White LED Based on Polyfluorene Co-Polymers Blend on Plastic Substrate

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***Abstract*—We report on high-performance, white light emission from polyfluorene co-polymers blend and study of the opto-electrical properties of polymer blend light-emitting devices (PLEDs) fabricated on plastic substrate. Our results show that efficient white light emission via energy transfer, producing higher device efficiencies and luminance in comparison with the conventional single PLEDs, can be realized by blending carrier donor (host) and acceptor (guest) organic polyfluorene co-polymers. A maximum luminance of $\sim$7400 cd/m^2 was achieved at 13 V with Internationale de L'Eclairage coordinates of (0.33, 0.33). Maximum emission efficiency of $\sim$2.0 cd/A and power efficiency of $\sim$1.1 lm/W are obtained for white light PLEDs on plastic substrate.**

***Index Terms*—Flexible plastic substrate, polymer blend, polymer light-emitting diodes (PLEDs), white polymer light-emitting diodes (WPLEDs).**

I. Introduction

Over the last several years, light-emitting devices (LEDs) based on organic materials have been attractive research subjects because of their potential applicability to large-size flat panel displays (FPDs) and solid-state lighting. The use of plastic substrates can add both device flexibility and reduced thickness, weight, and manufacturing costs of large-area FPDs [1]–[4]. Also, white light single-layer organic LEDs (OLEDs) can be used as a plane light source for current large-area liquid-crystal display (LCD) TVs and as back plane for future flexible full color displays in combination with color filters.

Since the early 1990s, there have been many studies reporting the white light emission from either small molecule- or polymer-based devices. In 1995, Kido *et al.* developed an OLED consisting of three emitter layers with different carrier transport properties, each emitting blue, green, and red light to generate the white light [5]. In 1999, Deshpande *et al.* also demonstrated a white light emitting OLED consisting of green and blue emitting layers doped with a red emitting material. Here, the light emission was controlled by varying the concentration of the doping material and the thickness of a thin hole-blocking layer [6]. In 2002, Mazzeo *et al.* successfully showed that the pair of blue emitting molecules, N, N'-bis(3-methyl-phenyl)-N,N'-diphenylbenzidine (TPD) and 2,5-bis(trimethylsilyl thiophene)-1,1-dioxide (STO), could produce the white electroluminescence from the exciplex recombination [7]. In 2004, Shao and Yang fabricated a white OLED from a single organic light-emitting layer doped with fluorescent dyes using the fused organic solid-solution technique [8]. Table I summarizes the opto-electronic performances of the devices reported above.

TABLE I
Opto-Electronic Characteristics of Various OLEDs Fabricated on Glass Substrates Are Summarized as (a) Small Molecule (b) Polymer-Based Devices

Parameters	Small molecule based devices on glass			
	[5]	[6]	[7]	[8]
Year	1995	1999	2002	2004
Voltage (V @ 1 cd/m^2)	~ 6	n/a	~ 8	~ 10
EE$_{max}$ (cd/A)	n/a	n/a	n/a	~ 2.5
PE$_{max}$ (lm/W)	n/a	~ 0.35	n/a	n/a
L$_{max}$ (cd/m^2)	~ 2200	~ 13500	~ 150	~ 15000
Voltage (V @ L$_{max}$)	~ 16	~ 18	~ 14	~ 13
CIE coordinate	n/a	(0.33, 0.33)	(0.34, 0.38)	(0.29, 0.33)

(a)

Parameters	Polymer based devices on glass				
	[9]	[10]	[12]	[13]	[14]
Year	1995	1996	2000	2004	2004
Voltage (V @ 1 cd/m^2)	~ 8	n/a	~ 15	~ 5	n/a
EE$_{max}$ (cd/A)	n/a	n/a	~ 0.9	~ 4.3	~ 1.6
PE$_{max}$ (lm/W)	n/a	n/a	~ 0.08	~ 1.0	n/a
L$_{max}$ (cd/m^2)	~ 4100	n/a	~ 1500	~ 12000	~ 3000
Voltage (V @ L$_{max}$)	~ 20	n/a	~ 45	~ 17	~ 10
CIE coordinate	(0.34, 0.38)	(0.34,0.32)	(0.30, 0.37)	(0.32, 0.33)	(0.34, 0.34)

(b)

White light emission from polymer films can also be accomplished by dispersing organic materials in a single light-emissive polymer layer or by blending different polymers. In 1995, Kido *et al.* reported that several fluorescent dyes, having different light emission colors, dispersed in poly(N-vinylcarbazole) (PVK) polymer could emit the white light with the high brightness [9]. Granström *et al.* showed in 1996 that white light emission could be produced from a polymer mixture in which an insulating polymer has been added to control the energy transfer from the high band gap to the low band gap polymers [10]. In 1998, Chao *et al.* showed that the generation of white light can also be achieved by the formation of exciplexes between two different blue emitting materials in a bilayer structure [11]. In

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Manuscript received July 6, 2005; revised December 2, 2005. The review of this paper was arranged by Editor L. Lunardi.

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Digital Object Identifier 10.1109/TED.2005.864378

2000, Yang *et al.* demonstrated the single layer white organic light-emitting diode by doping a blue light emitting material, phenylene-vinylene trimer, 1,4-bis(1,1-diphenyl-2-ethenyl) benzene (PEB), with a single orange dye, rubrene dispersed in a neutral matrix polymer, polystyrene [12]. Gong *et al.* reported in 2004 that the white-light emission can be produced from the semiconducting polymer blended with the organometallic emitters with a high power efficiency of ∼1 lm/W [13]. In the same year, Ho *et al.* showed that without involving dye or phosphorescent molecules, the white light-emission could be achieved from conjugate polymer blend of poly [2-methoxy-5 (2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) and poly (9,9-dioctylfluorene-2,7-diyl) (PFO), which showed the maximum luminance of ∼3000 cd/m^2 at 10 V [14]. The performances of devices mentioned above are summarized in Table I.

Until now, all white light-emitting devices from either small molecules or polymers have been fabricated on glass substrates. For the future flexible display or flexible solid-state lighting applications, however, the development of white light OLEDs on flexible plastic substrate is essential.

