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Recent development of polyfluorene-based RGB materials for light emitting diodes

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Abstract

As a continuation of our presentation at IUMRS-2000 in Hong Kong, we report the latest development of polyfluorene-based Red, Green and Blue (RGB) materials for light emitting diodes at The Dow Chemical Company. A modified Suzuki coupling process is used to synthesize RGB fluorene-based homopolymers and copolymers. Optimization of reaction conditions has led to a highly efficient procedure to generate polymers with controlled molecular weight (Mw), ranging from 10,000 to above 500,000 depending on the requirements of the desired applications. The optical and electronic properties of the polymers are tailored through selective incorporation of different aromatic units into the fluorene copolymer systems. By using this methodology, a portfolio of fluorene-based polymers has been designed and synthesized, achieving emissive colors that cover the entire visible spectrum.

The performance of fluorene-based polymers in light emitting devices has been optimized by modifying the polymer compositions so as to increase charge mobilities and to improve the carrier injection balance. As a result of these compositional changes, devices based on Dow's green emitters, using bi-layer structures on indium tin oxide substrates and evaporated metal cathodes, have demonstrated unprecedented high efficiencies at high brightness levels and long lifetime performance. A device comprised of a Dow green emitting polymer has a low turn-on voltage of 2.25 V and exhibits a peak efficiency of 10.5 Cd/A at 6600 Cd/m^2 at 4.85 V. These devices maintain an efficiency of greater than 10.0 Cd/A up to 50,000 Cd/m^{2}and demonstrate very good stability as exemplified by a device half-life of greater than 1500-h starting from 1100 Cd/m^2. Similar outstanding progress with red and blue emitters has also been made and will be discussed.
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1. Introduction

Polymer-based electroluminescent materials have been the subject of intense research in recent years due to their great potential in back light and full-color display applications [1–3]. Compared to small molecule system, which require high vacuum deposition, polymers offer the significant advantage of being directly processed from solution. A polymer film can be cast over a large area through spin-coating and other technologies, so 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 costly 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 polymer structures reported in the literature, poly(*p*-phenylenevinylene) (PPV) derivatives and fluorene-based polymers (PF) have received the most attention [5]. The basic PPV structure has not been very successful in generating useful blue emitters and is prone to fast oxidative degradation in the presence of air and light. The PF system has demonstrated versatility in color emission, including blue, and has excellent oxidative stability due to its 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 [7,8]. 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

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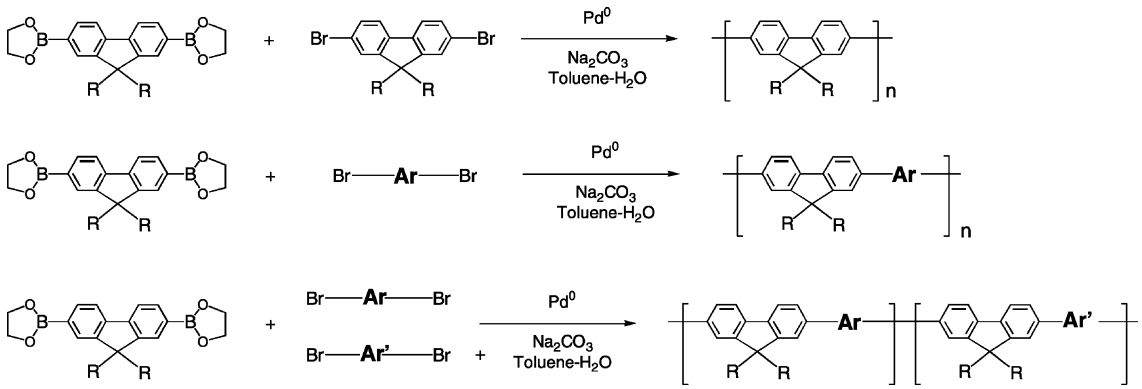

Scheme 1. Suzuki synthesis of fluorene-based polymers. Ar, Ar′ = aromatic groups.

simply using fluorene 2,7-diboronate as the building block to react with selected aromatic dibromide(s). The reaction uses a catalytic amount of palladium (0) with aqueous sodium carbonate as the base and a phase-transfer catalyst to provide better mixing. The reaction conditions are mild, tolerating a variety of functional groups. The polymers have controlled molecular weights ranging from 10,000 to 500,000 Da and are very pure, with ionic impurities typically in the ppm levels.

