

Synthesis and Characterization of Poly[9,10-diphenylanthracene-4',4''-ylenevinylene-3,6-(*N*-2-ethylhexyl)carbazole]

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Received May 22, 2001

A novel poly[9,10-diphenylanthracene-4',4''-ylenevinylene-3,6-(*N*-2-ethyl hexyl)carbazole] containing alternate diphenylanthracene and carbazole unit was synthesized by the Wittig reaction. The obtained polymer was soluble in common organic solvents and thermally stable up to 380 °C. The polymer gives rise to bright blue fluorescence both in solution and in thin solid films. The light emitted from the device (ITO/polymer/Al) was greenish-blue in color and clearly visible in daylight.

Keywords : Wittig reaction, Light emitting diodes, Blue fluorescence, Greenish-blue electroluminescence.

Introduction

Light-emitting polymers have been extensively investigated in recent years since the Cambridge group first reported a green light-emitting diode (LED) using poly(1,4-phenylenevinylene) (PPV) as an emitting layer.¹⁻⁴ Organic polymer LEDs have many advantages for the development of a large-area visible light-emitting display, because of the good processability, 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. Therefore, a considerable body of work now has been published on EL of conjugated polymer systems, such as PPV, poly(*p*-phenylene) (PPP) and poly(thiophene).¹⁻⁷ Current research interests on EL polymers include improvement of their processability and long-term stability and so on, but one of the most challenging problems is to optimize the radiative recombination efficiency and adjust the carrier injection and transport of the EL materials in order to active high quantum yields.⁸

It is known that diphenylanthracene had unit PL quantum yield, good electrochemical property and orthogonal structure between anthracene and substituted phenyl ring.^{9,10} Therefore, LED those containing diphenylanthracene as emitting layer are expected to have higher EL quantum yield, long lifetime and blue color. It is also known that carbazole unit is good hole transporting and electroluminescent material.¹¹

In this article we describe the synthesis, the characterization, and the application in light emitting diodes of a new blue-light emitting, poly[9,10-diphenylanthracene-4',4''-ylenevinylene-3,6-(*N*-2-ethylhexyl)carbazole] (DPAC) which has alternate diphenylanthracene and carbazole units.

Experimental Section

Materials. All reagent and solvents were purchased from Aldrich Chemical Co and Fluka. Only analytical grade quality chemicals were used. Quinine sulfate 7-hydrate was

obtained from Kodak Eastman. Spectroscopic grade CHCl₃ (Aldrich) was used for all absorption and emission experiments. All other compounds were used as received.

Preparation of monomers. 9,10-di(*p*-toluylphosphonium bromide)anthracene was prepared following methods.

Preparation of 9,10-dihydroxy-9,10-di(*p*-toluyl)anthracene. The *p*-toluyl magnesium bromide was obtained from *p*-toluyl bromide (85 g, 0.5 mol) and magnesium (12 g, 0.5 mol) was dropped in the ether solution of 9,10-anthraquinone (42 g, 0.2 mol) at -5~10 °C. The Grignard reaction was carried out by mechanical stir within 10 min for avoid the side reaction. After the reaction mixture was acidifying by aqueous ammonium chloride, the crude product was extracted by ether solution. The ether solvent was evaporated, product was recrystallized by THF and hexane solvent. The product yield was 40 g (50%). ¹H-NMR (300 MHz, acetone-*d*₆, ppm) δ 2.25 (s, 6H, -CH₃), 5.32 (s, 2H, -OH), 7.03 (d, 4H, ring protons), 7.11 (m, 4H, ring protons), 7.3 (m, 4H, ring protons), 7.45 (d, 4H, ring protons).

Preparation of 9,10-di(*p*-toluyl)anthracene. The obtained 9,10-dihydroxy-9,10-di(*p*-toluyl)anthracene (29.6 g, 0.05 mol) was dehydrated by potassium iodide (25 g, 0.15 mol) and NaH₂PO₄ · xH₂O (78 g, 0.5 mol) in acetic acid solvent (200 mL) during 4 h. After refluxing, the crude product was filtered and washed with water and ethyl ether. The product yield was 16.1 g (90%). ¹H-NMR (300 MHz, CDCl₃, ppm) δ 2.5 (s, 6H, -CH₃), 7.3 (m, 4H, ring protons), 7.4 (d, 4H, ring protons) 7.7 (m, 8H, ring protons).