In this paper, we report on opto-electronic properties of the single-layer co-polymer blend light-emitting devices (PLEDs) fabricated on plastic substrate [15]–[17]. Utilizing energy transfer concept from blue light-emitting (donor) to red light-emitting polyfluorene based co-polymer (acceptor), we could achieve both white light emission and a higher maximum luminance and device efficiency from PLEDs fabricated on plastic substrate. To our best knowledge, this paper represents the first investigation of the opto-electronic performance of white light PLEDs on plastic substrate.

II. Experimental Details

A. Polymer Blend Preparation

A polymer blend was made of polyfluorene based blue and red light-emitting co-polymers, the properties and possible chemical structures of which were reported previously [18]–[20]. Poly (fluorene-co-benzothiadiazol-co-thienyl-benzothiadiazol) and poly (fluorene-co-anthracene-co- p-tolylamine) will emit red and blue light, respectively. Blue polymer of 1.2 wt% in xylene was used as the carrier donor polymer with the red polymer as the carrier acceptor polymer. To control the blending ratio of red polymer to blue polymer, the weight of red polymer was fixed to 1 mg, and xylene was then added to achieve the desired concentration of red polymer in the solution (7.2×10^{-3} wt%). Finally, 1 mg of blue polymer was added to the red polymer solution to accommodate 1.2 wt% concentrations, and produce the blend solution with target ratios of blue to red polymer (99.5:0.5), (99.4:0.6), and (99.3:0.7). To avoid the possible degradation of polymers during the process, the blending step was performed inside a nitrogen atmosphere glove box.

B. Measurement of the Polymer Blend Optical and Electrochemical Properties

The absorption spectrum of the thin film (∼100 nm) deposited on a quartz substrate was measured in the air with a CARY 5 UV-visible spectrophotometer. The film was prepared from the solution described above by spin coating at 1500 rpm followed by a 90 °C bake in a vacuum oven outside the glove box for 1 h. The optical band gap E_G (eV) was estimated by following equation from the semiconductor theory: $E_G = hc/\lambda_{\text{abs}}$, where h is Plank constant, c is the velocity of light, and λ_{abs} (= 382 nm) is the peak wavelength in the polymer blend absorption spectrum. The resulting optical band gap was 3.25 eV. The photon energy values corresponding to maximum absorption for different polymers are given in Table II.

TABLE II
OPTO-ELECTRONIC CHARACTERISTICS OF RED, BLUE, AND POLYMER BLEND PLED ON PLASTIC SUBSTRATE ARE SUMMARIZED

PLED on plastic	White	Red	Blue
Abs$_{\text{max}}$ (nm)	382	323 / 463	379
Voltage (V @ 1 cd/m^2)	~ 5.6	~ 2.8	~ 4.8
Current (A/m^2 @ 1 cd/m^2)	~ 42.7	~3705*	~14128*
Voltage (@ 300 cd/m^2)	~ 8.3	~ 5.1	~ 7.0
EL$_{\text{max}}$ (nm)	466 / 607	637	477
EE$_{\text{max}}$ (cd/A)	~ 1.96	~ 0.27	~ 0.69
PE$_{\text{max}}$ (lm/W)	~ 1.09	~ 0.23	~ 0.33
L$_{\text{max}}$ (cd/m^2)	~ 7366	~ 1410	~ 2652
CIE coordinate	(0.33, 0.33)	(0.59, 0.29)	(0.16, 0.23)
HOMO (eV)	-5.9	-5.85	-5.8
LUMO (eV)	-2.1	-3.12	-2.1

* High current values for red and blue single polymer devices are due to current bumps in I-V characterstics which have been previously reported by other groups [27]

Electrochemical measurements were performed using a CH Instruments Electrochemical Workstation. The three-electrode cell consisted of a glassy carbon working electrode, a platinum counter electrode, and a Ag/Ag$^+$ reference electrode. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAPF6) in dry acetonitrile (MeCN) at a concentration of 0.1 M. The reference electrode is a 0.01 M solution of silver nitrate ($AgNO_3$) in dry MeCN in contact with a silver electrode. The electrolyte solution was bubbled with nitrogen for several minutes before measurements were taken to remove dissolved oxygen. The working electrode was modified by dip casting in polymer blend solution and dried in air.

Ferrocene is used as a pseudo-reference in these measurements. Ferrocene has a well-studied, reversible redox couple, estimated to be 4.8 eV below vacuum [21]. Using this estimation, we can develop an approximate relationship between the measured current-voltage characteristics and the absolute energy scale with the following equation:

$$E_{\text{vac}} = -q\left(4.8 + V_{\text{Ag/Ag}^+} - V^{\text{ferrocene}}_{\text{Ag/Ag}^+}\right) \qquad (1)$$

where $V^+_{\text{Ag/Ag}}$ is the voltage measured versus the Ag/Ag$^+$ reference and $V^{\text{ferrocene}}_{\text{Ag/Ag}^+}$ is the voltage at which the ferrocene redox couple occurs. For the data shown in Fig. 1, the ferrocene couple centered around 0.1 V versus Ag/Ag$^+$. The electron affinity (Ea) is found by substituting the reduction onset potential for $V^+_{\text{Ag/Ag}}$ while the ionization potential (Ip) is found by substituting the oxidation onset potential for $V^+_{\text{Ag/Ag}}$. The highest occupied molecular orbit (HOMO) and lowest unoccupied molec-

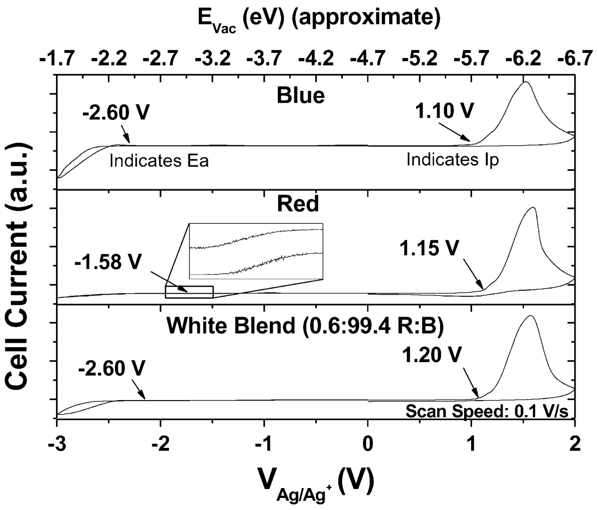

Fig. 1. Cyclic voltammetric current–voltage characteristics of blue, red, and (99.4:0.6) polymer blend coated on a glassy carbon electrode by dip-casting with supporting electrolyte of TBAPF6 in a 0.1-M dry MeCN. Scan rate was 0.1 V/s.

ular orbit (LUMO) levels for the polymer are then approximated by equating Ip to the HOMO and Ea to the LUMO [20], [21].

