ACS APPLIED MATERIALS & INTERFACES

White Light-Emitting Electrochemical Cell

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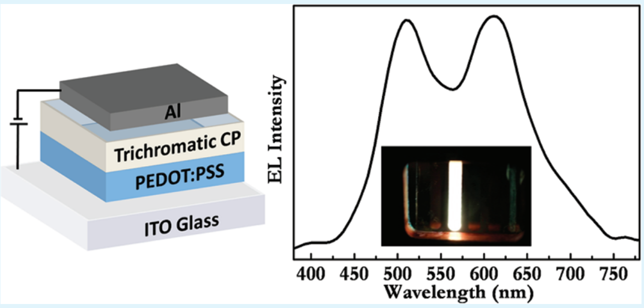
S *Supporting Information*



ABSTRACT: We report a light-emitting electrochemical cell (LEC) with air-stable electrodes and a solution-processed single-layer active material that emits warm-white light (CIE coordinates = (0.39, 0.43); color rendering index =83) with significant brightness (B) at a low voltage. The carefully tuned trichromatic device exhibits a short turn-on time (~5 s to $B >$ 100 cd/m^2), high efficiency (3.1 cd/A at B = 240 cd/m^2) and good operational stability (17 h at $B >$ 100 cd/m^2). We also report a blue LEC with a highly respectable set of device properties in the form of a turn-on time of ~5 s, an efficiency of 3.6 lm/W and 5.6 cd/A, and an uninterrupted operational lifetime of 25 h. Finally, by analyzing data from trichromatic and monochromatic devices as well as from the constituent fluorescent CPs, we are able to point out a viable path toward further improvements in the performance of the white-emitting LEC.

KEYWORDS: light-emitting electrochemical cell, white luminescence, solid-state lighting, conjugated polymer, solution-processed technology

INTRODUCTION

The light-emitting electrochemical cell (LEC) is defined by the existence of mobile ions within the active material, which allow for the formation of a light-emitting p−n junction doping structure when a voltage is applied.[1−8] The complex and intriguing doping process results in that the function of an LEC is largely independent of the thickness of the solution-processed active material and of the work function of the electrode materials.[9−13] These are important advantages from a fabrication and application perspective that distinguish the LEC from alternative emissive technologies, such as the polymer light-emitting diode (pLED), because they pave the way for a fault-tolerant and low-cost fabrication of conformable and/or large-area devices based solely on solution-processable organic materials.[14−17]

The in situ formation of a p−n junction doping structure also presents a drawback in that the related ion distribution process is slow, and that LECs as a consequence exhibit a slower turn-on time for light emission—typically ranging from a few tenths of a second up to several hours—[18−20] than pLEDs.[21−27] A second-long delay between application of electric power and significant light emission can, however, be acceptable in, e.g., solid-stage lighting applications. In this context, and in consideration of the aforementioned advantages as well as recent breakthroughs in LEC performance,[28−34] it is quite surprising that only a few reports on white-emitting LECs have appeared in the scientific literature.[35−39]

Yang and Pei presented the first white-emitting LEC, comprising a conjugated polymer (CP) with blue-green photoluminescence (PL) as the emissive material.[35] Interestingly, the blue-green PL transformed to white electroluminescence (EL) in an LEC device, when the CP was blended with a polymer electrolyte, presumably due to a phase separation event, but nothing was reported on the long-term stability of the somewhat anomalous white emission. In more recent LEC studies, phosphorescent ionic transition metal complexes have been preferentially employed as the active material, but even though good-quality white light at high efficiency was demonstrated, other device properties, notably the maximum attained brightness, the turn-on time, and/or the device stability, were inadequate for many applications.[36−38] Here, we report a carefully designed LEC that emits warm white light with good color rendering properties, and which importantly exhibits a high brightness at a respectable efficiency, as well as a comparatively fast turn-on time and long-term stability.

