Synthesis of fluorene-based polyelectrolytes tethering different counterions for single-component white light-emitting electrochemical cells

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ABSTRACT

A series of polyfluorene (PF) electrolytes bearing Br^-, BF_4^-, or PF_6^- counterions were synthesized and characterized. 2,1,3-benzoselenadiazole moieties were incorporated into polymer main chains to produce single-component white light-emitting polymers. The thermal stability of Br-containing ionic PF was decreased because of the Hofmann elimination occurred at higher temperature. By replacing Br^- with BF_4^- or PF_6^- counterions, the thermal stability of polymers was significantly improved. The emission intensity around 550 nm was decreased for ionic polyelectrolytes. The optimized spin-coated light-emitting electrochemical cell (LEC) with the configuration of ITO/PEDOT/polymer/Ag showed a maximum luminescence efficiency of 1.56 lm/W at a low operation bias of 3 V. The single-component LEC device exhibited pure white light emission with CIE'1931 coordinates approaching (0.33, 0.33) and high color rendering index (CRI > 85), referring to its potential use in solid-state-lighting application.

Keywords: polyelectrolytes, counterions, light-emitting electrochemical cells, solid-state lighting.

1. INTRODUCTION

Organic polymers based on polyfluorene (PF) have widely been used in organic optoelectronic devices such as organic light-emitting diodes (OLEDs) and organic solar cells[1,2]. PF and its derivatives, with their high photoluminescence (PL) quantum efficiencies, good thermal and chemical stability, excellent solubility in common organic solvents, are often used as good blue-light emitters. By properly adjusting the chemical structure and/or copolymerizing with suitable co-monomers, one can fine-tune their optical and electrical properties to obtain red, green, and even white emission[3,4]. Apart from being emitters in OLEDs, PF electrolytes carrying ionic groups on the end of C-9 substituents are also synthesized and utilized as electron-transporting layer to help carrier transport and to increase luminescence efficiency of devices[5,6].

Light-emitting electrochemical cells (LECs), demonstrated by Q. Pei et al. in 1995, have drawn a great deal of attention in the area of organic light-emitting devices[7]. The device structure of LECs is constructed as sandwiched layer with the configuration of anode/emissive layer/cathode, using organic materials blended with inorganic salts as active layer. The function of added salts includes better carrier transport and lower operation voltage[8]. The p-doped and n-doped regions are formed near the anode and cathode, respectively, under bias operation. The p-i-n interface is then constructed, confining emissive species in the intrinsic region[9]. However, the phase separation between organic materials and ionic salts are usually observed, resulting in reduced device performance for traditional LECs.

Considering the advantages of low voltage operation and simple layered structure, LECs are especially suitable for the application in solid-state lighting that requires high luminous efficiency and facile fabrication process. Several white emission LECs based on light-emitting polymers or ionic transition metal complexes have been reported in the literature. Alkoxyphenyl or ethylene oxide-containing PF derivatives doped with lithium salts were used as active layer in LECs to obtain white light[10,11]. In those cases, additional ion-transport materials such as polyethylene oxide, trimethylolpropane ethyloxylate, and lithium salts $LiCF_3SO_3$ were added, which increased complexity of active layer and might lead to phase separation. Iridium complexes coordinating with ionic ligands were reported to achieve high-efficiency white LECs[12,13]. In this system, however, the emissive layer is comprised of two (or more) complexes to emit white light that cannot be achieved by only one individual phosphorescent material so far. Furthermore, additional ionic liquid $BMIM^+PF_6^-$ was still added despite the incorporation of ionic groups on the ligands.

In this article, we demonstrate salt-free white LECs based on PF electrolytes. A series of fluorene-benzoselenadiazole copolymers bearing different counterions, including bromo Br$^-$, tetrafluoroborate BF$_4^-$, or hexafluorophosphate PF$_6^-$ ions were synthesized. Polymer main chains comprised of blue light-emitting fluorene segments and electron-deficient 2,1,3-benzoselenadiazole were designed to produce white light. Beside, ionic side chains on C-9 position of fluorene were built for carrier injection and transportation, i.e., no additional salt would be added. The thermal, optical, as well as electrochemical properties of the synthesized polymers were investigated to understand the influence of different counterions. Finally, single-component white emission LECs were fabricated and evaluated.

