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Improved Light Emission Properties and Operation Lifetime of Multi-Layered Organic Light-Emitting Diodes using Dyes Extracted from Spinach

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Abstract **– Multi-layered organic light-emitting diodes (OLEDs) containing chlorophyll as an emissive material were fabricated to improve their light emission efficiencies. The chlorophyll was extracted from spinach. In quintuple-layer OLEDs, the hole-blocking layer plays an important role to increase the emission intensity. In addition, we evaluated the antioxidant activities of the carotenoids that were also extracted from spinach. They were doped in the electron-transporting layer in one sample, and in the hole-blocking layer in another sample to change the distance from the carotenoids to the active layer. As a result, the OLED containing the carotenoid-doped hole-blocking layer revealed longer operation lifetime, because the hole-blocking layer was adjacent to the active layer, leading to more effective antioxidant activities.**

Keywords **– Organic Light-Emitting Diode, Chlorophyll, Carotenoid, Antioxidant Effect**

I. INTRODUCTION

Recently, organic light-emitting diodes (OLEDs) have been investigated for applications to flat panel displays and novel illumination light sources [1]. However, their operation lifetime is shorter than inorganic LEDs because organic materials are easily destroyed by oxidation and moisture [2]. Recently, OLEDs were fabricated from biomolecular compounds, in which refined chlorophyll a was used as an emissive material [3,4]. More recently, OLEDs were developed that contain chlorophyll as an emissive material that was extracted from spinach [5], suggesting that plants can supply low-price and abundant materials for OLEDs. In addition, the ref. [5] suggested that carotenoids, which are also extracted from spinach, have strong antioxidant effects [6,7], lengthening the operation lifetime of OLEDs. However, the luminance of these OLEDs containing chlorophyll was very weak. In this research, we fabricated multi-layered OLEDs containing chlorophyll in the active layers to improve their light emission efficiencies. To evaluate carotenoid's antioxidant effect, we also observed the time variation of two OLEDs that contain carotenoids in the hole-blocking and electron-injection layers.

II. EXPERIMENTAL

A. Sample fabrication

Poly(3,4-Ethyenedioxythiophene)/ poly(styrenesulfonate) (PEDOT-PSS) was used as the hole-injection layer (HIL) and poly(4-butylphenyl-diphenyl-amine) (Poly-TPD) was used as the hole-transporting layer (HTL). In addition, 3-(Biphenyl-4-yl)-5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole (TAZ) was used as the hole-blocking layer (HBL) and tris-(8-hydroxyquinoline)aluminum (Alq3) was used as the electron-transporting layer (ETL). Emissive material chlorophyll and carotenoids were extracted from spinach using a previous extraction method [5]. Poly[(m-phyenylenevinylene)-alt-(2.5-dihexyioxy-p-phenylene-vinylene)] (PPV) was used as a host material in the active layer. We fabricated OLEDs consisting of the following triple-, quadruple- and quintuple-layer structures:

A: ITO/PEDOT-PSS/Poly-TPD/active layer/Al,
B: ITO/PEDOT-PSS/Poly-TPD/active layer/TAZ/Al,
C: ITO/PEDOT-PSS/Poly-TPD/active layer/TAZ/Alq3/Al,
D: ITO/PEDOT-PSS/Poly-TPD/active layer/TAZ/(Alq3:carotenoid) /Al,
E: ITO/PEDOT-PSS/Poly-TPD/active layer/(TAZ:carotenoid) /Alq3/Al.

Note that in samples D and E, the carotenoids were doped in different layers. For sample E, they were doped in the hole-blocking layer, which is adjacent to the active layer, and they were doped in the electron-tranporting layer in sample D. Thus, for sample D, the carotenoids were separated from the active layer. All the organic layers were fabricated on indium-tin-oxide (ITO)-coated glass substrates using a spin-coating method. The thicknessses of the PEDOT-PSS and Poly-TPD layers were about 40 nm, and the active layer was about 80 nm thick. Finally, aluminum (Al) was vacuum deposited as a cathode metal.

B. Measurement setup

The current-voltage characteristics, the luminance and the electroluminescence (EL) spectra were observed using a multi-channel spectrometer (Hamamatsu Photonics PMA-12 C10027-02), a source meter (Keithley 2400), and an integrating sphere unit (Hamamatsu Photonics A10094). The thicknesses of the thin films were measured with a step profiler (AMBiOS XP-1). All measurements were performed at room temperature and in atmosphere.