Cyclic-voltammetry (*C–V*) scans were performed at a voltage scan speed of 0.1 V/s. The oxidative and reductive scans were done separately with new polymer films for each scan. *C–V* curves for red, blue and the blend polymer are shown in Fig. 1.

From the measurement results, for polymer blend, the oxidation and reduction onset potentials were found to be 1.2 and −2.6 V, respectively. Therefore, according to (1), the HOMO and LUMO (Ip and Ea) for the polymer blend with the ratio of (99.4:0.6) are −5.9 and −2.1 eV, respectively, giving an electrochemical gap of 3.8 eV. This carrier transport gap is 550 meV greater than the measured optical band gap E_G of 3.25 eV for the same material. As expected, the electrochemical characteristics of the blend, shown in Fig. 1, closely resemble that of the blue polymer.

C. Opto-Electronic Properties of PLED

The fabrication process of PLED on plastic substrate has been described previously [17]. Fig. 2 shows the schematic device crosssection and its top-view. A Ca/Al bi-layer and ITO layer were used as cathode and anode electrode, respectively.

The prepatterned ITO/plastic substrate was cleaned by acetone and isopropyl alcohol, and then air-dried by nitrogen. UV-ozone treatment was applied to the ITO surface for 20 min to clean the organic residue off the surface as well as modify its surface properties [16], [23]. The PEDOT:PSS (CH 8000) purchased from Bayer was spin-coated at 2000 rpm over the ITO surface outside the glove box, and it was baked at 90 °C for 1 hour inside glove box. PEDOT doped with PSS is used as a hole-injection layer (HIL) due to its high conductivity and large ionization potential. This layer allows for efficient injection of holes in to the polymer blend: the light emission layer (LEL). In addition, the PEDOT layer serves as a barrier to oxygen diffusion from the ITO layer [24].

The polymer blend solution with the ratio of 99.4:0.6 (blue : red) as LEL was deposited by spin coating at 1500 rpm inside the glove box, and baked at 90°C for 1.5 hours. Finally, the Ca/Al (150 Å/2000 Å) cathode was thermally evaporated through a shadow mask at $\sim 10^{-6}$ torr in a system directly connected to the nitrogen glove box. The dimension of complete PLED was 1.1×1.1 mm^2. The white light-emission from PLED is also shown in Fig. 2.

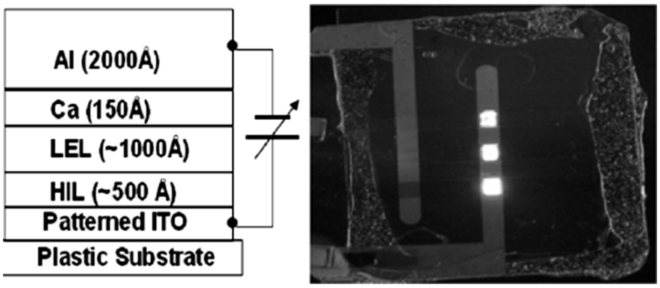

Fig. 2. PLED multilayer structure used in this paper is shown. An image of the white light emission from polymer blend PLED is also included.

To measure the PLED opto-electrical properties such as current–voltage (*I–V*) and luminance–voltage (*L–V*), the device was mounted on the input port of the integrating sphere in a nitrogen (N_2) atmosphere [25]. All optical and electrical measurements were performed in an integrating sphere system, which consists of a programmable electrometer (Keithley 2400), an IL 1700 Research Radiometer from International Light, and the photodiode. A LabView program was used to control the measurement system. The integrating sphere was calibrated to measure the total flux into the sphere system.

Electroluminescence (EL) spectrum of the complete PLED was measured in the air with an integrating sphere based measurement system [25]. The calibrated photodiode detector from JY Horiba was used to measure the EL spectrum. To prevent device degradation during the experiment, cover slide glass was attached with epoxy on the top of PLED. This simple packaging was done before removing the PLEDs from the nitrogen glove box. A dc power supply (BK 1670) was used to scan the voltage from 0 to 15 V. All measurements were performed at room temperature in the dark.

III. EXPERIMENTAL RESULTS

A. Opto-Electronic Characteristics

The energy band diagram of PLED multilayer structure with our polymer blend of (99.4:0.6) is shown in Fig. 3. The HOMO and LUMO levels of HIL and LEL were measured as discussed above. The band offsets between HOMO and LUMO levels of the HIL and LEL are defined as ΔE_H and ΔE_L, respectively while the potential barrier height between LUMO of LEL and the metal work function of Cathode (Φ_{Ca}) is defined as Φ_e $(= \Phi_{\mathrm{Ca}}$—LUMO). The ionization potential of PEDOT:PSS (5.0 eV) was taken from literature [26].

Fig. 4 shows the current density versus voltage (*J–V*) characteristics of polymer blend PLED. The *J–V* curve indicates a diode-like behavior, with a rectification ratio greater than 10^3 at voltages above 10.5 V. At a low voltage level, a current bump was observed, which has also been previously reported by other groups [27]–[29]. Berleb *et al.* associated this bump with the

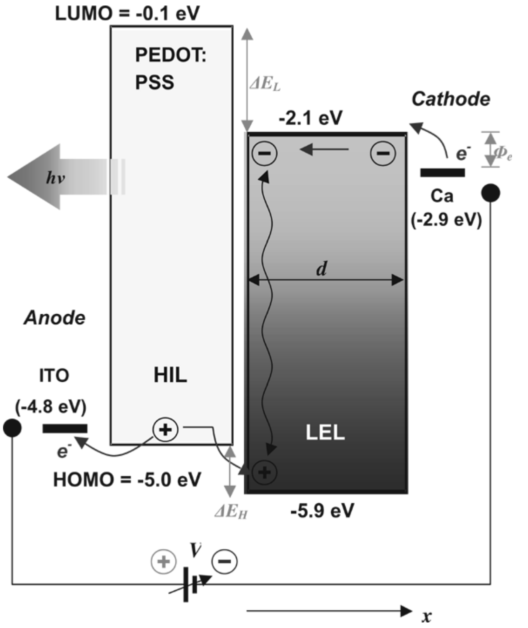

Fig. 3. Schematic energy band diagram for multilayer PLED before the electrical contact is established; all the energy values are relative to the vacuum level.

negative differential resistance (NDR) [27]. No light emission was observed when the diode was reverse-biased.

