(phenylene vinylene) (PPV)/Poly(styrene sulfonate) (PSS)) and (PPV/Poly(methacrylic acid) (PMA)) self-assembled bilayers exhibiting different hole transport properties, we investigated the competing effect on quantum efficiency of the variation of relative thicknesses of (PPV/PSS) and (PPV/PMA) bilayers in indium tin oxide (ITO)/(PPV/PSS)$_n$/(PPV/PMA)$_m$/Al devices with fixed 20 bilayers (i.e. $n+m=20$). The (PPV/PSS) bilayer is known to be better as a hole transport layer due to higher leakage current and lower quantum efficiency in comparison with the (PPV/PMA) emitting bilayers. With increasing the number of (PPV/PSS) bilayers from 0 to 20 bilayers, the quantum efficiency of the multilayer self-assembled device was at maximum with 3 bilayers of (PPV/PSS) in contact with the ITO anode and the efficiency montonically decreased upon further increase of the (PPV/PSS) bilayer above 3. In the case of the increase of (PPV/PSS) bilayer thickness by the addition of NaCl salt to the PSS solution during the layer deposition process, the quantum efficiency of the device was significantly improved and also maximized with the 3 (PPV/PSS) bilayers. The significant change on the quantum efficiency by a simple control of relative bilayer numbers is mainly attributed to the competing effects caused by the increase of hole transport (PPV/PSS) bilayer at the expense of reduced emitting (PPV/PMA) bilayer. It was also found that the enhancement of the quantum efficiency by the addition of NaCl salt to the PSS solution is mainly caused by sufficient surface coverage of the (PPV/PSS) hole transport bilayers on the ITO electrode.

*Keywords:* Poly(*p*-phenylene vinylene) (PPV); Polyelectrolyte; Self-assembly method; Electroluminescence (EL); Quantum efficiency

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## 1. Introduction

Since the first successful fabrication of polymer light emitting diodes using poly(*p*-phenylene vinylene) as an active material, there have been widespread research interests in enhancing the device efficiency due to their potential use in display technology. In typical polymer light emitting diodes (LEDs) composed of charge transport (i.e. hole transport or electron transport layer) and emitting layers, total thickness of the organic layers was restricted less than 150 nm in order to inject and transport charge carriers with low operating voltage [1,2]. Therefore, the relative thickness control of respective organic layers in ultrathin film devices should be taken into account because the excess increase or decrease of the respective layer thickness has significant effect on the efficiency of double-layer devices [3–7]. However, the conventional spin-coating method for the fabrication of a double layer device, due to the problem of layer thickness control on a nanometer scale, has difficulty in understanding the change of device efficiency by varying the thickness ratio of different layers in the device. The layer-by-layer self-assembly method, first introduced by Decher et al. in 1992, provides a versatile route to build up nanostructured polymer films by the sequential adsorption of polymer chains from solution [8]. It was shown that this self-assembly method could easily control the film thickness at a molecule level and allow one to insert desired layers in the

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organic devices. Using this method, Rubner et al. reported that ITO/(PPV/PSS)$_n$/(PPV/PMA)$_{20}$/Al device with inserting (PPV/PSS) bilayers at the interface between the ITO electrode and (PPV/PMA)$_{20}$ significantly enhanced the device efficiency in comparison with the ITO/(PPV/PMA)$_{20}$/Al device without containing the (PPV/PSS) bilayer [9,10]. They attributed the improved device efficiency to higher hole transporting characteristics of the (PPV/PSS) compared with the (PPV/PMA) bilayer. In addition, several research groups have recently employed this type of electrode modification to fabricate efficient light emitting devices based on self-assembled polymers or inorganic layers [3,6,11]. To date, no systematic study, however, has been carried out on the determination of optimal layer thickness in respective emission and modification layers exhibiting different electrical characteristics in a confined or fixed total organic thickness.

In the present study, we report the effect on quantum efficiency of the change in relative thickness of a hole transport layer (HTL) and an emitting layer (EML) in a restricted region of a film device and of the surface coverage of the HTL on ITO electrode. In order to investigate these effects in detail, we have used here a model of multilayer structure composed of (PPV/PSS) and (PPV/PMA) bilayers as proposed by Rubner et al. and have also controlled the HTL thickness by increasing the amount of ionic salt added to the PSS solution.

