

## Synthesis of Phenanthridine-Containing Conjugated Copolymer and OLED Device Properties

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### Abstract

*Polyazomethine type conjugated copolymers containing phenanthridine units, poly(PZ-PTI), were synthesized by Schiff-base reaction. This new conjugated copolymer exhibited improved solubility in common organic solvents due to the presence of alkyl side chains as well as phenanthridine groups. Double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) light emitting diode (LED) exhibited enhanced EL emission and efficiency compared to that of single layer (ITO/poly(PZ-PTI)/Mg) LED. With increasing the thickness of Alq<sub>3</sub> layer in double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) LED the emission peak gradually shifted to the single layer (ITO/Alq<sub>3</sub>/Mg) LED, confirming good hole transporting behaviour of the synthesized conjugated copolymer.*

### 1. Introduction

Conjugated polymers have been widely used as light emitting layers since R. H. Friend [1,2] reported polymer LEDs made with poly(*p*-phenylene vinylene)s. It has been shown so far that many polymeric electronic materials have an advantage on processing method in that polymers are usually spin-coated from solution.

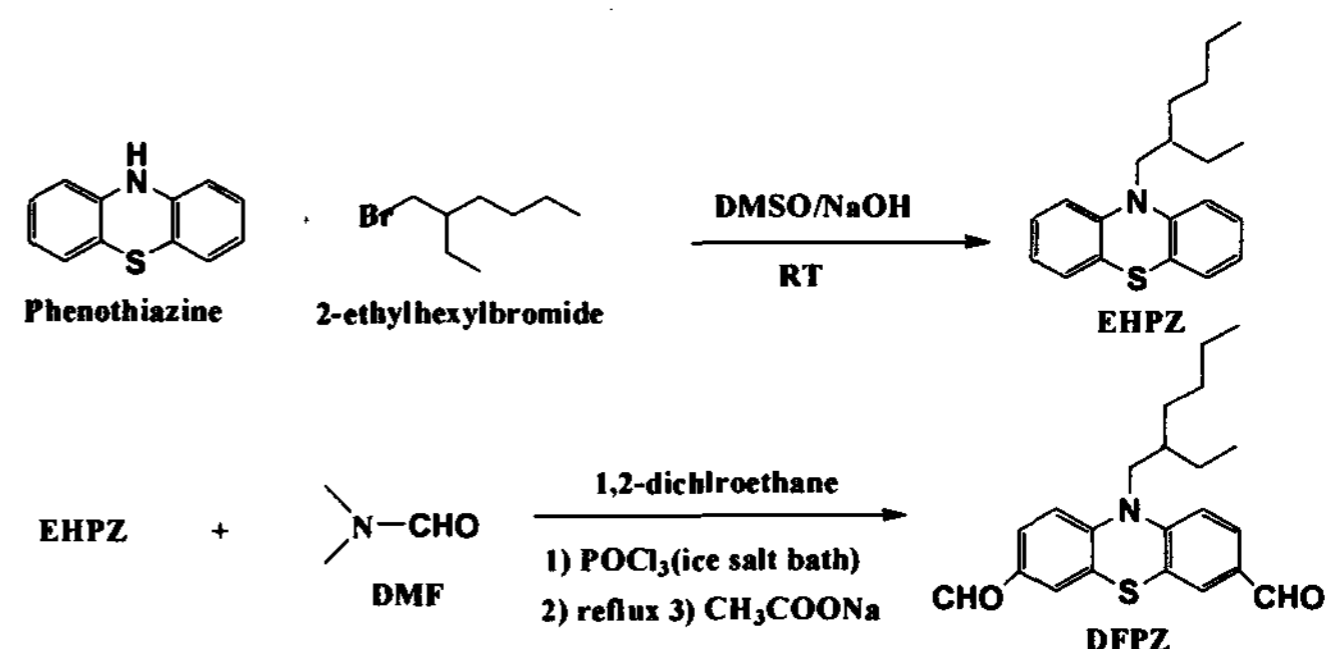
In this work, we present the synthesis of conjugated alternating copolymer that can be used for the fabrication of LEDs by spin-coating, and then the electro-optic properties of LEDs. The conjugated alternating copolymer containing phenanthridine moiety in the main chain was synthesized via Schiff-base reaction. Single and double layer LEDs were fabricated by spin-coating the conjugated copolymer as a light emitting layer on ITO glass and their electroluminescent properties such as emission color

and efficiency were studied from the viewpoint of polymer structure.