When forward bias (positive on anode, negative on cathode) is applied, it can be speculated that an electron injection from the cathode into the LUMO level of LEL, and an electron extraction from the HIL into the anode will take place. The electron extraction leaves positive charges (holes) in the HOMO level of HIL, and this process can be regarded as an hole injection process from anode into HOMO level of HIL over the HOMO level offset ($\Delta E_H = 0.9$ eV). The electrons are injected from cathode over Φ_e, and after drift/diffusion, they are confined at the interface between HIL and LEL due to the high LUMO levels offset ($\Delta E_L = 2.0$ eV). Under the applied bias, the opposite charges (polarons) will drift/diffuse toward each other under influence of the electric field, and eventually will recombine radiatively in LEL near the HIL/LEL interface to produce the white light-emission through ITO electrode that can be characterized by its luminance (*L*).

The luminance (*L*) versus voltage characteristics of polymer blend PLED are shown in Fig. 5. From this curve, we can define the following PLED characteristics: the turn-on voltage is the voltage which produces $L = 1$ cd/m^2, and the display operating voltage is the voltage which produces $L = 300$ cd/m^2. As shown in Table II, devices made with a single polymer of blue and red light-emitting material had average turn-on voltage of 4.8 and 2.8 V, respectively, whereas the white light-emitting device showed a turn on voltage of 5.6 ± 0.3 V, closely matching the turn-on voltage of the blue light-emitting polymer (donor). The polymer blend PLED shows a very high maximum luminance of $\sim$7400 cd/m^2 at 13 V, compared to 1410 and 2650 cd/m^2 produced by red and blue PLED, respectively.

Fig. 5 also shows the luminance versus current density (*L*–*J*) characteristic, which was extracted from *J*–*V* and *L*–*V* curves shown in Figs. 4 and 5.

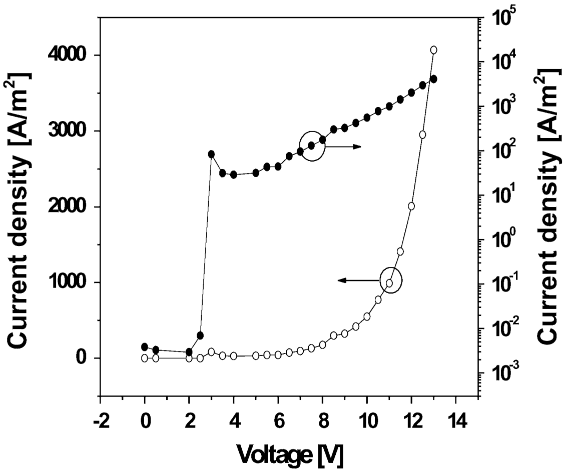

Fig. 4. Current density versus voltage characteristics of polymer blend PLED in linear and semilog plot. The solid lines are provided for eye guidance.

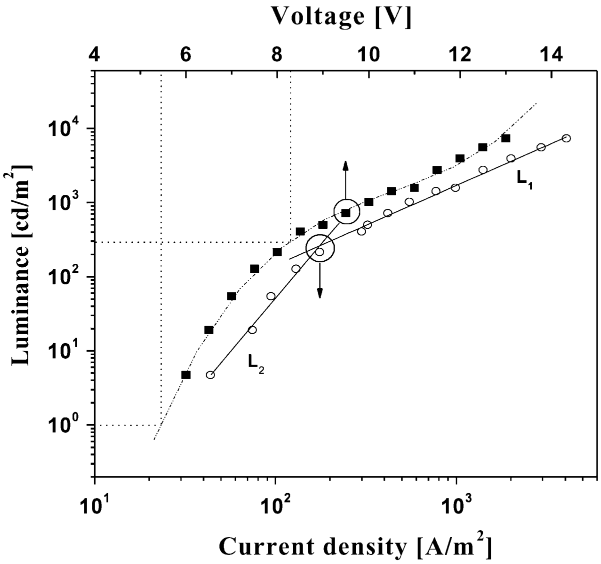

Fig. 5. Luminance versus voltage (closed square), and luminance versus current density (open circle) characteristics of polymer blend PLED. The solid lines represent fitting curves for each characteristic, and dotted line is provided for eye guidance.

If we assume that the PLED carrier injection at different interfaces is due to field-emission tunneling [30], the electron and hole injection currents can be expressed by

$$J_p = E^2 \exp\left[\frac{-4\sqrt{2m_h^*}(\Delta E_H)^{3/2}}{3q\eta E}\right], \text{ at } x = 0 \qquad (2)$$

$$J_n = E^2 \exp\left[\frac{-4\sqrt{2m_e^*}(\Delta \phi_e)^{3/2}}{3q\eta E}\right], \text{ at } x = d \qquad (3)$$

where m_h^* and m_e^* are the effective mass of holes and electrons, respectively, q is the electron charge, $\hbar$ is the reduced Plank constant, and E is the electric field. If we assume that the LEL behaves as a p-type semi-conductor [31] and the carrier transport in the LEL is a drift-type in a high electric field [32], we can describe the evolution of hole and electron density with the time by the following continuity equation [33]:

$$\frac{dp}{dt} = -\frac{1}{q}\frac{dJ_p}{dx} + G - R, \text{ with } p(0) = \frac{J_p}{q\mu_p E} \qquad (4)$$

$$\frac{dn}{dt} = \frac{1}{q}\frac{dJ_n}{dx} + G - R, \text{ with } n(d) = \frac{J_n}{q\mu_n E} \tag{5}$$

where the μ_n and μ_p are the electron and hole mobilities, respectively, G and R are the generation and recombination rate of carriers in the LEL, respectively, and d is the thickness of LEL. To solve the above nonlinear equations, several approximations must be made: 1) the time derivatives in (4) and (5) are set equal to zero; 2) The electric field throughout the LEL is uniform; 3) Recombination is dominant and has a constant value determined only by the electron lifetime (τ_n) in the entire LEL $(G = 0, R = n/\tau_n)$. By solving the carrier continuity equations under the boundary conditions mentioned above (which are similar to a-Si:H LED [34]), the distribution of electrons and holes in the LEL can be described by:

$$\begin{aligned} n(x) &= \frac{J_n}{q\mu_n E} e^{(x-d)/\gamma_n} \quad \text{and} \\ p(x) &= \frac{J_p}{q\mu_p E} - \frac{J_n}{q\mu_p E}\left(e^{(x-d)/\gamma_n} - e^{-d/\gamma_n}\right) \end{aligned} \tag{6}$$

where $\gamma_n = \mu_n \tau_n E$, the electron drift length.

