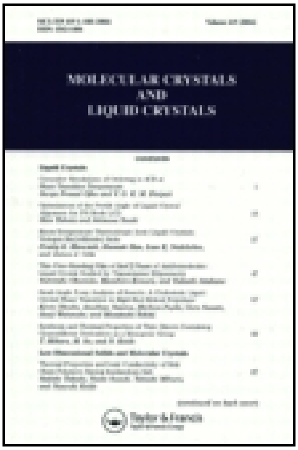

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Application of Soluble Poly(phenylenevinylene) Wrapped in Amylose to Organic Light-Emitting Diodes

Shunsuke Nishino [a], Tatsuo Mori [a], Sayaka Tanahara [b], Katsuhiro Maeda [b], Masato Ikeda [c], Yoshio Furusho [c] & Eiji Yashima [b] [c]

[a] Department of Electrical Engineering and Computer Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

[b] Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

[c] Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Shimoshidami, Moriyama-ku, Nagoya, Japan

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Shunsuke Nishino
Tatsuo Mori
Department of Electrical Engineering and Computer Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Sayaka Tanahara
Katsuhiro Maeda
Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Masato Ikeda
Yoshio Furusho
Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Shimoshidami, Moriyama-ku, Nagoya, Japan

Eiji Yashima
Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan; Yashima Super-structured Helix Project, Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Shimoshidami, Moriyama-ku, Nagoya, Japan

Non-substituted poly(phenylenevinylene) (PPV) is an insoluble material. Ikeda et al. synthesized Amylose-PPV (APPV), which is PPV wrapped in amylose, by applying precursor route synthesis of PPV in the presence of amylase; APPV is soluble in dimethylsulfoxide.

Comparison of the absorbance and the PL spectrum of APPV film with those of other organic films indicated the PL efficiency of APPV film as 0.28–0.43. The PL efficiency of PPV film is 0.27. Therefore, the amylose wrapping might

Address correspondence to Tatsuo Mori, Department of Electrical Engineering and Computer Science, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan. E-mail: t_mori@nuee.nagoya-u.ac.jp

improve the PL efficiency of PPV. The OLEDs emitted a green light when the OLEDs were fabricated with APPV as an emitting layer.

Keywords: amylose; organic light-emitting diode; PPV; solubilization; supramolecule

INTRODUCTION

Polymer light-emitting diodes (PLEDs) were first fabricated by J. H. Burroughes *et al.* [1]. The device structure is indium oxide/poly(phenylenevinylene) (PPV)/Al. Because the solubility of non-substituted PPV is too poor, a PPV film cannot be fabricated through a one-step wet processing. In that study [1], the PPV film was fabricated through a two-step process. First, a film of soluble PPV precursor was fabricated on a substrate by casting method. Secondly, PPV was polymerized on the substrate by annealing. This two-step process degenerates processability and leaves impurities in the film. Also, MEH-PPV, which is PPV solubilized by the introduction of the side chains, was reported by D. Braun *et al.* [2] as an emitting layer. Subsequently, many polymer materials came to be used in PLEDs. We reported effects of molecular weight on device performance using a light-emitting polymer: a polyfluorene derivative [3–5]. Ikeda *et al.* reported that the wrapping of amylose, i.e. helical polymer, can solubilize PPV [6]. We call the resultant supramolecule, which is PPV wrapped in amylase, APPV. It is soluble in dimethylsulfoxide (DMSO). For that reason, APPV film can be fabricated through a one-step process. Solubilization by wrapping of amylose was reported also on carbon nanotubes [7]. The substituents can be introduced to the amylose part of APPV. Therefore, substitution to the amylose part can append some functional groups without changing the features of the PPV inside, unlike direct substitution to PPV. Because PPV is a hole-transport material, APPV also might be a hole-transport material. Therefore, through introduction of an electron transportable substituent, the carrier balance might be improved even in a single-layer device. Additionally, the solvents determine whether the organic layer can be fabricated on another organic layer. We can fabricate a multi-layer structure through wet processing if the solubility of APPV can be controlled through selection of substituents.

