

Research Article

Light-Emission and Electricity-Generation Properties of Photovoltaic Organic Light-Emitting Diodes with Rubrene/DBP Light-Emission and Electron-Donating Layers

Mun Soo Choi¹ and Ho-Nyeon Lee²

¹ Department of Electric & Robotics Engineering, Soonchunhyang University, Asan 336-745, Republic of Korea

² Department of Display and Electronic Information Engineering, Soonchunhyang University, Asan 336-745, Republic of Korea

Correspondence should be addressed to Ho-Nyeon Lee; hnlee@sch.ac.kr

Received 22 December 2013; Accepted 6 March 2014; Published 6 April 2014

Academic Editor: Mark van Der Auweraer

Copyright © 2014 M. S. Choi and H.-N. Lee. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

We report the dependence of the characteristics of photovoltaic organic light-emitting diodes (PVOLEDs) on the composition of the light-emission and electron-donating layer (EL-EDL). 5,6,11,12-Tetraphenylnaphthacene (rubrene): dibenzo[*h*,*h'*]-4,4',7,7'-tetraphenyl]diindeno[1,2,3-*cd*:1',2',3'-*lm*]perylene (DBP) was used to form the EL-EDL, and C₆₀ was used as an electron-accepting layer (EAL) material. A half-gap junction was formed at the EAL/EL-EDL interface. As the rubrene ratio in the EL-EDL increased, the emission spectra became blue-shifted and the light-emission efficiency increased. The highest emission efficiency was achieved with an EL-EDL composed of 95% rubrene and 5% DBP. The short-circuit current decreased as the rubrene content increased up to 50% and then saturated, while the open-circuit voltage was almost unchanged regardless of the rubrene content. The power-conversion efficiency and fill factor increased as the composition of the EL-EDL approached that of pure materials. By controlling the rubrene : DBP ratio, the emission color could be adjusted. The emission efficiency of devices with mixed rubrene/DBP EL-EDLs could be greater than that of either pure rubrene or pure DBP devices. We obtained an overall power-conversion efficiency of 3% and a fill factor greater than 50%.

1. Introduction

Organic light-emitting diodes (OLEDs) and organic solar cells (OSCs) are two of the most widely used organic semiconductor devices. They are both fabricated using diode structures, and so they have similar configurations. Because of this, there has been much interest in creating combined OLED/OSC devices. By controlling the bias conditions, such dual-function photovoltaic organic light-emitting diodes (PVOLEDs) can operate as either an OLED or an OSC [1, 2]; this dual-function capability has the potential to considerably widen the range of applications of organic electronics. PVOLEDs can be used to develop extremely energy-efficient devices, for example, a display screen that can charge the battery when not in use. In addition, smart windows can be fabricated using PVOLEDs, which generate electricity during the day and can be used as a large-area display at night.

OLEDs and OSCs have somewhat contradictory requirements in terms of the behavior of electrons and holes. To obtain an efficient OLED, electrons and holes should recombine to generate light. In an OSC, photogenerated electrons and holes should be readily separated to contribute to a photocurrent. The device structure of OLEDs or OSCs is typically optimized for these particular requirements, and, as a result, we may expect that the device structure of a PVOLED will be different to those of either an OLED or OSC. There have been reports of dual-function organic diodes using a number of different device structures, including conventional organic diode structures [3–8], ionic junctions [9], half-gap junction structures [1, 2, 10], and tandem structures [11]. However, the reported efficiencies of both electrical power generation and light emission are considerably lower than the respective efficiencies of conventional OLEDs and OSCs. PVOLEDs with a structure similar to that of a conventional

OLED showed photovoltaic behavior under ultraviolet (UV) light rather than white light. Ionic junction PVOLEDs have stability issues due to the migration of the ions. Tandem structured PVOLEDs have complex stacked structures because of the separate units for the photovoltaic operation and light emission. Half-gap junction PVOLEDs are fabricated using a simple structure based on stable organic materials and can generate electricity under white light. For these reasons, we used a half-gap junction structure in this work.

