ARTICLE

Journal of Materials Chemistry
www.rsc.org/materials

A novel spiro-functionalized polyfluorene derivative with solubilizing side chains

Doojin Vak, Chaemin Chun, Chang Lyoul Lee,† Jang-Joo Kim† and Dong-Yu Kim*

Center for Frontier Materials, Department of Materials Science and Engineering,
Kwangju Institute of Science and Technology, 1 Oryong-dong, Puk-gu, Gwangju, Korea.
E-mail: kimdy@kjist.ac.kr; Fax: 82-62-970-2304; Tel: 82-62-970-2319

Received 5th January 2004, Accepted 11th February 2004
First published as an Advance Article on the web 9th March 2004

We report on a new polyfluorene derivative containing a spiroanthracenefluorene unit with a remote C-10 position that provides facile substitution of alkyl groups. An ethylhexyl group was introduced into the spiroanthracenefluorene unit and the ethylhexyl-substituted spiroanthracenefluorene was polymerized *via* an Ni(0)-mediated polymerization. The polymer showed a high spectral stability with respect to heat treatment, UV irradiation, and high current passage. A light-emitting device based on this polymer showed an emission in a deep blue region with CIE color coordinates of $x = 0.17$ and $y = 0.12$.

Introduction

Since the first fabrication of polymer light-emitting devices (PLEDs),[1] conjugated polymers have received a great deal of attention as light emitting materials.[2,3] However, despite various attempts to develop highly efficient PLEDs, these devices continue to suffer from a lack of efficient and stable blue-emitting materials for achieving a full color display.

Poly(*p*-phenylene)s (PPPs) have been extensively studied as candidates for PLED applications because of their chemical stability and large band-gap for blue light emission. Because PPP is insoluble in common organic solvents and consequently cannot be processed, soluble PPPs have been developed by introducing long alkyl chains onto the phenylene units.[4–6] However, the introduction of these bulky alkyl chains leads to steric strains that force the phenyl groups out of conjugation, thus limiting the intrinsic conjugation length.[7] Polyfluorenes (PFs), which can be regarded as a type of PPP with pairs of phenylene rings locked into a coplanar arrangement by the presence of the C-9 atom, are blue light emitting conjugated polymers that have generated considerable interest[8,9] because of their high photoluminescence (PL) quantum efficiencies and thermal stability.[10–12] The introduction of alkyl chains at the C-9 position increases the solubility of PFs without creating additional torsional strain. Because of these favorable properties, many research groups have studied these materials and several research groups reported on the preparation of PLEDs using PFs with a high degree of brightness.[13,14]

However, spectral stability has been a major problem of PFs. The pure blue emission of PFs changes to a greenish blue emission with an increase in broad band emission centered at 530–540 nm as the result of heat treatment, UV irradiation or the passage of an electrical current. This broad band has been extensively studied and has been attributed to formation of a physical defect aggregate.[15–21] Several research groups have recently reported that this long-wavelength emission is attributed to a chemical defect, an emissive keto defect, produced by thermo-, photo-, or electro-oxidative degradation rather than the aggregate formation.[22–25] Currently, the origin of this long-wavelength emission is the subject of considerable debate in the literature.[26–29]

Nevertheless in recent years, a number of reports have appeared showing that the spectral stability of PFs can be improved by various approaches which could reduce the aggregate formation. These include copolymerization with bulky phenyl groups,[17,29,30] the introduction of crosslinking groups,[31,32] blending,[33] the introduction of bulky dendrimer side groups,[34,35] and kinked backbone structures.[20]Among these methods, the introduction of a spiro structure appears to be one of the most promising solutions.[36,37] A spirobifluorene contains two biphenylene units connected by a tetrahedrally bonded carbon atom, where the planes of the biphenylene units lie perpendicular to each other. Once incorporated into the PFs, this three-dimensional structure should prevent the approach of other polymer backbones and therefore π-stacking of the conjugated polymer backbone could be minimized. This minimized π-stacking can not only prevent aggregate formation and/or excimer emission but can also increase the PL quantum efficiency. Recently, Wong *et al.*[38] reported that terfluorenes with spirobifluorene structure showed nearly a 100% PL quantum efficiency in solution and over 90% PL quantum efficiency even in a thin film. The results showed that the spiro-structure is effective with respect to PL quantum efficiency.

