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ARTICLE

A Fluorene−Oxadiazole Copolymer for White Light-Emitting Electrochemical Cells

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ABSTRACT: Solid-state, white light-emitting electrochemical cells (LECs) based on a fluorene−oxadiazole copolymer have been successfully demonstrated. The copolymer has a π-conjugated backbone consisting of 75 mol % fluorene and 25 mol % 5,5′-diphenyl-2,2′-bi-1,3,4-oxadiazole. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl attached on the 9-C of the fluorenes was introduced to promote ionic conductivity necessary for the operation of LECs. The copolymer, synthesized by Suzuki coupling reactions, has a number-average molecular weight of 8700 and polydispersity of 2.41. The LECs were fabricated by spin-coating the copolymer admixed with lithium trifluoromethanesulfonate onto indium−tin oxide (ITO) substrate coated with poly(ethylenedioxythiophene)−poly(styrenesulfonic acid) (PEDOT:PSS). The opposite electrode was vapor evaporated aluminum. The LEC devices showed a white electroluminescence with CIE coordinates of (0.24, 0.31). The emission spectrum consisted of emissions from both the individual polymer chains and excimers. The white LECs are promising for solid-state lighting devices with a simple device structure and low-cost fabrication.

Introduction

Compared with conventional polymer white light-emitting diodes (PLEDs), solid-state white light-emitting electrochemical cells (LECs) possess several potential advantages. The device performance of LECs is not critically dependent on the thickness of the active layer or on the work function of electrode materials. Typically, the component of the active layer of LEC devices is quite complicated, including conjugated polymer and ionic transporting material, such as poly(ethylene oxide) (PEO) and Li salt. The ions can induce doping (oxidation and reduction) of the emissive materials near the electrodes, that is, p-type doping near the anode and n-type doping near the cathode. The doped regions induce ohmic contacts with the electrodes and consequently facilitate the injection of both holes and electrons, which recombine at the p−n junction. As a result, a single-layered LEC device can be operated at low voltages using air-stable metals as cathode, for example, Al and Ag.[1−7]

White LECs based on polyfluorene and PEO mixture were reported as early as 1997. The white emission resulted from aggregation of polyfluorene. The morphological instability led to inherently low color stability in those devices.[8] More recently, white LECs using iridium-based cationic transition metal complexes were reported with high efficiencies. The active layer also consisted of a blend and exhibited voltage dependence of the emissive color.[9,10] White PLEDs have been obtained using a copolymer containing at least two covalently bonded chromophores.[11] These white PLEDs show significantly improved white color stability. It is interesting to explore copolymers for white polymer LECs.

We report the synthesis of a copolymer consisting of fluorene with 2-(2-(2-methoxyethoxy)ethoxy)ethyl side groups and diphenylbi(oxadiazole) (EO-PF-DPO). The polyether-type side groups are to promote the ionic conductivity necessary for the operation of LECs.[8] The bi(oxadiazole) moieties are introduced to enhance the n-doping capability of the polymer.[12a] Oxadiazole unit has been widely used to improve the color stability and electron transporting properties of polymer blue-light-emitting diodes based on polyfluorenes.[13−16] Bi(oxadiazole) is expected to be more effective than oxadiazole in promoting n-doping.[12] EO-PF-DPO exhibited blue photoluminescence in dilute solution and thin films. PLEDs based on this copolymer also emitted blue light. Interestingly, LECs based on EO-PF-DPO along with lithium trifluoromethanesulfonate admixed to provide the necessary ionic species, emitting white light with CIE (0.24, 0.31). This is the first report of white LECs using a single polymer in the emissive layer.

Experimental Section

Materials. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and used as received. 5,5′-Bis(4-bromophenyl)-2,2′-bi-1,3,4-oxadiazole (**1**)[17] and 2,7-dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene (**2**)[18] were prepared following published procedures, with modification, and characterized by ^{1}H NMR.