EXPERIMENTAL

As described in [6], APPV is synthesized by mixing PV monomer and amylose and NaOH in a DMSO water mixture while controlling the

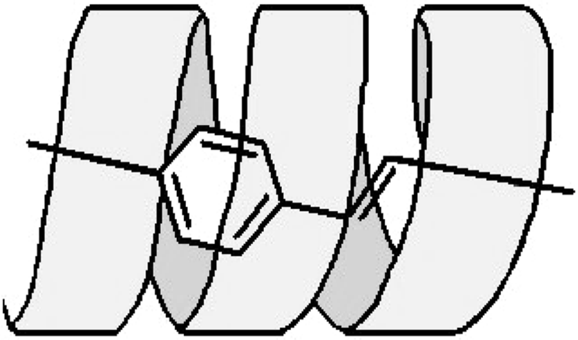


FIGURE 1 Schematic image of APPV.

temperature. In APPV, PPV is enveloped by amylose, as shown in Figure 1. The APPV was dissolved in DMSO to be 10 g/l and APPV film was fabricated by spin-coating method at 1000 rpm from the solution. The film was dried in vacuum for one day. We measured absorption spectra using a spectrophotometer (U-3000; Hitachi Ltd.), photoluminescence (PL) spectra using a spectrophotometer (FP-777; Jasco Inc.), ionization potential (Ip) using photoelectron spectroscopy in air (AC-2; Riken Keiki Co. Ltd.), and surface morphology using an atomic force microscope (VN-8000; Keyence Co.). Additionally, we fabricated OLEDs with APPV as the emitting layer. The OLED structures are indium-tin-oxide (ITO)/APPV/LiF [0.6 nm]/Al [ca. 200 nm] as single-layer devices and ITO/APPV/BCP [50 nm]/LiF [0.6 nm]/Al [ca. 200 nm] as double-layer devices. The APPV film was fabricated using spin-coating method and other films were fabricated using vacuum evaporation method at $2\text{–}5 \times 10^{-6}$ Torr. The effective electrode area was 2 × 2 mm. Luminance-current-voltage characteristics were measured using a source measurement unit (2400 Source Meter; Keithley Instruments, Inc.) and a luminance meter (BM-8 Luminance Meter; Topcon Corp.). We also measured electroluminescence spectra using a multi-channel photo detector (MCPD-4500; Otsuka Electronics Co., Ltd.).

RESULTS AND DISCUSSION

Figure 2 shows that little difference exists between absorption spectra and PL spectra of the APPV film and APPV solution. Woo *et al.* reported that two PL spectrum peaks are red-shifted with increasing polymerization degree and that energy spacing between two peaks is constant at about 0.16 eV [8]. The PL spectrum of APPV has two peaks

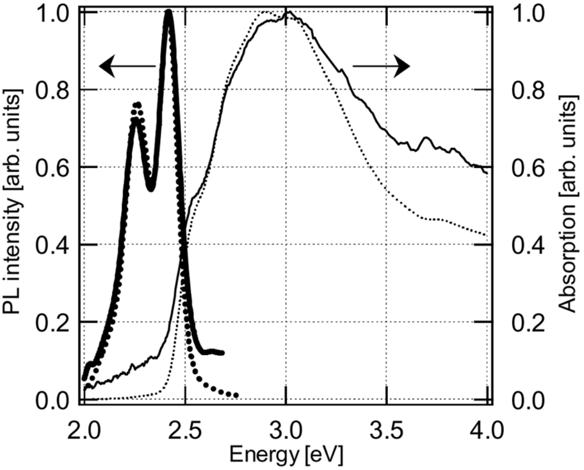


FIGURE 2 Absorption spectra and PL spectra of the APPV solution (solid line) and the APPV film (dash line).

at 2.27 eV and 2.43 eV; therefore, the energy spacing of two peaks is 0.16 eV. The PV 7mer has two peaks at 2.38 eV and 2.54 eV in the PL spectrum. Therefore, it is anticipated that the degree of polymerization is greater than 7. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of APPV showed that the degree of PPV polymerization is distributed between 5 and 14 [6]. Estimation using PL spectra might indicate that the degree of PPV polymerization is mainly distributed as 7 and more.

Figure 3 shows absorption spectra and the PL spectra of the APPV film and poly(2-methoxy-5-(2′-ethylhexyloxy)-phenylenevinylene) (MEH-PPV). The PL intensity at peak wavelength is calculated against absorbance at excitation. We define relative intensity I as that value. The relative PL intensity of APPV film I_{APPV} is given as

$$I_{\mathrm{APPV}} = \frac{\text{PL int.}}{\text{Abs.}(410\,\text{nm})} = \frac{94.7}{0.0226} = 4{,}192. \tag{1}$$

The relative PL intensity of MEH-PPV film I_{MEH} is given as

$$I_{\mathrm{MEH}} = \frac{\text{PL int.}}{\text{Abs.}(500\,\text{nm})} = \frac{1400}{0.952} = 1{,}470. \tag{2}$$

Therefore, the relative PL intensity of APPV is 2.9 times larger than that of MEH-PPV. It is anticipated that the ratio of PL efficiency approximately corresponds to the ratio of relative PL intensity.