III. RESULTS AND DISCUSSION

A. Triple- and quadruple-layer OLEDs

Figure 1(a) shows the EL spectra of samples A and B for an applied voltage of 20 V. Two peaking wavelengths were clearly observed, originating from PPV at about 510 nm and chlorophyll at about 680 nm. In this case, the luminance originating from the chlorophyll of sample B was twice as large as sample A, while that from PPV did not change. This means that most of the injected holes

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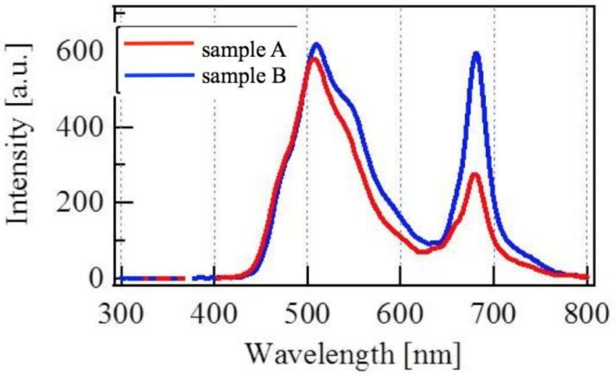
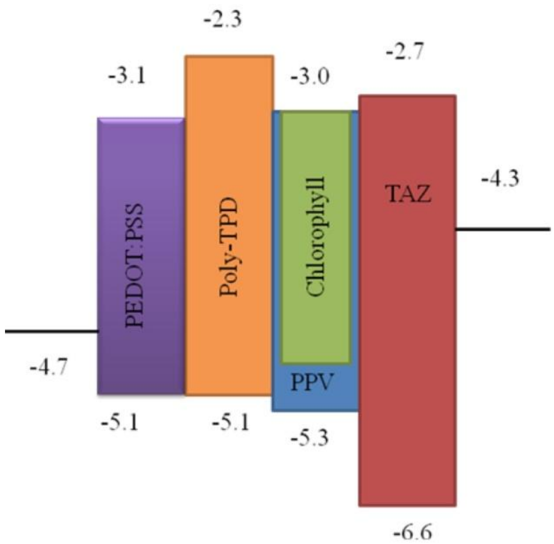
could not go to the cathode due to the hole-blocking layer TAZ, and so they contributed to the stronger light emission in the active layer. The large discontinuity of the highest occupied molecular orbital (HOMO) levels of the TAZ and active layers plays an important hole-blocking role (Fig. 1(b)). Since PPV also successfully suppressed the concentration quenching only the chlorophyll luminance was improved.



(a)

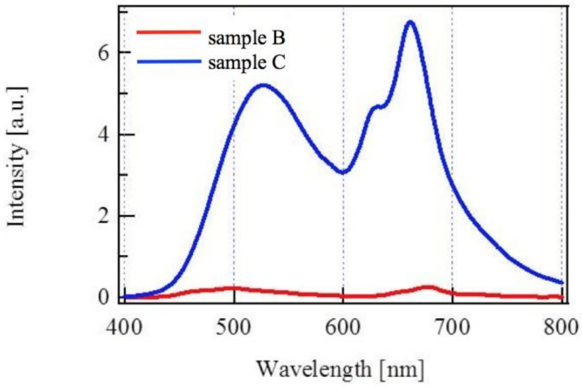


(b)

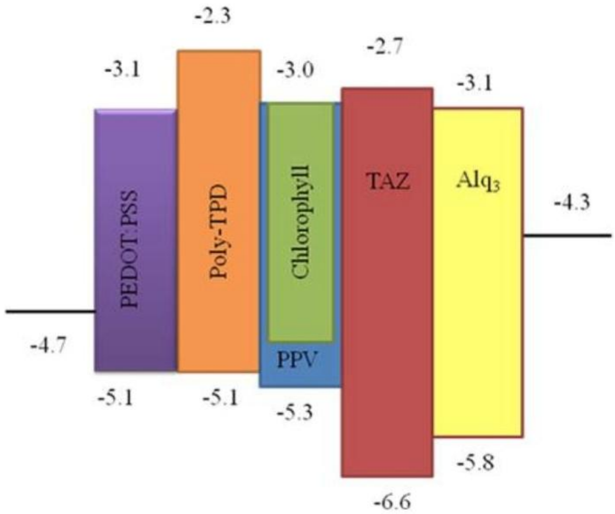
Fig.1. (a) EL spectra of samples A and B for an applied bias voltage of 20 V. (b) Energy band diagram of sample B. -4.7 on left and -4.3 on right are the work functions of ITO and Al cathode metal, respectively

B. Quadruple- and quintuple-layer OLEDs

Figure 2(a) shows the EL spectra of samples B and C. The applied voltages were 7.5 V for sample B and 10.0 V for sample C; they exhibited a maximum luminance of 2.06 cd/m2 (sample B) and 65.0 cd/m2 (sample C). Thus, the maximum luminance of sample C was about thirty times larger than that of sample B. This result can be attributed to the improved electron injection due to the electron-transporting layer of Alq3. As shown in Fig. 2(b), the lowest unoccupied molecular orbital (LUMO) level of Alq3 is located in the discontinuity between the LUMO level of TAZ and the work function of the Al cathode metal, increasing the electron injection into the TAZ and active layers.