## 2. Experimental sections

Polymer layers reported here were placed on the glass slides coated with ITO electrodes supplied by Samsung Corning Co. Poly(sodium 4-styrenesulfonate) (PSS) and poly(methacrylic acid) (PMA) were used as anionic polymers and poly(*p*-phenylene vinylene) (PPV) precursor which was further converted into conjugated PPV after thermal conversion was used as a cationic polymer. All solution concentrations were fixed at 0.01 mmol/l.

The thickness, root mean square (RMS) roughness and sheet resistance of the ITO electrode layer is approximately 1850 Å, 114 Å and 10∼20 Ω cm, respectively. The ITO substrates were cleaned by sonication in isopropyl alcohol for 1 h, followed by immersion into $H_2O/H_2O_2/NH_3$ (5/1/1) for 1 h. The fabrication of self-assembled films on the ITO substrates is as follows. The substrates were immersed alternately in the PPV precursor solution and in the PSS solution for 20 min each for deposition. After each adsorption step, the surface of the self-assembled film was rinsed by dipping in Milli-Q water three times for 2 min and then blown dry with a stream of nitrogen gas. After thermal conversion of the PPV precursor to a conjugated form of PPV, aluminum counter electrodes with a thickness of approximately 1500 Å were evaporated onto the PPV multilayer films. In this study, we employed the (PPV/PSS) layers as a hole transport layer on the ITO electrode and (PPV/PMA) layers as an emitting layer. This multilayer alignment is based on the fact that the (PPV/PMA) film device shows higher quantum efficiency and higher luminescence level in comparison with the (PPV/PSS) film device showing higher leakage current density.

## 3. Results and discussion

It is well known that self-assembled multilayer films based on PPV show unique structural, optical and electrical properties according to the type of polyanion employed to self-assemble the cationic PPV precursor compared with spin-coated or solution cast films [12,13]. In the case of (PPV/PSS) films, as the PSS doping of the PPV chains takes place during device operation, the self-assembled films composed of PPV and PSS usually have higher hole mobility than the (PPV/PMA) films. Therefore, if (PPV/PSS) and (PPV/PMA) films carrying different electrical properties are combined into an organic device, it is reasonable to think that the (PPV/PSS) and (PPV/PMA) films serve as a hole transporting and an emitting layer, respectively. As a result, we fabricated a series of ITO/(PPV/PSS)$_n$/(PPV/PMA)$_m$/Al devices in which the total number of (PPV/PSS) and (PPV/PMA) bilayers was fixed at 20 bilayers as schematically shown in Fig. 1. The total film thickness of the devices decreases with increasing the number of (PPV/PSS) bilayers because the thickness per bilayer of (PPV/PSS) and (PPV/PMA) measured from both X-ray reflectometer and ellipsometer is 6 Å and 22 Å, respectively.

Fig. 2a shows the change in relative quantum efficiency with increasing the number of (PPV/PSS) bilayer in contact with the ITO electrode from 0 to 20. The replacement with one bilayer of (PPV/PSS) on the ITO electrode has no significant effect on the device efficiency in comparison with the ITO/(PPV/PMA)$_{20}$/Al device (on the contrary, a slight decrease in the device efficiency was observed). In the case of three bilayers of (PPV/PSS) placed on top of the ITO electrode, both the quantum efficiency and brightness level were significantly improved. Although we did not quantitatively measure the surface coverage of the PPV/PSS bilayers on the ITO electrode, this electroluminescence behavior is expected because the increase of the (PPV/PSS) bilayer causes the uniform surface coverage on the ITO electrode with reduced surface defect and consequently accelerates the hole injection from the ITO electrode into the (PPV/PMA) emitting bilayer. We note, however, that the relative quantum efficiency and brightness level continuously decrease as the number of (PPV/PSS) bilayer is increased above 3 bilayers. This effect is manifested in the relationship between the quantum efficiency and the number of (PPV/PSS) bilayers as