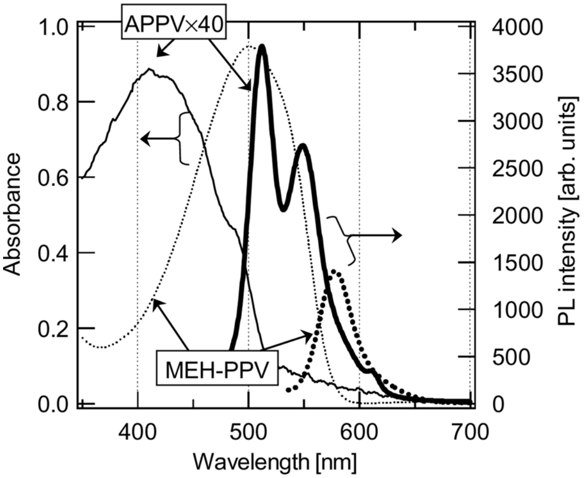
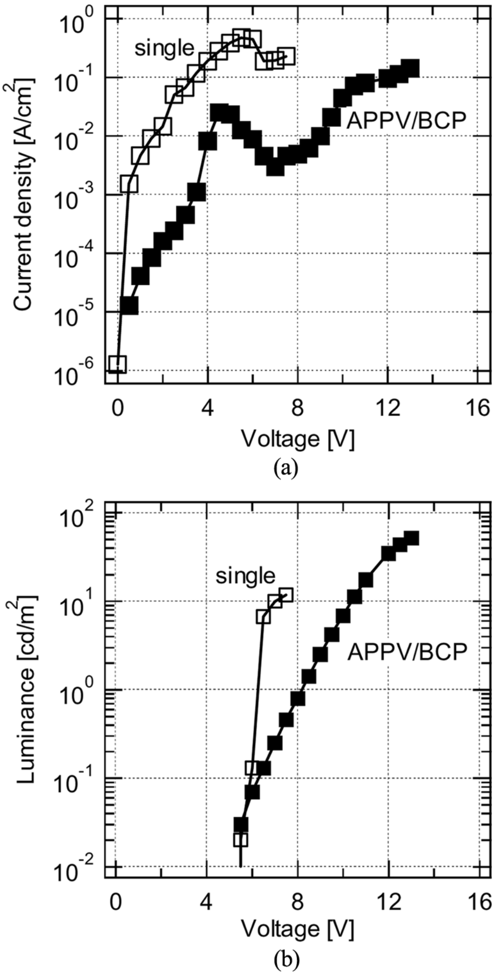


FIGURE 3 Absorption spectra and PL spectra of APPV film (solid line) and MEH-PPV film (dash line). Excitation wavelengths in APPV and MEH-PPV are, respectively, 410 nm and 500 nm.

Because it is reported that the PL efficiency of MEH-PPV film is 0.10–0.15 [9], the PL efficiency of APPV film is estimated at 0.29–0.44. Similar calculation of the relative PL intensity of Alq3 film I_{Alq3} shows that I_{APPV} is ca. 1.4 times larger than I_{Alq3}. Because the PL efficiency of Alq3 film is well known to be 0.20, the PL efficiency of APPV film is estimated at 0.28. To summarize our calculated PL efficiency of APPV film, the PL efficiency of APPV film is estimated at 0.28–0.44. Because the PL efficiency of non-substituted PPV film is 0.27 [9], it is thought that the wrapping of amylose improves the PL efficiency of PPV. Intermolecular interaction between PPV molecules is strong and the insolubility of PPV is ascribed to their strong interaction. Intermolecular interaction is known to cause concentration quenching. For that reason, the PL efficiency of PPV film might be decreased because of concentration quenching by the strong interaction. Reportedly, the interchain distance is 0.5 nm in PPV film [10]. Because the diameter of amylose in APPV is 1.4 nm [6], the PPV molecule is isolated from other PPV molecules by amylose in APPV. Because intermolecular interaction increases by shortening of the interchain distance, intermolecular interaction among PPV molecules in APPV film might be less than that in PPV film. Therefore, we deduce that higher PL efficiency of APPV films is attributable to inhibition of concentration quenching by the decrease in intermolecular interaction between PPV molecules. Additionally, it was reported by S. Doi *et al.* that the

PL intensity of dialkoxy-PPV film is improved by increasing the chain length of alkoxy group [11]. That paper describes that the ratio of non-radiative process is decreased because of prevention of exciton migration to traps by the alkoxy group. Insulator amylose is thought to have a wide energy gap. Therefore, amylose is suggested to prevent exciton migration between molecules.

