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An alternating copolymer for a blue light-emitting diode

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Summary

An alternating copolymer composed of 9,9'-dihexylfluorene and N-2-ethylhexyl carbazole was synthesized to use as an emissive polymer in a light-emitting diode(LED). The copolymer is soluble in organic solvents and spin-cast to make a fine film. An LED fabricated by sandwiching the alternating copolymer between indium-tin oxide and aluminum emits a white color with the full width at half maximum of 150 nm. The electroluminescence spectrum becomes simplified to have an emission peak at 460 nm for fine blue color when the copolymer is blended with poly(vinylcarbazole) with a ratio of 1 to 4 before the use as an emissive layer. The forward bias turn-on voltage for the LED is 13, and quantum efficiency is 0.002%.

Introduction

A light-emitting diode (LED) with organic chemicals as the emissive materials has some advantages over an LED with inorganic chemicals in terms of the operation voltage and the processibility of the emissive materials(1). However, the organic materials have a tendency to be crystallized during an operation of the LED to lose the original reactivity(2).

An emission of green-yellow color from the LED with poly (p-phenylenevinylene) (PPV) as the emissive layer is a great discovery for an ideal display system(3). A significant effort has gone into the improvements of the material since its introduction. The processibility was enhanced by increasing solubility of the material in organic solvents, which was accomplished by attaching a pendant group(4,5) or by inserting a chemical group on the main chain of the polymer(6). The emissive color was tuned by chemical

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modification of PPV(7,8). A ladder polymer based on PPV was also introduced for improvements in thermal stability and the stress life of LEDs(9). Polymers without a phenylenevinylene structure such as poly(p-phenylene)(10), poly(alkylthiophene)(11)and poly(alkylfluorene)(12)were introduced as emissive polymers in LEDs.

Fabrication techniques of a LED cell also attracted a great attention. Since light is emitted by a singlet decay of excitions formed by coupling between electrons and holes injected from the respective electrodes, a balanced charge transportation through the materials between two electrodes is prerequisite for a high quantum efficiency(13). Either an electron or a hole transporting layer or both were inserted between the electrodes and the emissive layer to enhance the quantum efficiency of an LED(14).

This work has tried to synthesize an emissive polymer which is soluble in organic solvents and gives blue light from an LED fabricated with the polymer.

Experimental

Synthesis of monomers

The sequences of syntheses of the monomers and the polymer are shown in Fig.1. 9.9'-Di-n-hexylfluorene was synthesized by the reaction of fluorene and n-hexylbromide using n-butyllithium in THF according to the literature procedure(15). A mixture of 33.4 g(0.1 mol) of 9,9'-di-n-hexylfluorene, 30 g(1.0 mol) of paraformaldehyde and 300 g of 30% HBr solution in acetic acid was stirred in a 1-L three-neck flask for 24 h at 60 ^{o}C. The reaction mixture was cooled to room temperature and 500 mL of cold water was added to it. The reaction mixture was extracted three times with 200 mL of dichloromethane each time. The extracted solution was washed subsequently with water and saturated aqueous solutions of $NaHCO_3$ and NaCl. The organic solution obtained was dried over anhydrous $MgSO_4$ which was then filtered. Pale yellow viscous liquid was obtained on evaporation of the solvent from the filtrate. The liquid was purified by a silica gel column using a solvent mixture of ethyl acetate and hexane with a ratio of 1 to 10 as an eluent. The resulting mixture was evaporated to afford 44.2 g (85% yield) of colorless viscous liquid of 2,7-bis(bromomethyl)-9.9'-di-n-hexylfluorene. ^{1}H-NMR ($CDCl_3$), δ(ppm): 0.59 (br, 6H, CH_3), 0.72-1.04(m, 16H, CH_2), 1.95(m, 4H, CH_2), 4.60(s, 4H, CH_2Br), 7.33-7.62(m, 6H, aromatic).

A mixture of 26.0 g (0.05 mol) of 2,7-bis(bromomethyl)-9,9'-di-n-hexylfluorene, 39.3 g (0.15 mol) of triphenylphosphine and 300 mL of dimethylformamide was heated to reflux in a 1-L three-neck flask with stirring for 12 h. The reactant was cooled to room temperature and added slowly to a flask with 1.5 L of ether while stirring. The white solid precipitate of 2,7-bis(bromomethyl)-9,9'-di-n-hexylfluorene triphenylphosphonium salt(I) was filtered, washed with ether three times and dried in a vacuum oven set temperature at 40 °C. Yield: 49.6 g (95 %). ^{1}H-NMR($CDCl_3$), δ(ppm): 0.11(br, 6H, CH_3), 0.62-1.09(m, 16H, CH_2),1.39(m, 4H, CH_2), 5.21-5.28(d, 4H, CH_2Br), 6,83-7.27(m, 6H, fluorenyl aromatic), 7.54-7.75(m, 30H, aromatic).