2. EXPERIMENTAL

2.1 Characterization of materials

The synthesized materials were characterized by the following techniques. ^{1}H-NMR spectra were recorded on a Bruker Avance 600 MHz NMR spectrometer. Gel permeation chromatography (GPC) data assembled from Viscotek with a VE3850 RI detector and three columns in series were used to measure the molecular weight distribution (MWD) relative to polystyrene standards at 35°C. TGA was undertaken on a Seiko TG/DTA 7200 instrument with a heating rate of 10 ^{o}C/min. UV-vis absorption and Photoluminescence (PL) spectra were obtained with a Princeton Instruments Acton 2150 spectrophotometer.

2.2 Preparation of polymers

The chemical structures of polymers P1 and corresponding polyelectrolytes tethering different counterions P1-Br, P1-BF$_4$, and P1-PF$_6$ are shown in Figure 1. The polymers P1 and P1-Br are prepared according to the previous literatures[14,15]. The polymers P1-BF$_4$ and P1-PF$_6$ are obtained by treating P1-Br with different ionic salts via ionic exchange reaction. Detailed synthetic procedures are listed as follows.

Synthesis of P1-BF$_4$. To a solution of P1-Br (100 mg) in methanol (20 mL) was slowly added a solution of sodium tetrafluoroborate (0.528 g, 4.8 mmol) in de-ionized water (20 mL). The mixture was stirred at room temperature for 48 hr, followed by removing the solvent by rotary evaporation. The previous procedure was repeated for 4 or 5 times to achieve high percentage of ionic exchange from Br to BF$_4$. The final product was collected and dried in oven as a yellow solid (80 mg, 78%).

Synthesis of P1-PF$_6$. To a solution of P1-Br (100 mg) in methanol (20 mL) was slowly added a solution of ammonium hexafluorophosphate (0.4 g, 4.8 mmol) in de-ionized water (20 mL). The mixture was stirred at room temperature for 48 hr, followed by removing the solvent by rotary evaporation. The previous procedure was repeated for 4 or 5 times to achieve high percentage of ionic exchange from Br to PF$_6$. The final product was collected and dried in oven as a yellow solid (79 mg, 77%).

2.3 Fabrication of LECs

ITO-coated glass substrates were cleaned and treated with UV/ozone prior to use. A PEDOT:PSS layer was spin-coated at 4000 rpm onto the ITO substrate in air and baked at 150 °C for 30 min. The emissive layer was then spin-coated at 3000 rpm from acetonitrile solutions. The thicknesses of P1-BF$_4$ and P1-PF$_6$ thin films from their solutions with concentrations of 150 mg/mL are 370 and 380 nm, respectively. The thickness of thin film was measured by employing ellipsometry. All solution preparing and spin-coating processes were carried out under ambient conditions. After spin coating, the thin films were then baked at 70 ^{o}C for 10 hours in a nitrogen glove box (oxygen and moisture levels below 1 ppm), followed by thermal evaporation of a 100-nm Ag top contact in a vacuum chamber (~10^{-6} torr). The electrical and emission characteristics of LEC devices were measured using a source-measurement unit and a calibrated Si photodiode. All device measurements were performed under a constant bias voltage (3.0, 3.3 and 3.5 V). The EL spectra were taken with a calibrated CCD spectrograph.
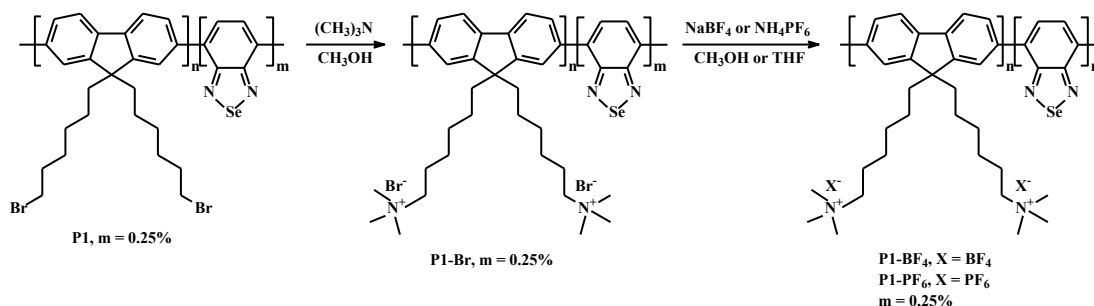
Figure 1. Chemical structures of polymers P1, P1-Br, P1-BF$_4$, and P1-PF$_6$.