The device characteristics of OLEDs with APPV as an emitting layer are shown in Figure 4. The maximum luminance is 12 cd/m^2



(a)

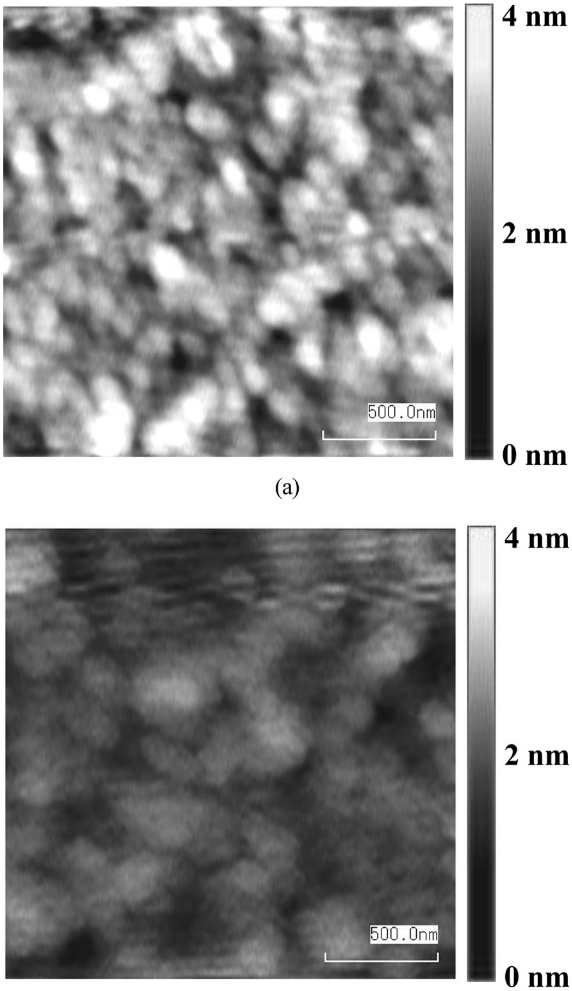
(b)

FIGURE 4 Device characteristics of OLEDs with APPV: (a) current-voltage characteristics, (b) luminance-voltage characteristics.

in a single-layer device. The APPV film is too thin to measure the film thickness. We measured the capacitance of a single-layer device and obtained the value of 9–11 nF at a device area 4 mm^2. Using 3, which is the general value of organic materials, as relative permittivity, we can calculate the thickness of APPV film d.

$$\begin{aligned} d &= \frac{\varepsilon S}{C} \\ &= \frac{8.854 \times 10^{-12} \times 3 \times 4 \times 10^{-6}}{C} \\ &= 10 - 12\,[\mathrm{nm}] \end{aligned} \tag{3}$$

The diameter of amylose in APPV is 1.4 nm [6]. Therefore, it is thought that, at most, eight APPV molecules are stacked in the film. Figure 5 shows the AFM images of APPV film and ITO film. The AFM image of APPV film shows the morphology of the APPV film fabricated on the ITO film. The surface roughness Ra of APPV film is 0.6 nm; that of the ITO film is 0.3 nm. The AFM image shows that the APPV film is formed by aggregation of 100-nm-wide PPV particles. Because the thickness of APPV film is 10–12 nm and the maximum peak-to-valley height of the APPV film is 4 nm, the film thickness differs by as much as 36% according to its position in a single-layer device. Therefore, the electrical field must be applied unequally in the position on a single-layer device. As a result, leakage current flows away in the device as a local maximum value appears in current-voltage characteristics. The ionization potential (Ip) of APPV is estimated at 5.8 eV using AC-2. The energy of the absorption edge, i.e. the energy gap (Eg), of APPV is also estimated at 2.4 eV. We can estimate the lowest unoccupied molecular orbital (LUMO) level of APPV at 3.4 eV from Ip and Eg. Figure 6 shows an energy diagram of the materials used in this study. We fabricated a double-layer device using BCP as a hole-blocking layer. Because the thickness is increased, an electrical field is thought to be applied equally in the position on the device. The maximum luminance of the double-layer device is 52 cd/m^2, which is higher than that of the single-layer device, as shown in Figure 4. The APPV devices emit a green light. Figure 7 shows the EL spectrum of the device. The EL spectrum has two peaks, similar to the PL spectrum of APPV film. Because current does not increase monotonically with increasing voltage, the leakage current seems to flow away in the device. However, most leakage current is inhibited by the BCP insertion. The BCP film quality is not good [12]. For that reason, we cannot measure the current-voltage characteristic of a single BCP film. Therefore, we infer that leakage current flows on the double-layer



