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Synthesis of PPV-PTV Alternating Copolymer and EL Devices Using the Polymer

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An alternating copolymer of PPV and PTV, poly[2-methoxy-5-(3,7-dimethyloctyloxy-1,4-phenylenevinylene-alt-2,5-thienylenevinylene)] (DAPPV-PTV) has been synthesized and light-emitting properties of the polymer have been studied. A single layer EL device using DAPPV-PTV as an emitting layer between ITO and Al electrodes (ITO/DAPPV-PTV/Al) has been fabricated, and light emission of the device becomes visible at 3 V. The EL emission maximum of the device is about 620 nm. Double layer EL device using DAPPV-PTV and Alq₃ (ITO/DAPPV-PTV/Alq₃/Al) has also been fabricated. The double layer EL device shows two-color emission depending on the applied voltage. The device emits a pale green color from 8 V, and then the color turns to red at about 18 V.

Introduction

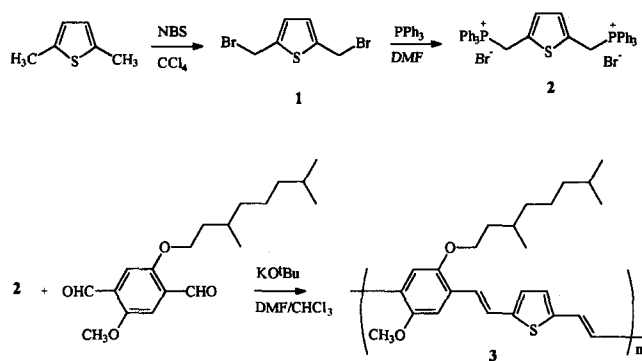
Electroluminescent (EL) devices based on organic materials have attracted much attention in the past ten years due to their potential applicability in display technology. Organic and polymer LEDs have many advantages for the development of a large-area visible light-emitting display, such as the good processibility, low operation voltage, fast response time and color tunability over the full visible range by control of the HOMO-LUMO bandgap of the emissive layer.¹⁻³ Conjugated polymers such as poly(1,4-phenylenevinylene) (PPV),^{1,3,4} polythiophene,⁵ polyfluorene,⁶ poly(*p*-phenylene) (PPP)⁷ derivatives have been most widely used as the emissive layer for the light-emitting diodes. EL devices using polymer blends,⁸⁻¹⁰ molecular doping¹¹ and organic or polymer multilayer structure¹²⁻¹⁴ have been extensively investigated in order to improve the quantum efficiency and stability of the device.

Recently we have synthesized an alternating copolymer of dialkoxyphenylenevinylene (DAPV) and thienylenevinylene (TV) units, poly[2-methoxy-5-(3,7-dimethyloctyloxy-1,

4-phenylenevinylene-alt-2,5-thienylenevinylene)] (DAPPV-PTV), and fabricated single and multilayer EL devices using the polymer in order to obtain a pure red light emission. Dialkoxy-PPV such as MEH-PPV shows an efficient electroluminescence, good processibility and good mechanical property, but the EL emission from the dialkoxy-PPV corresponds to orange red region.³ By the way, poly(thienylenevinylene) (PTV) shows an EL emission in pure red region but luminescence efficiency of PTV is very low.¹⁵ So we synthesized an alternating copolymer of dialkoxy-PPV and PTV in order to obtain an efficient pure red light emission. Here we report the synthesis and properties of DAPPV-PTV, and characteristics of the single and multilayer EL devices using the polymer. Synthetic route of the DAPPV-PTV is shown in Scheme 1.

Experimental

Synthesis of 2,5-bis(dibromomethyl)thiophene (1). Compound 1 was prepared by reacting 5.0 g (44.6 mmol) of 2,5-dimethylthiophene with 15.9 g (89.2 mmol) of



Scheme 1.

N-bromosuccinimide in 40 mL of carbon tetrachloride. A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 90 °C for 3 h under nitrogen atmosphere. Completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution. A yellow colored solution was obtained after filtration of the succinimide. The solution was concentrated and poured into *n*-hexane after nitrogen purging for 20 min. The resulting precipitate was filtered and dried under vacuum. The obtained product was highly unstable in air and moisture condition so it was stored under nitrogen. The product yield was 45% (5.4 g). ¹H NMR (200 MHz, CDCl₃) δ/ppm: 7.20 (s, 2H).

Synthesis of 2,5-dimethylenethiophenebis(triphenylphosphonium bromide) (2). A solution of 5.0 g (18.5 mmol) of compound 1 and 11.6 g (44.4 mmol) of triphenylphosphine in 30 mL of freshly distilled DMF was stirred and heated to 120 °C for 24 h under nitrogen atmosphere. The resulting mixture was poured into diethyl ether and then the precipitate was filtered and dried under vacuum for 24 h. The product yield was 87% (12.8 g). ¹H NMR (200 MHz, DMSO-*d*₆) δ/ppm: 7.77-7.50 (m, 30H), 6.66 (d, 2H), 5.55 (d, 4H).