EXPERIMENTAL SECTION

The blue-, green-, and red-emitting CPs were used as received, and termed B, G, and R, respectively, for convenience. The ion-transport material trimethylolpropane ethoxylate (TMPE) and the salt $LiCF_3SO_3$ were purchased from Aldrich (Steinheim, FRG), and the salt was dried in a vacuum oven at T = 473 K before use. All materials were dissolved separately in anhydrous tetrahydrofuran at a concentration of 10 mg/mL. The active material solutions were prepared by mixing the master solutions in a volume ratio of CP/TMPE/$LiCF_3SO_3$ = 1:0.1:0.03; note that CP represents the total mass of CP in the trichromatic devices. The

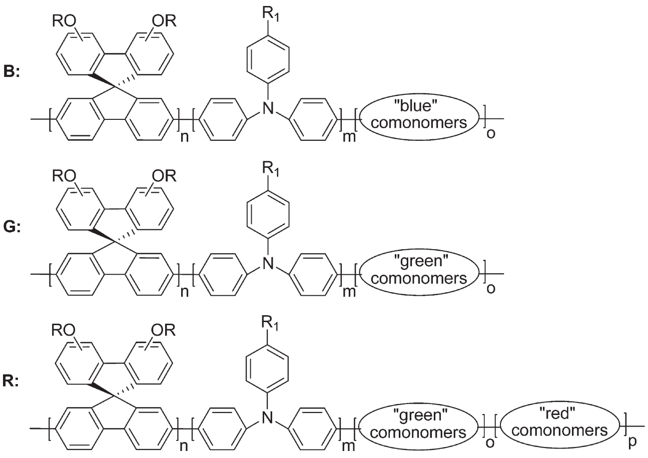
Received: May 5, 2011
Accepted: July 27, 2011
Published: July 27, 2011

active material solutions were stirred on a magnetic hot plate for 5 h at T = 323 K immediately before film fabrication.

LEC devices were fabricated by sequentially spin-coating ITO-coated glass substrates (1.5 × 1.5 cm^2, 20 ohms/square; Thin Film Devices, Anaheim, CA) with poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS, Aldrich; thickness: d = 50 nm) and active material. The thickness of the active material was 100 nm, as established with AFM. On top of the stack, Al cathodes were deposited by thermal evaporation through a shadow mask at $p < 2 \times 10^{-4}$ Pa. The active area of each LEC device was 13 mm^2. All of the above device preparation procedures and measurements, except the cleaning of the substrates and the deposition of PEDOT-PSS, were carried out in two interconnected N_2-filled glove boxes ($[O_2] < 3$ ppm, $[H_2O] < 0.5$ ppm).

The devices were driven by, and the current measured with, a Keithley 2400 source-meter. The brightness was measured using a calibrated photodiode with an eye response filter (Hamamatsu Photonics) connected through a current-to-voltage amplifier to a HP 34401A voltmeter. Electroluminescence (EL) measurements were performed using a calibrated USB2000 fiber optic spectrometer (Ocean Optics). The CRI and CIE coordinates were calculated using the SpectraWin software. For the cyclic voltammetry (CV) measurements, CP-coated Au was used as the working electrode, Pt was used as the counter electrode, and a silver wire was used as the pseudoreference electrode. The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in CH_3CN. The CV sweeps were driven and measured by an Autolab PGSTAT302 potentiostat. Directly after each CV scan, a calibration scan was run with a small amount of ferrocene added to the electrolyte. The onset potentials for oxidation and reduction were calculated as the intersection of the baseline with the tangent of the current at the half-maximum of the peak. The sample preparation and measurements were performed under inert atmosphere in a N_2-filled glovebox. The AFM images were recorded using a MultiMode SPM microscope with a Nanoscope IV Controller (Veeco Metrology) operating under ambient conditions.

Scheme 1. Chemical Structures of Copolymers B, G, R, Where *m*, *n*, *o*, and *p* are the Molar Percent of the Corresponding Monomers ($m + n + o = 1$ for B and G, and $m + n + o + p = 1$ for R), OR is an Alkoxyl Group, and R_1 is an Alkyl Group[a]



[a] The molecular weights for B, G, and R are M_w = 325 000, 470 000, and 470 000 g/mol, respectively.

