

Progress In Commercialization Of Light Emitting Polymers: Dow Polyfluorenes

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ABSTRACT

We report here our recent progress in the development and commercialization of polyfluorenes emitting red, green and blue (RGB) colors as materials for light emitting diodes (LEDs). Our patented version of the Suzuki coupling process has been used to synthesize a variety of fluorene-based homopolymers and copolymers emitting colors across the entire visible spectrum. The optical and electronic properties of the polymers are tailored through selective incorporation of different aromatic units into the polyfluorene backbone. Our latest green emitter, reported herein, provides very efficient devices with a low turn-on voltage of 2.25 V, a peak efficiency of 10.5 Cd/A at 6,600 Cd/m² at 4.85 V. These devices maintain an efficiency of greater than 10 Cd/A up to 50,000 Cd/m² and demonstrate very good stability as exemplified by a device half-life of greater than 1,500 hours starting from 1,100 Cd/m². Considerable progress has also been made with red and blue emitters and will be the subject of this presentation.

1. INTRODUCTION

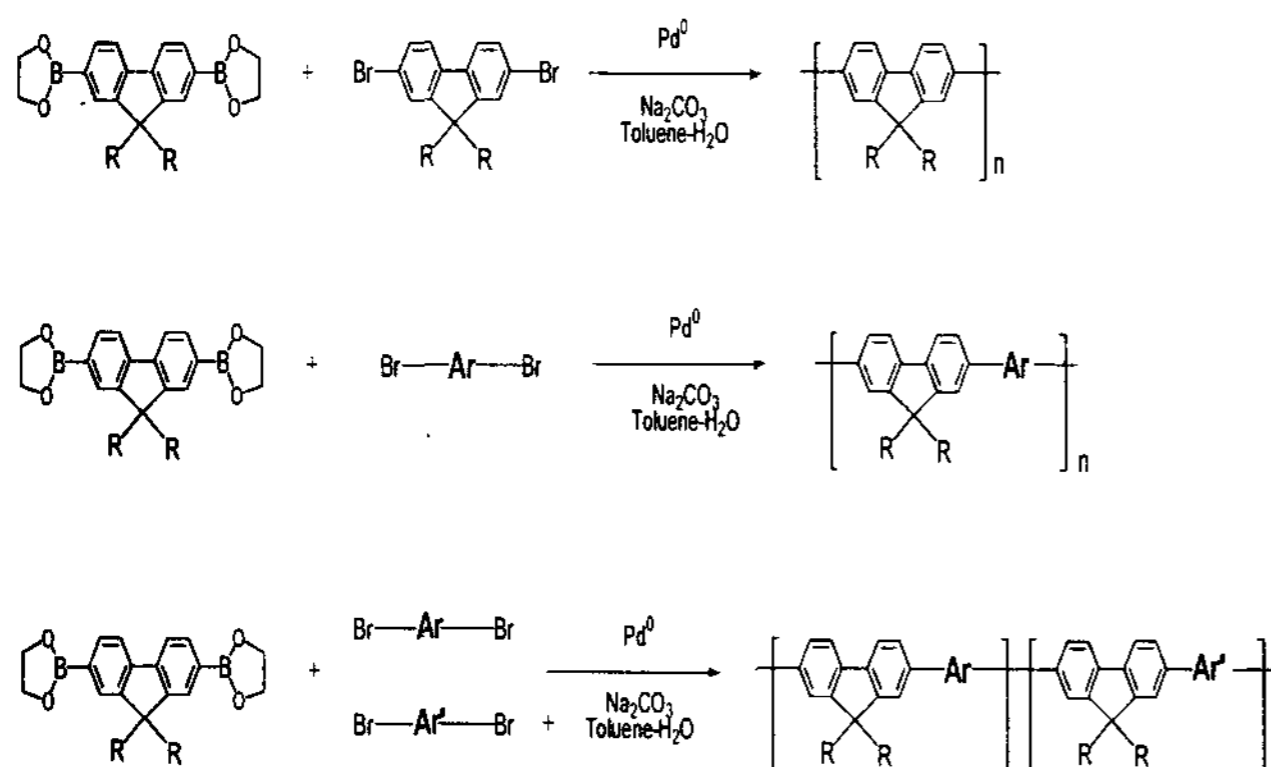
Polymer-based electroluminescent materials have been the subject of intense research in recent years due to their great potential for back light and full-color display applications [1-3]. Compared to emitters based on small molecules which require high vacuum deposition, polymers offer the significant advantage of easy processability from solution. A polymer film can be applied over a large surface area through spin-coating, ink jet printing and other techniques so that an array of devices can be readily assembled. In producing full color displays, polymer solutions can also be used directly to pattern red, green and blue pixels onto an active matrix array thus eliminating the need for expensive photolithographic processes. Ink jet printing is

particularly suitable for this purpose and great progress has recently been demonstrated in this area [4].