As exemplified in Fig. 1, a variety of chromophores can be incorporated into the fluorene polymer backbone. All of these copolymers are highly photoluminescent, and their band-gap, which defines the emissive wavelength, can be qualitatively correlated to the extent of de-localization in the co-monomers. For example, while the thiophene copolymer emits blue-green light, the 2,2′-bithiophene copolymer emits yellow light due to its more extended conjugation. Thus, the choice of comonomers in the fluorene-based polymer family has served as an excellent synthetic tool for designing polymers that have well-balanced hole and electron transport properties and emit a variety of colors. Through the years, a portfolio of polyfluorene-based polymers with efficient emission in red, green, blue and other colors spanning the entire visible range has been produced at The Dow Chemical Company.

2. Experimental

The synthesis, characterization and experimental examples of polyfluorene-based polymers have been described previously [6]. Following our established process, all polymers presented in this article were prepared in high yield and purity. As analyzed by fast neutron activation, the total level of inorganic impurities such as Cl, Na, Br, K, and Pd in each polymer sample was below 50 ppm. Poly(3,4-ethylenedioxythiophene) (PEDT) was used as the hole transporting polymer and was supplied by Bayer A. G. with the commercial name Baytron P.

The PLED devices were fabricated on patterned indium tin oxide (ITO) and each of the red, green and blue devices has an acting pixel area of 0.08 cm^2. After the substrates were cleaned and the surface was treated with an UV-ozone, an 80 nm PEDT film was spin-coated from a 2.5% aqueous dispersion. After the PEDT layer was baked on a hot plate to remove water, an 80 nm film of light emitting polymer (LEP) was spun onto 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 is completed with the deposition of calcium (35 nm) at pressures of 10^{-7}–10^{-8} mbar. A thick

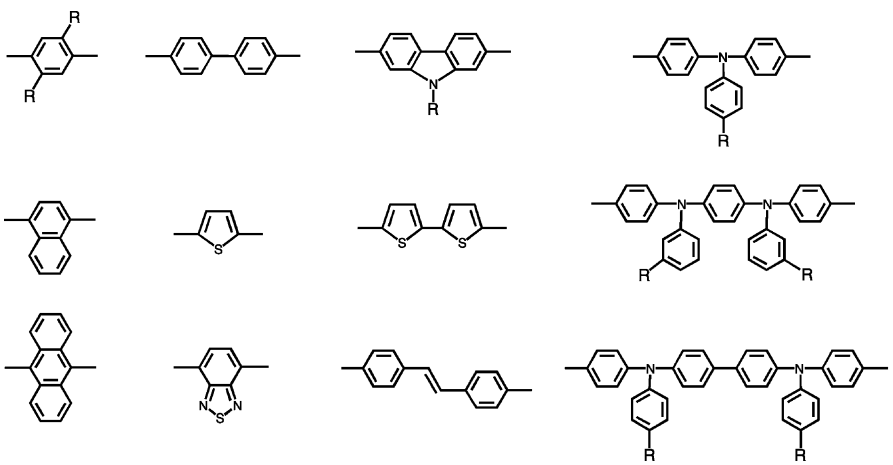

Fig. 1. Examples of monomers used in polyfluorene copolymers.

layer of silver or aluminum was deposited on top of the calcium as a capping protective layer. The thickness of both metal layers was measured with a calibrated oscillating crystal monitor. Finally, for ease of device characterization, the devices were encapsulated using a glass/epoxy resin package.

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

3. Results and discussion

The polymer characterization and device performance of red, green and blue polyfluorene polymers are discussed below (Tables 1 and Table 2). Although, the exact polymer structures are not disclosed, similar examples of polyfluorene-based light emitting systems have been published in the literature [7–9]. Table 1 illustrates the characteristic properties of three RGB polyfluorene polymers. The inherent viscosity (η_{in}) 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, from 220,000 to 433,000 Da with polydispersities of 2.26–3.27, respectively. As analyzed by Differential Scanning Calorimetry (DSC), the glass transition temperatures (T_g) of these polymers are all above 100 °C with the red polymer being significantly higher than the blue or green. Besides T_g, these polymers exhibit no other thermal transitions, such as melting and crystallization, indicating an amorphous characteristic in the solid state. All polymers are readily soluble in common organic solvents, such as tetrahydrofuran, toluene and xylenes.