Synthesis of poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene-alt-2,5-thienylenevinylene]. A mixture of 1.24 g (1.56 mmol) of compound 2 and 0.5 g (1.56 mmol) of 4-(3,7-dimethyloctyloxy)-1-methoxybenzene-2,5-dicarboxaldehyde was dissolved in 5 mL of DMF and 10 mL of CHCl₃. A potassium *t*-butoxide (1.05 g, 9.4 mmol) dissolved in 10 mL of ethanol was added to the monomer solution and stirred for 12 h at room temperature. The reaction mixture was precipitated into methanol, and the resulting precipitate was filtered and dried under vacuum for 12 hours. The polymer yield was 60% (0.37 g). GPC measurement of this polymer with polystyrene as the calibration standard showed a *M_w* of 10,000 and polydispersity index of 2.5.

ITO coated glass substrates were cleaned by successive ultrasonic treatments for an hour in acetone and isopropyl alcohol. The substrates were dried with nitrogen gas and heated at 100 °C for further drying to enhance the conductivity of transparent electrode. The DAPPV-PTV was dissolved in freshly distilled cyclohexanone. The polymer film thickness of about 100 nm was obtained by spin coating the filtered polymer solution on the substrates and drying in vacuum oven for several hours at 100 °C. Tris(8-hydroxyquinoline)

aluminum (Alq₃) was vapor deposited on the DAPPV-PTV coated substrate at the pressure below 1×10^{-7} Torr. The deposition rate for the organic layer was about 2-3 Å/s and the thickness of the organic layer was about 50 nm. Aluminum was vapor deposited for the top electrode at the pressure below 1×10^{-6} Torr, yielding active area of 0.02 cm². UV-VIS spectra were obtained with a Hitachi U-3501 spectrophotometer. Photoluminescence spectra were obtained by exciting the polymer film with 450 nm from Zenon lamp. EL spectra were measured using a monochromator (Jobin Yvon HR320) with the photomultiplier tube (Hamamatsu R928). Current-voltage (*I*-*V*) and light intensity-current (*I*-*I*) characteristics were measured using the current/voltage source and the calibrated silicon photodetector (Newport 818SL). The emitted light was collected with the photodetector placed in front of the device. All the measurements were performed in air at room temperature.

Results and Discussion

The synthesized DAPPV-PTV is completely soluble in common organic solvents such as chloroform, THF and cyclohexanone etc. The DAPPV-PTV shows an absorption maximum and edge at about 460 nm and 610 nm, respectively. The PL emission maximum of the DAPPV-PTV film is about 610 nm. UV-visible and PL spectrum of the DAPPV-PTV film are shown in Figure 1.

A single layer EL device using DAPPV-PTV as the emissive layer, and ITO and aluminum as the anode and cathode (ITO/DAPPV-PTV/Al) has been fabricated. Figure 2 shows the *I*-*V* and *I*-*V* characteristics of the single layer EL device. The current and the luminous power increase with increasing applied voltage. The voltage dependence of emission intensity from the device shows that light emission becomes observable at a bias of about 3 V.

EL spectra of the single layer device using DAPPV-PTV is shown in Figure 3. The EL emission maximum of the ITO/DAPPV-PTV/Al device is at about 616 nm.

Double layer EL device using DAPPV-PTV and Alq₃ (ITO/DAPPV-PTV/Alq₃/Al) has also been fabricated. Interestingly the double layer EL device shows two different colors depending on the applied voltage. The device shows a pale green emission from 8 V, and then the color turns to red at higher voltage from 18 V. Wu *et al.* reported the EL

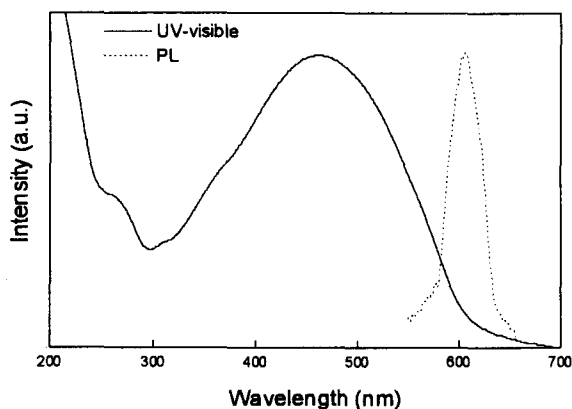


Figure 1. UV-visible (solid) and PL (dot) spectra of DAPPV-PTV film.