Measurement. Photoluminescence (PL) spectra were measured on a Photon Technology International spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz. Cyclic voltammetry was measured on a potentiostat/galvanostat model 283 electrochemical workstation (Princeton Applied Research) at a scan rate of 50 mV/s in a 1 M $LiClO_4$ solution in acetonitrile (CH_3CN), with platinum working electrode and saturated calomel electrodes (SCE) as reference electrode. The polymer molecular

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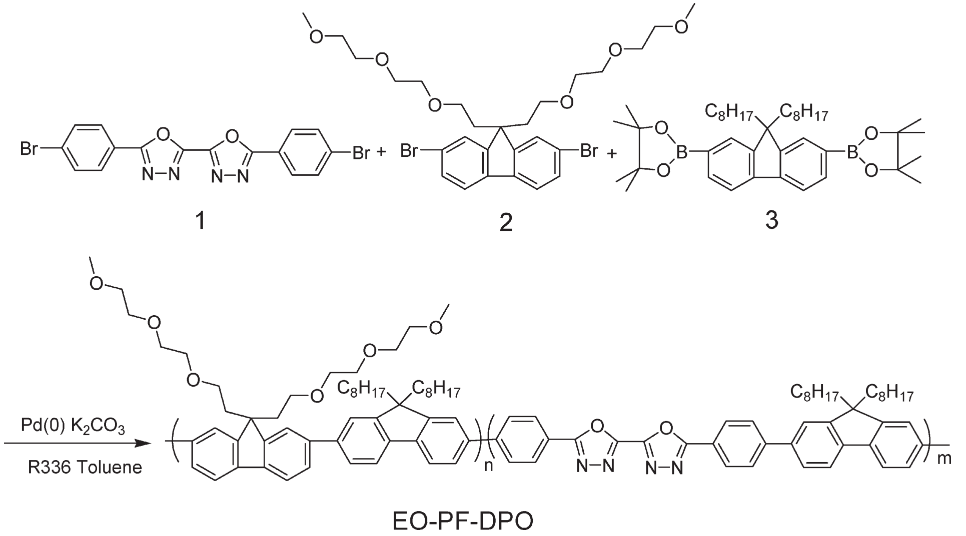
Scheme 1. Synthesis Route of the Polymer



weights were determined by GPC (Waters) using polystyrene standards and THF as eluent.

Devices. Light-emitting diodes (LED) was fabricated on prepatterned indium–tin oxide (ITO) with a sheet resistance of 10–20 Ω/□. The substrate was ultrasonically cleaned with acetone, detergent, deionized water, and 2-propanol subsequently. Oxygen plasma treatment was made for 10 min as the final step of substrate cleaning to improve the contact angle just before film coating. Onto the ITO glass a 50 nm thick layer of poly(ethylenedioxythiophene)–poly(styrenesulfonic acid) (PEDOT:PSS) film was spin-coated from its aqueous dispersion (Baytron P 4083, Bayer AG). This PEDOT:PSS layer was included to improve the hole injection and reduce the possibility of leakage. It was dried at 80 °C for 2 h in a vacuum oven. Then the solution of the copolymer was spin-coated on top of the ITO/PEDOT:PSS surface. The typical thickness of the emitting layer was 70–80 nm. A thin layer of barium as an electron injection cathode and a 200 nm thick aluminum layer were successively deposited by vacuum thermal evaporation through a mask. The vacuum pressure was below 2×10^{-4}Pa. The deposition speed and thickness of the barium and aluminum layers were monitored by a thickness/rate meter (model STM-100, Sycon). The active area of the devices in this study was 0.17 cm^2. The spin-coating of the EL layer and device testing were carried out within a glovebox (Vacuum Atmosphere Co.) with nitrogen circulation. Current–luminance–voltage (I–L–V) characteristics were measured with a computer-controlled Keithley 236 source measure unit and calibrated by a Si photodiode. Luminance was calibrated by a PR705 spectragraph–photometer after the encapsulation of the devices with UV-curing epoxy and thin cover glass. EL spectra were taken by InstaSpec IV CCD spectragraph.

LECs were fabricated similar to the PLED devices except that the LECs has a layered configuration of ITO/PEDOT:PSS/EO-PF-DPO: lithium trifluoromethanesulfonate blend/Al. The polymer and lithium trifluoromethanesulfonate (Aldrich) blend (weight ratio of 5.2–5.6:1) was spin-coated from a cyclopentanone solution. The coating thickness was 50–80 nm.

