Syntheses of Vinyl Polymers Containing Phenylanthracene Pendants and Their Application ro Organic EL Device

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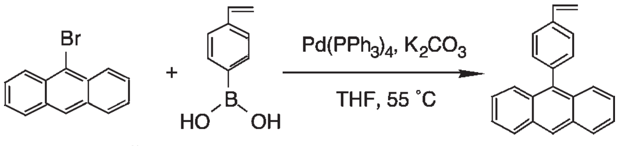
Fluorescent vinyl polymers containing 9-phenylanthracene pendants were synthesized and examined as an emitter layer in organic electroluminescent devices. The single layer polymer EL device using the homopolymer emitted green light originating from the excimer of the anthracene units. On the other hand, blue emission was observed from the devices using the copolymer with vinylcarbazole.

In organic electroluminescent devices (OELDs), two types of organic materials, small molecules and polymers, are used in device fabrication. Among polymers, π-conjugated polymers, such as poly(1,4-phenylenevinylene)[1] and its derivertives[2–4] have been widely used as the emitting layer in OELDs. However, it is still difficult to obtain blue emission due to extended π-conjugation. On the other hand, non-conjugated polymers such as poly(*N*-vinylcarbazole) (PVK)[5] emit in purplish blue region. In addition, emission color can be changed to various colors by doping fluorescent dyes. For example, we demonstrated white emission from the device using PVK doped with red, green and blue dyes.[6] In this case, hole-transporting PVK was doped with electron-transporting material, 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) to inject electrons to the PVK emitter layer.

In this study, our objective is to develop non-conjugated polymers and their OELDs emiting blue light. We synthesized vinyl polymers containing blue fluorescent 9-phenylanthracene pendants.

9-(4-Vinyl phenyl)anthracene (VPA) was synthesized by palladium-catalyzed Suzuki cross-coupling reaction as shown in Scheme 1. 9-Bromoanthracene was reacted at 55 °C with 1,4-vinylphenylboronic acid in tetrahydrofuran (THF) in the presence of $Pd(PPh_3)_4$ as a catalyst under nitrogen for 24 hours. The residue was chromatographed on silica-gel using chloroform-hexane (1 : 5) as eluent to yield the light yellow solid VPA (45%). Anal. Calcd for ($C_{22}H_{16}$): C, 94.25; H, 5.75%. Found: C, 94.03; H, 5.85%. mp 159.6–160.5 °C. 1H NMR ($CDCl_3$, 270 MHz, ppm): d 5.4–5.9 (2H, m, CH2), d 6.8–6.9 (1H, m, CH), d 7.2–8.0 (12H, m, Ar-H), d 8.5 (1H, s, Ar-H). The homopolymer and copolymer with N-vinylcarbazole (90 mol%) were synthesized by radical polymerization. 2,2′-Azobis (isobutyronitrile) (AIBN) as an initiator and the corresponding monomers reacted at 65 °C in THF under nitrogen for 24 h. The polymers were then dissolved in THF and precipitated into methanol, washed with methanol, and dried under vacuum at 60 °C to give light yellow polymers. Homopolymer: Anal. Calcd for ($C_{22}H_{16}$): C, 94.25; H, 5.75%. Found: C, 93.81; H, 5.85%. The composition of copolymer, molecular ratio of carbazole unit and phenylanthracene unit, was determined to be 9 : 1 (VK : VPA) from elemental analysis. Found: C, 87.46; H, 5.48; N, 6.25%. Molecular weights were determined by GPC using polystyrene as a standard. Weight average molecular weight of the homopolymer and copolymer were 12000 and 11300 with polydispersibilities of 1.92 and 1.88, respectively. The homopolymer and copolymer showed the glass transition temperatures at 173 and 168 °C, and decomposition temperatures at 427 and 405 °C, respectively.



Scheme 1. Synthesis of a monomer.

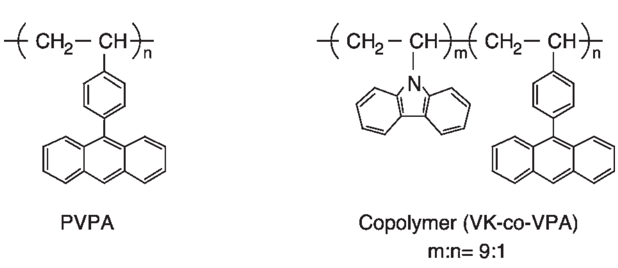


Figure 1. The molecular structures of polymers.

The polymers were examined as an emitter layer in single-layer-type devices. The device structure is a glass substrate/indium-tin-oxide (ITO)/polyethylenedioxithiophene (PEDOT) (600 Å)/emitting polymer (1000 Å)/LiF (5 Å)/Al (1000 Å). ITO-coated glass substrates were cleaned in a ultrasonic bath using several solvents and were treated in a UV-ozone chamber just before device fabrication. The organic layers were formed by spin coating from the solution onto ITO, and LiF and Al top electrode were deposited at 5×10^{-6} Torr. PEDOT, doped with polystyrene sulfonic acid, was received from Bayer Co. Ltd. ITO-coated glasses were received from Asahi Glass Co. Ltd. Luminance was measured using a Topcon BM-8 luminance meter and electroluminescence (EL) spectra were taken on a Hamamatsu photonics PMA-10 optical multi channel analyzer and photoluminescence (PL) spectra were taken on a fluorescence spectrometer, Instruments SA Fluoro Max-2. Ionization potential (Ip) was measured by atmosphere ultra violet photoelectron analysis using a Riken Keiki AC-1 under ambient atmosphere.