3.1. Green

The green device efficiency and brightness as a function of applied bias are shown in Fig. 2(a). The device has a low turn-on voltage of 2.25 V and reaches a brightness of 10,000 Cd/m^2 at 5.6 V. The inset shows the luminous efficiency as a function of light output. The device peaks at

Table 1
The characteristics properties of green, red and blue polyfluorene polymers

	Green	Red	Blue
η_{inh} (dl/g)	2.27	2.02	2.47
Mw	330,000	220,000	433,000
Polydispersity	2.26	2.41	3.27
T_g (°C)	115	123	110

The peaks of electroluminescent (EL) emission, CIE color coordinates, and device efficiency at different brightness level (200, 1000, 4000 and 10,000 Cd/m^2) 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 λ_{max} (nm)	534	648	476
CIE[a]			
x	0.40	0.68	0.16
y	0.58	0.32	0.19
200 Cd/m^2			
Lm/W	7.64	1.43	1.31
Cd/A	6.92	1.50	2.82
1000 Cd/m^2			
Lm/W	8.31	0.68	0.90
Cd/A	8.84	1.20	2.60
4000 Cd/m^2			
Lm/W	7.36	–	0.48
Cd/A	10.01	–	2.00
10,000 Cd/m^2			
Lm/W	5.62	–	–
Cd/A	10.25	–	–

[a] Measured at 200 Cd/m^2.

10.5 Cd/A at 6600 Cd/m^2 and maintains an efficiency of greater than 10.0 Cd/A up to 50,000 Cd/m^2. 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/m^2 is a very attractive feature for passive matrix displays, which are known to require high efficiencies at high brightness levels under pulsed excitation [10].

In addition to their high efficiencies the green devices have demonstrated excellent lifetime characteristics. Fig. 2(b) displays the lifetime parameters of a typical green device starting from a brightness of 1100 Cd/m^2 and driven by dc with a current density of 12.8 mA/cm^2 at ambient temperature. The test was terminated at 940 h with an extrapolated lifetime of greater than 1500 h. Over 940 h, the drive voltage of the device only increased by 0.52 mV/h.

When lifetime measurements are performed at high luminance levels and ambient temperature, decay mechanisms are accelerated and the lifetime can be extrapolated over a reduced time scale [5]. Similar experimental results using accelerated lifetime testing have also been reported with other polymer systems [11]. Based on a composite engineering plot of this green emitter, a lifetime in excess of 10,000 h with an acceptable high brightness level has been projected.

The green devices have also demonstrated very good color stability over time and at different brightness levels. Fig. 3(a) illustrates a negligible chromaticity change ($\Delta x, \Delta y$) when the device is operated at different brightness levels. The changes in the *x* and *y* CIE color coordinates from 200 to 15,000 Cd/m^2 are only $\Delta x = 0.006$ and $\Delta y = 0.004$. Fig. 3(b) illustrates the EL spectra of a device before and after continuous operation for 570 h at 1000 Cd/m^2. Again, the changes in CIE coordinates (Δx, Δy), measured at 200 Cd/m^2, are only 0.003 and −0.004, respectively.

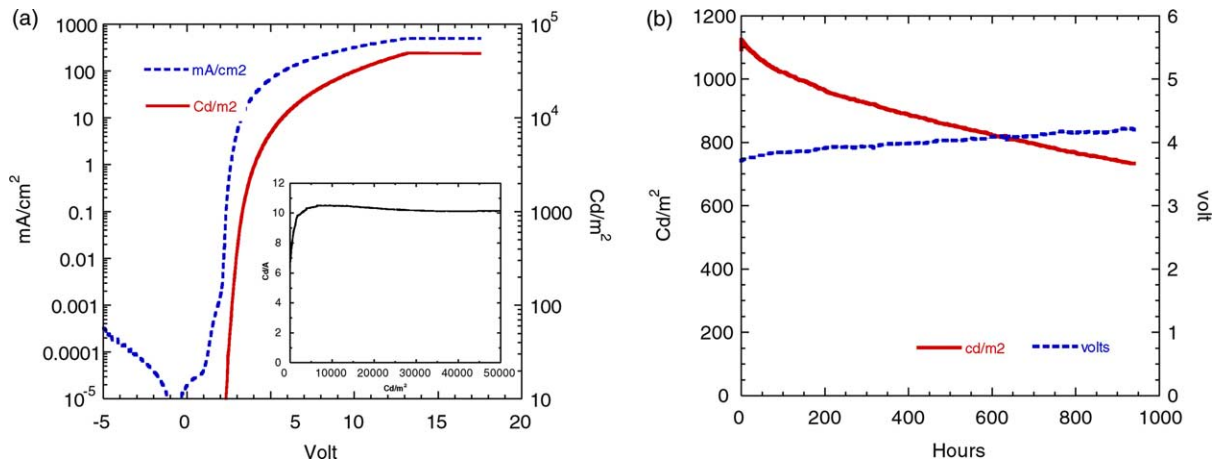

Fig. 2. Characteristics of the green device with PEDT as the hole-transporting layer and Ca as the cathode. (a) Current-luminance vs. voltage. Inset shows device efficiency (Cd/A) vs. Luminance (Cd/m^2). (b) Lifetime with light output (Cd/m^2) vs. time (hour).