### 2. Experimental

#### 2.1. Monomer

Aromatic dialdehyde monomer, *N*-(2-ethylhexyl)-3,6-diformylphenothiazine (DFPZ) containing phenothiazine moiety was synthesized as shown in Scheme 1.

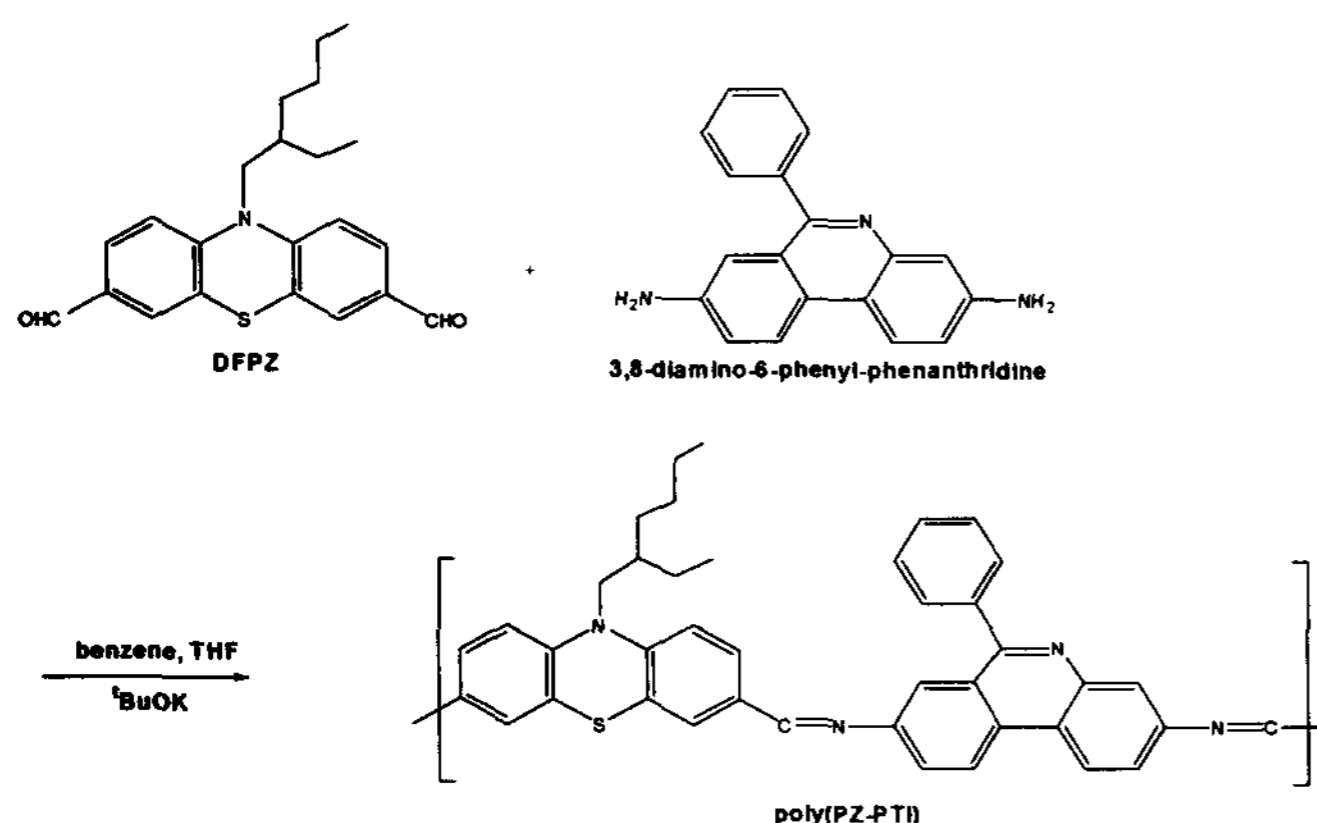


**Scheme 1. Synthesis of DFPZ dialdehyde monomer.**

#### 2.2. Polymerization

Schiff-base reaction was used to obtain conjugated copolymer which contains phenanthridine linkage and phenothiazine moiety [3,4,5]. The polymerization was carried out as presented in Scheme 2. 3,8-Diamino-6-phenyl-phenanthridine (2.85g, 0.01 mol, Aldrich Co., 98%) was added dropwise to a mixture solution of DFPZ (3.67 g, 0.01 mol) in benzene (60 ml) at room temperature under nitrogen atmosphere. The solution was then heated to reflux temperature. After reaction, the resulting mixture was concentrated under reduced

pressure, and then washed with methanol and water. After filtration and vacuum drying at 50 °C for 48hr the poly(PZ-PTI) was obtained as orange color powder.



**Scheme 2. Synthesis of conjugated copolymer [poly(PZ-PTI)].**

### 2.3. LED Device Fabrication

Single layer (ITO/poly(PZ-PTI)/Mg) LED was made by using the synthesized poly(PZ-PTI) conjugated copolymer as an emitting layer which has good solubility in common organic solvents. Indium-tin oxide coated (ITO) glass with a sheet resistance of 30  $\Omega/\square$  was cut into 2.0  $\times$  2.0 cm<sup>2</sup>, and electrode area was prepared by photo-etching technique. It was cleaned successively with acetone, methanol, and mixture of isopropyl alcohol and water (1:1 by vol.) in an ultrasonic bath. Filtered solutions of conjugated copolymer in benzene were cast on patterned ITO glass by spin coating and the solvent was evaporated to give an emitting layer with thickness about 600 Å measured by scanning probe microscope (Nanoscope Multimode SPM & Bio Scope). Thin Mg film was deposited at the rate of 20 Å/sec on top of the emitting layer as cathode (approximately 0.4 cm<sup>2</sup>) by E-beam method to about 4000 Å thickness.

Double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) LED with Alq<sub>3</sub> as an additional electron transporting layer between an emitting layer and a metal electrode was also fabricated. After spin-coating and drying of poly(PZ-PTI) emission layer, vacuum deposition of Alq<sub>3</sub> was performed on top of the emitting layer at the rate of 3-5 Å/sec, yielding 100 - 400 Å thickness. The Mg metal was deposited on Alq<sub>3</sub> thin film to give

ITO/conjugated copolymer/Alq<sub>3</sub>/Mg type double layer LEDs.

### 3. Results and Discussion

The UV absorption maximum ( $\lambda_{\max,UV}$ ) of synthesized copolymer, poly(PZ-PTI), appeared at 414 nm. The maximum of EL spectra ( $\lambda_{\max,EL}$ ) of single layer (ITO/poly(PZ-PTI)/Mg) LED was observed at 572 nm. The electro-optical properties such as maximum  $\pi$ - $\pi^*$  transition ( $\lambda_{\max,UV}$ ), HOMO-LUMO band gap energy ( $\lambda_{\text{edg},UV}$ ) and emission maximum ( $\lambda_{\max,EL}$ ) obtained from UV-visible and EL spectra are summarized in Table 2.

**Table 2. Electro-optical properties of conjugated copolymers**

Conjugated copolymer	$\lambda_{\max,uv}$ (nm) (eV)	$\lambda_{\text{edg},UV}^1$ (nm) (eV)	$\lambda_{\max,EL}$ (nm) (eV)
	414	514	572
Poly(PZ-PTI)	(2.99)	(2.41)	(2.17)