3. RESULTS AND DISCUSSION

3.1 Characterization of polymers

The number-average and weight-average molecular weights of P1 were determined by GPC to be 7.1×10^3 and 2.8×10^4 g/mol, respectively, with its polydispersity index of 3.9. The molecular weights of polymers P1-Br, P1-BF$_4$, and P1-PF$_6$ were not measured by GPC because of low solubility in THF. Since the polymer backbone of these three polymers are the same before and after ionic exchange, the molecular weights of ionic polymers are assumed to be similar to their original polymer P1.

The electron spectroscopy for chemical analysis (ESCA) was used to examine the ionic exchange of polymers. Figure 2 (a) shows the ESCA spectra of ionic polymers P1-Br, P1-BF$_4$, and P1-PF$_6$. For P1-Br, a clear peak at 400 eV is found and assigned as N *1s* signal; three discrete peaks at 260, 180, and 80 eV are assigned as Br *3s*, *3p*, and *3d* signals, respectively, which means the incorporation of trimethylammonium bromide —N(CH$_3$)$_3$Br group on alkyl chain ends. For P1-BF$_4$, three new peaks are observed at 700, 190, 20 eV, belonging to F *1s*, B *1s*, and F *2s* signals, while Br signals are vanished, referring to successful replacement of Br$^-$ by BF$_4^-$. As for P1-PF$_6$, two additional peaks at 195 and 150 eV (assigned as P *2s* and *2p* signals) and existence of N *1s*, F *1s*, *2s* signals also prove that Br$^-$ is replaced by PF$_6^-$ after ionic exchange.

The solubility test also provides evidence of ionic exchange. P1 are soluble in many organic solvents, such as toluene, tetrahydrofuran (THF), dichloromethane, and chlorobenzene (CB), while polymers P1-Br, P1-BF$_4$, and P1-PF$_6$ are not. P1-Br can be dissolved in some high polar solvents, such as methanol, dimethyl sulfoxide (DMSO), and *N,N*-dimethylformamide (DMF). After ionic exchange from Br$^-$ to BF$_4^-$ or PF$_6^-$, the solubility of resulting polymers P1-BF$_4$ and P1-PF$_6$ is significantly decreased in methanol, indicating change of nature of ionic polymers.