The same excellent color stability has also been observed for both red and blue devices.

3.2. Red

Devices made with the red polyfluorene polymers have exceeded the efficiencies of those reported in the literature [11] and exhibit a saturated red color chromaticity. The efficiency characteristics of a red device are shown in Fig. 4(a). The device has a low turn on voltage of 2.1 V, achieves a maximum efficiency of 1.5 Cd/A at 210 Cd/m^2 and reaches a brightness of 2000 Cd/m^2 at 8.4 V.

The light output of the red device as a function of time is illustrated in Fig. 4(b). Starting from of 200 Cd/m^2, the device was operated at ambient temperature for 3050 h. The light output was 163 Cd/m^2 when the current running through the device was turned off and the overall voltage increase was only 0.46 V, corresponding to a ΔV of 0.15 mV/h. The extrapolated time to reach half of the initial light output is 7000–8000 h. For a device starting from 100 Cd/m^2, the projected lifetime is in excess of 10,000 h.

3.3. Blue

Among all RGB polymers, devices made from blue emitters commonly exhibit lower device efficiencies and poor lifetimes [12]. In polymeric semiconductors, the majority charge carriers are typically holes because of the polymers ability to be easily oxidized and due to the typically smaller injection barriers at the anode/polymer interface. This is especially true in the case of current polyfluorene systems and more general in wide band gap blue emitting polymers. The blue systems are characterized by a relatively low electron affinity, which makes electron injection difficult with the use of conventional cathode metals such as calcium. Therefore, lowering the cathode energy barrier height and enhancing electron injection is especially important in providing efficient recombination of

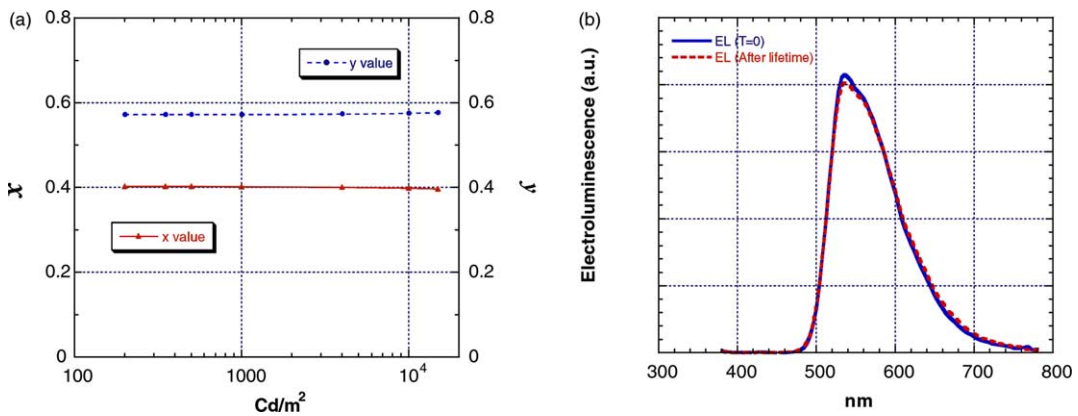

Fig. 3. (a) Green device chromaticity at varies brightness levels. (b) Green device emission spectra before and after continuous operation at 1000 Cd/m^2 for 570 h.