Among the numerous light emitting polymer structures reported in the literature, poly(*p*-phenylenevinylene) (PPV) derivatives and polyfluorenes (PF) have received the most attention [3]. While progress with yellow, orange and green polymers based on PPV chemistry has been demonstrated, the successful development of stable blue emitters from PPV has yet to be reported in the literature. The PF system, on the other hand, has demonstrated greater versatility in color emission, including blue color, and exhibits high oxidative stability due to its robust polyphenylene-like backbone structure.

Over the past years, considerable research effort at The Dow Chemical Company has been devoted to developing polyfluorene-based light emitting polymers with a modified Suzuki coupling technique [5,6]. As illustrated in Scheme 1, the modified Suzuki polymerization process can be used to synthesize homopolymers, alternating copolymers as well as copolymers containing more than one co-monomer by simply using fluorene 2,7-diboronate as the building block to react with selected dibromoarenes. The reaction uses a catalytic amount of palladium (0) complex along with aqueous sodium carbonate as the base and a phase-transfer catalyst to accelerate the polymerization process. The reaction conditions are mild and tolerate a variety of functional groups. The polymers have controlled molecular weights ranging from 10,000 to 500,000 Daltons with a typical polydispersity between 2 and 3. Depending upon the choice of the co-monomers a range of copolymers emitting colors

across the entire visible spectrum can be synthesized. charge carrier (holes and electrons) transport properties can be prepared in high yield and purity.



Scheme 1. Modified Suzuki process for making polyfluorenes. Ar and Ar' denote aromatic structures

2. EXPERIMENTAL

The synthesis and characterization of polyfluorenes have been described in detail previously [5,6]. Poly(3,4-ethylenedioxythiophene) (PEDT) was used as the hole injecting polymer and was supplied by H. C. Starck under the commercial name of Baytron P. The PLED devices were fabricated on patterned indium tin oxide (ITO) and each of the red, green and blue devices had an acting pixel area of 0.08 cm². After the substrates were cleaned and the surface was treated with UV-ozone, PEDT film (80 nm) was spin-coated from a 2.5% aqueous dispersion. After the PEDT layer was baked on a hot plate to remove water, light emitting polymer (LEP, 80 nm) was spun over the PEDT from a 1-2% xylenes solution. The LEP film was subsequently baked in nitrogen to remove the solvent residue. The devices were then loaded into an evaporation mask and transferred into an evaporator where the device structure was completed with the deposition of calcium (35 nm) at pressures of 10⁻⁷-10⁻⁸ mbar. A thick layer of silver or aluminum (200-300 nm) was then deposited on top of the calcium as a protective layer. The thickness of both metal layers was measured with a calibrated oscillating crystal monitor. Devices were encapsulated using a glass/epoxy resin package for ease of device

Additionally, polymers with specific characterization. The emission spectra as well as the CIE chromaticity coordinates were obtained using a Photo Research Spectrascan PR-650. The IVL characteristics were measured using a test apparatus that combines a calibrated photo-optically corrected photodiode and an Agilent 4155 semiconductor parameter analyzer.

3. RESULTS AND DISCUSSION

Table 1 illustrates the characterisation of three RGB polyfluorene polymers. The inherent viscosity of these polymers ranges from 2.02 to 2.47 dL/g (0.5 g/dL, THF, 25 °C) and the molecular weights (Mw), determined by GPC using polystyrene as the standard, vary from 220,000 to 433,000 Dalton with polydispersities of 2.26 to 3.27, respectively. As analyzed by Differential Scanning Calorimetry (DSC), the glass transition temperatures (Tg) of these polymers are all above 100 °C. Besides Tg, these polymers exhibit no other thermal transitions such as melting and crystallization indicating an amorphous nature in the solid state. All polymers are readily soluble in common organic solvents such as tetrahydrofuran, toluene and xylenes.

Table 1. Physical properties of green, red and blue polyfluorene polymers.

	Green	Red	Blue
Inherent Visc. (dL/g)	2.27	2.02	2.47
Mw	330,000	220,000	433,000
Polydispersity	2.26	2.41	3.27
Tg (°C)	115	123	110

The peaks of electroluminescent (EL) emission, CIE color coordinates and device efficiency at different brightness level (200, 1000, 4,000 and 10,000 Cd/m²) from these polymers are summarized in Table 2.