Since the luminance is proportional to the rate of the radiative recombination of injected carriers in LEL, it can be related by the following equation:

$$L \propto \int_0^d n(x)^{\alpha_c} \cdot p(x)^{\alpha_v}\, dx \tag{7}$$

where α_c and α_v are the dispersive parameters associated with the bulk dispersive transport of electrons and holes within LEL. From (4) and (5), we can get a simplified equation for the luminance in terms of the current density by integrating the product of electron and hole density over the LEL thickness. Since $J_n + J_p \approx J_p \equiv J$, L can be expressed by

$$\begin{aligned} L \propto & \left(\frac{J}{q\mu_p E}\right)^{\alpha_v} \\ & \cdot \left(\frac{J_n}{q\mu_n E}\right)^{\alpha_c} \int_0^d \left(1 - \frac{J_n}{J}\exp[-(x-d)/\gamma_n]\right)^{\alpha_v} \\ & \times \exp[-\alpha_c(x-d)/\gamma_n]dx. \end{aligned} \tag{8}$$

If we simplify (8)

$$\begin{aligned} J_n^{\alpha_c} &= J_p^{\alpha_c}\exp[\frac{\alpha_c}{d_c}] \approx J^{\alpha_c}\exp[\frac{\alpha_c}{d_c}] \text{ with } d_c \\ &\equiv \frac{3q\eta E}{4\sqrt{2m^*}(\Delta E_h^{3/2} - \phi_e^{3/2})} \end{aligned} \tag{9}$$

then (8) becomes

$$L \propto \frac{d}{E^{\alpha_c+\alpha_v}} \exp\left[\frac{\alpha_c}{d_c}\right] J^{\alpha_c+\alpha_v} \tag{10}$$

and if $\alpha_c + \alpha_v = 1$, then (10) becomes

$$L \propto \frac{d}{E} \exp\left[\frac{\alpha_c}{d_c}\right] J. \tag{11}$$

From this equation, the PLED luminance is expected to increase linearly with the current density. Experimentally we observe this linear relationship in the current range from ~3 × 10^2 up to ~10^4 cd/m^2, Fig. 5, and in this case, L can be expressed by

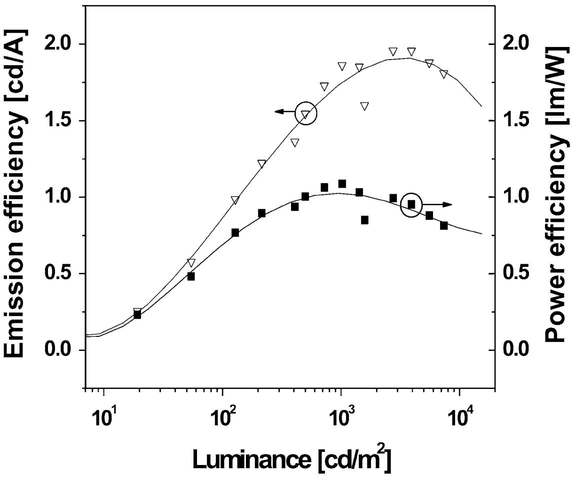

Fig. 6. Emission efficiency and power efficiency versus luminance characteristics of polymer blend PLED are shown. The solid lines are provided for eye guidance.

$$L_1 \propto J^{\alpha}, \text{ with } \alpha = 1.07 \pm 0.01. \tag{12}$$

At low luminance (< 3 × 10^2 cd/m^2), the *L*–*J* relationship deviates from this linearity and can be expressed by

$$L_2 \propto 0.04 J^{\alpha}, \text{ with } \alpha = 1.82 \pm 0.19. \tag{13}$$

The origin of this deviation at low luminance regime is under present investigation. Therefore, the total PLED luminance L is the sum of both L_1 and L_2, which can be expressed generally by (10).

Knowing L and J, the emission efficiency $(\mathrm{EE} = L/J)$ versus luminance characteristics can be defined for polymer blend PLED, Fig. 6. Enhanced EE was obtained for our polymer blend PLED in comparison with both single blue and red polymer PLEDs as shown in Table II. This increase in EE will be addressed in the next section. For the polymer blend device, an EE larger than ~1.8 cd/A was obtained over the luminance ranging from 1000 to 7400 cd/m^2, whereas the red PLED showed a maximum EE of 0.27 cd/A at ~1460 cd/m^2 and the blue PLED showed an EE about 0.69 cd/A at 2650 cd/m^2.

The power efficiency ($\mathrm{PE} = \Phi/IV = \pi L/JAV = \pi EE/AV)$) is defined as the ratio of the total luminous flux (Φ) of the PLED to the input electrical power, and was obtained by dividing the measured total luminous flux by the products of the corresponding input current (*I*) and voltage (*V*), where *A* is the area of PLED. The power efficiency versus luminance characteristics of polymer blend PLED is also shown in Fig. 6. As expected, the measured PE shows similar behavior to the EE, e.g., efficiency increases with luminance and a higher PE value was observed for the polymer blend PLED in comparison with both blue and red PLEDs as shown in Table II. The maximum PE of 1.1 lm/W was obtained at ~1023 cd/m^2 for polymer blend PLED with the white light emission, whereas the red PLED showed a maximum PE of

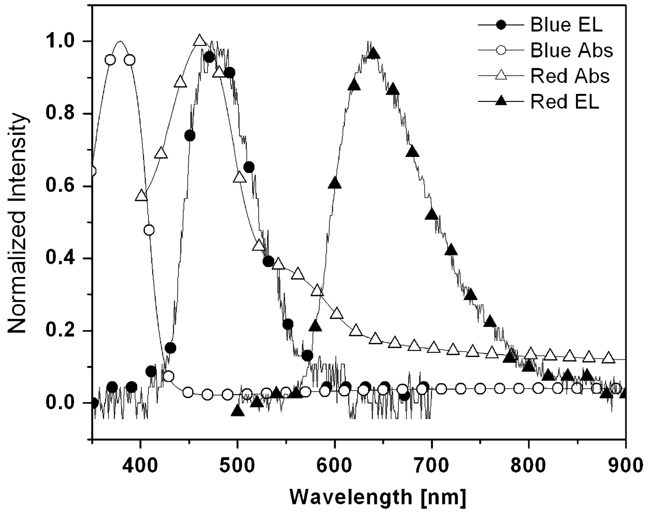

Fig. 7. Normalized absorption spectra of thin red and blue polymer films, and EL spectra of corresponding PLED are shown.