300 mL of dried THF in a 500-mL three-neck flask was purged with nitrogen and then 6.0 g (0.25 mol) of NaH was added into the flask to be stirred. 33.4 g (0.2 mol) of carbazole was added slowly into the mixture. 48.3 g (0.25 mol) of 1-bromo-2-ethylhexane diluted by 50 mL of THF was added dropwise into the flask and the content in the flask was refluxed for 12 h. The reactant was cooled to room temperature and then the solvent was stripped off by evaporation. The residue was added by 300 mL of H_2O and extracted with methylene chloride. The extracted solution was dried with anhydrous $MgSO_4$ and then filtered. Yellowish viscous liquid obtained on evaporation of the solvent from the filtrate was purified by employing a silica gel column with an eluent of an ethylacetate-hexane mixture of 1 to 10 ratio to get pale yellowish viscous liquid, N-(2-ethylhexyl) carbazole. Yield : 44.6g (80%), ^{1}H-NMR($CDCl_3$), δ(ppm) : 0.84-0.92(m, 6H, CH_3), 1.24-1.34(m, 8CH, CH_2), 2.03(m, 1H, CH), 4.12(d, 2H, NCH_2), 7.17-7.45(m, 6H, aromatic), 8.10(d, 2H, aromatic).

191 g (2.61 mol) of N,N-dimethyl formamide(DMF) and 100 mL of 1,2-dichloroethane in 1-L three-neck flask were purged with nitrogen and chilled to 0 °C. 197.6 g (1.29 mol) of phosphorous oxychloride was added slowly into the flask. The reactant was warmed up to room temperature and stirred for one hour, which was chilled again to 0 °C and added by 18.7 g (0.067 mol) of N-(2-ethylhexyl) carbazole diluted with 30 mL of 1.2-dichloroethane. In an hour, the reaction temperature was raised to 90 °C and then kept for 24 h to complete the reaction. After cooling to room temperature, the reaction mixture was poured into 1.5 L of ice water and extracted three times with 200 mL of methylene chloride. The extracted solution was subsequently washed with H_2O, saturated $NaHCO_3$ aqueous solution and aqueous NaCl solution to obtain organic liquid, which was then dried with anhydrous $MgSO_4$ and filtered. Yellowish viscous liquid was left on evaporation of the solvent and turned into crystal of N-(2-ethylhexyl)-3, 6-diformyl carbazole(II) with a melting temperature range of 110-111 °C after recrystallization three times with a small amount of ethylacetate. Yield : 16.8 g(75%), ^{1}H-NMR($CDCl_3$), δ(ppm):0.84-0.97(m, 6H, CH_3), 1.26-1.38(m, 8H, CH_2), 2.05(m, 1H, CH), 4.23(d, 2H, NCH_2), 7.49-8.62(m, 6H, aromatic), 10.11(S, 2H, CHO).

Polymer Synthesis

2.09 g (2 mmol) of I and 0.67 g (2 mmol) of II were dissolved in a mixture of 60 mL of anhydrous ethyl alcohol and 20 mL of chloroform in a three-neck flask, and 2.3 g of 5 % solution of sodium metal in anhydrous ethyl alcohol was added dropwise through syringe. The mixture was kept at room temperature for 12 h and 1 mL of 0.1 N aqueous HCl solution was added to it to end the reaction. The precipitated yellow solid, poly(9,9-n-dihexyl-2,7-fluorenediylvinylene-alt-N-ethylhexyl-3,6-carbazolevinylene)(PDFOK) was washed thoroughly with water and methyl alcohol, and then dried in a vacuum oven set temperature at 40 °C. Yield : 0.84 g. ^{1}H-NMR ($CDCl_3$), δ(ppm) : 0.8-2.1(br, m, aliphatic), 4.2(br, s, NCH_2), 6.7-8.3(br, m, vinyl and aromatic), weight average molecular weight(Mw) and molecular weight distribution (MWD) measured by gel permeation chromatography(GPC) based on polystyrene standards using THF as an eluent were 5,500 g/mol and 1.81, respectively.