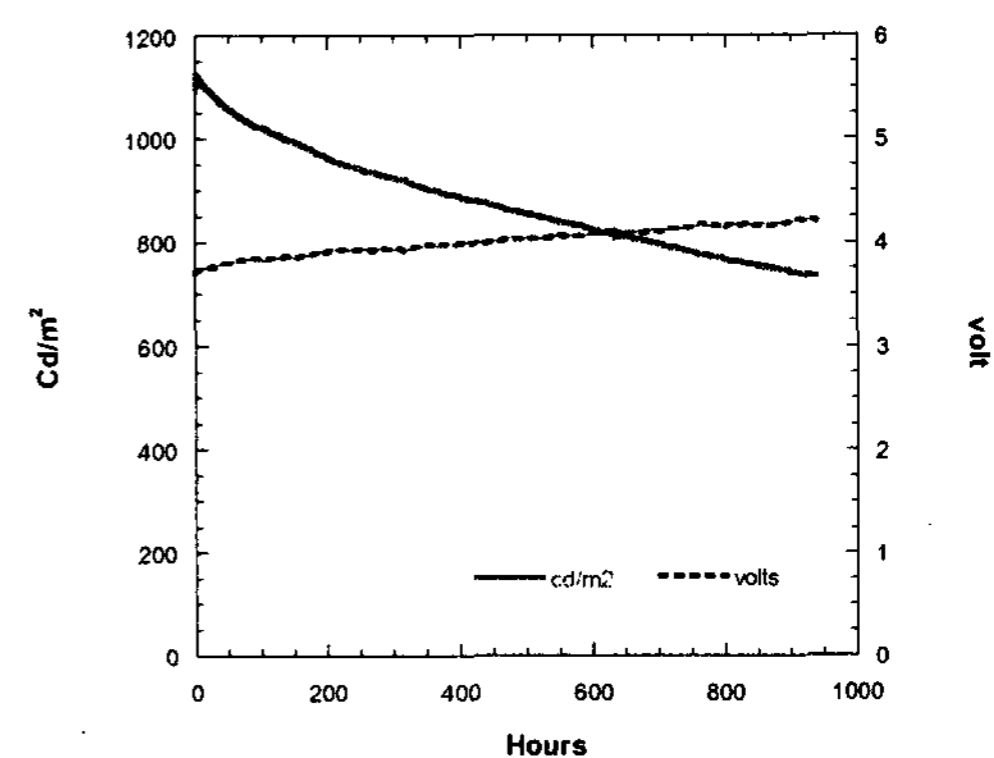
Table 2. Emission color and device characteristics of Dow Green, Red and Blue.

	Green	Red	Blue
EL max (nm)	534	648	476
CIE*			
x	0.40	0.68	0.16
y	0.58	0.32	0.19
200 Cd/m²			
Lm/W	7.64	1.43	1.31
Cd/A	6.92	1.50	2.82
1,000 Cd/m²			
Lm/W	8.31	0.68	0.90
Cd/A	8.84	1.20	2.60
4,000 Cd/m²			
Lm/W	7.36	-	0.48
Cd/A	10.01	-	2.00
10,000 Cd/m²			
Lm/W	5.62	-	-
Cd/A	10.25	-	-