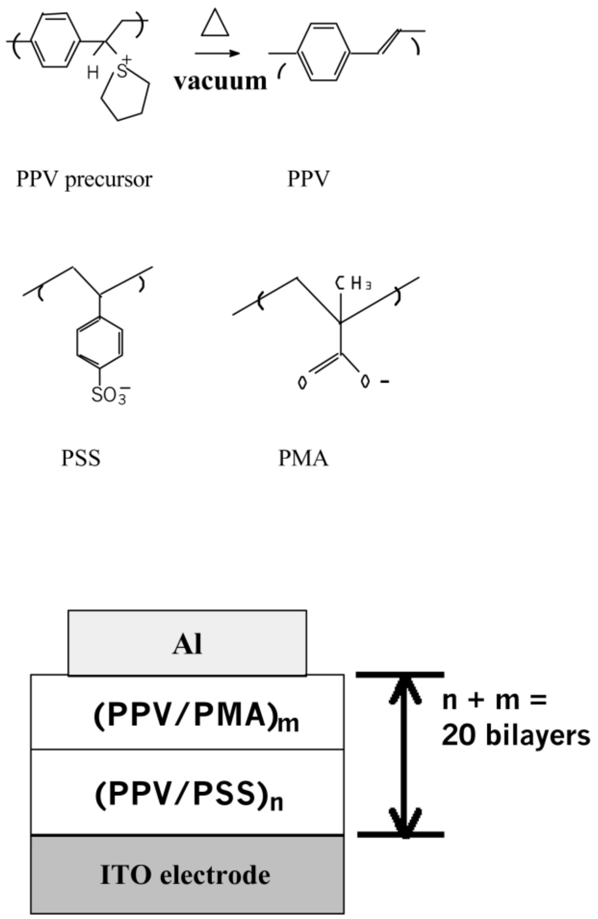

Fig. 1. Chemical structures of polyelectrolytes used in this study and a schematic layer alignment in EL device.

shown in Fig. 2b. This implies that heterogeneous self-assembled devices composed of (PPV/PSS)$_n$ and (PPV/PMA)$_m$ bilayers have the maximum quantum efficiency during the transition from the efficiency of (PPV/PMA)$_{20}$ to the efficiency of (PPV/PSS)$_{20}$ film with increasing the number of (PPV/PSS) bilayers from 0 to 20 bilayers. Consequently, we believe that the device efficiency is significantly improved at the optimal thickness balance of the HTL and EML layers although component polymers used for the multilayer films and multilayer alignment structure are the same [5,6].

As further evidence to support these changes in the quantum efficiency, Fig. 3a shows the change in relative quantum efficiency when the thickness per bilayer of (PPV/PSS) is increased up to 22 Å by the addition of 1 M NaCl salt in the PSS solution during the deposition [14]. For the ITO/(PPV/PSS)$_n$/(PPV/PMA)$_m$/Al heterostructure devices, the one bilayer thickness of (PPV/PSS) deposited in the existence of NaCl electrolyte is almost equivalent to that of the (PPV/PMA) bilayer. In this case, the insertion of only one bilayer of the (PPV/PSS) bilayer dramatically improved the quantum efficiency in contrast to the (PPV/PSS)$_1$/(PPV/PMA)$_{19}$ film device shown in Fig. 2 exhibiting no virtual improvement of the device efficiency. This distinct improvement in the device efficiency by the salt addition can be clearly shown in Fig. 3b. In the self-assembled film devices based on PPV, the overall improvement of the quantum efficiency by the NaCl salt addition is generally attributed to a couple of different factors: first, as the (PPV/PSS) hole transport layer becomes thicker, the hole transporting characteristics is enhanced due to the sufficient surface coverage on the ITO electrode, blocking the direct contact of the ITO electrode and the (PPV/PMA) emitting layer. This possibility is supported by the observation that there is no appreciable enhancement in the quantum efficiency in the case of the (PPV/PSS)$_1$/(PPV/PMA)$_{19}$ film device containing a HTL thickness of 6 Å obtained without the addition of NaCl salt to the PSS solution. Second, in a fixed 20 layered device composed of both HTL and EML, the number of (PPV/PMA) emitting layer can be maximized because the hole transporting property is sufficiently guaranteed even with a small