Synthesis of EO-PF-DPO. 5,5′-Bis(4-bromophenyl)-2,2′-bi-1,3,4-oxadiazole (**1**), 2,7-dibromo-9,9-bis(2-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (**2**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**), $(PPh_3)_4Pd(0)$ (0.5–2.0 mol %), and several drops of Aliquat 336 (methyltrioctylammonium chloride as the phase transfer catalyst) were dissolved in a mixture of toluene and aqueous 2 M K_2CO_3. The solution was refluxed with vigorous stirring for 24 h in an argon atmosphere. At the end of polymerization, the polymers were end-capped with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene and bromobenzene. The organic mixture was then poured into methanol, and the polymer precipitate was separated by filtration. The polymer was redissolved in THF, filtered through a 1.5 μm filter, and precipitated in methanol. The polymer was air-dried, followed by drying in vacuum at ambient temperature. In the process of polymerization, the comonomer feed ratios of **1**:**2**:**3** were 25:25:50. The yield of the resulting copolymer, EO-PF-DPO, was around 85%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.30, 7.87, 7.67, 3.51, 3.44, 3.30, 2.94, 2.59, 2.13, 1.19, 1.12, 0.80. Elemental analyses: Calcd: C, 79.70; H, 8.21; N, 3.68; O, 8.41. Found: C, 79.92; H, 8.76; N, 3.52. M_n = 8700, M_w = 20 900, and M_w/M_n = 2.41.

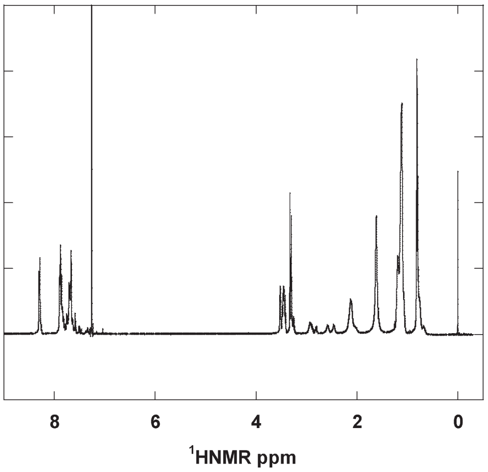


Figure 1. ^{1}H NMR spectrum of EO-PF-DPO in $CDCl_3$ at 500 MHz.

Results and Discussion

Synthesis and Characterization. The general synthetic route toward copolymer EO-PF-DPO is outlined in Scheme 1. The obtained copolymer is readily soluble in common organic solvents, such as THF and chloroform. The ^{1}H NMR spectrum of EO-PF-DPO is shown in Figure 1. ^{1}H NMR chemical shifts at ca. δ = 3.51, 3.44, 3.30, 2.94, and 2.59 ppm are assigned to the polar 2-(2-(2-methoxyethoxy)ethoxy)ethyl side group. ^{1}H NMR chemical shifts at ca. δ = 8.30 are assigned to the four hydrogens ortho to oxadiazole in the 5,5′-diphenyl-2,2′-bi-1,3,4-oxadiazole unit.[17] The peaks at ca. δ = 7.87 are assigned to the

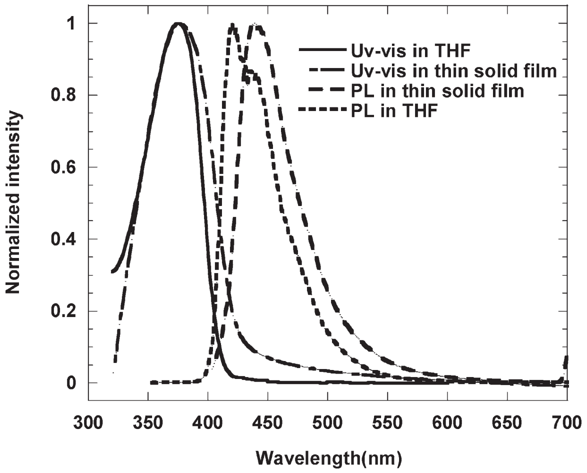


Figure 2. UV−vis absorption and PL (excitation: 350 nm) spectra of EO-PF-DPO in THF solution and thin solid film.

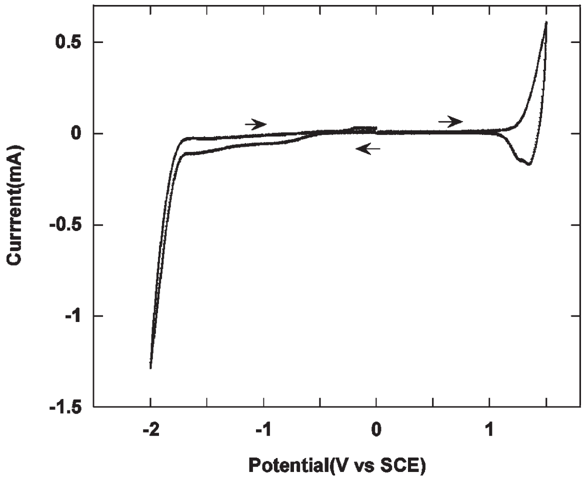


Figure 3. Cyclic voltammogram of EO-PF-DPO coated on a platinum working electrode in a 1 M LiClO$_4$ solution in acetonitrile. Scan rate is 50 mV/s.

