

Synthesis and Light-Emitting Properties of Poly(phenylene ethynylene) derivative Containing Cyano substituent

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Abstract

A novel poly(phenylene ethynylene) derivative containing cyano group as electron-transporting moiety was synthesized via Pd-catalyzed coupling reaction. The structures of the monomers and polymer were confirmed by spectroscopy. The polymer demonstrated a wide variation of solubility, optical absorption, electrical conductivity and electrochemical properties.

1. Introduction

Conjugated polymers with extended π -system have drawn a great attention owing to both their rigid backbone structure and unique optical properties.¹ Poly(phenylene ethynylene)s (PPEs) are a special class of π -conjugated polymers that have potential applications as molecular wires^{2,3} due to their excellent conductivity, optical nonlinear susceptibility, and magnetic susceptibility.

In this work, we describe the synthesis of a novel poly(phenylene ethynylene) derivative containing cyano group as electron transporting moiety. The cyano group is introduced into the polymer main chain to achieve desirable properties of luminescence and enhanced electron injection/transporting ability.⁴

Electronic conductivities of the polymers were measured by the conventional four-probe method after it was doped by iodine.⁵ Light-emitting devices of double-layer polymer films were fabricated in the construction of ITO/PEDOT/PPE-CN/Mg:Ag/Ag and their electrical performances were measured and discussed