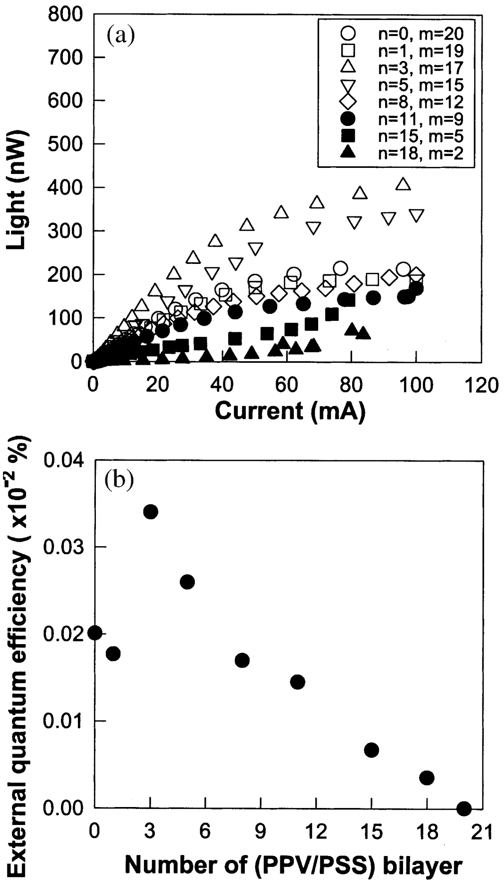

Fig. 2. Changes (a) in relative quantum efficiency and (b) in external quantum efficiency of ITO/(PPV/PSS)$_n$/(PPV/PMA)$_m$/Al devices with $n+m=20$ as a function of number of (PPV/PSS) bilayer in contact with ITO electrode. No ionic salt was added to the PSS solution.

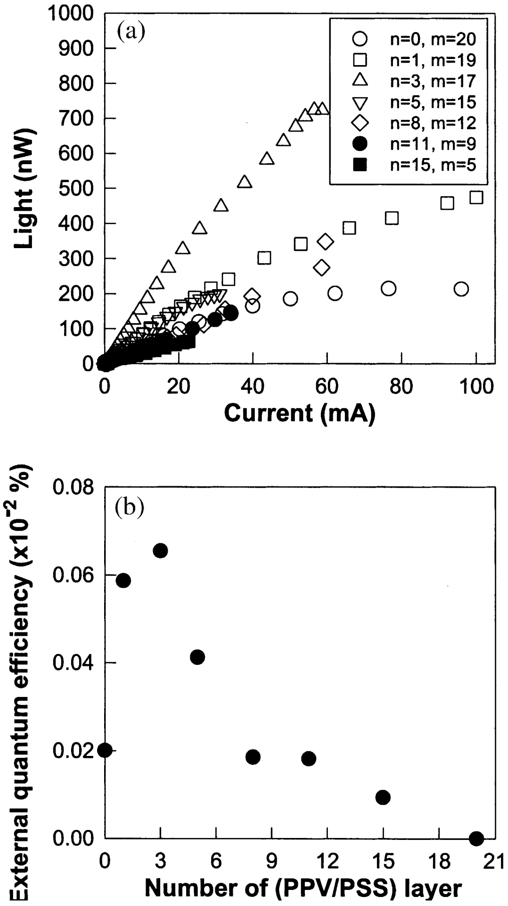

Fig. 3. Changes (a) in relative quantum efficiency and (b) in external quantum efficiency of ITO/$(PPV/PSS)_n$/$(PPV/PMA)_m$/Al devices with $n+m=20$ as a function of number of (PPV/PSS) bilayer in contact with ITO electrode. 1 M NaCl salt was added to the PSS solution.

number of HTL. We, thus, believe that the HTL thickness in the $(PPV/PSS)_3/(PPV/PMA)_{17}$ film device without the addition of ionic salt to the PSS solution is still insufficient despite showing the maximum quantum efficiency. We attribute these characteristics to the competing effects based on the relative thicknesses of the hole transport layer and the emitting layer in a device with a fixed number of bilayers. In the devices fixed with a restricted number of bilayers, either the decrease in the emitting layer in exchange for the increase in the HTL thickness or vice versa deteriorates the device efficiency when the relative thicknesses of the HTL and EML are out of balance as represented by the cases given in Figs. 2 and 3. In other words, although the hole transporting characteristics are reinforced in the case of the excess increase of the (PPV/PSS) bilayer number, the device efficiency continuously decreases due to the higher leakage current and the narrower recombination region of the (PPV/PMA) bilayers.