(a)



(b)

Fig.2. (a) EL spectra of samples B and C. Applied voltages were 7.5 V for sample B and 10.0 V for sample C, at which the samples exhibited the maximum luminance. (b) Energy band diagram of sample C. -4.7 on left and -4.3 on right are the work functions of ITO and Al cathode metal, respectively

C. Antioxidant activities of carotenoids doped in the different layers

The carotenoids extracted from spinach improved the operation lifetime of OLEDs [5]. In this case, the carotenoids were doped in the active layer in which the chlorophyll that was extracted from spinach was used as an emissive material. In addition, the samples we studied had a bilayer structure that consisted of hole-injection and active layers.

We doped the carotenoids in the electron-transporting layer (sample D) and in the hole-blocking layer (sample E). Therefore, they were adjacent to the active layer in sample E, but they were unattached to it in sample D. We observed the EL intensities of samples D and E three days after the fabrication. The operation lifetime of the sample D did not improve; its luminance decreased to about 18% due to the oxidation in three days. On the other hand, the luminance of sample E decreased but maintained a leve of about 70% in three days. This indicates that the

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carotenoids in the adjacent layer to the active layer resulted in strong antioxidant activities, lengthening the operation lifetime of the OLEDs.

We also evaluated the luminance-voltage characteristice of samples D and E (Fig. 3). This measurement was performed just after their fabrication. The maximum luminance of sample D was very weak; only about one-sixth of sample E. This is probably because the carotenoids suppressed the electron-transporting activities of Alq3. In addition, the luminance of sample E became maximum at about 12.5 V, and that of sample D became maximum at a different applied voltage of about 9 V. These results clearly indicate that the antioxidant activities of carotenoids were strongly activated and improved the operation lifetime of the OLEDs when they were adjacent to the active layer.

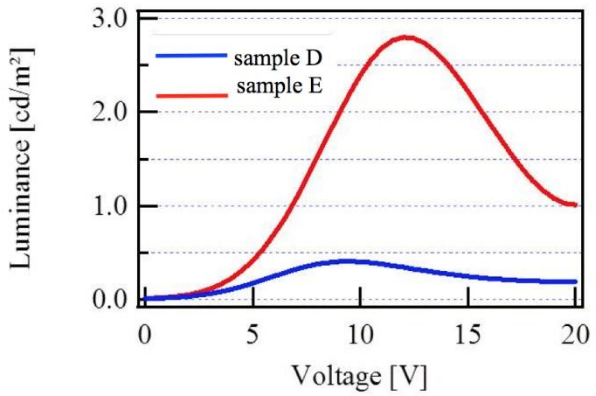

Fig.3. Luminance-voltage characteristics of samples D and E.

Figure 4 shows the time variation of the luminances of samples C and E, which were measured at three and four days after their fabrications. It is obvious that the luminance of sample C in which carotenoids were not doped decreased to about 30% in four days. On the other hand, sample E's luminance decreased but maintained a level of about 70% in four days. These results indicate that the antioxidant activities of the carotenoids extracted from spinach effectively improved the operation lifetime of the OLEDs.

IV. Conclusion

We fabricated multi-layered organic light-emitting diodes (OLEDs) and used the chlorophyll extracted from spinach as an emissive material to improve their light emission efficiencies. In quintuple-layer OLEDs, the hole-blocking layer plays an important role to improve the luminance. We also evaluated the antioxidant activities of carotenoids that were also extracted from spinach. When they were doped in the hole-blocking layer that was adjacent to the active layer, the quintuple-layer OLED revealed a longer operation lifetime. On the other hand, when they were doped in the electron-transporting layer, which was unattached to the active layer, the luminance was very weak and the sample's operation lifetime did not improve. Thus, the antioxidant activities of the carotenoids were activated when they were adjacent to the active layer. Therefore, carotenoids extracted from plants are strong candidates for low-price materials to improve the operation lifetime of OLEDs.

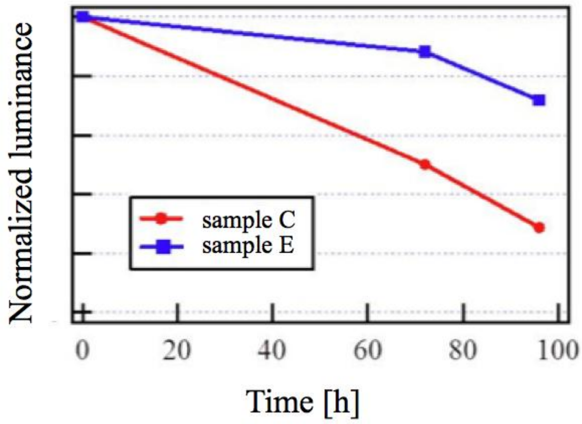

Fig.4. Time variation of luminances of samples C and E normalized by value measured just after fabrication. Luminances were measured at three and four days after fabrication.

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