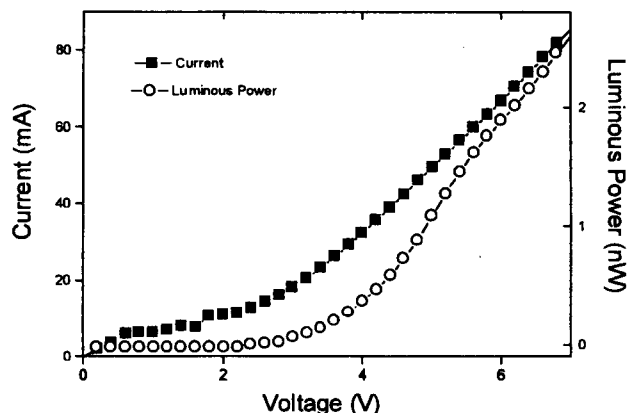


Figure 2. I-V (filled square) and L-V (open circle) curves of ITO/DAPPV-PTV/Al single layer device.

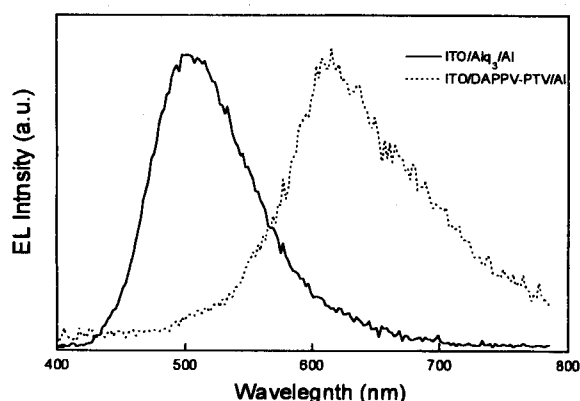


Figure 3. EL spectra from ITO/Alq₃/Al (solid) and ITO/DAPPV-PTV (dot) single layer device.

properties of a heterostructure EL device using PPV and Alq₃ (ITO/PPV/Alq₃/Mg:Ag).¹⁶ They reported that both Alq₃ and PPV emit light in the device, but no spectral change on bias was observed.

Figure 4 shows the EL spectra of the device taken at 13 V and 20 V. In both spectra, two major emission peaks are positioned at 520 nm and 630 nm which are originated from Alq₃ and DAPPV-PTV respectively, suggesting that both DAPPV-PTV and Alq₃ layer participate in the light emission.

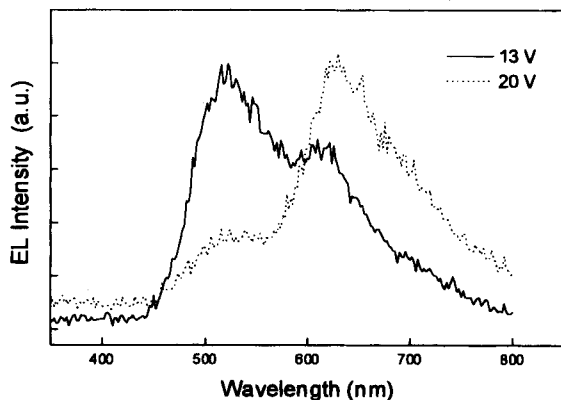


Figure 4. EL spectra from ITO/DAPPV-PTV/Alq₃/Al double layer device at 13 V (solid) and 20 V (dot).

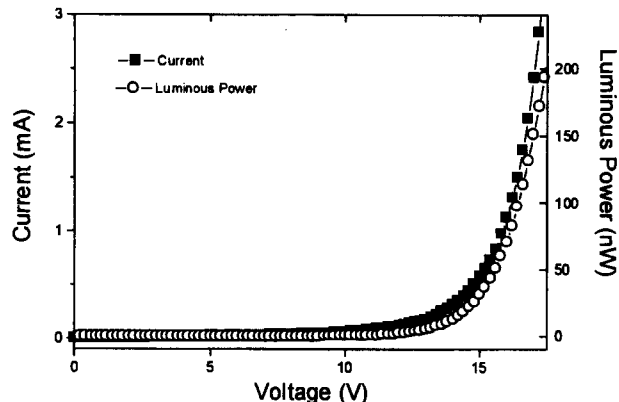


Figure 5. I-V (filled square) and L-V (open circle) curves of ITO/DAPPV-PTV/Alq₃/Al double layer device.