<sup>1</sup>: onset point of UV-visible absorption spectrum

Figure 1 shows the luminance vs. voltage profile of single layer (ITO/poly(PZ-PTI)/Mg) and double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg and ITO/Poly(*N*-vinylcarbazole) (PVK)/poly(PZ-PTI)/Mg) LEDs. Double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) LED exhibited both enhanced emission intensity (168 cd/cm<sup>2</sup> at 21 V) and efficiency compared to the single layer (ITO/poly(PZ-PTI)/Mg) LED (7.9 cd/cm<sup>2</sup> at 19 V). Turn-on voltage of single layer (ITO/poly(PZ-PTI)/Mg) LED was higher than that of double layer (ITO/poly(PZ-PTI)/Mg) LED. These results indicated that energy barrier at the interface between poly(PZ-PTI) and Mg cathode in single layer LED is higher than that at Alq<sub>3</sub>/Mg interface in the double layer LED. Luminance and efficiency of double layer (ITO/PVK/poly(PZ-PTI)/Mg) LED made with PVK known as a hole transporting layer, however, were lower than those of single layer (ITO/poly(PZ-PTI)/Mg) LED. In addition, the threshold luminance maximum of ITO/PVK/poly(PZ-PTI)/Mg devices was lower than that of ITO/poly(PZ-PTI)/Mg device. From these results, it could be concluded that conjugated poly(PZ-PTI) synthesized had hole transporting and

electron working property under the induced electric field. This may be due to the presence of alkyl substituted phenothiazine units in the polymer since the aromatic amines are well known to be as a hole transporting layer in the EL devices [6].