2. Experimental

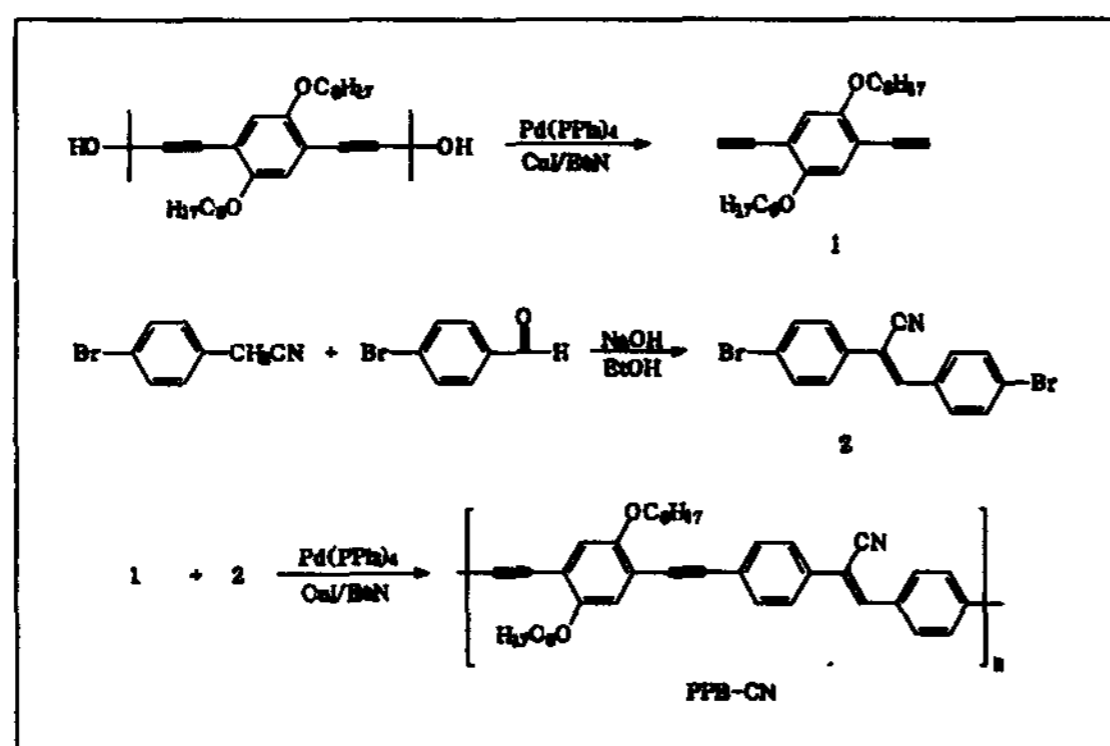
2.1. Monomer synthesis

1, 4-Diethynyl-2,5-bis(octyloxy)benzene(1)⁶

Toluene(50ml) and NaH(1.13g) were added at room temperature to a toluene(100ml) solution of 1,4-bis(3-hydroxy-3-methyl but-1-ynyl)-2,5-dioctylbenzene (4.7g) and the reaction mixture was stirred for 18hrs at 110°C. When the mixture was filtered and solvent was evaporated, a yellow solid was obtained. This crude product was purified by recrystallization from ethanol twice to yield 3.35g (89%) as light-yellow crystal. The raw material was prepared according to previous literature.⁶

1,2-Bis(4-bromophenyl)1-cyanovinylene(2)⁷

4-bromophenylacetonitrile(1.96g) and 4-bromobenzaldehyde(1.85g) were dissolved in ethanol(50ml). To



Scheme 1. Synthetic route to monomers and polymer

the mixture was added dropwise a solution of NaOH (50mg) in ethanol(20ml) under nitrogen atmosphere.

The reaction mixture was stirred at room temperature for 1h. The product obtained as a precipitate was filtered and washed with water to yield 2.9g (80%) as a white crystal.

2.2. Polymer synthesis⁸

Polymer was prepared by Heck's Pd(PPh₃)₄/CuI-catalyzed cross coupling of an aryl acetylene with aryl bromide in a mixture of toluene and triethylamine for 24hrs at 70 °C, as shown in Scheme1. The polymer remained soluble during the reaction. The solution was filtered and then dropped into excess ethanol to precipitate out the polymer. It was filtered, washed thoroughly, and dried in vacuo.

2.3. Conductivity

The conductivity of polymer was measured by the conventional four-probe method, known as Van der Pauw method, with a Keithley Sourcemeter(Model 2400). The polymer was doped by exposing it to the iodine vapor.

2.4. EL device

The EL device was fabricated as follows. For the double-layer device, a modified water dispersion of PEDOT was used as a hole injection/transport layer(~400 Å). The polymer film was prepared by spin-coating a polymer solution onto ITO glass. Uniform and pin hole-free film with thickness of around 600 Å was easily obtained. Metal contact(Mg:Ag) was deposited on top of polymer film through a shadow mask by vacuum evaporation at a pressure less than 3×10^{-6} torr(~1000 Å), and an additional encapsulating layer of Ag(~200 Å) was thermally evaporated

The measurement of device characteristics and current-voltage-luminescence (I-V-L) change were made by a current/voltage source and EL emission fluorescence spectrophotometer.

3. Results and discussion

3.1. Polymer synthesis

The synthesized poly (phenylene ethynylene) derivative (PPE-CN) was prepared through Heck reaction. Number average molecular weight (M_n) of the purified polymer was determined to be around 8200 by gel permeation chromatography using a polystyrene standard, and a polydispersity index to be