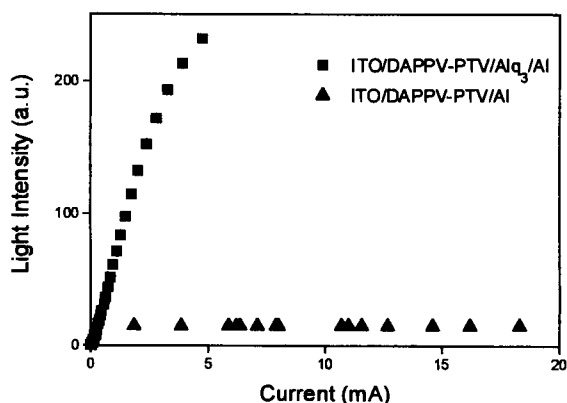


Figure 6. L-I curves of single (filled triangle) and double layer devices (filled square).

ission. Green emission from Alq₃ is bigger than that from DAPPV-PTV at lower voltage, but with increasing bias voltage, the emission from DAPPV-PTV becomes dominant. We suppose that electron injection from the Al cathode is not efficient at lower voltage, so holes and electrons are recombine and form excitons mainly at Alq₃ layer near DAPPV-PTV/Alq₃ interface. But at higher voltage, electrons injected from the cathode are highly increased and the recombination zone moves to the DAPPV-PTV layer near the DAPPV-PTV interface.

A similar result was reported by Matsumura *et al.*¹⁷ They reported the voltage dependence light-emitting zone in double layer organic EL device. They fabricated a double layer EL device with diamine derivative and alq₃ (ITO/diamine/alq₃/Mg:Ag), and the EL spectra from the device was changed on bias. The exchange in the emissive zone was explained on the basis of the difference in the barrier heights for the injections of electrons and holes from electrodes and the difference in the mobility of electrons and holes.

Figure 5 shows the I-V and L-V characteristics of the double layer device. The current of the double device significantly reduced compared with that of the DAPPV-PTV single layer device at the same voltage due to the hole blocking effect of the Alq₃ layer. Alq₃ layer efficiently blocks holes from DAPPV-PTV layer due to the difference in barrier height of HOMO level between DAPPV-PTV (ca 5.0 eV) and Alq₃ (ca 5.4 eV), thus reduces the hole current

and improves the quantum efficiency of the device. Figure 6 shows the L-I curves of the single and double layer EL devices.

Good processibility and pure red emission of the DAPPV-PTV, and the dramatic voltage dependent spectral change and the quantum efficiency improvement in the double layer device may make it a good candidate for application in polymer LEDs.

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Synthetic Studies on Carbapenam Skeletons. (II)

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Syntheses of carbapenam skeletons were achieved from 3-benzyloxypropanal through 1,3-dipolar cycloaddition. 3-Benzyloxypropanal was reacted with *N*-hydroxyglycine ester to give *C*-(2-benzyloxyethyl)-*N*-alkoxycarbonylmethyl-nitron (6). 1,3-Dipolar cycloaddition of the nitron with ethyl crotonate gave 3-(2-benzyloxyethyl)isoxazolidine (7). Compound 7 was transformed to 4-(2-hydroxyethyl)-2-azetidinone (11). Compound 11 was converted to 4-(2-iodoethyl)-2-azetidinone (13) or 4-phenylthiocarbonylmethyl-2-azetidinone (16) which was cyclized to give 6-(1-hydroxyethyl)carbapenam-3-carboxylate (14, 17).

Introduction

Thienamycin (1) has a unique structure and shows broad and strong antimicrobial activity.^{1,2} Many synthetic studies, therefore, have been carried out to obtain thienamycin and its derivatives. One of the synthetic approach was through 1,3-dipolar cycloaddition of crotonates with nitrones to give isoxazolidine derivatives, which were transformed to carbapenems.³⁻⁵

During the development of a new route for the synthesis of carbapenam analogs, the isoxazolidine derivatives (3) produced by 1,3-dipolar cycloaddition of *C*-(2-hydroxyethyl)-*N*-alkoxycarbonylmethyl-nitron (2) with crotonate were cyclized to give 3-methyl-7-oxo-2-azabicyclo[3.3.0]octane-4,8-dicarboxylate (4). The N-O bond of 4 was reduced to give β -amino esters, which could be cyclized by treatment with

a Grignard reagent to yield 6-(1-hydroxyethyl)-2-oxocarbapenam-3-carboxylate (5). The results were published in the previous paper⁶ (Scheme 1).

As a part of the continued study, the present paper covers another conversion of isoxazolidine derivatives to carbapenam skeletons.

Results and Discussion

Synthesis of 1-(*t*-butoxycarbonylmethyl)-3-[1-(*t*-butyldimethylsilyloxy)ethyl]-4-(2-hydroxyethyl)-2-azetidinone. Reflux of the benzene solution of *N*-hydroxyglycine *t*-butyl ester⁷ and 3-benzyloxypropanal⁸ for 30 min yielded *N*-(3-benzyloxypropylidene)glycine *N*-oxide *t*-butyl ester (6) in a good yield (89%). The product showed a triplet (*J*=5.7 Hz) at 6.82 ppm for N=CH, a singlet at 4.43