The half-gap junction is composed of a light-emission and electron-donating layer (LE-EDL) and an electron-accepting layer (EAL). The lowest unoccupied molecular orbital (LUMO) level of the EAL is located close to the middle of band gap of the LE-EDL. A schematic diagram illustrating the operation of a PVOLED based on a half-gap junction structure is shown in Figure 1. In photovoltaic mode, electron-hole pairs generated by incident light are separated as shown in Figure 1(a). In the light-emission mode, the excess energy generated from electron-hole recombination at the interface between the LE-EDL and the EAL supplies energy for another electron at the LUMO of the EAL to move into the EL-EDL, as shown in Figure 1(b).

Here, we investigate the properties of PVOLEDs with various compositions of the EL-EDL. The EL-EDL was fabricated using 5,6,11,12-tetraphenylanthracene (rubrene) [12, 13] and dibenzo[*[f,f']*-4,4',7,7'-tetraphenyl]diindeno[1,2,3-cd:1',2',3'-lm]perylene (DBP) [14, 15]. DBP has a similar HOMO level to that of rubrene, but a slightly lower LUMO level, as shown in Figure 2(a). The composition of DBP and rubrene in the EL-EDL is expected to influence the light-emission and electricity-generation properties of the PVOLEDs. We describe the characteristics of PVOLEDs for various ratios of DBP : rubrene in the EL-EDL.

2. Experiments

The stacked structure of the PVOLEDs is shown in Figure 2(b), and it consisted of a 0.5 mm thick glass substrate, a 150 nm thick indium tin oxide (ITO) anode layer, a 30 nm thick N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) layer, a 30 nm thick rubrene:DBP layer, a 45 nm thick C₆₀ layer, a 5 nm thick 4-7-diphenyl-1,10-phenanthroline (BPhen) layer, a 1 nm thick LiF layer, and a 100 nm thick Al cathode layer. Chemical structures of above organic materials are shown in Figure 3. The rubrene:DBP layer functioned as an EL-EDL, and C₆₀ was used as an EAL. The ITO layer deposited using plasma-beam deposition had a sheet resistance of 10 Ω/sq. Anodes were patterned using photolithography and wet etching. Following anode patterning, oxygen-plasma treatment was carried out using the inductively coupled plasma (ICP) machine. The organic layers and the LiF/Al layer were then deposited sequentially using thermal evaporation at a pressure of 10⁻⁶ Torr. The EL-EDL was deposited using a codeposition process. The ratio of rubrene:DBP was controlled by adjusting the deposition rates of rubrene and DBP independently and was calculated as the volume ratio, that is, (rubrene volume)/(rubrene volume + DBP volume). An encapsulation process employing a glass cap in a nitrogen environment was carried out following

the fabrication of the diodes. The light-emitting properties were measured using a spectroradiometer in a dark box, and the photovoltaic properties were measured using a solar simulator with an air-mass coefficient (AM) specification of AM1.5.

3. Results and Discussion

In this work, the electron injection process to the EL-EDL may be explained as follows [10]. In the light-emission mode, injected electrons and holes should be accumulated at each side of the EAL/EL-EDL interface due to the large barrier. Hence, exciplex states could be formed at the interface. Due to the large concentration of electrons at the interface, the electron-hole recombination energy of the exciplex could contribute to exciting an electron in the LUMO of C₆₀ to a C₆₀⁻ excited state [16] located at 1.1 eV above the ground state. Because the height of the C₆₀⁻ excited state and the electron-injection barrier height at the EAL/EL-EDL interface are similar, the excited electron may be injected into the EL-EDL.