Although the introduction of spirobifluorene into PF has been shown to alleviate the spectral stability problem, the incorporation of the spirobifluorene unit into the polymer structure at greatly reduces its solubility in common organic solvents. Therefore, a homopolymer of spirobifluorene has never been used due to its low solubility. In the present study, we report on the synthesis, characterization and greatly enhanced spectral stability of poly[10,10-bis(2-ethylhexyl)-10*H*-spiro(anthracene-9,9′-fluorene)-2′,7′-diyl] (PEHSAF, see Scheme 1), which contains a spiroanthracenefluorene rather than a spirobifluorene. This spiroanthracenefluorene structure was synthesized in 1930,[39] but has never been used for PLED applications. This structure still maintains the useful spiro structure and at the same time provides for facile functionalization at the C-10 position of the dihydroanthracene unit, where various solubilizing side chains could be easily introduced.

Experimental

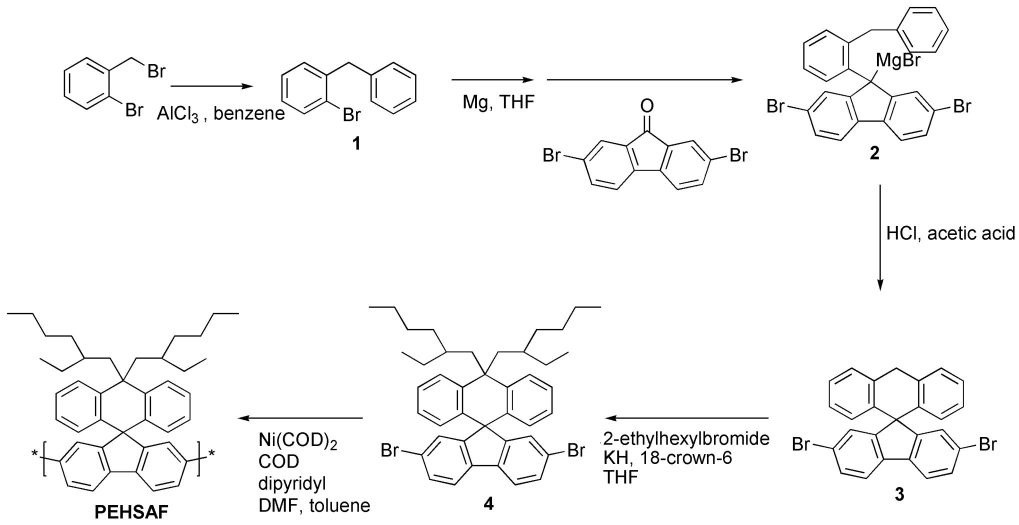
Characterization and measurements

Materials were characterized by means of ^{1}H, ^{13}C NMR spectroscopy (JEOL JNM-LA300WB 300 MHz). Thermal

---

† Present address: Department of Materials Science and Engineering, Seoul National University, San 56-1 Shilim-dong Gwanak-gu, Seoul, Korea.

DOI: 10.1039/b317028d



Scheme 1 Synthetic scheme for PEHSAF.

properties including glass transition temperature (T_g) were determined by means of differential scanning calorimetry (DSC; TA2010) and thermo-gravimetric analysis (TGA; TA-2050) at a heating rate of 10 °C min^{-1} under nitrogen. Boiling (bp) and melting points (mp) were determined by means of TGA and DSC, respectively. Elemental analyses were performed by the Korean Basic Science Institute, Seoul Branch Analytical Laboratory (Elemental analyzer; CE Instruments Flash EA 1112 series). Absorption spectra were measured using a UV/Vis spectrophotometer (K-MAC, Spectraview-2000). Molecular weights were measured by gas chromatography mass spectrometry (GCMS, Shimadzu, GCMS-QP2010) and by gel permeation chromatography (GPC, Futecs, NS2001) for polymers. PL spectra were obtained using an ACTON spectrometer connected to a photo-multiplier tube (Acton Research Co. SpectraPro-300i) with a xenon lamp as the excitation source. The current–voltage-luminescence characteristics of the devices were measured using a Keithley 237 Source Measurement Unit and an optical power meter (Newport, 1835C) with a calibrated photodiode (Newport, 818 UV).

