Organic Light-Emitting Diodes Using Octafluorobiphenyl-Based Polymer Synthesized by Direct C–H/C–H Cross Coupling Reaction

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Organic light-emitting diodes (OLEDs) were prepared using the P1 polymer and then characterized. P1 was synthesized via the direct C–H/C–H cross coupling reaction between octafluorobiphenyl and bithiophene monomers. By analyzing the electroluminescence properties of various OLED structures, P1 was found to exhibit more favorable ambipolar transport, compared with F6T2, which consists of fluorene and bithiophene units. The octafluorobiphenyl monomer was already known to exhibit fewer undesired homocoupling defects in P1. Thus, our experimental results in this study proved that octafluorobiphenyl was useful not only for the cross coupling reaction but also for adding new functions to polymers.

Keywords: Octafluorobiphenyl, π -Conjugated polymer, Organic light-emitting diode, Cross coupling, Electroluminescence

1. Introduction

Interest in π -conjugated polymer-based thin-film devices such as organic light-emitting diodes (OLEDs), organic photovoltaics, and organic transistors has been increasing due to the growth in the flexible electronics and circuit market. Interest has also grown due to the ability of this class of materials to be solution-processed over large areas at a low cost [1,2]. To date, highly efficient polymer-based thin-film devices have depended on the development of novel π -conjugated polymers synthesized via cross coupling reactions [3,4]. Conventional polycondensation procedures are essentially based on coupling reactions between organometallic monomers and halogenated monomers. These are typically multistep syntheses. Hence, production is energy intensive and expensive [5].

To reduce synthetic steps and material costs, a polycondensation reaction with a direct C–H

arylation mechanism has been developed in recent years. The mechanism causes the activated C–H bond of one monomer to react with an aryl halide on another monomer [6,7]. This polycondensation reaction reduces the number of synthetic steps, toxic byproducts, and the quantity of impurities produced. The latter point is important, as it simplifies the purification process compared with conventional polycondensation processes [8]. However, it is important to note that it has been reported that the performance of polymer-based thin-film devices deteriorates when the devices are fabricated using polymers with an aryl halide on the terminal structure [9]. Thus, further developments of cross coupling reactions without the use of pre-functionalized starting monomers are necessary [10].

To address this issue, we recently developed a new polymer, P1 prepared via the direct C–H/C–H cross coupling reaction (cross-dehydrogenative-coupling reaction) between

octafluorobiphenyl and dihexyl-bithiophene monomers as shown in Fig. 1 [11]. This mechanism allows straightforward access to alternating π -conjugated polymers with no possibility that aryl halides remain at the terminal positions. The obtained polymer was evaluated as a light emitting and hole transport polymer in OLEDs exhibiting external quantum efficiencies (EQEs) of 0.12% [11].

In the reaction mentioned above, octafluoro biphenyl proved to be the most suitable monomer, exhibiting fewer undesired homocoupling defects in P1. In subsequent research, we will focus on the function of octafluorobiphenyl in P1-based OLEDs, because fluorinated acenes have been known to lower the HOMO-LUMO energy levels in organic semiconductors, and lead to electron transporting materials [12-15]. In this study, by fabricating various OLED structures and analyzing their electroluminescence (EL) properties, it is indicated that P1 exhibits ambipolar (hole-electron balanced) carrier transport, in comparison to the reference F6T2 polymer which consists of fluorene and bithiophene units.

2. Experimental

2.1. Materials and methods

P1 was prepared via a Pd-catalyzed C–H/C–H cross coupling reaction described in the literature [11]. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of P1 were estimated to be 53400 and 2.9, respectively. As a reference light emitting (hole transport) polymer, F6T2 was purchased from American Dye Source, Inc. The

M_n and polydispersity were estimated to be 7200 and 1.8, respectively. Poly(3,4-ethylenedioxy thiophene)-poly(styrenesulfonate) (PEDOT:PSS, Clevis P VP AI 4083) was purchased from Heraeus. Poly(N-vinylcarbazole) (PVK) was purchased from Tokyo Chemical Industry. 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenylbenzimidazole) (TPBi) was purchased from Luminescence Technology Corp. UV-vis absorption spectra were recorded on a Hitachi U-3010 spectrometer. The photoluminescence (PL) spectra and the internal PL quantum efficiency were measured using a Jasco FP-6500 spectrofluorometer with an integrating sphere. The thicknesses of the films were measured using an automatic micro-figure measuring instrument (Surfcoorder ET200, Kosaka Laboratory Ltd.). The HOMO energy levels of P1 and F6T2 in the thin-film state were measured by photoelectron yield spectroscopy using an AC-3 spectrometer (Riken Keiki). The LUMO energy levels of the polymers in the thin-film state were estimated using optical bandgaps and their HOMO energy levels.