The thermal stabilities of P1 and its corresponding ionic polymers were investigated by TGA. Figure 2 (b) shows the TGA thermograms of all polymers by heating from 100 to 600 ^{o}C. The decomposition temperatures T$_d$ (defined as 5% weight loss) were determined at 298, 211, 289, and 274 ^{o}C for P1, P1-Br, P1-BF$_4$, and P1-PF$_6$, respectively. It is seen that T$_d$ of three ionic polymers is lower than that of the original polymer P1, which is explained by the formation of Hofmann elimination[16]. Nguyen et al. proposed that quaternary ammonium group on the side chain is cleaved and eliminated by heating over 180 ^{o}C. Besides, it is found that T$_d$ of P1-BF$_4$ and P1-PF$_6$ are much higher than that of P1-Br, revealing that BF$_4^-$ and PF$_6^-$ groups possess resistance to thermal heating. It is concluded that ionic polymers bearing PF$_4^-$ and PF$_6^-$ groups show improved thermal stability and bring benefit in device application, since the inner temperature is usually increased under bias operation.
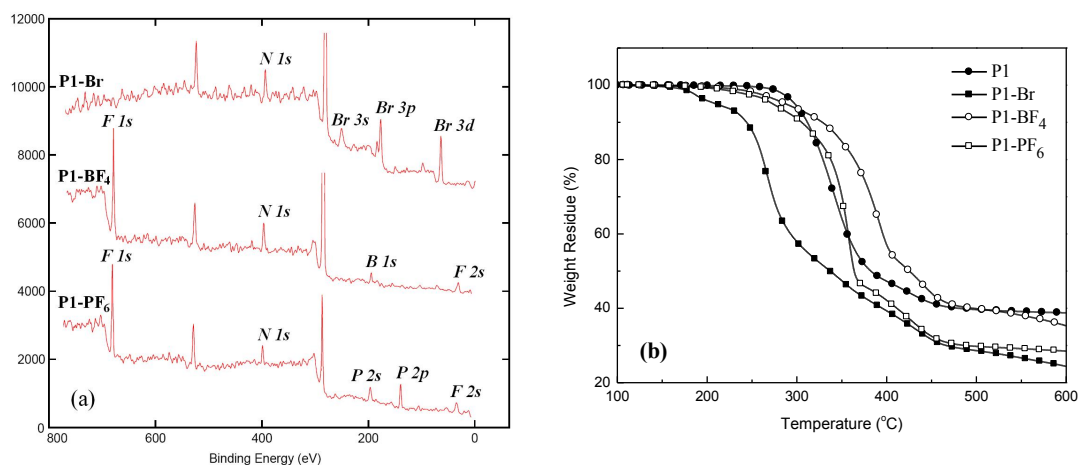
Figure 2. (a) ESCA spectra and (b) TGA thermograms of polymers P1, P1-Br, P1-BF$_4$, and P1-PF$_6$.

3.2 Optical properties of polymers

The UV-vis absorption spectra of polymers in film state are depicted in Figure 3 (a). The absorption maxima (λ_{max}) of polymers are located in the range of 388-400 nm, belonging to π-π* transition along the main chain. It is noted absorption λ_{max} of three ionic polymers are red-shifted compared with original polymer P1. The difference in absorption spectra between original and ionic polymers can be attributed to polar effect. Polymers P1-Br, P1-BF$_4$, and P1-PF$_6$ contain many ionic groups, i.e., —N(CH$_3$)$_3$Br, —N(CH$_3$)$_3$BF$_4$, and —N(CH$_3$)$_3$PF$_6$, bringing closer packing of polymer chains and leading to red-shift in absorption measurement.

The PL emission spectra of polymers in film state are shown in Figure 3 (b). All polymers reveal a major emission at 430 nm and an additional yellow emission around 560 mm arises, owing to energy transfer from fluorene to 2,1,3-benzoselenadiazole moieties. Combining two bands would bring white emission that can be utilized for lighting application. Furthermore, it is observed that intensity of the yellow emission band is decreased as quaternary ammonium group is tethered. The reason to this phenomenon is explained as follows. The heterocyclic 2,1,3-benzoselenadiazole is known as an electron-deficient moiety; the nature of quaternary ammonium groups —N(CH$_3$)$_3$Br, —N(CH$_3$)$_3$BF$_4$, and —N(CH$_3$)$_3$PF$_6$ are also electron-transport dominating. The competition between these two moieties would lower the ratio of carrier recombination on 2,1,3-benzoselenadiazole and, in consequence, decrease yellow emission band for those ionic polymers.
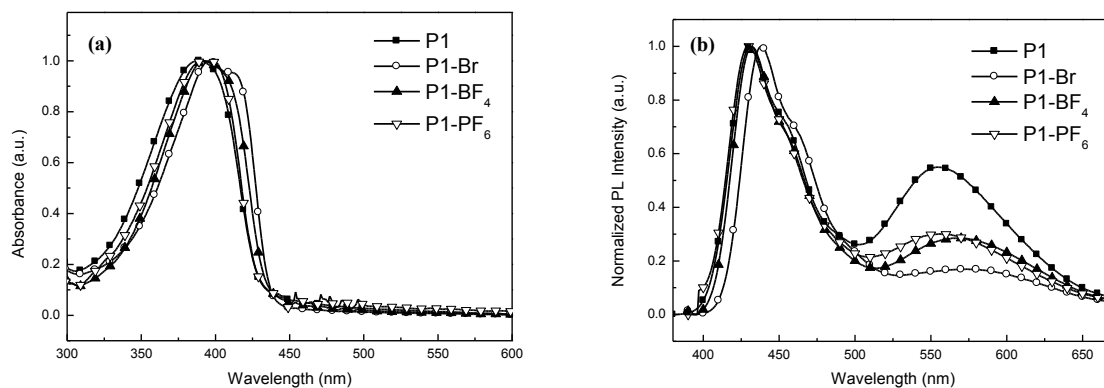