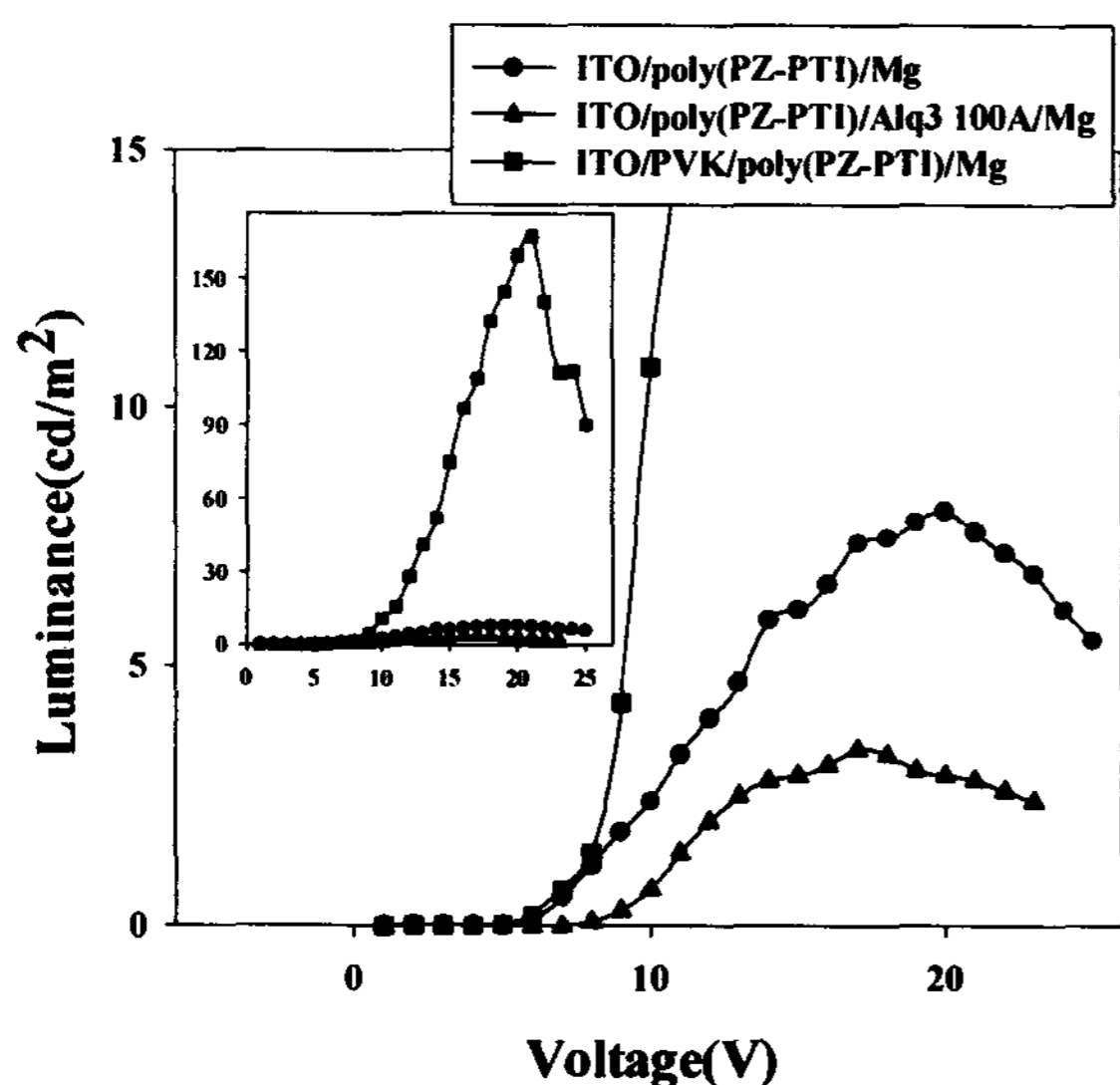
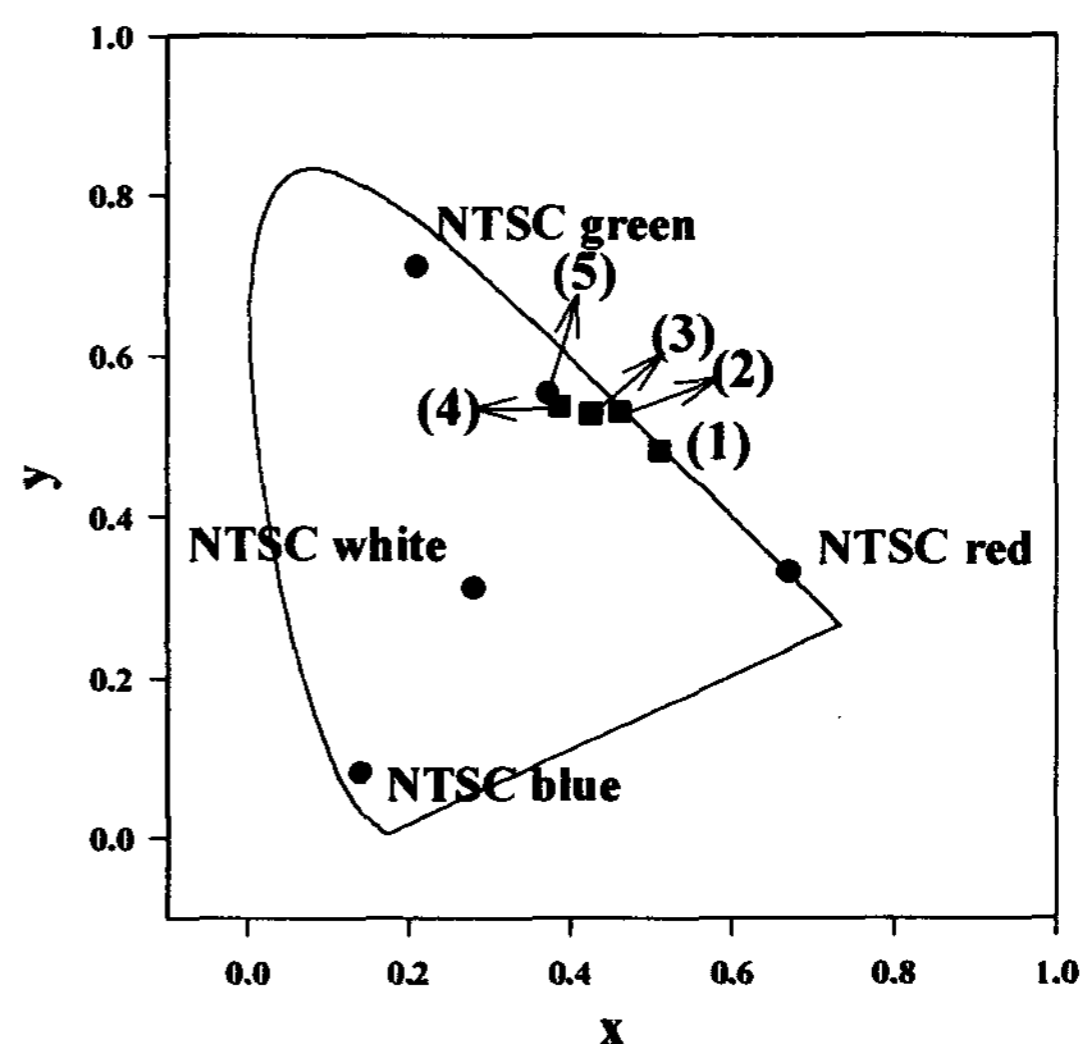


Figure 1. Luminance versus voltage profile of single and double layer LED fabricated with poly(PZ-PTI) as light emitting layer.