2.2. Fabrication and characterization of OLEDs

The OLEDs were fabricated in the following configurations: Device A: ITO/PEDOT:PSS/P1 (79 nm)/LiF/Al; device B: ITO/PEDOT:PSS/PVK (33 nm)/P1 (47 nm)/LiF/Al; device C: ITO/PEDOT:PSS/P1 (49 nm)/TPBi (40 nm)/LiF/Al; and device D: ITO/PEDOT:PSS/PVK (22 nm)/P1 (32 nm)/TPBi (30 nm)/LiF/Al. Patterned indium tin oxide (ITO) glass with a sheet resistance of 10 Ω /square was pre-cleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet/ozone chamber. A 40 nm hole injection layer of PEDOT:PSS was spin-coated and subsequently dried at 110 $^{\circ}$ C for 10 min on a hot plate under air. The substrates were transferred to a N_2 glove box and then dried again at 110 $^{\circ}$ C for 10 min on a hot plate. A hole transport layer of PVK was spin-coated from chloroform solution and then annealed at 150 $^{\circ}$ C for 10 min in the fabrication of devices B and D. After annealing treatment, the solubility of the PVK layer is reduced. This allowed us to fabricate a multilayer architecture by subsequent spin-coating [16]. A light emitting layer of P1 was spin-coated from a chloroform solution in the fabrication of devices A and C (or spin-coated from a toluene solution in the fabrication of devices B and D) and then annealed at 80 $^{\circ}$ C for 10 min. Subsequently, an electron transport layer

Fig. 1. Chemical structures of P1 and monomers used in the direct C–H/C–H cross coupling reaction.

of TPBi was deposited by conventional thermal evaporation at a chamber pressure lower than 5×10^{-4} Pa in the fabrication of devices C and D. Finally, LiF (1 nm) and Al (100 nm) were deposited onto the active layer by vacuum evaporation. An active area of 2×2 mm² of the devices was determined by the overlap area of the anode and cathode.

Current density (J), voltage (V) characteristics and luminance (L) of the OLEDs were simultaneously measured using an ADCMT 6246 DC voltage current source/monitor (ADC Corporation) and an LS-100 luminance meter (Konica Minolta Japan, Inc.), respectively. The EL spectra and the coordinates of the CIE chromaticity were measured using an array spectrometer (MCPD-9800-311C, Otsuka Electronics Co., Ltd.).

3. Results and discussion

Figures 2 and 3 show the EL spectra, and J - V , L - V characteristics of devices A, B, C, and D. The EL spectra of all devices are consistent with the PL spectrum of P1 in thin-film state, as shown in Fig. 2. Thus, all EL spectra are originated from P1 in these devices. Probably due to a low carrier mobility of P1 or a high carrier injection barrier between the electrodes and P1 with the HOMO (LUMO) energy of 6.07 (3.11) eV, a high turn on voltage in device A is observed in Figs. 3(a) and (b). This high driving voltage can be reduced somewhat by stacking PVK and P1 [16], as done in device B or by stacking P1 and TPBi [17], as done in device C.

Fig. 2. PL spectrum of P1 in thin-film state and EL spectra from OLEDs.

Fig. 3. (a) Current density–voltage and (b) luminance–voltage of OLEDs using P1.

Device A (P1) shows the poorest performance, with a maximum EQE of 0.10%. However, this is comparable to the maximum EQE of 0.12% in device B (PVK/P1) and the maximum EQE of 0.12% in device C (P1/TPBi), as shown in Fig. 4. The experimental results using P1 in OLEDs are quite different from those using F6T2 with a HOMO energy of 5.52 eV and a hole mobility of 8.4×10^{-5} cm²V⁻¹s⁻¹ [18]. Two kinds of OLEDs were fabricated as a reference experiment: Device I: ITO/PEDOT:PSS/F6T2 (90 nm)/LiF/Al and device II: ITO/PEDOT:PSS/F6T2 (54 nm)/TPBi (40 nm)/LiF/Al. The fabrication methods for devices I and II are the same methods used for devices A and C, respectively. As shown in Figs. 4 and 5, device II (F6T2/TPBi) and device C

Fig. 4. EQE–current density of OLEDs using P1.

Fig. 5. Chemical structure of F6T2 and EQE–current density of OLEDs using F6T2.

(P1/TPBi) present similar maximum EQEs of 0.17% and 0.12%, respectively. This similarity arises because the internal PL quantum efficiency of the F6T2 film (8.5%) is similar to the PL efficiency of the P1 film (8.7%). On the other hand, device I (F6T2) shows a maximum EQE of 0.00023% (as seen in Fig. 5), which is about 430 times smaller than the EQE of 0.10% which was estimated in device A (P1). These results indicate that the current density in device I stems mainly from the hole only transport [19]. F6T2 has a similar LUMO energy as P1 (3.14 eV and 3.11 eV,

respectively). Therefore, considering the fact that F6T2 and P1 have the same electron injection barrier, it is implied that ambipolar (hole–electron balanced) transport is more easily realized in device A using P1, than in device I using F6T2.