The electroluminescence as a function of the current density is shown in Figure 4(a) for various rubrene ratios in the EL-EDL. In general, a higher rubrene ratio resulted in more luminance; however, a pure rubrene EL-EDL showed a less luminance than the 95% rubrene EL-EDL. A small doping of 5% DBP to 95% rubrene resulted in the most efficient light emission. The normalized emission spectra of PVOLEDs are shown in Figure 4(b) as a function of the rubrene composition. With a small addition of DBP to rubrene (95% rubrene ratio), the emission spectrum was changed from that of rubrene [17, 18] to DBP [15, 17, 19]. The emission spectra from high DBP ratio devices (rubrene ratio of 0~50%) became red-shifted from the previously known DBP emission spectra. The high DBP ratio could cause the formation of DBP aggregates. The DBP aggregates may cause the red shift [20]. By changing the rubrene content, the color of the emitted light could be changed from red to green. DBP has a lower LUMO level than rubrene, so electrons can be excited from the LUMO of C₆₀ to the LUMO of DBP more easily than from the LUMO of C₆₀ to the LUMO of rubrene. Hence, electron transfer from the EAL to the EL-EDL could be enhanced by using DBP as a dopant. However, when the DBP ratio was larger than 50%, the emission efficiency decreased according to the DBP-ratio increase. DBP-aggregate concentration may increase according to the DBP-ratio increase. The increased DBP aggregate concentration may reduce the emission efficiency.

Figure 5(a) shows current density curves as a function of the bias voltage for various rubrene ratios. The short-circuit current, I_{SC} , decreased as the rubrene ratio increased up to 50% and then saturated. The increase in I_{SC} with the DBP ratio may be related to the lower light-emission efficiency at the higher DBP ratio. The lower light-emission efficiency may imply that exciton in EL-EDL diffuses farther before a recombination reaction. The longer exciton diffusion length can result in a larger I_{SC} . Whereas there was a significant change in I_{SC} , the change in the open-circuit voltage, V_{OC} , was small. Figure 5(b) shows the power-conversion efficiency, η , and the fill factor (FF) as a function of the rubrene ratio. The

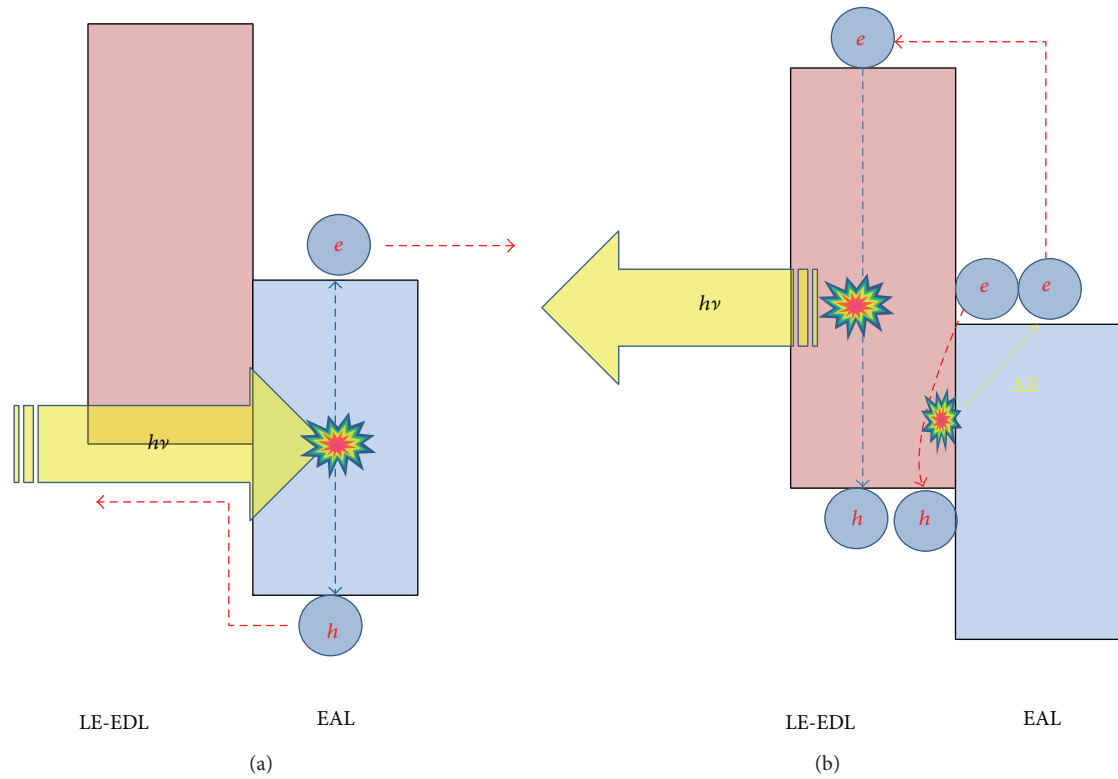


FIGURE 1: Schematic diagram showing the operation of a PVOLED with a half-gap junction structure: (a) electricity-generation mode and (b) light-emission mode.