RESULTS AND DISCUSSION

To attain a broad-band white emission, we utilized a trichromatic LEC device configuration based on three different CPs with complementary and broad EL spectra centered in the blue, green and red region, respectively. These polyspirobifluorene-based copolymers, termed B, G, and R for convenience, were synthesized by the Suzuki-coupling method, and their chemical structures are depicted in Scheme 1. The B:G:R mass ratio was carefully tuned for the purpose of white light emission. For the electrolyte, we employed the salt $LiCF_3SO_3$ dissolved in TMPE, since this electrolyte's wide electrochemical stability window and transport properties recently have been demonstrated to allow for the attainment of stable and efficient monochromatic (yellow-emitting) LECs.[30] The LEC devices were fabricated in a sandwich-cell configuration by spin-coating a single layer of active material blend on top of an indium−tin oxide/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) anode, and thereafter evaporating an Al contact on top of the active material. The mass stoichiometry of the active material was invariably {conjugated polymer:TMPE:$LiCF_3SO_3$} = {1:0.1:0.03}, but it is notable that "conjugated polymer" represents the total mass of the three different polymers in different proportions in the trichromatic devices.

Figure 1 presents the EL spectra (a) and the long-term operational stability (b) of monochromatic B-, G-, and R-LECs driven at a constant current density, as specified in the inset in Figure 1b. The peak efficiency is 3.6 lm/W and 5.6 cd/A for the B-LEC, 3.3 lm/W and 6.4 cd/A for the G-LEC, and 0.25 lm/W and 0.27 cd/A for the R-LEC. The operational lifetime (here, defined to be the time during which the device emits at a brightness >100 cd/m^2) is 25 h for the B-LEC, 33 h for the G-LEC, and 7 h for the R-LEC. The device performance data are summarized in Table 1. These are notable numbers for the B-LEC, and the operational lifetime is to our knowledge the best

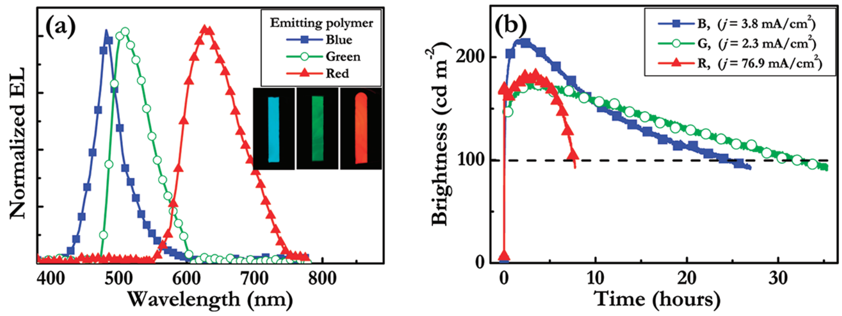


Figure 1. (a) Normalized EL spectra and (b) the temporal evolution of the brightness of the monochromatic blue-, green-, and red-emitting LEC devices driven at a constant current density, as specified in the inset in b. The inset in a shows photographs of operating devices.

reported to date. Moreover, the turn-on time to significant brightness (>100 cd/m^2) is relatively fast at ~5 s for all three device types.

A large number of trichromatic LECs with varying B:G:R stoichiometry were fabricated and screened for performance. The goal was to find an appropriate B:G:R mass ratio so that good-quality and stable white light emission could be attained. An example of the optimization procedure is shown in Figure 2a, where the concentration of R was varied while keeping the B and G concentrations constant; and the resulting EL spectra, CIE (Commision Internationale de l'Éclairage) coordinates and color rendering index (CRI) values were measured as a function of R (see upper inset for CIE and CRI data). High-quality white light emission with CIE coordinates of (0.39, 0.43) and a CRI value of 83 was achieved for a B:G:R mass ratio of 100:1:3. This device exhibited a warm-white appearance (see photograph in the inset of Figure 2b), and the color rendering is considered sufficient for, e.g., indoor lighting applications.[40]