Figure 3. (a) UV-vis absorption and (b) photoluminescent spectra of polymers P1, P1-Br, P1-BF$_4$, and P1-PF$_6$.

3.3 Evaluation of LECs

EL characteristics of white LECs based on P1-BF$_4$ and P1-PF$_6$ were measured to evaluate their applications in LECs. The data of devices based on P1-Br is not involved since it is rather unstable under electrical driving. It would be attributed to the degradation of polymers caused by Hofmann elimination, as discussed in the section 3.2. The white LECs have the structure of indium tin oxide (ITO) (120 nm)/ PEDOT:PSS (30 nm)/emissive layer/Ag (100 nm), where the emissive layer is a thin film of P1-BF$_4$ 370 nm or P1-PF$_6$ 380 nm for each device. The EL spectra of white LECs based on two polyelectrolytes under various bias voltages are shown in Figure 4. Simultaneous EL emissions from the blue emitting fluorene segments and the yellow emission were measured in all devices. However, the bias voltage and the thickness of the emissive layer affect the relative amount of the yellow emission with respect to the blue one, resulting in altered white EL spectra. In these white LECs, electrochemically doped regions of the emissive layer result in ohmic contact with metal electrodes and consequently facilitate carrier injection onto both the fluorene segments and the 2,1,3-benzoselenadiazole moieties. Hence, both exciton formation on the higher-gap fluorene followed by energy transfer to the lower-gap 2,1,3-benzoselenadiazole and direct exciton formation on the lower-gap 2,1,3-benzoselenadiazole induced by charge trapping contribute to the yellow emission. At a lower bias, e.g., 3 V, carrier injection and trapping on the smaller-gap 2,1,3-benzoselenadiazole would be favored and thus direct exciton formation on the lower-gap chromophore would lead to more significant yellow emission, as shown in Figure 4 (a). As the bias increases, carrier injection and exciton formation on the higher-gap fluorene is facilitated and subsequent partial energy transfer dominates the yellow emission, resulting in less significant yellow emission. Yellow emission mainly comes from partial energy transfer from blue excitons on the fluorene to electron-deficient 2,1,3-benzoselenadiazole. EL spectra of P1-PF$_6$ exhibited similar evolution trends when the bias voltage and the thickness of the emissive layer are varied, as shown in Figure 4 (b). These results show that white LECs based on these PF electrolytes at 3.3 V show CIE'1931 coordinates close to (0.33, 0.33) and good CRI > 85, which are essential for solid-state lighting applications.

All white LECs based on polyelectrolytes P1-BF$_4$ and P1-PF$_6$ showed similar time-dependent EL characteristics. The time-dependent brightness and current density of P1-BF$_4$ device under constant biases of 3.0~3.5 V are shown in Figure 5 (a). After the bias was applied, the device current first rose and then stayed rather constant. On the other hand, the brightness first increased with the device current, reaching maximum values before undergoing gradual decreases over time. The time required for the brightness to reach its maximum value decreased as the bias voltage increased, presumably because a higher accumulation rate of mobile ions facilitated the formation of electrochemically doped regions under a higher electric field. The maximum brightness of P1-BF$_4$ device reached 17, 151, and 226 cd/m^2 under biases of 3.0, 3.3 and 3.5 V, respectively. The brightness then dropped with time with a rate depending on the bias voltage (or current). The lifetime of devices was decreased upon increasing the bias voltage. It results from that higher current density induced by a higher bias voltage led to a higher rate of irreversible multiple oxidation and subsequent decomposition of the emissive material, thereby accelerating the degradation of the LEC devices[17]. The external quantum efficiency (EQE) and power efficiency of P1-BF$_4$ device under constant biases of 3.0~3.5 V are shown in Figure 5 (b). Immediately after a forward bias was applied, the EQE was rather low because of unbalanced carrier injection. During the formation of the doped regions near the electrodes, the balance of the carrier injection was improved and, accordingly, the EQE of the device increased rapidly. The peak EQE and peak power efficiency for P1-BF$_4$ device under 3 V were 0.4% and 0.79 lm W^{-1}, respectively.