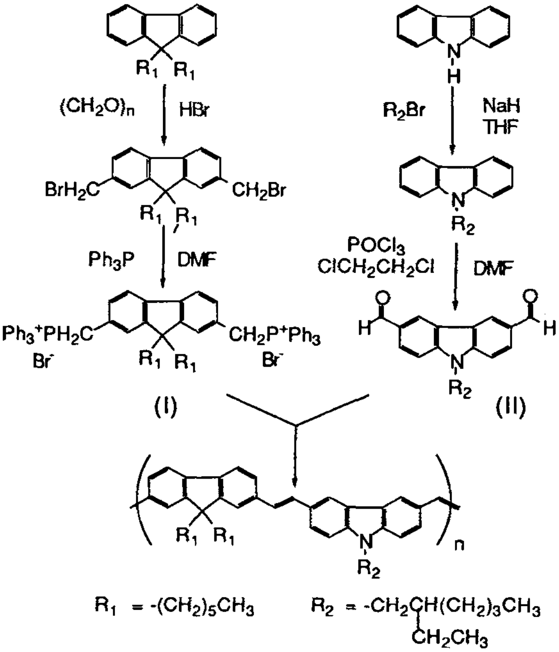

Figure 1. Synthesis route to PDFOK.

LED device fabrication

PDFOK is soluble in $CHCl_3$. Thus, 100 mg of each of the polymer was dissolved in 5 mL of chloroform to make a 2% solution which was filtered with a pore size of 0.2 µm. The LED structure consists of an aluminum contact on the surface of the polymer which was spin-cast on ITO glass. The spin-cast film with thickness of 100 nm was formed by controlling the spin rate of 1000 rpm. Aluminum was deposited onto the surface of the spin-cast film by vacuum evaporation at pressure below 10^{-6} torr, yielding an active layer of a circle with a diameter of 5 mm. All processing steps were carried out in air.

UV-VIS spectra were recorded with a HP 8452A Diode Array Spectrophotometer. Photoluminescence(PL) and electroluminescence(EL) spectra were recorded with an ISS K-2 Fluorometer. I-V-L characteristics were recorded by a Keithley 236 Source/Measure Unit for voltage-current relationship and by a Newport 818-SL photodiode for voltage-electroluminescence intensity.

Results and Discussion

The polymer gradually lost weight of 7% on heating to 285 °C and showed a fast decrease in weight starting at 370 °C as shown in Fig. 2. The weight loss on the thermal treatment at the low temperature might be due to evaporation of the oligomers which might exist since Mw and MWD were low and broad, respectively. The glass transition temperature was measured as 90 °C.

The optical absorption(AB) and PL spectra of a PDFOK film are shown in Fig. 3 along the EL spectrum of a single layer LED fabricated with the polymer. The absorption due to the π–π^* transition rises rapidly at a wavelength of 470 nm and shows a shoulder at 435 nm before reaching the peak at 410 nm. There is another shoulder detected at 380 nm. There may be more than one absorption structure in the polymer.

The PL spectrum shows rather a small Stokes shift (50 nm) and the full width at half maximum (FWHM) of 50 nm. The peak at 460 nm has a vibronic structure with a shoulder at 480 nm. The weak shoulder at 530 nm is not sure to have the same emissive center as that at 460 nm. There must be some absorption of EL by the emissive polymer based on the overlap between the AB and PL spectra, which suggests that quantum efficiency of the LED will be enhanced with a thinner layer of the polymer.

The EL spectrum covers almost the full color range with the FWHM of 150 nm. The spectrum composes of the EL peak at 480 nm and two shoulders at 460 and 530 nm. There might be a vibronic coupling between the peaks at 460 and 480 nm. The PL peak at 530 nm might be generated by interchain excimer emission as claimed in the literature (16, 17) or an emissive center different from that of the peak at 480 nm.

The variation of forward current with bias voltage in the LED is shown in Fig. 4. The forward current is detected at a forward bias voltage of 13 V and increases with the increasing bias voltage but the reverse bias current is negligible. A rather white light emission is visible at the bias voltage higher than 16 V in a dim-lighted room with quantum efficiency of 0.002%.

The EL spectrum changed when the emissive polymer used in an LED was blended with poly(vinylcarbazole)(PVK) as shown in Fig. 5. The LED fabricated with a blend of PDFOK and PVK as a ratio of 1 to 4 shows the EL spectrum much simplified from that of the LED with PDFOK alone. The EL spectrum of the LED with the blend shows the EL peak at 460 nm with a shoulder at 480 nm and a small bump at 530 nm.

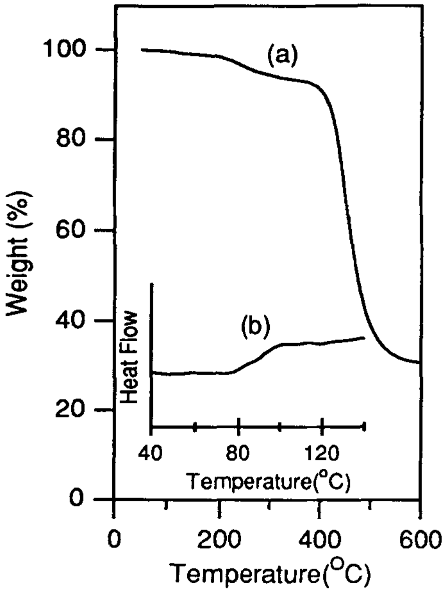

Figure 2. TGA(a) and DSC(b) thermograms of PDFOK.