Preparation of 9,10-di(*p*-bromotoluyl)anthracene. When the 9,10-di(*p*-toluyl)anthracene (7.2 g, 0.02 mol) was refluxed in the CCl₄ solvent (100 mL), NBS (9 g, 0.04 mol) and catalytic amount BPO was added. After the reaction mixture was refluxed during 3 h, cooled to room temperature. Solvent was evaporated and the crude product was washed by methanol for elimination of succinimide. The product was recrystallized by methylen dichloride and ethanol. The product yield was 3.6 g (35 %). ¹H-NMR (300 MHz, CD₂Cl₂, ppm) δ 4.7 (s, 4H, -CH₂Br), 7.35 (m, 4H,

ring protons), 7.5 (d, 4H, ring protons), 7.7 (m, 8H, ring protons).

Preparation of 9,10-di(*p*-toluylphosphonium bromide)-anthracene. The mixture of 9,10-di(*p*-bromotoluy)anthracene (3.6 g, 6.3 mmol) and triphenylphosphine (3.4 g, 13.0 mmol) was refluxed in the DMF (50 mL) during 10 h. The reaction mixture was cooled and the crude product was filtered. The product was washed several times by ether solvent. The product yield was $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, ppm) δ 5.4 (d, 4H, $-\text{CH}_2-$), 7.3 (m, 4H, diphenyl anthracene ring protons), 7.5 (m, 8H, diphenyl anthracene ring protons), 7.8-7.9 (m, 30H, phenyl ring protons), 8.0 (m, 4H, diphenyl anthracene ring protons), Anal. Cald for $\text{C}_{64}\text{H}_{50}\text{P}_2\text{Br}_2$: C, 73.8%; H, 4.8%. Found C, 73.08%; H, 5.0%.

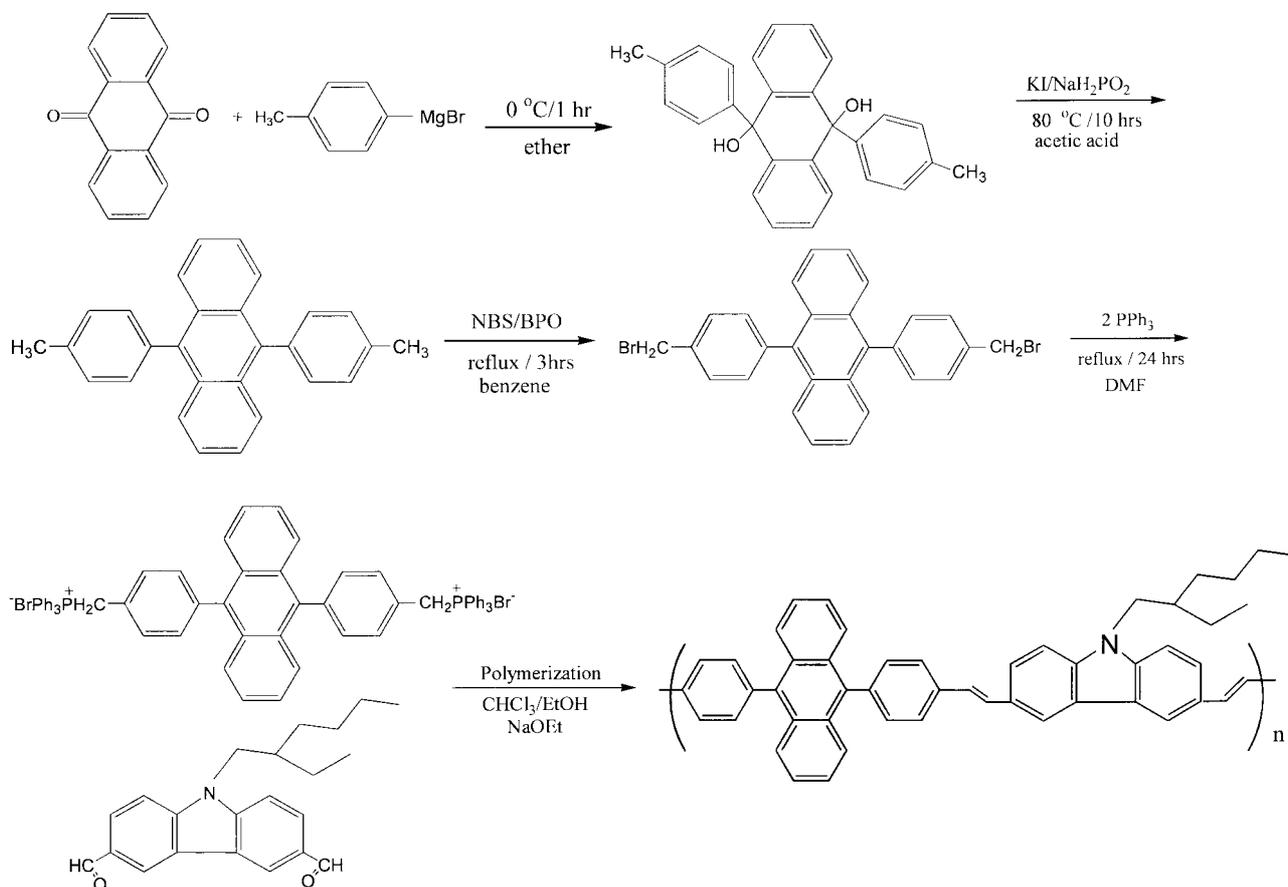
3,6-Diformyl-9-(2-ethylhexyl)carbazole. 3,6-Diformyl-9-(2-ethylhexyl)carbazole was prepared by the previous work.¹¹

