doi:10.1246/cl.2012.257
Published on the web February 25, 2012

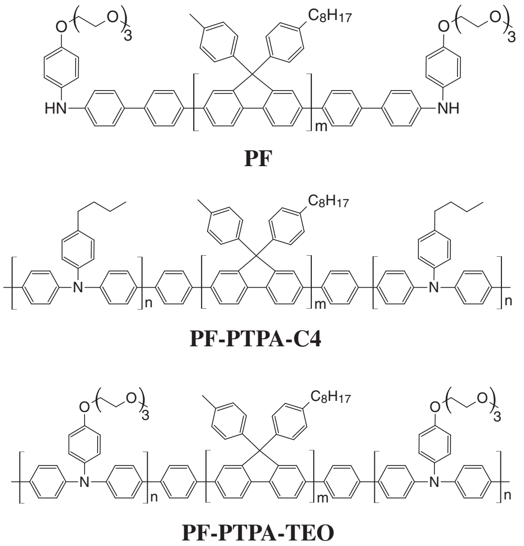
Synthesis of Polyfluorene Block Copolymers and Effect of Side Chain Group on Electroluminescent Device Performance

Ying Tan, Kousuke Tsuchiya, and Kenji Ogino*
Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology,
2-24-16 Nakacho, Koganei, Tokyo 184-8588

(Received December 19, 2011; CL-111206; E-mail: kogino@cc.tuat.ac.jp)

Blue-light-emitting block copolymers based on polyfluorene (PF) and poly(triphenylamine) (PTPA) were synthesized for polymeric electroluminescent (EL) materials. PF with diphenylamine terminals were prepared by the Suzuki coupling polymerization, and converted to PTPA-*block*-PF-*block*-PTPA triblock copolymers by C–N coupling polymerization. The block copolymers with different substituents on PTPA segment, hydrophilic trioxyethylene (TEO) group (PF–PTPA–TEO) or hydrophobic *n*-butyl group (PF–PTPA–C4), were prepared in order to investigate their effect on device performance. The block copolymers showed relatively high HOMO levels compared with PF. EL devices based on the block copolymers showed higher luminance and current efficiency than that of PF homopolymer because of the improvement of hole injection by the introduction of PTPA segment. Modification by TEO group provided higher device performance than *n*-butyl group, indicating that PTPA segment segregated at the interface with PEDOT:PSS by the hydrogen-bonding interaction.

Polyfluorenes (PFs) have been attracting much attention for blue polymeric light-emitting material because of their superior properties such as highly efficient luminescence, excellent thermal stability, and good solubility in common organic solvents.[1,2] However, some disadvantages using PFs for electroluminescent (EL) devices impedes their practical application. One of the problems is low reliability in long time usage, originating from insufficient color stability of PFs. This causes a troublesome long-wavelength emission band above 500 nm, assigned to aggregates/excimers, interchain interactions, and/or an emissive keto defect generated by thermo-, photo-, or electrooxidative degradation during device operation.[3–6] Some researchers have proposed structural modifications such that an alkylphenyl group was introduced at the C-9 position of fluorene to reduce the aggregation and keto defect.[7–10] Another serious problem is poor EL efficiency due to an imbalance in charge carriers caused by large hole-injection barriers and different charge carrier mobilities.[11] In addition, this mismatch of the number of carriers brings an emission to near the interface with hole injection layer, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), where the emitting units can be damaged by proton or impurities originating from PEDOT:PSS. Therefore, an additional buffer layer with hole injecting/transporting ability is required between PF and PEDOT:PSS layers. In this communication, novel block copolymers consisting of PF and poly(triphenylamine) (PTPA) were prepared in order to improve the performance of blue-emitting EL devices. We demonstrate here that introduction of PTPA segment as a hole-transporting material into PF terminals can facilitate hole injection and transport from the anode. A hydrophilic trioxyethylene (TEO) group was attached to the side chain of PTPA, which will help PTPA segments segregate into the interface by hydrogen-bonding interaction with PEDOT:PSS layer. The effect of TEO on the device performance was compared with hydrophobic *n*-butyl group.[12,13]



Scheme 1. Structures of PF, PF–PTPA–C4, and PF–PTPA–TEO.

PF homopolymer and block copolymers were synthesized for EL application (Scheme 1). PF homopolymer was prepared by the Suzuki coupling polymerization followed by terminal modification with diphenylamine moiety. In order to suppress the formation of aggregates/excimers and interchain interactions, the C-9 of fluorene was substituted by alkylphenyl groups. C–N coupling polymerization in the presence of the PF homopolymer provided PF-*block*-PTPA-*block*-PF triblock copolymers.[14] PTPA block, attached to the ends of PF backbone, is considered to decrease the concentration of keto defects.[6] The two block copolymers consisting of PF and PTPA substituted with TEO group (PF–PTPA–TEO) or *n*-butyl group (PF–PTPA–C4) were prepared.