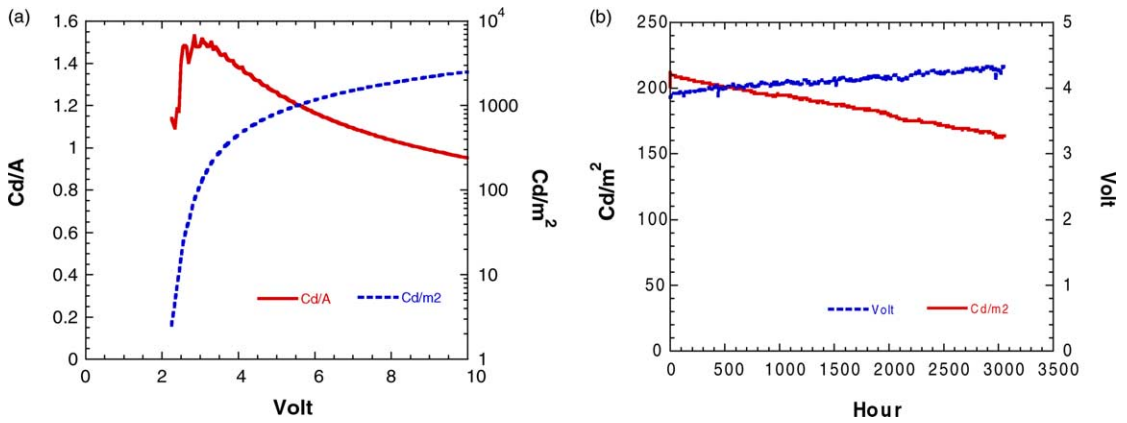

Fig. 4. Characteristics of the red device with PEDT as the hole transporting layer and Ca as the cathode. (a) Luminance (Cd/m^2) and efficiency (Cd/A) as the function of voltage (V). (b) Light output (Cd/m^2) as a function of time (hour) at ambient temperature.

electrical charges in the luminescent segments of the polymers. The incorporation of interlayer such as LiF at the cathode/polymer junctions has been shown to significantly improve device efficiency and lifetime of blue emitting devices [13].

As a result of our continuous optimization of polymer compositions, the efficiency of blue devices has been significantly improved over last few years. As shown in Fig. 5(a), 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/m^2. Even at 4000 Cd/m^2 the efficiency remains above 2.0 Cd/A.

In Fig. 5(b) shows the lifetime of a blue device starting from an initial brightness of 100 Cd/m^2. The device was operated at ambient temperature and reached 500 h at half of the initial light output. Considering calcium is used as the cathode in this case, a significantly higher efficiency and longer lifetime can be expected when a modified cathode is used.

While the intrinsic properties of blue polymers are critical to achieving good device performance, the same importance lies in optimizing device design. The device fabricating capabilities at Cambridge Display Technologies (CDT) have enabled a blue device made with a polymer produced at Dow to perform with very low turn-on voltage (~2.7 V), good efficiency (3–4 Cd/A between 100 and 1000 Cd/m^2), acceptable color ($x = 0.17$, $y = 0.21$) and excellent lifetime. Starting from 100 Cd/m^2 the device suffered only 30% luminance loss after 2100 h and has a projected lifetime exceeding 4000 h.

4. Summary

With our modified Suzuki polymerization, the synthesis of a broad range of polyfluorene-based light emitting polymers with high molecular weight, excellent quality and tunable color have been developed. Red, green and blue PLED devices with high efficiency, low operating voltage and long lifetime have been demonstrated. Furthermore, excellent color stability at different brightness levels and

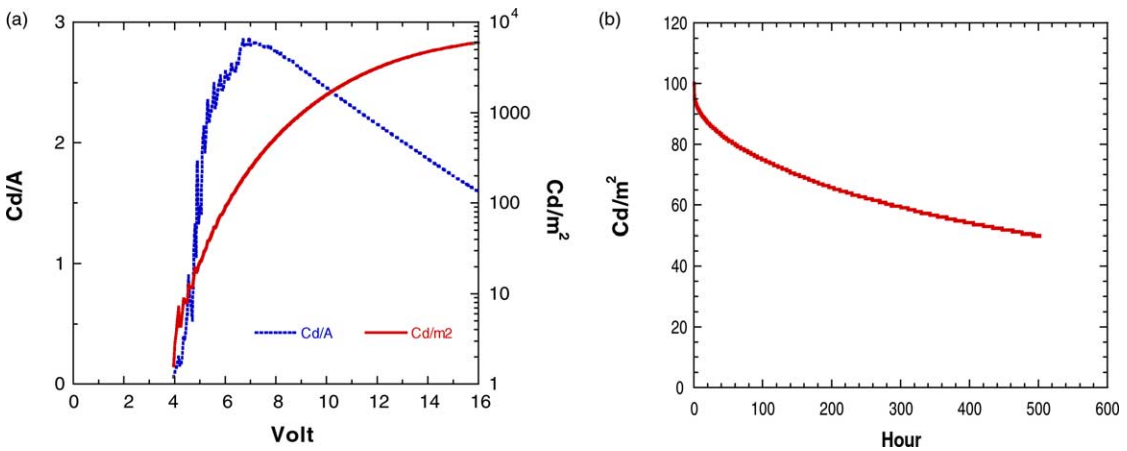

Fig. 5. Characteristics of the blue device with PEDT as the hole transporting layer and Ca as the cathode. (a) Luminance (Cd/m^2) and efficiency (Cd/A) as the function of voltage (V). (b) Light output (Cd/m^2) as a function of time (hr) at ambient temperature.

over thousands of hours of continuous operation has been shown for all three colors.

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