Table 1. Device Performance of Monochromatic and White LECs

emission color	EL peak (nm)	current efficacy (cd/A)	power efficacy (lm/W)	lifetime (at B > 100 cd/m^2) (h)
blue	480	5.6	3.6	25
green	504	6.4	3.3	33
red	630	0.27	0.25	7
white	510, 610	3.1	1.6	17

Figure 2b reveals that the optimized white LEC exhibits a low-energy EL peak at 610 nm (open downward triangles), which is blue-shifted in comparison to the single EL peak at 630 nm from the monochromatic R-LEC (solid upward triangles). This blue-shift is attributed to a reduced intermolecular interaction for the R component in the white LEC, since the mass concentration of R in the active material is quite low at 3% and because an atomic force microscopy study (see Figure S1 in the Supporting Information) of the active material film in the white LEC showed no indications of phase separation. The single EL peak from the monochromatic B-LEC at 480 nm (solid squares) is not distinguishable in the white EL, but instead a notably broad high-energy EL peak is found at 510 nm, which is in close proximity to the major EL peak of the monochromatic G-LEC at 504 nm (open circles), despite the fact that the B component dominates the G component by a factor of 100.

The PL spectrum from the active material film in the white LEC is clearly blue-shifted with respect to the EL from the same device; compare dashed line with line marked with open downward triangles in Figure 2b. This observation strongly suggests that the broad-band white EL stems from a combination of B-to-G and G-to-R energy transfer via Förster and exciton diffusion processes and charge trapping, where the latter is manifested in the distinct difference between the PL and EL spectra. The inset in Figure 2a shows the energy levels of the three CPs, as measured with cyclic voltammetry, and in consideration of the similarly positioned HOMO levels (at −5.15 eV vs. vacuum), we

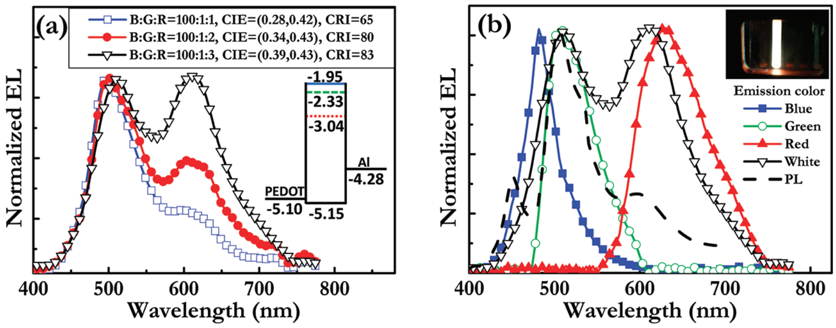


Figure 2. (a) Normalized EL spectra of three different trichromatic LECs, with the B:G:R mass ratio and the measured color data specified in the upper inset. The energy levels of the constituent CPs and the electrodes are presented in the right part of the figure. (b) Normalized EL and PL spectra from the trichromatic white-emitting LEC (B:G:R = 100:1:3) and the EL spectra from the monochromatic B-, G-, and R-LECs. The inset in the upper-right corner presents a photograph of the emission from the white trichromatic LEC.

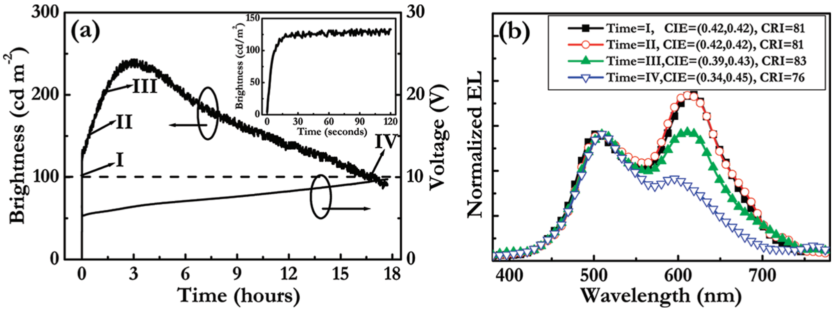


Figure 3. (a) Temporal evolution of the brightness and voltage of the white LEC driven at a constant current density of 7.7 mA/cm^2. The inset shows the turn on kinetics during the initial 2 min of a pristine device. (b) The normalized EL spectra, with corresponding color values indicated in the inset, of the white LEC measured at the times marked with Roman numerals in (a).