Polymerization. To a stirred solution of 0.167 g (0.5 mmol) of the *N*-(2-ethylhexyl)-4,4'-diformyl carbazole and 0.52 g (0.5 mmol) of 9,10-bis(*p*-toluylphosphonium bromide)-anthracene in 10 mL of anhydrous ethanol and 20 mL of anhydrous chloroform was added dropwise a solution of 0.0288 g (1.2 mmol)/5 mL of EtOH at room temperature. The reaction mixture was stirred for 12 h after addition, and then 20 mL of 2% HCl was added. The crude product was extracted with chloroform. The extracted solution was evaporated to give pale-yellow polymer. The polymer was

dissolved in chloroform and precipitated in methanol, and then filtered and dried in vacuum at 60 °C.

Instrument. Melting points were determined on a Hoover capillary melting point apparatus. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral data are expressed in ppm relative to internal standard and were obtained in CDCl_3 or dimethyl sulfoxide ($\text{DMSO-}d_6$) on a Varian XL 300 NMR spectrometer. Elemental analyses were performed by Leco Co. CHNS-932. TGA measurement was performed on a Perkin-Elmer Series 7 analysis system under N_2 at a heating rate of 10 °C/min. DSC measurement was performed on a Perkin-Elmer Series 7 analysis system under N_2 at a heating rate of 10 °C/min. UV-vis spectra and optical density measurements were obtained on a Hp 8452A diode array spectrometer. The photoluminescence spectra were recorded with a SPEX 312 scanning fluorimeter. The excitation wavelength in all cases was 360 nm. Thickness was determined with a Sloan Dektak. Light intensities were measured with a silicon-photodiode (Model 1830-C from Newport Instruments). We have determined that the light output in nW. The current-voltage and light-voltage curves were recorded automatically *via* the use of custom LabView program written specially for this task.

Device fabrication. Substrate for device fabrication typically consisted of four ITO lines. 2-mm-wide lines of Al were deposited perpendicular to the ITO lines via thermal evaporation at a pressure of 5×10^{-6} torr. The aluminum was evaporated at a rate of 200 Å per second onto the films. The



Scheme 1

resultant thickness of the aluminum lines was typically between 1500 and 2000 Å. Each sample therefore has four ITO lines and four aluminum lines, the intersections of which give 16 pixels or active devices that can be addressed individually by hooking up the appropriate leads to power source.