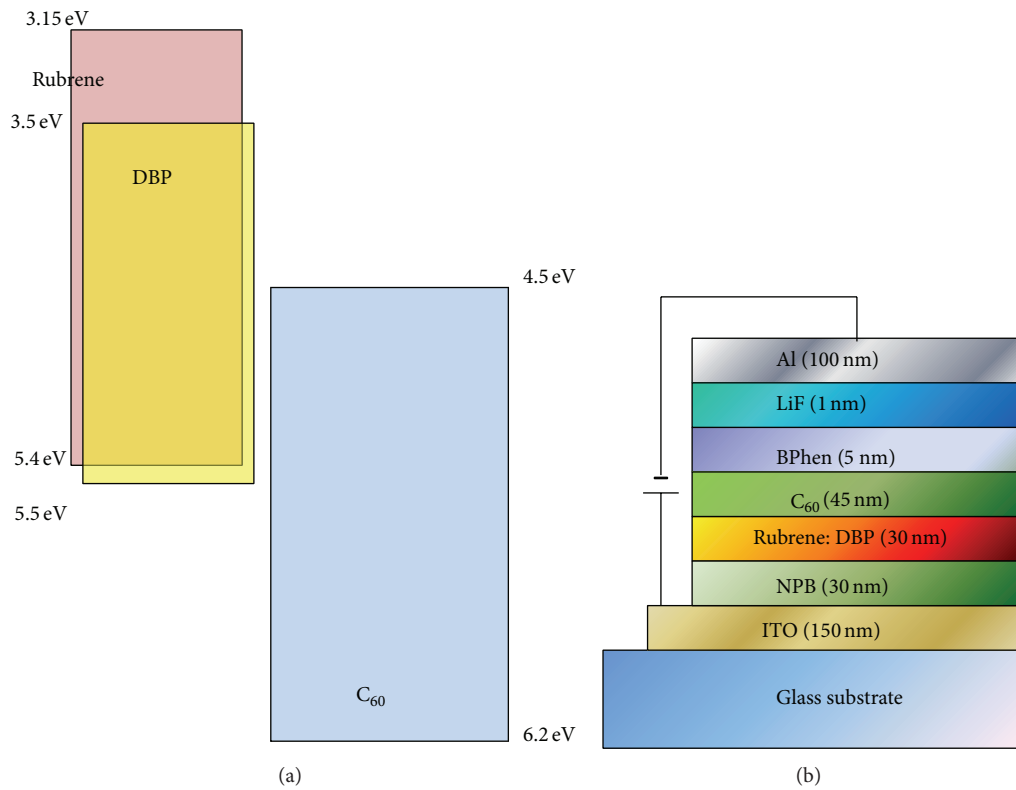


FIGURE 2: Schematic diagram showing (a) the energy bands of the junction materials and (b) the stacked structure of the devices.