EL emissions of double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) LEDs with different thickness of Alq<sub>3</sub> are shown in the NTSC chromaticity diagram in Figure 2. As the thickness of Alq<sub>3</sub> layer increased, the emission color of double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) LED exhibited gradual shift to that of the single layer (ITO/Alq<sub>3</sub>/Mg) LED fabricated with only Alq<sub>3</sub> as an emitting layer. This result indicated that recombination of holes and electrons took place close to the Alq<sub>3</sub> layer with increasing the thickness of Alq<sub>3</sub> layer, since the Alq<sub>3</sub> layer could function both as an emitting layer and an electron transporting layer. This phenomenon further supported that the synthesized conjugated copolymer had good hole transporting property, which has been suggested to originate from phenothiazine functional groups in the main chain.



Structure of LED	Color coordinate		Color
	x	y	
(1) ITO/polymer/Mg	0.5109	0.4811	yellow
(2) ITO/polymer/Alq <sub>3</sub> 100 Å/Mg	0.4868	0.5031	greenish yellow
(3) ITO/polymer/Alq <sub>3</sub> 200 Å/Mg	0.4154	0.5273	greenish yellow
(4) ITO/polymer/Alq <sub>3</sub> 400 Å/Mg	0.3861	0.5362	yellow green
(5) ITO/Alq <sub>3</sub> 300 Å/Mg	0.3477	0.5329	yellowish green

Figure 2. Effect of thickness of Alq<sub>3</sub> layer in the CIE chromaticity diagram of LED made with poly(PZ-PTI); (1) single LED, (2) double layer (Alq<sub>3</sub>-100 Å), (3) double layer (Alq<sub>3</sub>-200 Å), (4) double layer (Alq<sub>3</sub>-400 Å) and (5) single layer LED made with Alq<sub>3</sub>.

#### 4. Conclusion

Conjugated copolymers containing phenothiazine moiety and phenanthridine linkage in the main chain could be easily synthesized by Schiff-base type reaction. The polymers exhibited good solubility in common organic solvents due to the polar phenanthridine linkages. Double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) LEDs made with the synthesized polymers as emitting layer and Alq<sub>3</sub> as electron transporting layer exhibited enhanced EL emission and efficiency compared to those of single layer

(ITO/poly(PZ-PTI)/Mg) LEDs. As the thickness of the Alq<sub>3</sub> layer increased, the emission color of double layer (ITO/poly(PZ-PTI)/Alq<sub>3</sub>/Mg) LEDs approached to that of single layer (ITO/Alq<sub>3</sub>/Mg) LEDs made with only Alq<sub>3</sub> as emitting layer, indicating that the synthesized copolymers have good hole transporting property.

## 5. Acknowledgements

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## 6. References

- [1] 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, 1990, vol.347(6293), pp.539.
- [2] N.C.Greenham, S.C.Moratti, D.D.C.Bradley, R.H.Friend, and A.B.Holmes, Nature, 365,628(1993)
- [3] Y. Wei, Y. Yang, and J. M. Yeh ,Chemistry of Materials, 1996, vol.8, no.11, pp.2659.
- [4] S. Destri, M. Pasini, C. Pelissi, W. Porzio, G. Predieri,, Macromolecules, 1999, vol.32, no.2, pp.353.
- [5] L. A. Paquette, John Wiley & Sons, New York, 1995, vol.6, pp.4133.
- [6] T. Kobayashi, Y.Matsushima, H.Sugiyama, and T. Hagiwara, ; 1999, U. S. Patent 5,942, 615.