Synthesis

All starting materials were obtained from Aldrich Chemical Co. and used without further purification except THF, which was dried by refluxing over calcium hydride.

1-Bromo-2-benzyl-benzene (1). 12.5 g of 2-bromobenzyl bromide was dissolved in 150 ml of benzene. 2.5 ml of 1 M $AlCl_3$ in nitrobenzene solution was injected under nitrogen. The solution was refluxed for 5 h. The reaction mixture was extrated using 500 ml of ether. The solution was dried over $MgSO_4$ and the solvent evaporated. The reaction mixture was purified by column chromatography using hexane as the eluent. (R_f = 0.35) The product was a colorless liquid, produced in 93% yield. Bp: 128–132 °C, ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.10 (s, 2H), 7.0–7.3 (m, 8H), 7.56 (d, 1H, J = 9.17 Hz). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 41.57, 124.89, 126.23, 127.42, 127.85, 128.45, 128.98, 131.05, 132.81, 139.42, 140.35. Anal. calc. for $C_{13}H_{11}Br$: C, 63.18; H, 4.49. Found: C, 62.61; H, 5.03%, MS (EI): m/z 246.0 (M$^+$).

10*H*-Spiro[anthracene-9,9′-(2′,7′-dibromofluorene)] (3). 0.18 g of Mg was charged into a two-neck flask and flame-dried. 1.8 g of **1** in 40 ml of THF was added to the flask. The reaction mixture was refluxed for 1 h under nitrogen and cooled to room temperature. 2,7-Dibromofluorenone was rapidly added to the reaction mixture, which was then refluxed for 2 h. After cooling the reaction mixture, precipitate was obtained and 400 ml of hexane was added to obtain more precipitate. The reaction mixture was filtered and the filtrate was transferred to a two-neck flask. 50 ml of acetic acid and a few drops of concentrated HCl was added to the flask and followed by refluxing for 3 h. The reaction mixture was cooled and 20 ml of water was slowly added. The resulting white crystals were collected and recrystallized from dichloromethane and methanol (Yield 77%). Mp: 273 °C, ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 4.48 (s, 2H), 6.42 (d, 2H, J = 7.5 Hz), 6.97 (dd, 2H, J = 7.7, 7.3 Hz), 7.11 (d, 2H, J = 1.8 Hz), 7.22 (dd, 2H, J = 7.5, 7.3 Hz), 7.41 (d, 2H, J = 7.7 Hz), 7.47 (dd, 2H, J = 8.2, 1.8 Hz), 7.63 (d, 2H, J = 8.2). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 34.41, 59.48, 121.46, 122.25, 126.90, 127.20, 127.62, 128.66, 128.68, 131.00, 134.12, 137.30, 138.27, 157.37. Anal. calc. for $C_{26}H_{16}Br_2$: C, 63.96; H, 3.30. Found: C, 63.60; H, 3.46%, MS (EI): m/z 488.0 (M$^+$).