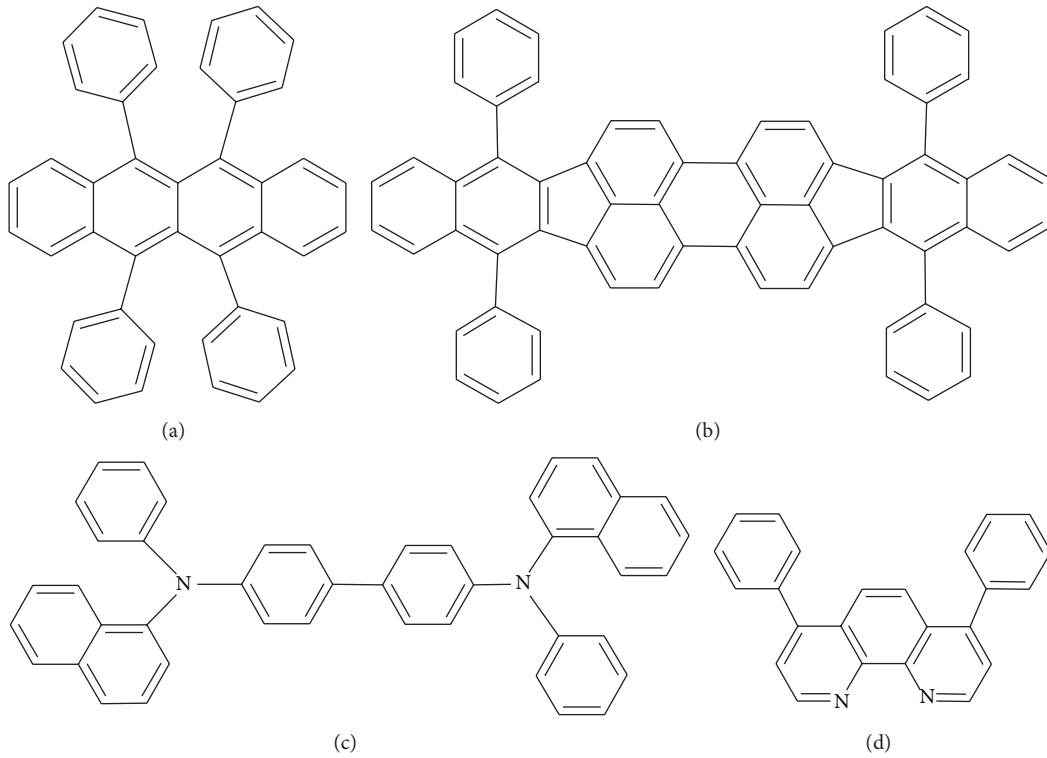


FIGURE 3: Chemical structure of (a) rubrene, (b) DBP, (c) NPB, and (d) BPhen.