suggest that the charge trapping is effectuated at the LUMO level, which spans from −3.04 eV for R, over −2.33 eV for G, to reach −1.95 eV for B.

We now shift our attention to the turn-on kinetics, efficiency and long-term stability of the white LEC device. Figure 3a presents the brightness and voltage as a function of time during operation at a constant current density of j = 7.7 mA/cm^2, and Figure 3b shows EL spectra recorded at discrete times during the long-term operation, as specified by the Roman numerals indicated in Figure 3a. The pristine device turns on and emits significant white light in ∼5 s (see inset in Figure 3a), which represents a distinct improvement over previous white LECs based on cationic transition metal complexes.[37,38,41,42] We attribute the relatively fast turn-on process to the lack of phase separation between the electrolyte and the CPs (see Figure S1 in the Supporting Information), and also point out that CP-LECs typically exhibit an advantage over their cationic transition metal complex-LECs counterparts from a kinetic perspective, because both the cation and anion are mobile in the former, whereas only the anion is mobile in the latter. The peak current and power conversion efficacy (recorded at a significant brightness of B = 240 cd/m^2) is 3.1 cd/A and 1.6 lm/W, respectively, which is respectable numbers even in comparison to monochromatic CP-based LECs. The white LEC exhibits a relatively impressive uninterrupted operational lifetime of 17 h (see Figure 3a), but suffers from a gradual decrease of the low-energy EL peak with time (see Figure 3b). The latter change is quantified by that the CIE coordinates change from an initial value of (0.42, 0.42) to (0.34, 0.45) at t = 17 h, whereas the CRI value drops from 81 to 83 during the first hours of operation to reach 76 at t = 17 h. It is, however, notable that the device still emits white light to the eye with significant intensity at this predefined end-of-operation stage.

The observed loss of the low-energy peak in the white EL implies that the dominant degradation is due to a gradual loss of the EL capacity of the low-energy R component in the active material. This conclusion is further supported by that the performance of the monochromatic R-LEC was inferior to the monochromatic B- and G-LECs from a stability (and also an efficiency) viewpoint (see Figure 1 and Table 1); and that a distinct blue-shift in the PL was observed in post-mortem white devices in comparison to pristine white devices (see Figure S2 in the Supporting Information and related text). We further note that the employed B component ideally should exhibit a slightly more deep-blue emission in order to facilitate for ideal equal-energy white emission at CIE coordinates of (0.33, 0.33) and a higher CRI value. These observations thus point out a path toward further improvements of the herein introduced white LEC devices via the identification and appropriate utilization of more stabile and efficient red emitters and the development of deeper-blue emitters.

CONCLUSIONS

To summarize, we demonstrate that it is possible to realize white-emitting LECs with air-stable electrodes and with a solution-processed single-layer active material, which exhibit a promising combination of device properties from a solid-state lighting perspective. Specifically, we show that an appropriately tuned trichromatic LEC device can turn on relatively fast, exhibit respectable efficiency and lifetime, and emit bright warm-white light with good color rendering properties at low voltage.

ASSOCIATED CONTENT

Ⓢ Supporting Information. AFM image and photograph of device under UV light. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

The authors acknowledge Kempestiftelserna, Carl Tryggers Stiftelse, and the Swedish Research Council (Vetenskapsrådet) for financial support. L.E. is a "Royal Swedish Academy of Sciences Research Fellow" supported by a grant from the Knut and Alice Wallenberg Foundation. S.T. and L.E. are grateful to Merck KGaA for the access to high-quality materials.

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