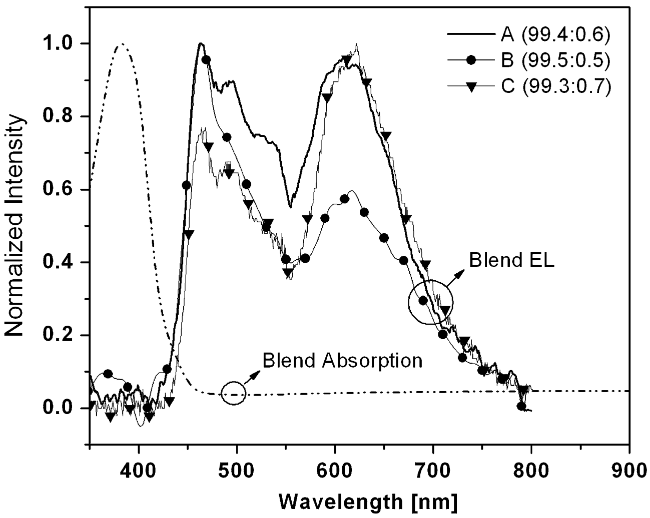

Fig. 8. Normalized EL spectra from polymer blend PLEDs of various blending ratios are shown.

0.23 lm/W at ~1410 cd/m^2 and the blue PLED showed an PE about 0.33 lm/W at 2650 cd/m^2. The increase of PE value will be addressed in the next section.

B. Energy Transfer in the Blend Polymer

The polymer blend used in PLEDs consists of blue and red light-emitting polymers, of which the absorption spectrum of the thin film and the EL spectra of each PLED are shown in Fig. 7. Since the major component of the polymer blend is blue light-emitting polymer (host), we expect that the polymer blend based PLED will emit mainly blue light. However, experimentally we observed both blue and red light emission from polymer blend PLED, Fig. 8. Since we have an overlap between the absorption spectrum of red polymer and the emission spectrum of blue polymer, it is expected, and is experimentally observed that the blue emitted light is absorbed by the red polymer dispersed within the blue polymer host, Fig. 7. Therefore, the light emitted from blue polymer will be absorbed by the red polymer (guest) and will be used to produce excited states within the red polymer that will emit light in a different photon energy region, Fig. 7.

Knowing that the maximum luminance of blue and red PLED is 1450 and 760 cd/m^2, respectively, we would expect that the maximum luminance of polymer blend PLED should be equivalent to blue PLED performance in the best condition. Experimentally, we observe that the polymer blend PLED performance is much higher than the blue PLED. This enhancement of the luminance is due to the energy transfer between blue light-emitting material (donor) and red light-emitting material (acceptor). It is expected that when energy transfer takes place between donor and acceptor, the polymer blend PLED will display much higher opto-electronic performance than donor itself [35]; this was observed experimentally in this case. Energy transfer will take place between donor and acceptor when the following conditions are satisfied: 1) there is an overlap between the light emission spectrum of donor polymer and the absorption spectrum of acceptor polymer; 2) the spacing between uniformly mixed donor and acceptor polymers is on the order of tens of Augstroms; and 3) the energy transfer rate between donor and acceptor should be faster than any decay rate of excited states in donor polymer.

Energy transfer competes with both radiative and nonradiative decay inside the donor polymer. If the rate of energy transfer between donor and acceptor materials is faster than other decay mechanisms, a majority of the excitations created in the donor polymer will be transferred to the acceptor polymer before they can decay either radiatively or nonradiatively. Since, in this polymer blend, the energy transfer rate is much faster than nonradiative decay rate [36], we expect that its EL spectra will be composed of blue and red light emission, as experimentally observed, Fig. 8. Indeed, the EL spectra of the polymer blend PLED shows peaks at 466 nm (2.66 eV) and 607 nm (2.04 eV) corresponding to the blue and red light-emitting polymer components, respectively (see Table II). As shown in the Fig. 8, EL spectra are very sensitive to polymer blend composition. Therefore, a slight change in blending ratio from 99.4:0.6 (sample A) to 99.5:0.5 (sample B) or 99.3:0.7 (sample C) could result in the prominent red (sample B) or blue (sample C) light-emission, respectively.

Since luminescent polymers have nonzero absorption at their emission wavelength, reabsorption of emitted photons can play a major role in reducing the efficiency and luminance of PLEDs [37]. As shown in Fig. 8, the blend polymer showed the dominance of the blue polymer component and there was no appreciable absorption corresponding to the red polymer. Hence, it provides a transparent medium for the emission of red light. With negligible self-reabsorption due to the low mass content of the red acceptor polymer, it is expected that the blend PLED could produce much higher luminance than single blue and red PLEDs. It is also expected that a diluted material in a matrix can produce enhanced light emission intensity [37] since increasing the interchain separation between the polymer chains by diluting the polymer in a solid-state matrix can reduce the nonradiative transitions as observed in solution. Since luminance is enhanced for the polymer blend PLED, we expect a higher PE