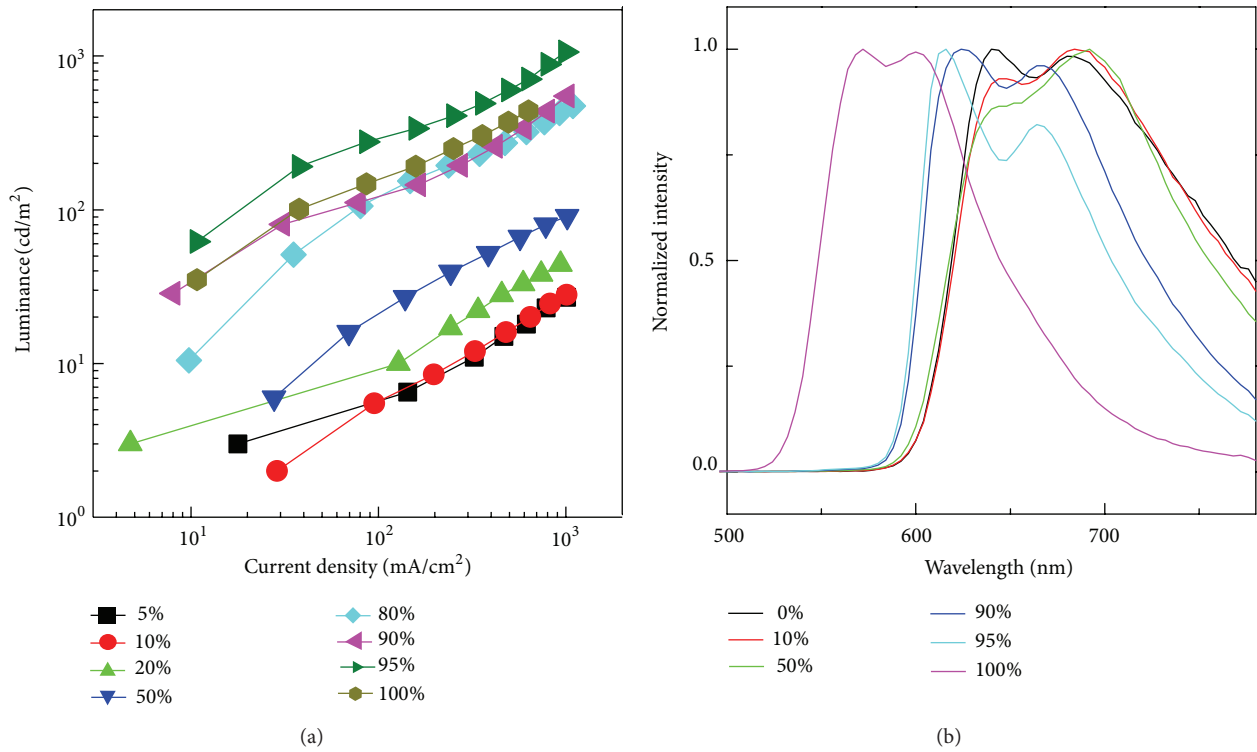


FIGURE 4: (a) Luminance as a function of current density and (b) normalized emission spectra for various rubrene ratios of the EL-EDL. Legends in the figures show the rubrene percent ratios.