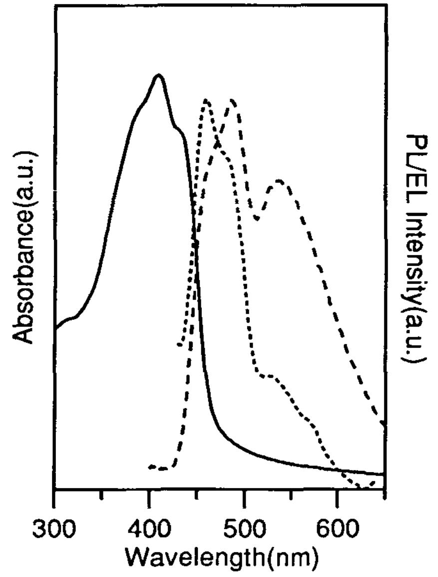

Figure 3. AB(——), PL(······), and EL(- - -) spectra of PDFOK.

The PL spectrum of the polymer blend with the blend ratio of PDFOK and PVK as 1 to 4 is almost identical to that of PDFOK alone. It is interesting to note that the EL spectrum of the blend LED is the same as the PL spectrum, which means that the exciton state for a singlet decay of EL is the same as that of the 0-0 transition for PL.

There is a strong possibility that the LED fabricated with PDFOK alone has two emissive centers; one for the peak at 480 nm and the other at 530 nm. The alternating copolymer with the stiff monomeric units may develop either a planar structure for a long conjugation length in the molecule or a lattice structure by molecular aggregations to give a low energy state which generates the EL peak at 530 nm. The long planar structure may be disturbed to loose the EL peak at 530 nm when the copolymer is blended with PVK.

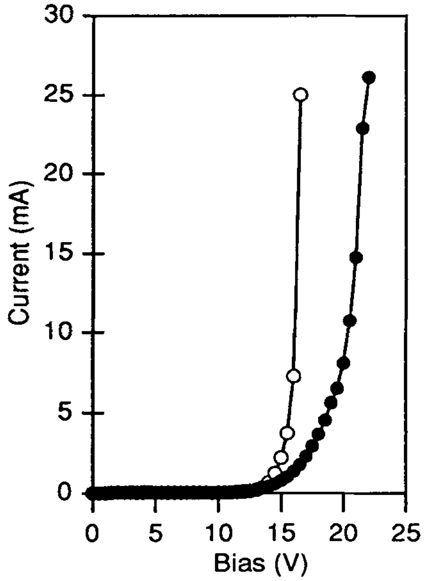

Figure 4. I-V characteristics of PDFOK (○) and PDFOK/PVK(1/4) blend(●).

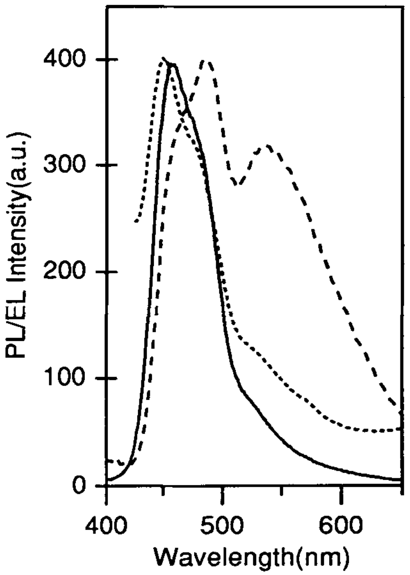

Figure 5. EL(——) and PL(·····) spectra of PDFOK/PVK(1/4) blend and EL spectrum of PDFOK(- - -)

Conclusion

An alternating copolymer with two monomeric units of which homopolymers are emissive in LEDs is also emissive when used in an LED. The copolymer is designed to be soluble in organic solvents and spin-cast to produce a fine film. The PL and EL spectra are much different from each other indicating different emissive centers present. The EL spectrum becomes almost identical to the PL spectrum when the copolymer is blended with PVK. Good miscibility between PDFOK and PVK may disturb the planarity in the molecule to shorten the conjugation lengths or break the lattice structure developed by molecular aggregation. The LED based on the polymer blend generates a blue-light emission on forward bias voltage of 13 V while the LED fabricated with the copolymer alone produces a white-light emission.

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