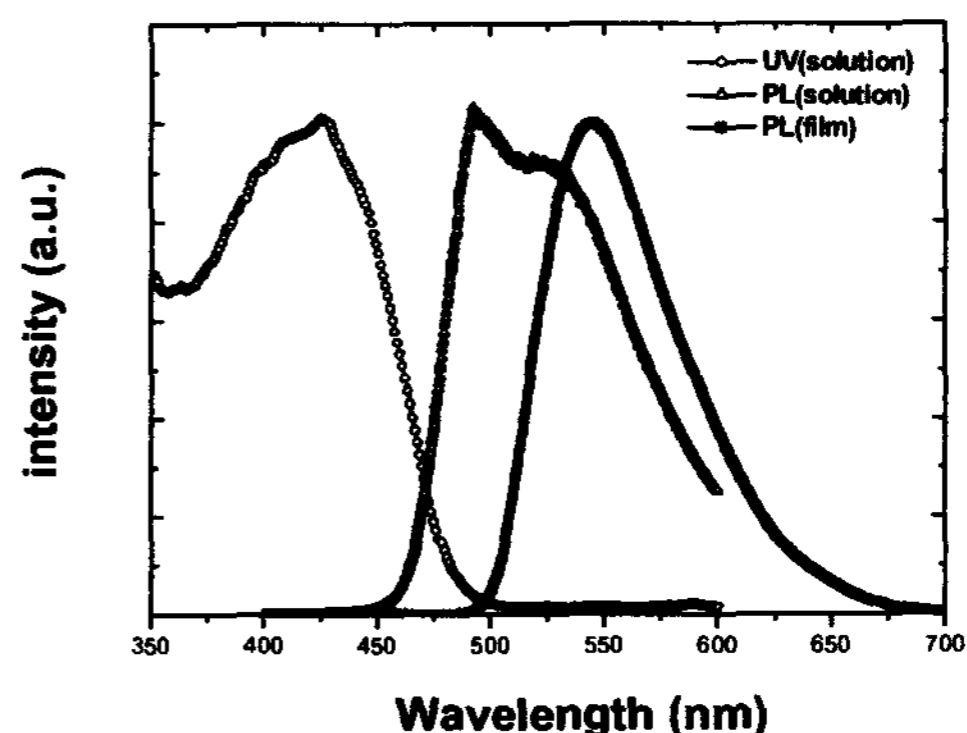


Fig.1. Absorption and PL spectra of PPE-CN

Table1. Physical and electrical properties of polymer

Mn/Mw ^{a)}	Thermal		UV absorption (nm)(solution) ^{d)}	PL emission (nm) ^{e)}		EL emission (nm)	Conductivity(S/cm)		
	Stability(°C)			solution	film		Undoped(σ)	Doped(σ_0)	(σ/σ_0)
	T _{5%} ^{b)}	T ₀ ^{c)}							
8,200/20,000	390	345	425	492	544	498	4.0×10^{-10}	3.9×10^{-6}	0.97×10^4

a) PS Standards, in THF, 0.80 mL/min b) Temperature at 5% weight loss c) Onset Temperature of degradation

d) In CHCl₃ solution e) In CHCl₃ solution

2.4. The polymer exhibited high thermal stability, and the weight losses were less than 5% on heating to 390°C

3.2. Conductivity

The color of the polymer changed from yellow to the dark -brown by the iodine doping. The conductivity of chemically prepared polymer in both the undoped and doped states are summarized in Table1. The conductivity of PPE-CN in undoped state was less than 4×10^{-10} S/cm, while the conductivity of the iodine doped polymer increased to 3.9×10^{-6} S/cm. Between undoped and doped polymer there is an increase in conductivity by four orders of magnitude.

3.3. Optoelectric properties

Fig.1. shows UV-Vis absorption and PL emission spectra of the polymer in toluene solution and in film state. UV-Vis. absorption and PL emission shows a peak at 425nm and 492nm in the solution, respectively. The PL emission maximum of the polymer thin film coated onto ITO glass appears at 544nm. The PL emission of the polymer film was 52nm red-shifted relative to that of polymer in solution. This behavior can be ascribed for the formation of an excited state complex between neighboring chains of the polymer known as an excimer. Double-layered EL device with ITO/PEDOT/PPE-CN/Mg:Ag/Ag construction was fabricated and characterized as a function of applied voltage. The typical current-voltage-luminescence (I-V-L) curve of the devices is shown in Fig.2. The