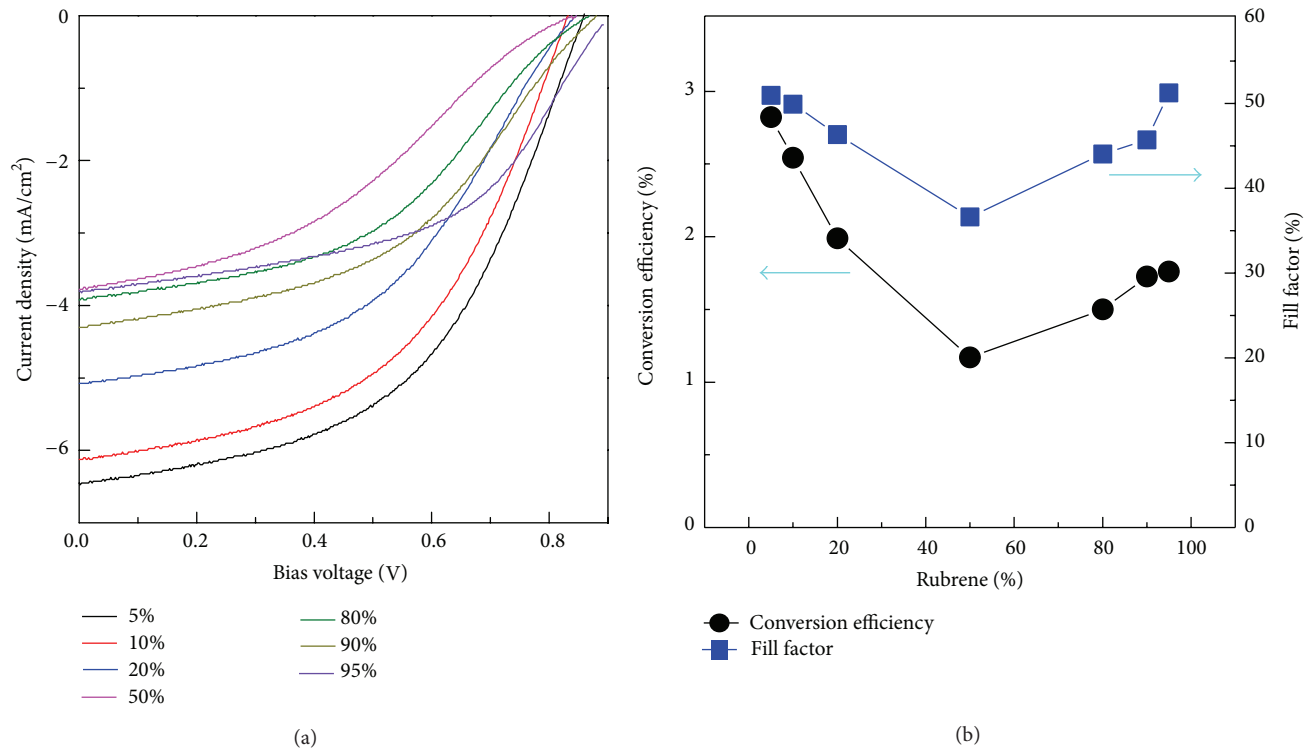


FIGURE 5: (a) Current density as a function of bias voltage for various rubrene ratios and (b) power-conversion efficiency and fill factor as a function of the rubrene ratio. Legends in (a) show the rubrene percent ratios.

value of η decreased as the rubrene ratio increased from 0% to 50% and then increased again as the rubrene ratio increased above 50%, and finally saturated when the rubrene ratio was above 95%. The FF showed a similar behavior to that of η ; the FF increased as the composition of EL-EDL approached that of pure DBP or pure rubrene. The dependence of the FF on the composition ratio may be related to a conductivity change of the EL-EDL according to the composition ratio.

4. Conclusion

We successfully fabricated PVOLEDs employing a rubrene:DBP EL-EDL/C₆₀ EAL junction structure, which could operate as either an OLED or an OSC, depending on the bias conditions. The dependence of the operating characteristics of the PVOLEDs on the rubrene:DBP ratio was investigated using stacked ITO/NPB/rubrene:DBP/C₆₀/BPhen/LiF/Al diode structures. When operating in light-emission mode, as the rubrene ratio increased, the emission spectra became blue-shifted and the light-emission efficiency increased. The highest light-emission efficiency was archived with a 95% rubrene:5% DBP EL-EDL. This optimum efficiency could be explained by a doping effect of DBP. The doping effect and aggregate formation of DBP could explain the overall dependence of the light-emission behavior on the rubrene:DBP ratio.

When operating in photovoltaic mode, I_{SC} increased as the rubrene ratio increased up to 50% and then saturated, and V_{OC} remained almost unchanged. η and FF showed a similar

dependence on the rubrene ratio, and, as the composition of EL-EDL approached that of the pure materials, η and FF increased. Changes in exciton diffusion length and conductivity according to the composition of EL-EDL could explain these phenomena. However, additional works are required to confirm the explanation.

The emission color could be controlled by varying the rubrene ratio. The emission efficiency of the 95% rubrene devices was higher than that of pure rubrene or pure DBP EL-EDL devices. A power-conversion efficiency of approximately 3% and a FF greater than 50% were obtained. The work described here is expected to be useful in developing methods to control the light-emission and electricity-generation properties of PVOLEDs.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (Grant no. 2010-0023459) and by the Soonchunhyang University Research Fund.