Results and Discussion

The new polymer was synthesized by using well-known Wittig reaction between the aldehyde and the phosphonium salts as shown in Scheme 1. The obtained polymer was soluble in common organic solvents such as chloroform, dichloromethane and toluene. GPC measurement of the polymer with polystyrene as the calibration standard shows that the weight average molecular weight (Mw) is 8500 with a polydispersity of 1.5. Figure 1 shows the IR and $^1\text{H-NMR}$ spectrum of poly(DPAC). The IR spectrum of the synthesized polymer showed drastic decrease of intensity of strong aldehyde carbonyl stretching band of the dialdehyde comonomer. On the other hand, a weak sharp absorption peak at 962 due to the out-of plane bending mode of the trans-vinylene groups appeared, indicating that the vinylene double bonds newly formed are mainly trans configuration. The $^1\text{H-NMR}$ spectrum of the polymer shows that the aldehyde proton peak of the monomer present at 9.8 ppm decreased and new vinylic proton peak appeared at 6.7-7.8 ppm along with aromatic protons. The thermal property of the synthesized polymer was evaluated by means of TGA under nitrogen atmosphere. TGA curve shows that the polymer exhibits good thermal stability. The weight loss of the polymer is less than 5% on heating to 380 °C. (Figure 2) The DSC measurement showed glass transition at around 126 °C.

The UV-vis absorption and fluorescence spectra of poly(DPAC) in CHCl_3 are shown in Figure 3. The characteristic absorption maxima of the polymer were shown at 237, 312,

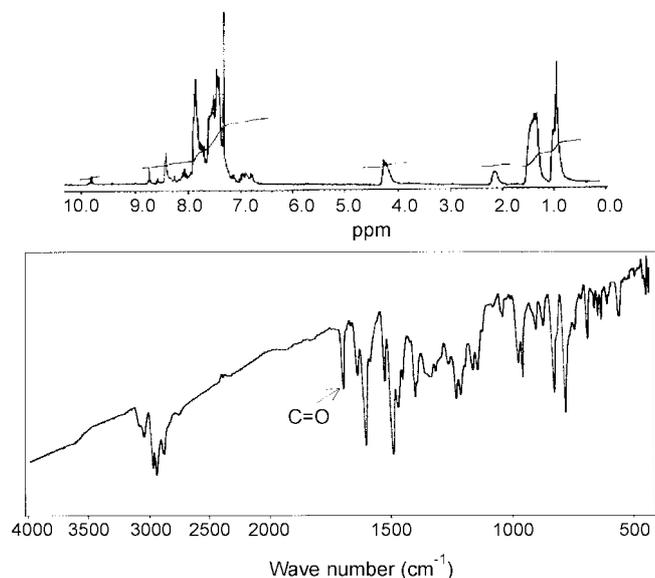


Figure 1. The IR and $^1\text{H-NMR}$ spectrum of poly(DPAC).

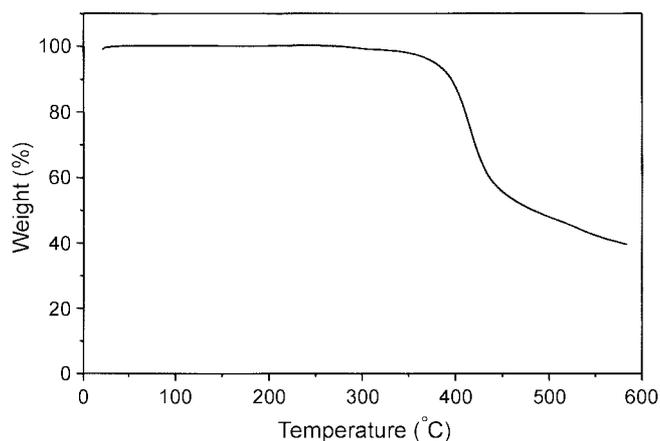


Figure 2. The TGA thermogram of poly(DPAC).

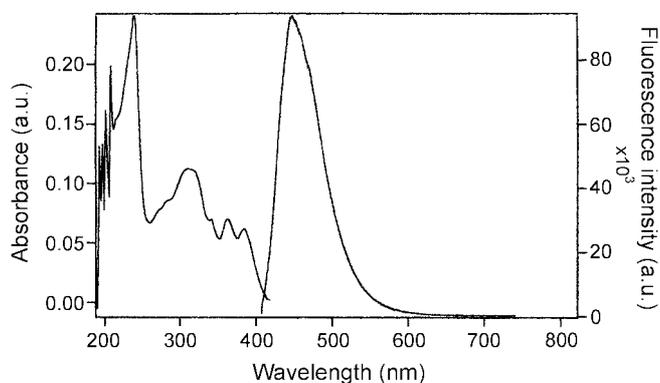


Figure 3. The UV-vis absorption and fluorescence spectra of poly(DPAC) in CHCl_3 .