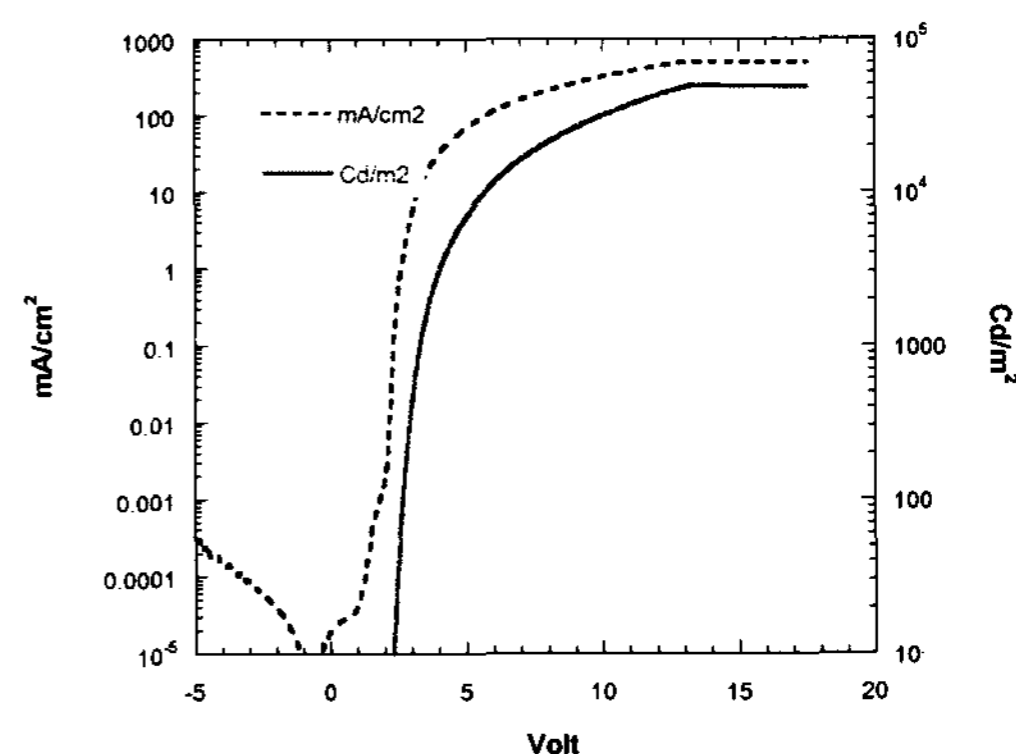
*Measured at 200 Cd/m²

4. GREEN EMITTER

The device efficiency based on our green emitter and brightness as a function of applied bias are shown in Figure 1a. The device has a low turn-on voltage of 2.25 V and reaches a brightness of 10,000 Cd/m² at 5.6 V. The inset shows the luminous efficiency as a function of light output. The device peaks at 10.5 Cd/A at 6,600 Cd/m² and maintains an efficiency of greater than 10.0 Cd/A up to 50,000 Cd/m². Such a steady correlation between device efficiency and light output has never been reported from any other polymer system. The high efficiency at a brightness as high as 50,000 Cd/m² is a very attractive feature for passive matrix displays which are known to require high efficiencies at high brightness levels under pulsed excitation [8].



a)



b)

Figure 1. Characteristics of the green device with PEDT as the hole-transporting layer and Ca as the cathode. (a) Current-luminance vs. voltage. Inset shows device efficiency (Cd/A) vs. Luminance (Cd/m²); (b) Lifetime with light output (Cd/m²) vs. time (hour).

In addition to their high efficiencies the green devices have demonstrated excellent lifetime characteristics. Figure 1b displays the lifetime parameters of a typical green device starting from a brightness of 1,100 Cd/m² and driven by dc with a current density of 12.8 mA/cm² at ambient temperature. The test was terminated at 940 hours with an extrapolated lifetime of greater than 1,500 hours. Over 940 hours, the voltage change was minimal at 0.52 mV/hour.

5. RED EMITTER

Devices based on our red polymer have exceeded the efficiencies of those reported in the literature [9] and exhibit a saturated red color chromaticity. The

device has a low turn on voltage of 2.1 V, achieves a maximum efficiency of 1.5 Cd/A at 210 Cd/m² and reaches a brightness of 2,000 Cd/m² at 8.4 V. The projected half life for a red device with L₀= 200 Cd/m² is 8000 hours with a voltage change of 0.15 mV/h.

6. BLUE EMITTER

As a result of our continuous optimization of polymer compositions, the efficiency of blue devices has been significantly improved over the last few years. A double layer Blue device using PEDT as the hole transporting layer and calcium as the cathode turns on at less than 4.0 V and reaches a maximum efficiency of 2.9 Cd/A at 190 Cd/m². Even at 4,000 Cd/m² the efficiency remains above 2.0 Cd/A. In addition to the material optimization, improvements in device engineering and cathode modification at Cambridge Display Technologies (CDT) have resulted in blue devices based on polyfluorenes with low turn-on voltage (~2.7 V), good efficiency and color (3-4 Cd/A between 100-1000 Cd/m²; x = 0.17, y = 0.21) and improved lifetime. Starting from 100 Cd/m² the device suffered only 30% luminance loss after 2,100 hr and has a projected lifetime exceeding 4,000 hours.

7. TIMELINES FOR COMMERCIALIZATION

We have synthesized RGB polymers in our pre-production facility successfully over the past two years. Green emitting polymers have been commercially available since the fourth quarter of 2000 and were transitioned to the full-scale production facility in the fourth quarter of 2001. The red emitting polymer has been commercially available since the first quarter of 2002 and is expected to be moved to full-scale production in the fourth quarter of year 2002. Commercial production of blue emitter will commence in the first quarter of

2003.

8. SUMMARY

We have developed a broad range of light emitting polymers based on polyfluorenes with controlled molecular weight, high purity and tunable color. Red, green and blue PLED devices with high efficiency, low operating voltage and long lifetime have been demonstrated. Commercial production has been initiated for our green and red polymers and plans for the blue emitters are in progress.

9. ACKNOWLEDGEMENT

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