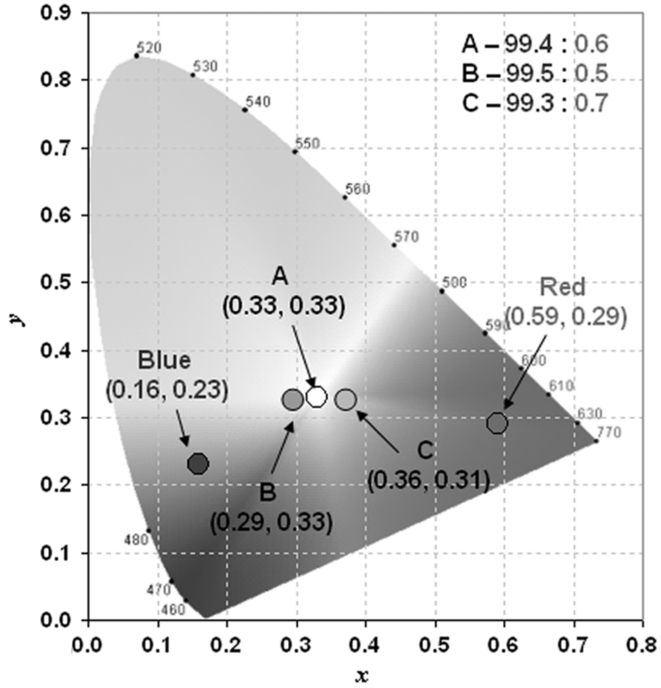

Fig. 9. CIE 1931 chromaticity diagram with coordinates corresponding to the EL emission from polymer blend PLEDs of various blending ratios. The optimum polymer blend ratio for the pure white light emission (0.33, 0.33) is (99.4:0.6).

and EE as experimentally observed; both parameters are directly associated with the luminance of PLED.

C. CIE Color Coordinates of the Blend Polymer PLED

The color of the resulting EL spectra from polymer blend PLEDs were characterized by the CIE chromaticity coordinates. They were obtained from CIE 1931 chromaticity calculation [38] using a home made MATLAB routine. By integrating the products of the measured EL spectrum with three color matching functions, the three fundamental tristimulus values of *X, Y,* and *Z* were calculated. By projecting these tristimulus values on to the unit plane $(X + Y + Z = 1)$, the color of the EL spectrum can be expressed in a two-dimensional plane. The color can be specified by the chromaticity coordinates (*x, y*) defined by $x = X/(X + Y + Z)$ and $y = Y/(X + Y + Z)$, which is shown in Fig. 9.

From the EL spectrum shown in Fig. 8, we can calculate the following CIE color coordinates: (0.33, 0.33). These coordinates correspond to pure white light, Fig. 9. In this case, the optimal polymer blend ratio for the white light was 99.4:0.6 (sample A). It should be noticed that these pure white light coordinates are very sensitive to polymer blend composition as shown in Figs. 8 and 9; a slight change in polymer blend composition could cause either bluish (sample B) or reddish (sample C) change in CIE coordinates. The CIE coordinates of red and blue single polymer PLED used in this work are also plotted on the same figure as reference.

Using color simulation approach, we have established that to achieve CIE coordinates (0.33, 0.33), we need to combine red (0.59, 0.29) and blue (0.16, 0.23) CIE coordinates in the following ratio: 22.7% to 77.3%. Hence, we can speculate that 0.6% of the total polymer weight (red polymer) is responsible for 22.7% of the polymer blend PLED red light emission and 99.4% of the total polymer weight (blue polymer) is responsible for the remaining 77.7% of the polymer blend PLED blue light emission.

IV. CONCLUSION

In this paper, we demonstrated that by blending a red light-emitting polymer as acceptor (guest) in a donor blue light-emitting polymer (host), we could successfully produce pure white light-emission from our polymer blend device with a CIE coordinate of (0.33, 0.33). In comparison with the single red or blue polymer light-emitting devices on plastic substrates, increased luminance and improved device efficiency has been obtained from single-layer polymer blend device due to energy transfer from donor (blue) to acceptor (red) polymer: EE$\sim$ 2.0 cd/A, PE $\sim$ 1.1 lm/W, and L $_{\max} \sim 7400$ cd/m^2.

ACKNOWLEDGMENT

The authors would like to thank Dr. S. Lee, Intel Corporation, for useful discussions about the PLED opto-electrical measurements, Dow Chemical for providing polymers used in this paper, and D. Banach at UC Santa Barbara (Chemistry Department) for initial work done in this area during J. Kanicki's sabbatical at UCSB within Prof. A. Heeger's group that lead to improved device performance described in this paper.

REFERENCES

[1] G. Gu, P. E. Burrow, S. Venkatesh, S. R. Forrest, and M. E. Thompson, "Vacuum deposited, nonpolymeric flexible organic light-emitting devices," *Opt. Lett.*, vol. 22, no. 3, pp. 172–174, 1997.

[2] Y. Hong, Z. Hong, and J. Kanicki, "Materials and devices structures for high performance poly OLEDs on flexible plastic substrates," *Proc. SPIE*, vol. 4105, pp. 356–361, 2000.

[3] Y. Hong, Z. He, S. Lee, and J. Kanicki, "Air-stable organic polymer red light-emitting devices on flexible plastic substrates," *Proc. SPIE*, vol. 4464, pp. 329–335, 2001.

[4] H. Lim, W. J. Cho, C. S. Ha, S. Ando, Y. K. Kim, C. H. Park, and K. Lee, "Flexible organic electroluminescent devices based on fluorine-containing colorless polyimide substrates," *Adv. Mater.*, vol. 14, no. 18, pp. 1275–1279, 2002.

[5] J. Kido, M. Kimura, and K. Nagai, "Multilayer white light-emitting organic electroluminescent devices," *Science*, vol. 267, no. 5202, pp. 1332–1334, 1995.

[6] R. S. Deshpande, V. Bulovic, and S. R. Forrest, "White-light-emitting organic electroluminescent devices based on interlayer sequential energy transfer," *Appl. Phys. Lett.*, vol. 75, pp. 888–890, 1999.

[7] M. Mazzeo, J. Thompson, R. I. R. Blyth, M. Anni, G. Gigli, and R. Cingolani, "White light from blue: White emitting organic LEDs based on spin coated blends of blue-emitting molecules," *Physica E*, vol. 13, pp. 1243–1246, 2002.

[8] Y. Shao and Y. Yang, "White organic light-emitting diodes prepared by a fused organic solid solution method," *Appl. Phys. Lett.*, vol. 86, 2004. 073 510.

[9] J. Kido, H. Shinoya, and K. Nagai, "Single-layer white light-emitting organic electroluminescent devices based on dye-dispersed poly(N-vinylcarbazole)," *Appl. Phys. Lett.*, vol. 67, pp. 2281–2283, 1995.