Figure 2 shows the EL spectra of the devices, which are identical with the PL spectra. Green EL from the homopolymer peaking at 490 nm was obtained from the devices as shown in Figure 2 (a), while, blue EL peaking at 435 nm was obtained from the device using copolymer as shown in Figure 2 (b). These results indicate that the decreasing of anthracene units in the copolymer composition suppresses the formation of the excimer of anthracene moiety.

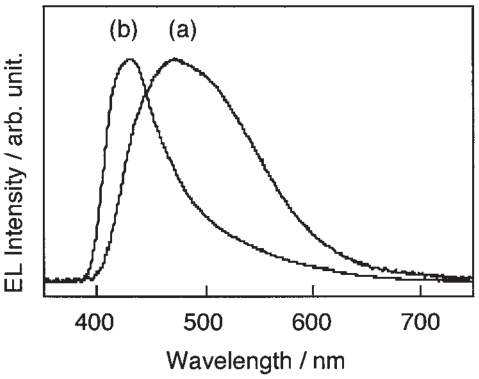


Figure 2. EL spectra of the devices. (a): ITO/PEDOT (600 Å)/homopolymer (1000 Å)/LiF/Al (b): ITO/PEDOT (600 Å)/copolymer (molecular ratio of monomer VK : VPA = 9 : 1 (1000 Å)/LiF/Al.

Luminance-voltage (L-V) and current density-voltage (J-V) characteristics of ITO/PEDOT (600 Å)/homopolymer (1000 Å)/LiF/Al device are plotted in Figure 3 (circles). The maximum luminance of the device using homopolymer is 25 cd/m^2 at 18 V. The external quantum efficiency (QE) of this device is calculated to be 0.004% at 15 V. In contrast, the maximum luminance of 60 cd/m^2 at 18 V and the external QE of 0.018% at 16 V are obtained from ITO/PEDOT (600 Å)/copolymer (1000 Å)/LiF/Al device (Figure 3 (triangles)). In this device, the barrier height for hole injection is smaller than that of the homopolymer-based device, due to smaller Ip value of the copolymer (Ip = 5.8 eV) compared with that of the homopolymer (Ip = 6.0 eV), which may improve carrier recombination efficiency. Figure 3 (squares) shows the L-V and J-V characteristics of ITO/PEDOT (600 Å)/copolymer doped with PBD (30 wt%) (1000 Å)/LiF/Al device. The maximum luminance and the external QE of the device using copolymer doped with 30 wt% PBD are improved to be 480 cd/m^2 at 18 V and 0.152% at 17 V, respectively, because of further balancing the electron-hole injection. The device performance is comparable to a blue-light-emitting OELDs using PVK doped with PBD and blue fluorescent dye, 1,1,4,4-tetraphenyl butadiene (TPB) peaking at 450 nm.[6]

In conclusion, we have succeeded in obtaining blue electroluminescence by the use of vinyl polymers having 9-phenylanthracene pendants as an emitter layer. Lifetime of the devices will be measured and reported elsewhere.

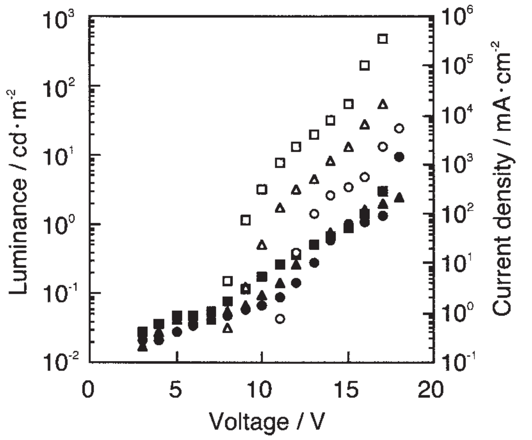


Figure 3. Luminance-Voltage (open symbols) and Current density-Voltage (close symbols) characteristics of the devices. (circles): ITO/PEDPT (600 Å)/homopolymer (1000 Å/LiF/Al, (triangle): ITO/PEDOT (600 Å)/copolymer (1000 Å)/LiF/Al, (squares): ITO/PEDOT (600 Å)/copolymer doped with PBD (30 wt%) (1000 Å)/LiF/Al.

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References and Notes

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature*, **347**, 539 (1990).

2 P. L. Burns, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, *Nature*, **356**, 47 (1992).

3 A. R. Brown, D. D. C. Bradley, J. H. Burroughes, R. H. Friend, N. C. Greenham, P. L. Burns, A. B. Holmes, and A. Kraft, *Appl. Phys. Lett.*, **61**, 2793 (1992).

4 G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature*, **357**, 477 (1992).

5 J. Kido, K. Hongawa, K. Okuyama, and K. Nagai, *Appl. Phys. Lett.*, **63**, 19, 2627 (1993).

6 J. Kido, H. Shionoya, and K. Nagai, *Appl. Phys. Lett.*, **67**, 16, 2281 (1995).