The number average molecular weights (M_n) of PF, PF–PTPA–TEO, and PF–PTPA–C4 estimated by GPC were 13400, 23100, and 19000 with a molecular-weight dispersity (M_w/M_n) of 2.42, 2.67, and 2.43, respectively. The polymer structure was confirmed by ^{1}H NMR spectra (Figure S1[16]). The signals assignable to TEO group were observed at 3.4–4.2 ppm, whereas those of *n*-butyl group at 0.9 ppm in ^{1}H NMR spectrum, indicating that PTPA segment was introduced at the ends of PF backbone. The molar ratio of PF and PTPA repeating units

($N_{\mathrm{PF}}/N_{\mathrm{PTPA}}$) for PF–PTPA–TEO and PF–PTPA–C4 were determined to be 34/29 and 34/26 by ^{1}H NMR spectra, respectively. PF homopolymer, PF–PTPA–TEO and PF–PTPA–C4 block copolymers showed a T_g of 111, 150, and 148 °C in differential scanning calorimetric (DSC) analysis, respectively.

The optical properties of the polymers in chloroform solution and in film state are shown in Figure S2.[16] In the absorption spectra of solution state, polymers showed $\lambda_{\mathrm{abs,max}}$ of 388–389 nm. Similar results were obtained in film state. All the polymers exhibited similar PL spectra both in solution state and in film state, having distinct vibronic bands at 418 and 445 nm and a shoulder around 470 nm upon excitation at 380 nm. Both of the block copolymers exhibit similar emission properties to PF homopolymer, which suggests that the attachment of PTPA block to the PF backbone has no influence on the luminescent properties of PF.

The electrochemical properties of the polymers were investigated by cyclic voltammetry (CV) with a reference electrode of Ag/AgCl. As shown in Figure S3,[16] the oxidation process of PF started at 1.39 V, and the reversible redox peak appeared at −0.79 V. The same result was also found in the case of the block copolymers except that a new redox peak in the anodic sweep were observed at around 0.90 V. The block copolymers exhibited lower oxidation onset in comparison with PF, which was attributed to oxidation of PTPA segment. Furthermore, the oxidation potentials of PF–PTPA–TEO and PF–PTPA–C4 were nearly the same.

The energy levels of the highest occupied molecular orbital (HOMO) of the polymers were estimated from their oxidation potential according to an empirical formula, $E_{\mathrm{HOMO}} = -\mathrm{e}(E_{\mathrm{ox}} + 4.4)\,\mathrm{V}$. The HOMO level of PF was −5.79 eV, whereas PF–PTPA–PEO and PF–PTPA–C4 showed higher HOMO level of −5.29 and −5.28 eV, respectively. The results indicate that the introduction of PTPA segment into the polymer chain ends efficiently raised their HOMO levels, thus could facilitate the hole injection from an anode to the emitting polymer.

Figure 1 shows the energy level diagram for PF–PTPA–TEO. The HOMO levels of PTPA segment of block copolymers suitably match the HOMO level of PEDOT:PSS (−5.2 eV), while there was an energy barrier over 0.50 eV between the HOMO level of PEDOT:PSS and that of PF. This suggests that facile hole injection from PEDOT:PSS into PF emission layer passing through PTPA segment can be expected in comparison with PF.

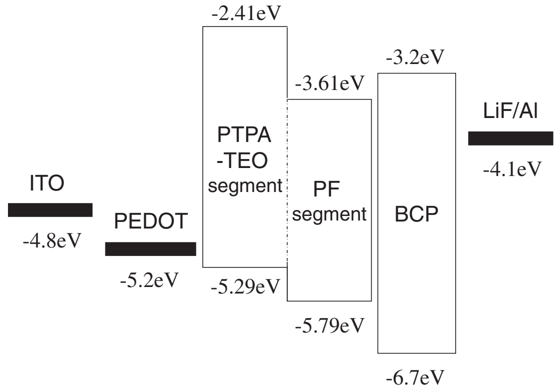


Figure 1. Energy level diagram of PF–PTPA–TEO.