Fig. 4 displays the change in the relative quantum efficiency of ITO/$(PPV/PSS)_3/(PPV/PMA)_{17}$/Al devices fabricated with different amount of NaCl salt added to the PSS solution. The average thickness per (PPV/PSS) bilayer increases from 6 Å to 22 Å with the increase of NaCl salt concentration and also, the average thickness per (PPV/PMA) bilayer slightly increases from 22 Å to 24 Å presumably due to the higher ionic strength of the (PPV/PSS) bilayers upon the salt addition. The turn-on voltage of these devices was almost constantly maintained at 2.8 ~ 3 V. In a fixed number of emitting bilayers composed of PPV and PMA, we are convinced that the improved quantum efficiency with the increase in ionic strength of the PSS solution was mainly caused by the increased surface coverage of the hole transport layer along with the slight increase of the (PPV/PMA) emitting layer. Although the increase of the (PPV/PSS) bilayer thickness due to the addition of ionic salt has an effect on the increase in the total film thickness of the light-emitting device, it has been reported that the slight thickness increase of the (PPV/PSS) bilayers cannot significantly improve the device efficiency [13].

In the light of experimental results reported here, it is reasonable to conclude that the significant improvement of device efficiency is caused by the reinforcement of the hole transporting characteristics of the (PPV/PSS) bilayers avoiding the direct contact between the ITO anode and the (PPV/PMA) emitting bilayers. As a result, these competing effects by changing the relative thicknesses of both HTL and EML clearly demonstrate that the HTL and EML thicknesses of ultrathin double layer devices should be optimized; the HTL thickness is minimized until sufficient surface coverage on ITO electrode is guaranteed while the EML thickness is maximized to achieve the high quantum efficiency.

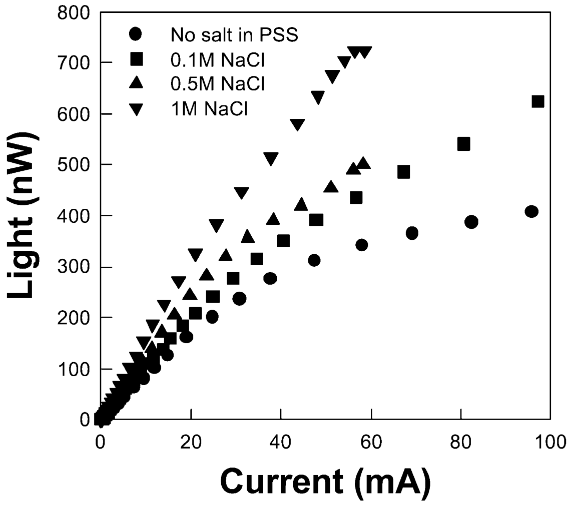

Fig. 4. Relative quantum efficiency of ITO/$(PPV/PSS)_3$/$(PPV/PMA)_{17}$/Al devices fabricated with different amounts of NaCl salt in the PSS solution during the self-assembly deposition.

## 4. Conclusion

We report the change in the quantum efficiency of multilayer film devices by the variation of relative thicknesses of hole transport layer (HTL) and emitting layer (EML) for a fixed number of total bilayer as well as by the increase in the HTL thickness with a fixed number of EML. Self-assembled multilayer devices composed of both the (PPV/PSS) HTL and the (PPV/PMA) EML with a fixed number of total 20 bilayers (i.e. $n_{\mathrm{HTL}}+n_{\mathrm{EL}}=20$) have the maximum device efficiency at an optimal number of respective bilayers (i.e. $n_{\mathrm{HTL}}=3$) due to the competing effect provided by the increase of the hole transport characteristics at the expense of the reduced emitting (recombination) region by increasing the number of (PPV/PSS) bilayer. In addition, instead of simply increasing the (PPV/PSS) bilayer number as a way to improve the device efficiency, the increase of the (PPV/PSS) bilayer thickness by the ionic salt addition to PSS solution is proven to dramatically improve the device efficiency. This enhanced quantum efficiency is mainly attributed to the improvement of the hole transporting characteristics by the sufficient surface coverage of the (PPV/PSS) layer on the ITO electrode without sacrifice of the (PPV/PMA) recombination layers.

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