364, 383 nm. Upon uv excitation, solution of the copolymer exhibits the very intense blue fluorescence with a maximum at 446 nm. The lack of mirror image relationship between the absorption and emission spectra is related to the vibronic coupling.⁹ The fact that the emission band is much narrower than the absorption bands and shows well-resolved vibronic bands are consistent with emission from localized excited states, most likely after a migration of the excitons along the polymer main chains to segments that represent low energy states.

Homogeneous and pinhole-free thin film can be obtained by spin-casting from either CHCl_3 or toluene solution. Figure 4 shows the photoluminescence spectrum of a thin film of poly(DPAC) and electroluminescence spectrum of an ITO/poly(DPAC)/Al device. The PL spectrum of thin film shows a maximum peak at 475 nm. The bathochromic shift from that of the solution can be attributed either to the difference in the energy transfer process between the film and solution due to the presence of rotational conformers in the solution reducing the π conjugation of the chromophore, or to the effect of packing and local geometry of polymer. The electroluminescence spectrum has a maximum at 495 nm. The shape and position of the photoluminescent and electroluminescent emission are similar but not identical. The bathochromic shift and peak broadened in electro-

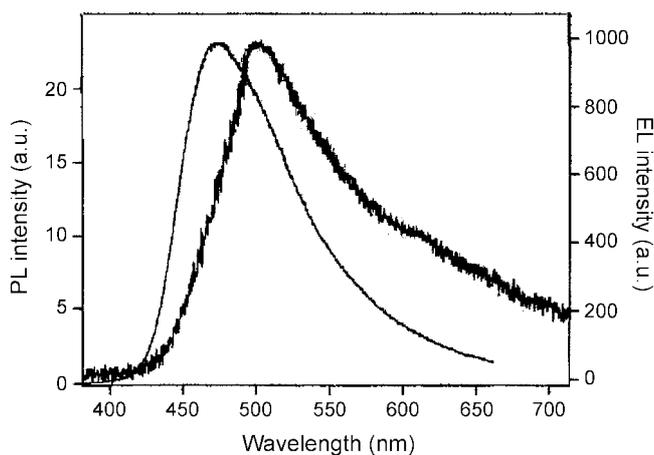


Figure 4. PL and EL spectra of thin film of poly(DPAC).

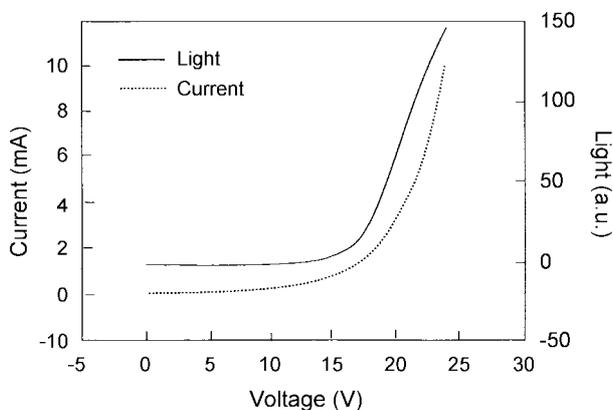


Figure 5. Light-voltage and current-voltage plots of ITO/poly(DPAC)/Al device.

luminescent emission relative that of fluorescence may be attributable to formation of excimer.¹²

Figure 5 represents typical current-voltage and luminescence-voltage measurements in a device. Current and light arise at almost the same voltage, which increase with the

film thickness. The polymer has turn-on voltage at 12.5 V in a 130 nm thick film. The light emitted from the device appears greenish-blue in color and is clearly visible in daylight. In here, we use a nonoptimized device configuration. The turn-on voltage and quantum efficiency are expected to be lowered and enhanced, respectively, by optimization of the device characteristics.

Acknowledgment. This work was supported from the KRF (Y00275) and the Basic Research Program of the KOSEF.

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