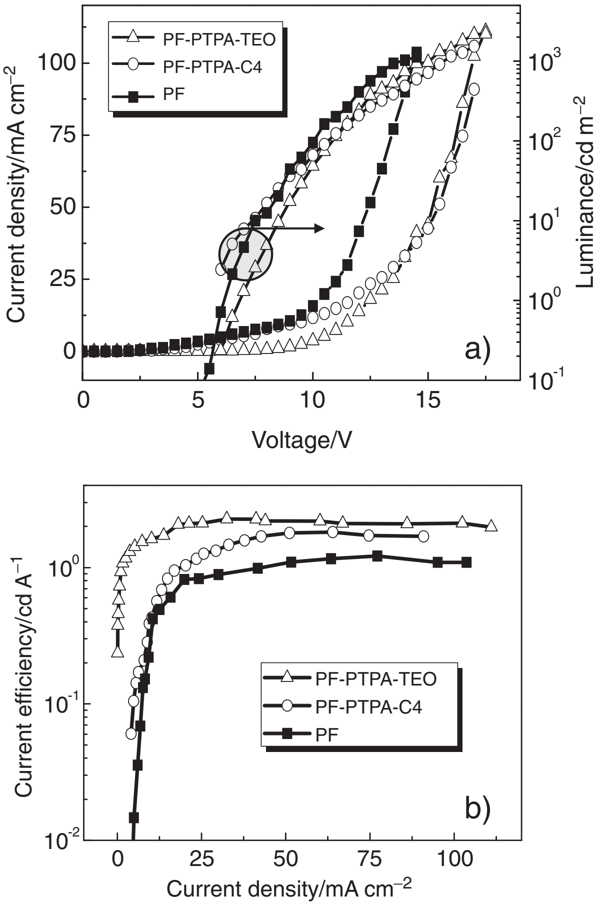


Figure 2. Device performance of blue-emitting PLEDs based on PF, PF–PTPA–C4, and PF–PTPA–TEO.

The performance of the EL devices based on PF homopolymer and the block copolymers with the device structure of ITO/PEDOT:PSS/polymer/BCP/LiF/Al was evaluated. As a hole blocking layer, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (bathocuproine, BCP) was used between the emission layer and cathode. Figure 2 shows current density and luminance vs. voltage, and current efficiency vs. current density characteristics. The device performance was summarized in Table 1. The turn-on voltages of all the devices were about 5.0–6.0 V. The luminance was exponentially increased with an increase in voltage. At the similar current density (for example, 30 mA cm^{-2}), PF–PTPA–C4 and PF–PTPA–TEO showed higher luminance (388 and 732 cd m^{-2}) than PF homopolymer (266 cd m^{-2}). Moreover, similar results were obtained for the maximum luminance. The maximum current efficiencies of PF homopolymer was 1.21 cd A^{-1}, whereas those of PF–PTPA–C4 and PF–PTPA–TEO increased to 1.87 and 2.27 cd A^{-1}. The improvement of the device performance using block copolymers is probably attributed to an efficient hole injection, which leads good balance between hole and electron charges in the emitting layer, by the attachment of PTPA block to PF backbone. In addition, it is suggested that the microphase-separated structure created by the block copolymers offered large interface between PF and PTPA segments for the efficient charge recombination.[15]

Table 1. Device performance of PF, PF–PTPA–C4, and PF–PTPA–TEO

Polymer	Turn-on voltage/V	Luminance[a] /cd m^{-2}	Maximum luminance /cd m^{-2}	Maximum current efficiency /cd A^{-1}
PF	5.0	266	1130	1.21
PF–PTPA–C4	6.5	388	1540	1.87
PF–PTPA–TEO	6.5	732	2194	2.27

[a]At 30 mA cm^{-2}.

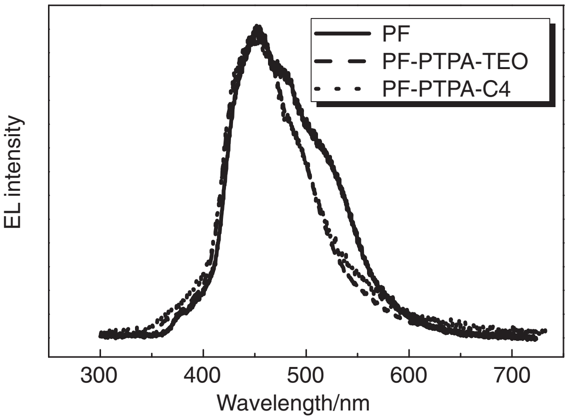


Figure 3. Electroluminescence spectra of devices based on PF, PF–PTPA–TEO, and PF–PTPA–C4 at 14 V.