The time-dependent brightness/current density and EQE/power efficiency of P1-PF$_6$ device under constant biases of 3.0~3.5 V are shown in Figure 6 (a) and (b), respectively. Replacing BF$_4^-$ anions with larger PF$_6^-$ anions did not significantly alter the trend in the time-dependent EL characteristics of the white LECs. However, the device response is slower in devices containing larger PF$_6^-$ anions due to a lower ionic mobility of larger anions in the emissive layer[18]. In addition, devices employing PF$_6^-$ counterions exhibited lower device current density and thus longer device lifetimes were obtained compared with P1-BF$_4$ device. It is noted that the thicker P1-PF$_6$ device showed high peak EQE and power efficiency up to 0.69% and 1.56 lm W^{-1}, respectively. These results are approaching the upper limit (~0.8%) that one would expect from the PLQY of the thin film of P1-PF$_6$ (16%, measured by fluorescent spectrophotometer equipped with integrating sphere) when fluorescent spin statistics of ca. 25% and an optical out-coupling efficiency of ca. 20% are estimated. Thus, superior carrier balance in white LECs based on P1-PF$_6$ could be speculated. It may result from the bipolar characteristic of the molecular structure of P1-PF$_6$, which is consisted of hole transporting fluorene segments and electron transporting 2,1,3-benzoselenadiazole moieties. Such device efficiencies are among the highest reported for

white-light polymer LECs[9]. Furthermore, white EL spectra with CIE coordinates approaching (0.33, 0.33) and high CRI > 85 have been reported for the first time in polymer white LECs to the best of our knowledge.
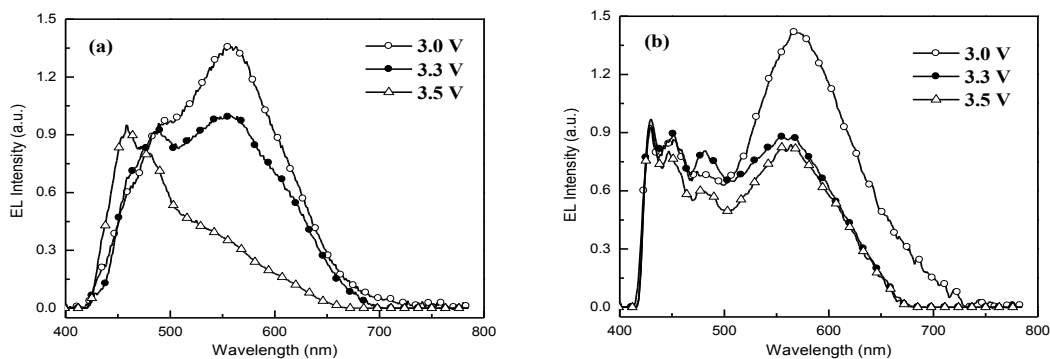