fluorene hydrogens. The peaks at ca. 7.67 are from the four hydrogens on the 5,5′-diphenyl-2,2′-bi-1,3,4-oxadiazole unit ortho to the fluorenes.[11c,17] The molar ratio of substituted fluorene to 5,5′-diphenyl-2,2′-bi-1,3,4-oxadiazole (DPO) in the copolymer estimated by ^{1}H NMR peak areas and elemental analyses are 76.5:23.5 and 76.1:23.9, respectively, which are in good agreement with the feed ratio (75:25) of the comonomers. The number-average molecular weight of EO-PF-DPO determined by GPC using a polystyrene standard is 8700 with a polydispersity index (M_w/M_n) of 2.41.

UV−vis Absorption and Electrochemical Properties. The UV−vis absorption spectrum of EO-PF-DPO in THF solution (Figure 2) shows a peak at 375 nm with onset wavelength around 415 nm, which is in the similar range as the $\pi-\pi^*$ transition in polyfluorene[19] and poly(l,4-phenylene-1,3,4-oxadiazole).[12a] The UV−vis absorption spectrum of EO-PF-DPO in thin solid film shows a peak at 376 nm with red-shifted onset wavelength around 425 nm.

The electrochemical properties of EO-PF-DPO were investigated by cyclic voltammetry (CV). The CV in Figure 3 shows both a p-doping and n-doping processes in the copolymer. The onset potentials of the p-doping and n-doping are 1.3 and −1.8 V, respectively. Using the empirical formulas[20]

$$E_{\mathrm{HOMO}} = -(E_{\mathrm{ox}} + 4.4)\ (\mathrm{eV})$$

$$E_{\mathrm{LUMO}} = -(E_{\mathrm{re}} + 4.4)\ (\mathrm{eV})$$

The HOMO and LUMO of EO-PF-DPO are calculated with $E_{\mathrm{HOMO}} = -5.7$ eV and $E_{\mathrm{LUMO}} = -2.6$ eV. The energy band gap (E_g) calculated from the difference of the HOMO and LUMO levels is around 3.1 eV. The band gap of the polymer calculated from the onset wavelength of the UV−vis absorption spectrum in thin solid thin, λ, is 2.92 eV.

The E_{LUMO} of EO-PF-DPO is fairly low compared to typical light-emitting polymers (LEPs) with such a large bandgap. The E_{LUMO} of poly(dioctylfluorene) is 2.12−2.6 eV.[21] Apparently, the incorporation of bioxadiazole units into the polymer backbone was effective to reduce the LUMO energy and thus the n-dopability.

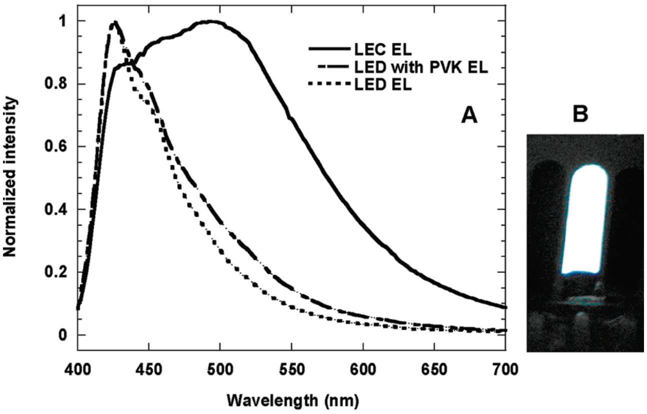


Figure 4. (A) EL spectra of the polymer LEDs (ITO/PEDOT:PSS/polymer/Ba/Al and ITO/PEDOT:PSS/PVK/polymer/Ba/Al) and LEC (ITO/PEDOT:PSS/polymer:Li salt blend/Al). (B) Photograph of the white LEC device.

Photoluminescent and Electroluminescent Properties. The PL spectrum of EO-PF-DPO in THF solution (Figure 2) shows a main peak at 420 nm and a shoulder at 440 nm. The PL spectrum of the solid film only shows one peak at 439 nm. The emission wavelength range also coincides with those of polyfluorene and poly(l,4-phenylene-1,3,4-oxadiazole).[12a,19] The red shift of the UV−vis spectrum and PL spectrum of EO-PF-DPO in thin solid film than in THF solutions could result from the molecular aggregations.