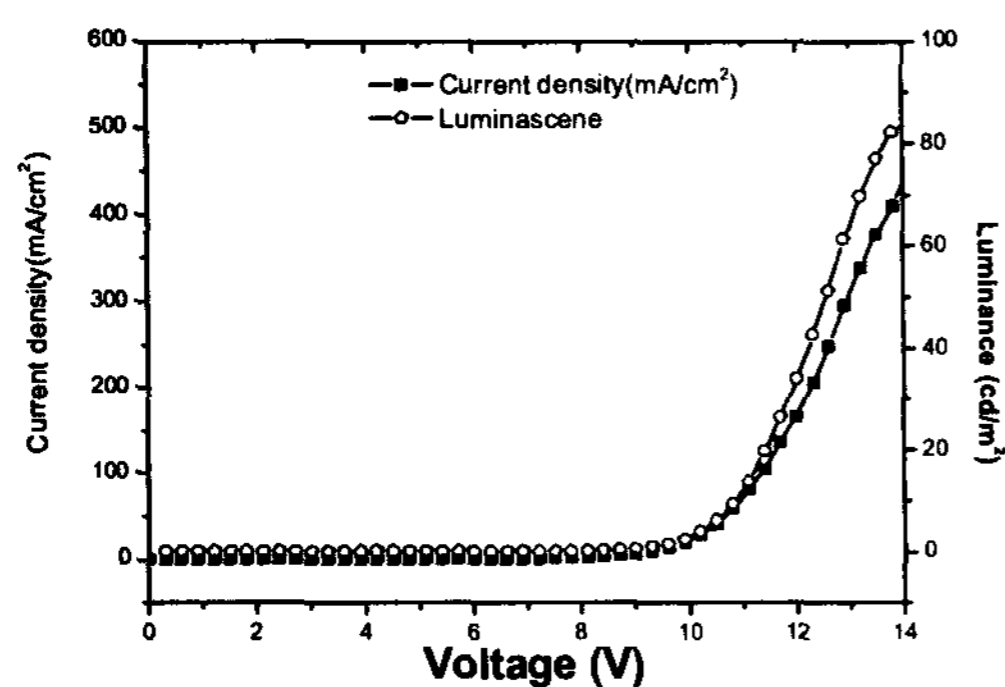


Fig.2. I-V-L curve for the device of ITO/PEDOT/PPE-CN/Mg:Ag/Ag

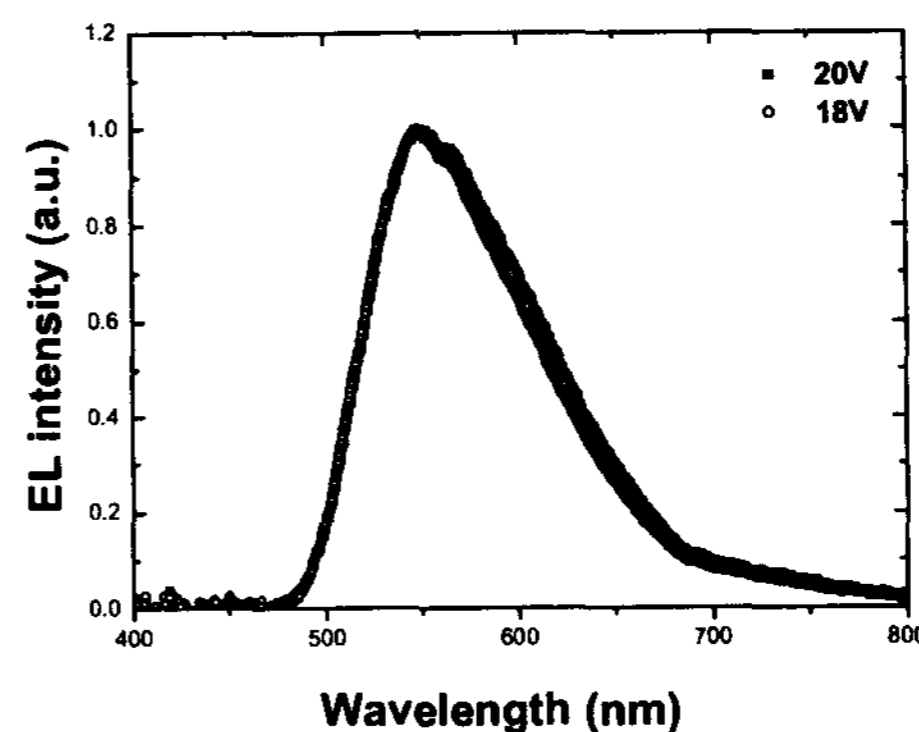


Fig.3. EL spectra of PPE-CN

current-voltage-luminescence characteristics of the device revealed an excellent diode behavior(Fig.2), i.e. under the forward bias, the current and the intensity of the emitting light increases strictly linearly with the increase of applied voltage. The turn-on voltage is determined to be 9V.