Figure 4. EL spectra of LEC devices based on (a) P1-BF$_4$ and (b) P1-PF$_6$ under different bias operation.
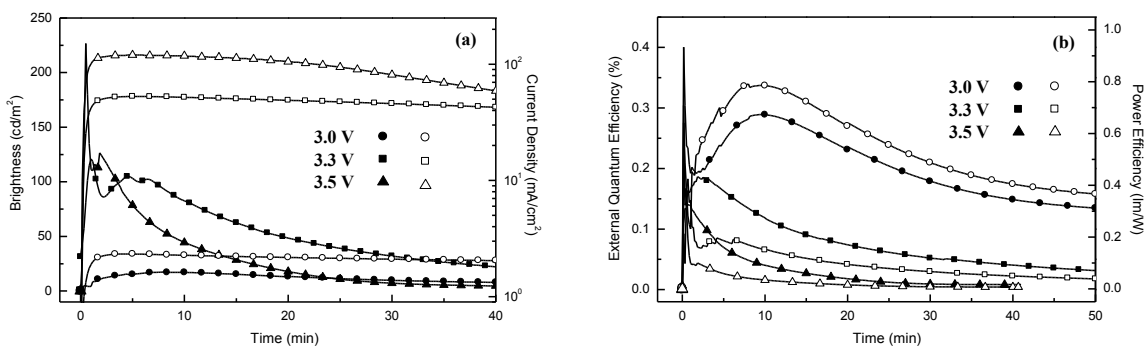

Figure 5. (a) Brightness-time-current density and (b) external quantum efficiency-time-power efficiency curves of LEC device based on P1-BF$_4$.
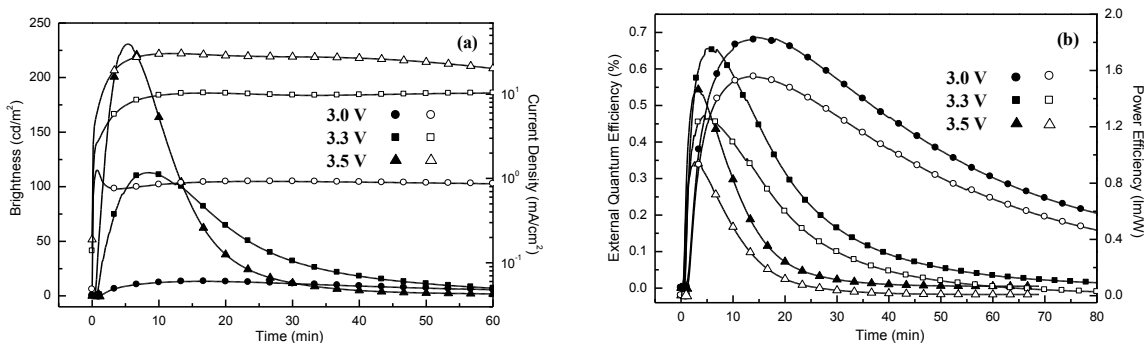

Figure 6. (a) Brightness-time-current density and (b) external quantum efficiency-time-power efficiency curves of LEC device based on P1-PF$_6$.

4. CONCLUSIONS

A series of PF electrolytes bearing Br^-, BF_4^-, and PF_6^- counterions on the side chains were synthesized and characterized. Electron-deficient 2,1,3-benzoselenadiazole moieties were copolymerized into PF main chains to produce white light. Polymers P1-BF$_4$ and P1-PF$_6$ were found to suppress the formation of Hoffmann elimination and to increase thermal stabilities. All polymers showed two emission bands around 430 and 560 nm in thin film state; in addition, the intensity of the yellow emission band was decreased as quaternary ammonium group is tethered. Electrochemical analysis revealed that oxidation potentials of P1-BF$_4$ and P1-PF$_6$ were significantly decreased compared to their original polymer P1. Single-component white LECs were fabricated using P1-BF$_4$ and P1-PF$_6$ as active layer, without adding additional inorganic salts. Characteristics including high luminescence efficiency of 1.56 lm/W, pure white EL emission, and high CRI values demonstrated the best device result among white-light polymer LECs so far.

REFERENCES

[1] Grimsdale, A. C., Chan, K. L., Martin, R. E., Jokisz, P. G., and Holmes, A.B., "Synthesis of light-emitting conjugated polymers for applications in electroluminescent devices," Chem. Rev. 109, 897-1091 (2009).

[2] Cheng, Y. J., Yang, S. H., and Hsu, C.S., "Synthesis of conjugated polymers for organic solar cell applications," Chem. Rev. 109, 5868-5923 (2009).