Finally, to obtain the best performance of OLEDs using P1, both PVK and TPBi were used in device D, further improving the EL performance [20]. The maximum luminance and the maximum EQE were 2600 cd/m² and 0.37%, respectively, with the CIE chromaticity coordinates at (0.24, 0.46). A rough estimate of the upper limit for the EQE of OLEDs was given as 5%, when the light emitting layer from singlet excited states has the internal PL quantum efficiency of 100%. Thus, the upper limit for EQE using P1 with the internal PL quantum efficiency of 8.7% is estimated to be 0.44%. Since the EQE obtained in the experiment is close to the upper limit value, the ideal carrier balance in the multilayer device D has been realized [19]. Moreover, with the aim of solution processing all polymeric and organic layers in device D, the TPBi layer was fabricated by spin-coating from methanol solution [21]. The device showed an EQE of 0.32%, which is comparable to the EQE of 0.37% obtained with the vacuum-deposited TPBi layer.

4. Conclusion

By fabricating various OLED structures and analyzing their EL properties, it is indicated that P1 synthesized via the direct C–H/C–H cross coupling reaction between octafluorobiphenyl and bithiophene monomers exhibits more ambipolar carrier transport, than F6T2, which consists of fluorene and bithiophene units. Octafluorobiphenyl is known to be a useful monomer as it causes fewer undesired homocoupling defects in P1. Thus, in this study, we found that octafluorobiphenyl is useful not only for the direct C–H/C–H cross coupling reaction but also for adding a new function to polymers. Moreover, the multilayer OLEDs using P1 sandwiched between a hole-transport layer (PVK) and an electron-transport layer (TPBi) exhibited an EQE of 0.37%.

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References

1. L. Ying, F. Huang, and G. C. Bazan, *Nat. Commun.*, **8** (2017) 14047.
2. M. U. Ocheje, B. P. Charron, A. Nyayachavadi, and S. Rondeau-Gagné, *Flex. Print. Electron.*, **2** (2017) 043002.
3. S. Yu, F. Liu, J. Yu, S. Zhang, C. Cabanetos, Y. Gao, and W. Huang, *J. Mater. Chem. C*, **5** (2017) 29.
4. N. S. Gobalasingham, S. Ekiz, R. M. Pankow, F. Livi, E. Bundgaard, and B. C. Thompson, *Polym. Chem.*, **8** (2017) 4393.
5. T. P. Osedach, T. L. Andrew, and V. Bulović, *Energy Environ. Sci.*, **6** (2013) 711.
6. J.-R. Pouliot, F. Grenier, J. T. Blaskovits, S. Beaupré, and M. Leclerc, *Chem. Rev.*, **116** (2016) 14225.
7. T. Yasuda, J. Kuwabara, L. Han, and T. Kanbara, *J. Photopolym. Sci. Technol.*, **29** (2016) 347.
8. J. Kuwabara, T. Yasuda, S. J. Choi, W. Lu, K. Yamazaki, S. Kagaya, L. Han, and T. Kanbara, *Adv. Funct. Mater.*, **24** (2014) 3226.
9. J. Kuwabara, T. Yasuda, N. Takase, and T. Kanbara, *ACS Appl. Mater. Interfaces*, **8** (2016) 1752.
10. Q. Zhang, M. Chang, Y. Lu, Y. Sun, C. Li, X. Yang, M. Zhang, and Y. Chen, *Macromolecules*, **51** (2018) 379.
11. H. Aoki, H. Saito, Y. Shimoyama, J. Kuwabara, T. Yasuda, and T. Kanbara, *ACS Macro Lett.*, **7** (2018) 90.
12. W. Lu, J. Kuwabara, T. Iijima, H. Higashimura, H. Hayashi, and T. Kanbara, *Macromolecules*, **45** (2012) 4128.
13. F. Babudri, G. M. Farinola, F. Naso, and R. Ragni, *Chem. Commun.*, (2007) 1003.
14. T. Yasuda, K. Kashiwagi, Y. Morizawa, and T. Tsutsui, *J. Phys. D: Appl. Phys.*, **40** (2007) 4471.
15. A. M. Assaka, P. C. Rodrigues, A. R. M. de Oliveira, L. Ding, B. Hu, F. E. Karasz, and L. Akcelrud, *Polymer*, **45** (2004) 7071.
16. U. Giovanella, P. Betti, C. Botta, S. Destri, J. Moreau, M. Pasini, W. Porzio, B. Vercelli, and A. Bolognesi, *Chem. Mater.*, **23** (2011) 810.
17. L. Chen, G. Lin, H. Peng, H. Nie, Z. Zhuang, P. Shen, S. Ding, D. Huang, R. Hu, S. Chen, F. Huang, A. Qin, Z. Zhao, and B. Z. Tang, *J. Mater. Chem. C*, **4** (2016) 5241.
18. W. Tang, V. Chellappan, M. Liu, Z.-K. Chen, and L. Ke, *ACS Appl. Mater. Interfaces*, **1** (2009) 1467.
19. T. Tsutsui and N. Takada, *Jpn. J. Appl. Phys.*, **52** (2013) 110001.
20. U. Giovanella, C. Botta, F. Galeotti, B. Vercelli, S. Battiato, and M. Pasini, *J. Mater. Chem. C*, **1** (2013) 5322.
21. Z.-Y. Liu, S.-R. Tseng, Y.-C. Chao, C.-Y. Chen, H.-F. Meng, S.-F. Horng, Y.-H. Wu, and S.-H. Chen, *Synth. Met.*, **161** (2011) 426.