References

- [1] H. N. Lee and M. S. Choi, "Dependence of light-emitting and photovoltaic properties of dual-function organic diodes on carrier-transporting layers," *Electronic Materials Letters*, vol. 9, no. 1, pp. 29–32, 2013.
- [2] H. N. Lee and M. S. Choi, "Dependence of the characteristics of photovoltaic organic light-emitting diodes on device structure," *Molecular Crystals and Liquid Crystals*, vol. 584, no. 1, pp. 139–144, 2013.
- [3] S. Sahu and A. J. Pal, "Multifunctionality of organic devices: light emission, photovoltage generation, and photodetection," *The Journal of Physical Chemistry C*, vol. 112, no. 22, pp. 8446–8451, 2008.
- [4] L. L. Chen, W. L. Li, M. T. Li, and B. Chu, "Bifunctional electroluminescent and photovoltaic devices using bathocuproine as electron-transporting material and an electron acceptor," *Journal of Luminescence*, vol. 122–123, no. 1–2, pp. 667–670, 2007.
- [5] H. Wei, W. Li, M. Li et al., "White organic electroluminescent device with photovoltaic performances," *Applied Surface Science*, vol. 252, no. 6, pp. 2204–2208, 2006.
- [6] Z. R. Hong, C. S. Lee, S. T. Lee, W. L. Li, and Y. Shirota, "Bifunctional photovoltaic and electroluminescent devices using a starburst amine as an electron donor and hole-transporting material," *Applied Physics Letters*, vol. 81, no. 15, pp. 2878–2880, 2002.
- [7] B. Chu, D. Fan, W. L. Li, Z. R. Hong, and R. G. Li, "Organic-film photovoltaic cell with electroluminescence," *Applied Physics Letters*, vol. 81, no. 1, pp. 10–12, 2002.
- [8] A. Cravino, P. Leriche, O. Alévêque, S. Roquet, and J. Roncali, "Light-emitting organic solar cells based on a 3D conjugated system with internal charge transfer," *Advanced Materials*, vol. 18, no. 22, pp. 3033–3037, 2006.
- [9] D. A. Bernardis, S. Flores-Torres, H. D. Abruña, and G. G. Malliaras, "Observation of electroluminescence and photovoltaic response in ionic junctions," *Science*, vol. 313, no. 5792, pp. 1416–1419, 2006.
- [10] A. K. Pandey and J.-M. Nunzi, "Rubrene/fullerene heterostructures with a half-gap electroluminescence threshold and large photovoltage," *Advanced Materials*, vol. 19, no. 21, pp. 3613–3617, 2007.
- [11] C.-J. Yang, T.-Y. Cho, C.-L. Lin, and C.-C. Wu, "Organic light-emitting devices integrated with solar cells: high contrast and energy recycling," *Applied Physics Letters*, vol. 90, no. 17, Article ID 173507, 2007.
- [12] Z. Wang, Y. Lou, S. Naka, and H. Okada, "Direct comparison of solution- and vacuum-processed small molecular organic light-emitting devices with a mixed single layer," *ACS Applied Materials and Interfaces*, vol. 3, no. 7, pp. 2496–2503, 2011.
- [13] D. Wang, Z. Wu, X. Zhang et al., "Solution-processed organic films of multiple small-molecules and white light-emitting diodes," *Organic Electronics: Physics, Materials, Applications*, vol. 11, no. 4, pp. 641–648, 2010.
- [14] K. Okumoto, H. Kanno, Y. Hamada, H. Takahashi, and K. Shibata, "Organic light-emitting devices using polyacene derivatives as a hole-transporting layer," *Journal of Applied Physics*, vol. 100, no. 4, Article ID 044507, 2006.
- [15] K. Okumoto, H. Kanno, Y. Hamada, H. Takahashi, and K. Shibata, "High efficiency red organic light-emitting devices using tetraphenyl-dibenzoperiflanthene-doped rubrene as an emitting layer," *Applied Physics Letters*, vol. 89, no. 1, Article ID 013502, 2006.
- [16] K. Matsumoto, M. Fujitsuka, T. Sato, S. Onodera, and O. Ito, "Photoinduced electron transfer from oligothiophenes/polythiophene to fullerenes (C_{60}/C_{70}) in solution: comprehensive study by nanosecond laser flash photolysis method," *Journal of Physical Chemistry B*, vol. 104, no. 49, pp. 11632–11638, 2000.
- [17] T. Kasahara and J. Mizuno, "Variable multi-color microfluidic organic light emitting device based on mixing of electrochemiluminescence solutions," in *Proceedings of the 17th International Conference on Solid-State Sensors, Actuators Microsystems, 27th Transducers Eurosensors*, pp. 2596–2599, 2013.
- [18] R. Petre and T. Zecheru, "Synthesis and characterization of new oxalate ester-polymer composites for practical applications," *Journal of Luminescence*, vol. 135, no. 1, pp. 288–294, 2013.
- [19] Y. Zhang and S. R. Forrest, "Triplets contribute to both an increase and loss in fluorescent yield in organic light emitting diodes," *Physical Review Letters*, vol. 108, no. 26, Article ID 267404, 2012.
- [20] S. K. Saikin, A. Eisfeld, S. Valleau, and A. Aspuru-Guzik, "Photonics meets excitonics: natural and artificial molecular aggregates," *Nanophotonics*, vol. 2, no. 1, pp. 21–38, 2013.