[10] M. Granström and O. Inganäs, "White light emission from a polymer blend light emitting diode," *Appl. Phys. Lett.*, vol. 68, pp. 147–149, 1996.

[11] C. Chao and S. Chen, "White light emission from exciplex in a bilayer device with two blue light-emitting polymers," *Appl. Phys. Lett.*, vol. 73, pp. 426–428, 1998.

[12] J. P. Yang, Y. D. Jin, P. L. Heremans, R. Hoefnagels, P. Dieltiens, F. Blockhuys, H. J. Geise, M. V. Auweraer, and G. Borghs, "White light emission from a single layer organic light emitting diode fabricated by spincoating," *Chem. Phys. Lett.*, vol. 325, pp. 251–256, 2000.

[13] X. Gong, W. Ma, J. C. Ostrowski, G. C. Bazan, D. Moses, and A. J. Heeger, "White electrophosphorescence from semiconducting polymer blends," *Adv. Mater.*, vol. 16, pp. 8601–8605, 2004.

[14] G. Ho, H. Meng, S. Lin, S. Horng, C. Hsu, L. Chen, and S. Chang, "Efficient white light emission in conjugated polymer homojuctions," *Appl. Phys. Lett.*, vol. 85, pp. 4576–4578, 2004.

[15] Y. He and J. Kanicki, "High efficiency organic polymer light-emitting devices on the flexible plastic substrates," *Appl. Phys. Lett.*, vol. 76, no. 6, pp. 661–663, 2000.

[16] Y. Hong, Z. He, L. S. Lennhoff, D. Banach, and J. Kanicki, "Transparent flexible substrates for organic light-emitting devices and other devices," *J. Electron. Mater.*, vol. 33, pp. 312–320, 2004.

[17] Y. Hong and J. Kanicki, "Opto-electronic properties of poly (fluorene) co-polymer red light- emitting devices on flexible plastic substrate," *IEEE Trans. Electron Devices*, vol. 51, no. 10, pp. 1562–1569, Oct. 2004.

[18] J. Kanicki, S. Lee, Y. Hong, and C. C. Su, "Organic polymer light-emitting devices on flexible plastic substrate," in *IMID Dig.*, 2004.

[19] M. T. Bernius, M. Inbasekaran, J. O'brien, and W. Wu, "Progress with light-emitting polymers," *Adv. Mater.*, vol. 12, no. 23, pp. 1737–1750, 2000.

[20] M. Inbasekaran, W. Wu, E. P. Woo, and M. T. Bernius, "Fluorene Copolymers and Devices Made Therefrom," U.S. Patent 6 353 083, Mar. 5, 2002.

[21] A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*. New York, NY: Wiley, 2001.

[22] J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch, and J. Daub, "Efficient two layer LEDs on a polymer blend basis," *Adv. Mater.*, vol. 7, no. 6, pp. 551–554, 1995.

[23] J. S. Kim, R. H. Friend, and F. Cacialli, "Surface energy and polarity of treated indium- tin- oxide anodes for polymer light-emitting diodes studied by contact-angle measurements," *J. Appl. Phys.*, vol. 86, no. 5, pp. 2774–2778, 1999.

[24] M. P. de Jong, L. J. van Ijzendoorn, and M. J. A. de Voigt, "Stability of the interface between indium-tin-oxide and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in polymer light-emitting diodes," *Appl. Phys. Lett.*, vol. 77, pp. 2255–2257, 2000.

[25] Y. Hong and J. Kanicki, "Integrating sphere CCD-based measurement method of organic light-emitting devices," *Rev. Sci. Instrum.*, vol. 78, no. 7, pp. 3572–3575, 2003.

[26] R. Friend, J. Burroughes, and T. Shimoda, "Polymer diodes," *Phys. World*, pp. 35–40, 1999.

[27] S. Berleb, W. Brütting, and M. Schwoerer, "Anomalous current-voltage characteristics in organic light-emitting devices," *Synth. Met.*, vol. 102, pp. 1034–1037, 1999.

[28] H. Kusano, N. Shiraishi, S. Hosaka, I. Kuruma, M. Kitagawa, K. Ichino, and H. Kobayashi, "Carrier transport mechanism of PVCz-based multilayered electroluminescent devices," *Synth. Met.*, vol. 91, pp. 341–343, 1997.

[29] P. S. Smertenko, O. P. Dimitriev, S. Schrader, and L. Brehmer, "Doping of polyaniline by transition metal salts: Current-voltage characteristics of the ITO/polymer film/metal heterostructures," *Synth. Met.*, vol. 146, pp. 187–196, 2004.

[30] I. D. Parker, "Carrier tunneling and device characteristics in polymer light-emitting diodes," *J. Appl. Phys.*, vol. 75, pp. 1656–1666, 1994.

[31] S. Martin, M. Hamilton, and J. Kanicki, "Organic-polymer thin-film transistors for active-matric flat-panel displays?," *J. Soc. Inf. Disp.*, vol. 11, pp. 543–549, 2003.

[32] I. H. Campbell, D. L. Smith, C. J. Neef, and J. P. Ferraris, "Consistent time-of-flight mobility measurements and polymer light-emitting diode current-voltage characteristics," *Appl. Phys. Lett.*, vol. 74, pp. 2809–2811, 1999.

[33] R. S. Crandall, "Modeling of thin film solar cells: Uniform field approximation," *J. Appl. Phys.*, vol. 54, pp. 7176–7186, 1983.

[34] J. Kanicki, *Amorphous & Microcrstalline Semiconductor Devices*. Boston, MA: Artech, 1991.

[35] X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan, and A. J. Heeger, "High-efficiency polymer-based electrophosphorescent devices," *Adv. Mater.*, vol. 14, pp. 581–585, 2002.

[36] H. Lee, D. Banach, and J. Kanicki, "High-performance light-emitting devices via energy transfer in polymer blends," , to be published.

[37] R. Gupta, M. Stevenson, A. Dogariu, M. D. McGehee, J. Y. Park, V. Srdanov, and A. J. Heeger, "Low-threshold amplified spontaneous emission in blends of conjugated polymers," *Appl. Phys. Lett.*, vol. 73, pp. 3492–3494, 1998.

[38] Y. Ohno, "CIE fundamentals for color measurements," in *Proc. IS&T NIP16 Conf.*, 2000.

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