Polymer light-emitting diodes (PLEDs) were fabricated using spin-cast EO-PF-DPO films as the emitting layer. A PEDOT:PSS layer was used to improve the hole injection and reduce current leakage. Two device configurations were used: ITO/PEDOT:PSS/EO-PF-DPO/Ba/Al and ITO/PEDOT:PSS/PVK/EO-PF-DPO/Ba/Al. PVK was employed in the latter devices to boost hole injection, as the E_{HOMO} of PVK, 5.5−5.6 eV, falls in between those of EO-PF-DPO (5.7 eV) and PEDOT:PSS (5.0−5.2 eV). Figure 4 shows the EL spectra of the two LEDs. Both EL spectra peak at 420 nm with a minor shoulder at 440 nm, similar to that of the polymer in THF solution. The EL spectra have full width at half-maximum being 56 and 67 nm, with CIE (0.17, 0.12) and (0.18, 0.16), respectively, for the devices without and with PVK layer. The LED performances are further tabulated in Table 1. The highest luminance efficiency of 0.6 cd/A is achieved with the LEDs consisting of a PVK layer. These results agree with literature reports that oxadiazole-based polyfluorenes can be used as the light-emitting polymers for color-stable blue LEDs.[13−16]

Table 1. LED and LEC Devices Performances of the Polymer[a]

hole transport layer	V^b (V)	J^c (mA/cm^2)	LE^d (cd/A)	$L_{max}{}^e$ (cd/m^2)	CIE $(x,y)^f$	$\lambda_{fwhm}{}^g$ (nm)
PEDOT:PSS (LED)	5	8.9	0.07	78	0.17, 0.12	56
PEDOT:PSS/PVK(LED)	7	11	0.6	706	0.18, 0.16	67
PEDOT:PSS (LEC)	6.4	34	0.15	257	0.24, 0.31	160

[a] Device configurations are ITO/PEDOT:PSS/polymer/Ba/Al (LED), ITO/PEDOT:PSS/PVK/polymer/Ba/Al (LED), and ITO/PEDOT:PSS/polymer:Li salt blend/Al (LEC). [b] Voltage at maximum luminance efficiency. [c] Current density at maximum luminance efficiency. [d] Maximum luminance efficiency. [e] Maximum luminance. [f] CIE 1931 coordinate. [g] Full width at half-maximum of EL spectrum.

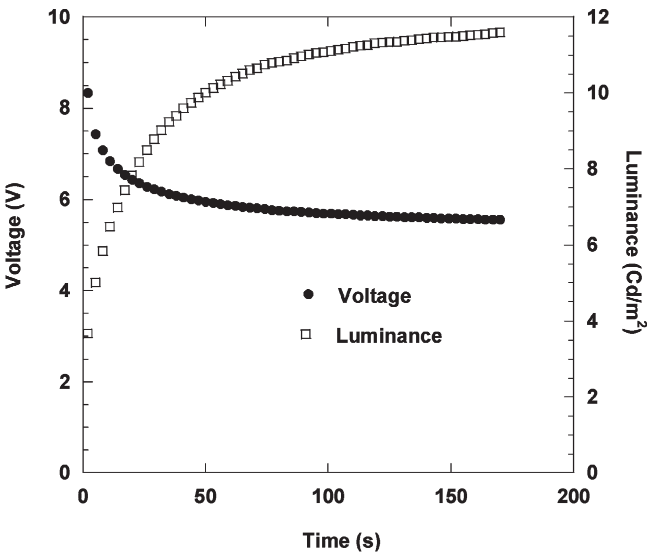


Figure 5. Voltage−light intensity−time curves of an LEC operated at a constant current density of 29.4 mA/cm^2.

Light-emitting electrochemical cells (LECs) were fabricated in a similar manner as the LEDs with a device configuration of ITO/PEDOT:PSS/polymer:Li salt blend/Al. The LEC devices had a slow turn-on at 4.6 V. When operated at a constant current density of 29.4 mA/cm^2, the devices turned on rapidly. The rising emission intensity started to plateau at about 82 s (see Figure 5). The maximum luminance of the white LEC device is 257 cd/m^2 as shown in Table 1.

The EL spectrum of the LEC devices, shown in Figure 4, exhibits an intense emission in the green and red regions. The emission color with a CIE (0.24, 0.31) is fairly white, which is in stark difference from the LEDs and the PL emission. The full width at half-maximum of the LEC emission is 160 nm. The photograph of the device (Figure 4B) shows uniform white emission.