Although the two kinds of block copolymers (PF–PTPA–TEO and PF–PTPA–C4) possessed similar hole injection capability (because they showed similar electrochemical properties), comparing with PF–PTPA–C4, the EL device based on PF–PTPA–TEO showed higher performance (both luminance and current efficiency). The TEO moiety is polar and hydrophilic; it is indicated that an interaction between TEO attached to PTPA segment and sulfonic acid in PEDOT:PSS layer probably built a graded skin layer of PTPA, which worked as a buffer layer to prevent the migration of proton or impurities from the PEDOT:PSS layer to PF emitting layer as well as to facilitate a hole injection. The difference of polarity between PF and PTPA with TEO moiety may promote greater microphase separation than with PF–PTPA–C4, which also contributes to the improvement of current efficiency. The EL spectra of the devices based on PF and PF–PTPA–TEO are shown in Figure 3. All the devices exhibited a blue emission without unnecessary green-emitting bands. No spectral change was observed by the introduction of PTPA segment. Similar EL spectrum to PF–PTPA–TEO was also obtained for a device based on PF–PTPA–C4.

In summary, novel PF-based block copolymers containing PTPA as a hole-transporting segment were prepared for a blue-light-emitting devices, and the effect on device performance was evaluated for the difference of the structure, namely hydrophilic and hydrophobic side chains on PTPA. PF homopolymer with diphenylamine terminals was synthesized by the Suzuki coupling polymerization. PTPA block was introduced at the terminals of PF via C–N coupling polymerization to give PTPA-*block*-PF-*block*-PTPA triblock copolymers with different substituents, TEO and *n*-butyl groups. The photophysical analysis revealed that the PTPA chains had no influence on the blue emission of PF segment. Compared with PF, the EL devices based on block copolymers showed higher luminance and current efficiency, resulting from the improvement of hole injection from PEDOT:PSS into the emitting layer. Furthermore, the device performance of PF–PTPA–TEO exceeded that of PF–PTPA–C4. It can be concluded that TEO allows PTPA segments to segregate at the interface with PEDOT:PSS layer, triggered by hydrogen-bonding interaction between the TEO and sulfonic acid in the PEDOT:PSS layer.

References and Notes

1 E. Lim, B.-J. Jung, H.-K. Shim, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 243.

2 N. S. Cho, J.-H. Park, S.-K. Lee, J. Lee, H.-K. Shim, M.-J. Park, D.-H. Hwang, B.-J. Jung, *Macromolecules* **2006**, *39*, 177.

3 E. J. W. List, R. Guentner, P. S. de Freitas, U. Scherf, *Adv. Mater.* **2002**, *14*, 374.

4 L. Romaner, A. Pogantsch, P. S. de Freitas, U. Scherf, M. Gaal, E. Zojer, E. J. W. List, *Adv. Funct. Mater.* **2003**, *13*, 597.

5 J.-K. Jin, S.-K. Kwon, Y.-H. Kim, D.-C. Shin, H. You, H.-T. Jung, *Macromolecules* **2009**, *42*, 6339.

6 A. Bolognesi, P. Betti, C. Botta, S. Destri, U. Giovanella, J. Moreau, M. Pasini, W. Porzio, *Macromolecules* **2009**, *42*, 1107.

7 M. Kreyenschmidt, G. Klaerner, T. Fuhrer, J. Ashenhurst, S. Karg, W. D. Chen, V. Y. Lee, J. C. Scott, R. D. Miller, *Macromolecules* **1998**, *31*, 1099.

8 J.-I. Lee, G. Klaerner, R. D. Miller, *Chem. Mater.* **1999**, *11*, 1083.

9 X. Gong, P. K. Iyer, D. Moses, G. C. Bazan, A. J. Heeger, S. S. Xiao, *Adv. Funct. Mater.* **2003**, *13*, 325.

10 G. Klärner, J.-I. Lee, V. Y. Lee, E. Chan, J.-P. Chen, A. Nelson, D. Markiewicz, R. Siemens, J. C. Scott, R. D. Miller, *Chem. Mater.* **1999**, *11*, 1800.

11 S. K. Lee, T. Ahn, N. S. Cho, J.-I. Lee, Y. K. Jung, J. Lee, H. K. Shim, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1199.

12 T. Wang, Y. Qi, J. Xu, X. Hu, P. Chen, *Appl. Surf. Sci.* **2005**, *250*, 188.

13 K. Tsuchiya, K. Sakaguchi, H. Kasuga, A. Kawakami, H. Taka, H. Kita, K. Ogino, *Polymer* **2010**, *51*, 616.

14 K. Tsuchiya, T. Shimomura, K. Ogino, *Polymer* **2009**, *50*, 95.

15 K. Tsuchiya, K. Sakaguchi, A. Kawakami, H. Taka, H. Kita, T. Shimomura, K. Ogino, *Synth. Met.* **2010**, *160*, 1679.

16 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.