[3] Herguth, P., Jiang, X., Liu, M. S., and Jen, A. K.-Y., "Highly efficient fluorene- and benzothiadiazole-based conjugated copolymers for polymer light-emitting diodes," Macromolecules 35, 6094-6100 (2002).

[4] Luo, J., Li, X., Hou, Q.. Peng, J., Yang, W., and Cao, Y., "High-efficiency white-light emission from a single copolymer: fluorescent blue, green, and red chromophores on a conjugated polymer backbone," Adv. Mater. 19, 1113-1117 (2007).

[5] Oh, S. H., Na, S. I., Nah, Y. C., Vak, D., Kim, S. S., and Kim, D. Y., "Novel cationic water-soluble polyfluorene derivatives with ion-transporting side groups for efficient electron injection in PLEDs," Org. Electron. 8, 773-783 (2007).

[6] Hoven, C. V., Garcia, A., Bazan, G. C., and Nguyen, T. Q., "Recent applications of conjugated polyelectrolytes in optoelectronic devices," Adv. Mater. 20, 3793-3810 (2008).

[7] Pei, Q., Yu, G., Zhang, C., Yang, Y., and Heeger, A. J., "Polymer light-emitting electrochemical cells," Science 269, 1086-1088 (1995).

[8] Kosilkin, I. V., Martens, M. S., Murphy, M. P., and Leger, J. M., "Polymerizable ionic liquids for fixed-junction polymer light-emitting electrochemical cells," Chem. Mater. 22, 4838-4840 (2010).

[9] Norell Bader, A. J., Ilkevich, A. A., Kosilkin, I. V., and Leger, J. M., "Precise color tuning via hybrid light-emitting electrochemical cells," Nano Lett. 11, 461-465 (2011).

[10] Sun, M., Zhong, C., Li, F., Cao, Y., and Pei, Q., "A fluorene-oxadiazole copolymer for white light-emitting electrochemical cells," Macromolecules 43, 1714-1718 (2010).

[11] Tang, S., Pan, J., Buchholz, H., and Edman, L., "white light-emitting electrochemical cell," Appl. Mater. Interfaces 3, 3384-3388 (2011).

[12] He, L., Qiao, J., Duan, L., Dong, G., Zhang, D., Wang, L., and Qiu, Y., "Toward highly efficient solid-state white light-emitting electrochemical cells: blue-green to red emitting cationic iridium complexes with imidazole-type ancillary ligands," Adv. Funct. Mater. 19, 2950-2960 (2009).

[13] He, L., Duan, L., Qiao, J., Dong, G., Wang, L., and Qiu, Y., "Highly efficient blue-green and white light-emitting electrochemical cells based on a cationic iridium complex with a bulky side group," Chem. Mater. 22, 3535-3542 (2010).

[14] Liu, B. and Bazan, G. C., "Optimization of the molecular orbital energies of conjugated polymers for optical amplification of fluorescent sensors," J. Am. Chem. Soc. 128, 1188-1196 (2006).

[15] Guo, X., Qin, C., Cheng, Y., Xie, Z., Geng, Y., Jing, X., Wang, F., and Wang, L., "White electroluminescence from a phosphonate-functionalized single-polymer system with electron-trapping effect," Adv. Mater. 21, 3682-3688 (2009).

[16] Lin, C. Y., Garcia, A., Zalar, P., Brzezinski, J. Z., and Nguyen, T. Q., "Effect of thermal annealing on polymer light-emitting diodes utilizing cationic conjugated polyelectrolytes as electron injection layers," J. Phys. Chem. C 114, 15786-15790 (2010).

[17] Parker, S. T., Slinker, J. D., Lowry, M. S., Cox, M. P., Bernhard, S., and Malliaras, G. G., "Improved turn-on times of iridium electroluminescent devices by use of ionic liquids," Chem. Mater. 17, 3187-3190 (2005).

[18] Rudmann, H., Shimada, S., and Rubner, M. F., "Solid-state light-emitting devices based on the tris-chelated ruthenium(II) complex. 4. High-efficiency light-emitting devices based on derivatives of the tris(2,2'-bipyridyl)ruthenium(II) complex," J. Am. Chem. Soc. 124, 4918-4921 (2002).