White EL from a single emissive polymer has been reported in the literature by (1) covalent bonding of green and red or orange chromophores in a largely blue polymer backbone,[11] (2) electron-trapping effect,[22] and (3) excimer emission.[8] In the case of polyfluorenes, both excimer or keto defects have been used to to achieve white LEDs.[8,23] Oxadiazole units have been reported to affect the photophysics properties of polyfluorene-based LEDs.[24] The major color shift of in the EO-PF-DPO LEDs and LECs may be explained by charge trapping: the emission is dominated by the lowest electronic states. Further study is needed to elucidate the color shift.

Results of preliminary evaluation of color stability of the white LECs are shown in Figure 6. The fresh LEC devices EL spectra taken at a current density of 58.8 mA/cm^2 after 2, 6, 10, and 15 min of continuous lighting show little change. The emission colors are CIE (0.24, 0.31), (0.26, 0.34), (0.27, 0.35), and (0.28, 0.37) for 2, 6, 10, and 15 min lighting, respectively.

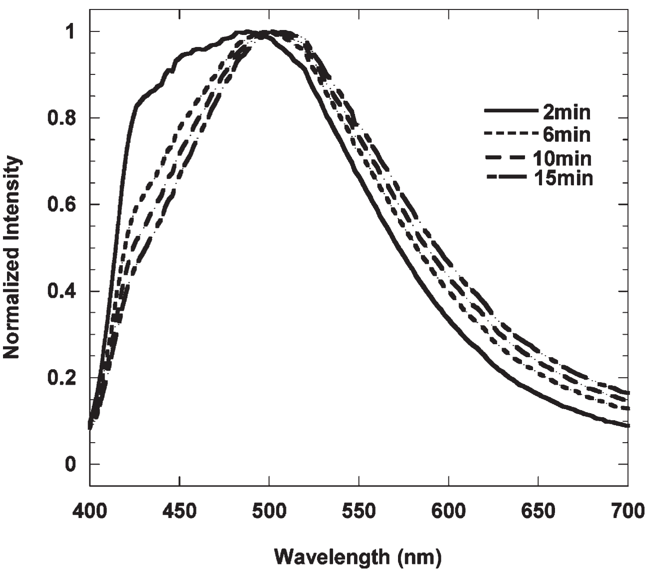


Figure 6. Normalized LEC EL spectra after continuous operation at a current density of 58.8 mA/cm^2.

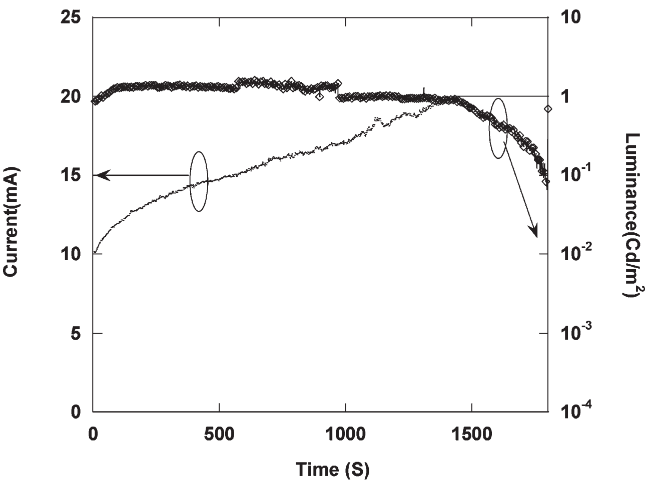


Figure 7. Current−luminance−time response of an LEC operated at a constant 9 V. The device was prebiased at 9 V for 5 min to established the dynamic *p*−*i*−*n* junction.

Results of preliminary lifetime testing are shown in Figure 7. The device was prebiased at 9 V for 5 min to establish the *p*−*i*−*n* junction. The subsequent biasing at 9 V produced a fairly stable emission intensity for 1500 s. Thereafter, a rapid degradation was observed. The driving current gradually increased until reaching the compliance set at 20 mA.

Conclusion

EO-PF-DFO, conveniently synthesized by Suzuki coupling, shows absorption and photoluminescence characteristic of polyfluorenes and poly(paraphenylenes). The LECs using a blend of EO-PF-DPO and lithium trifluoromethanesulfonate emitted white light with a broad spectrum. Further electronic characterization and device optimization should further improve LEC performance.

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