(a)

(b)

FIGURE 5 AFM images of (a) APPV film on ITO, and (b) ITO.

device are attributable to the poor BCP film quality. As a result, it is thought that the causes of leakage current on the single-layer device are an overly thin film, poor film quality, and metal penetration. We consider that film thickness is increased by the increased concentration of the APPV solution because of the introduction of a substituent that improves solubility to the amylose part. Metal penetration is inhibited by increased thickness. The film-quality improvement is

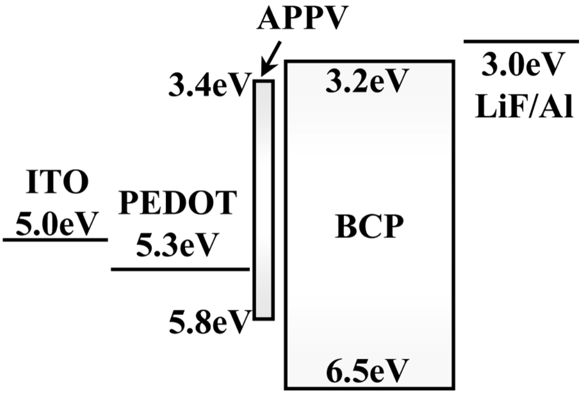


FIGURE 6 Energy diagram of materials used in this study.

achieved if the poor film quality is caused by the solvent. However, because amylose is an insulator and the intermolecular distance of PPV is increased by introduction of the substituent, the APPV film conductance is not good. In addition, we are considering introducing a substituent that contributes to the improvement of conductance.

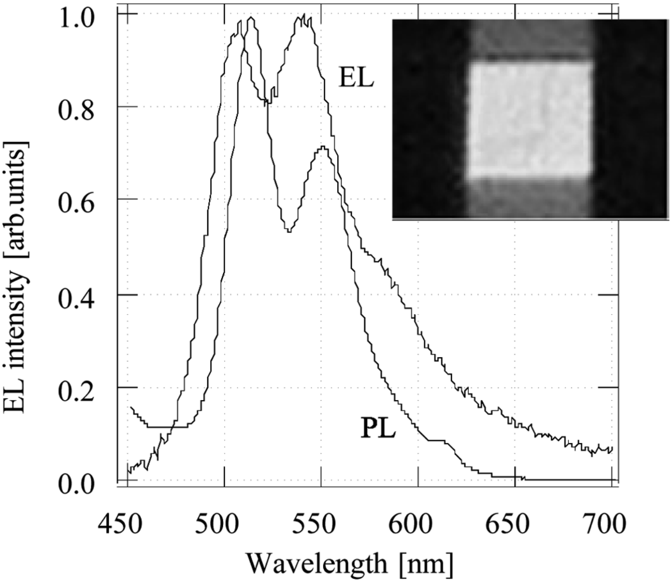


FIGURE 7 An EL spectrum of the double-layer device and a PL spectrum of APPV film. The inset shows a light from double-layer device with a 2 × 2 mm emission area.

CONCLUSION

We reported characteristics of an APPV film and those of OLEDs with APPV as an emitting layer. By comparing the absorbance and the PL spectrum of APPV film with those of the other films, we estimated the PL efficiency of APPV film at 0.28–0.44. The PL efficiency of non-substituted PPV film is 0.27. Therefore, it is thought that the wrapping of amylose improves the PL efficiency of PPV. We think that the causes of the improvement of PL efficiency are inhibition of concentration quenching by the decrease of intermolecular interaction between PPV molecules, and prevention of exciton migration to traps. A green light is visible from OLEDs with APPV. However, the maximum luminance of the device is not so high ($52\,\mathrm{cd/m^2}$). We were able to improve the PL efficiency of PPV by enveloping it in an amylose sheath. However, in terms of carrier conduction, we infer that the APPV film conductance is less than that of PPV film because of that insulator wrapping. Therefore, we seek to improve the APPV film conductance by introducing a carrier transport substituent to the amylose part. Additionally, because the solubility of APPV is insufficiently high, we are considering the introduction of a substituent that improves the solubility to the amylose part.

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