The electroluminescence spectra of the device under different drive voltage of thin film PPE-CN are shown in Fig. 3. EL spectra were obtained at 18V and 20V using a pulse voltage source. The EL spectra from the device were almost identical with the PL emission spectrum (Fig.1) of the polymer, indicating that the same excitation state is involved. But although the maximum is located in the green region, the peak is broader and red-shifted up to 6nm compared to the corresponding PL spectrum of the film. These results could be much improved when our device constellation is optimized. The external quantum efficiency of the device fabricated is shown in Fig 4.

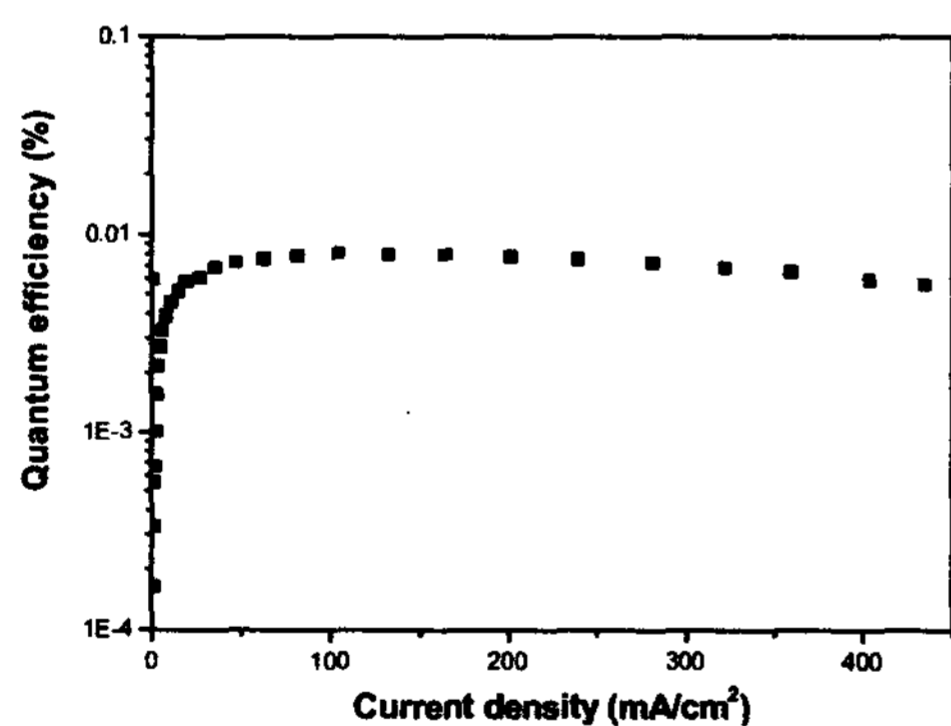


Fig.4. Quantum efficiency of PPE-CN

4. Conclusion

In conclusion, a light-emitting polymer containing the electron-transporting moiety of cyano group was

synthesized via a Pd-catalyzed cross coupling. The resulting polymer possesses excellent thermal stability, solubility and thin film forming properties. Conductivity difference between undoped and doped polymer was about four orders of magnitude. In addition, we have shown the EL properties of the PPE-CN in LED and greenish-yellow light emission was achieved for the LED fabricated with this polymer

5. Acknowledgement

The work supported by the Korea Research Foundation Grant(KRF 2002-005-0009) and the Center for Advanced Functional Polymers(R11-1997-044-05017-0)

6. References

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