10,10-Bis(2-ethylhexyl)-10*H*-spiro[anthracene-9,9′-(2′,7′-dibromofluorene)] (4). 1.46 g of **2**, an excess of KH, a catalytic amount of 18-crown-6 and 25 ml of THF were placed in a two-neck flask. 0.64 ml of 2-ethylhexyl bromide was injected and the solution stirred for 5 h at room temperature. The remaining KH was deactivated by the addition of methanol. The reaction mixture was extracted with 300 ml of ether. The solution was dried over $MgSO_4$ and evaporated. The reaction mixture was purified by column chromatography using hexane as the eluent (R_f = 0.29, Yield 80%). Mp: 150–155 °C, ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.63 (t, 6H, J = 7.0 Hz), 0.72 (t, 6H, J = 6.8 Hz), 0.75–1.10 (m, 16H), 1.26 (m, 2H), 2.17 (m, 4H), 6.24 (d, 2H, J = 7.9 Hz), 6.86 (dd, 2H, J = 8.1, 7.2 Hz), 7.01 (d, 2H, J = 1.8 Hz), 7.17 (dd, 2H, J = 7.9, 7.2), 7.45 (dd, 2H, J = 8.1, 1.8 Hz), 7.50(d, 2H, J = 8.1 Hz), 7.64 (d, 2H, J = 8.1 Hz). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): δ 9.45, 13.86, 22.82, 25.81, 27.24, 32.99, 34.12, 45.53, 50.14, 58.09, 121.23, 122.44, 126.39, 126.79, 127.59, 128.75, 128.97, 130.69, 135.85, 138.30, 139.30, 159.95. Anal. calc. for $C_{42}H_{48}Br_2$: C, 70.79; H, 7.79. Found: C, 70.41; H, 7.27%, MS (EI): m/z 712.3 (M$^+$).

Poly[10,10-bis(2-ethylhexyl)-10*H*-spiro(anthracene-9,9′-fluorene)-2′,7′-diyl] (PEHSAF). 0.69 g of bis(2,5-cyclooctadiene)-nickel(0), 0.39 g of dipyridyl and 0.30 ml of 1,5-cyclooctadiene were placed in a two-neck flask. 15 ml of anhydrous DMF was injected and the solution then stirred at 80 °C for 30 min. 0.712 g of **3** in 60 ml of toluene was injected into the solution which was then stirred at 80 °C for 48 h. The reaction mixture was poured into a mixture of 250 ml of methanol and concentrated HCl (methanol : HCl = 8 : 2). The precipitate was collected, redissolved in chloroform and reprecipitated several times using methanol. The resulting polymer was a yellowish powder (Yield 61%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 0.61 (br, 12H), 0.94 (br, 16H), 1.47 (br, 4H), 2.19 (br, 2H), 6.24 (br, 2H), 6.74 (br, 2H), 7.14 (br, 6H), 7.50 (br, 4H). Anal. calc. for $C_{42}H_{48}$: C, 91.25; H, 8.75. Found: C, 89.74; H: 10.01%.

Device fabrication

The PEHSAF based polymer LEDs were fabricated with the structure of ITO/PEDOT (60 nm)/PEHSAF (70 nm)/LiF (5 nm)/Ca (10 nm)/Ag. The glass substrate pre-coated with indium-tin-oxide was cleaned in an ultrasonic bath with acetone, followed by boiling 2-propanol. Surface treatment was carried out by exposing the ITO to UV-ozone. The hole injecting poly(3,4-ethylene dioxythiophene) (PEDOT) layer was spin coated on the ITO with a thickness of 60 nm and baked at 130 °C for 10 min on a hot plate. A 1.5 wt% solution of PEHSAF in a toluene was spin coated on the PEDOT layer as an emitting layer and baked at 130 °C for 1 h. LiF and Ca were deposited as the cathode through a shadow mask by thermal evaporation. Finally, a Ag layer was deposited as a protecting layer. The sample spot size was 1 mm in diameter in our measurement.

Results and discussion

Synthesis and characterization

The synthetic scheme for the polymer is shown in Scheme 1. **1** was synthesized from bromobenzyl bromide *via* a Friedel–Craft alkylation using benzene as the solvent. The reaction was monitored by gas chromatography rather than TLC because **1** had the same R_f value as the starting material. **1** was obtained as a colorless liquid in 93% yield. **3** was prepared using a method very similar to that employed to synthesize spirobifluorene.[17] A solution of **1** in anhydrous THF was added to flame dried magnesium and the solution refluxed for 2 h. After Grignard reagent formation, the colorless reaction mixture became yellowish. The solution was cooled to rt and 2,7-dibromofluorenone was added to the solution. The reaction mixture was refluxed for 1 h and cooled to room temperature again. When the temperature of the reaction mixture reached rt, **2** was precipitated as a white powder due to its low solubility in THF. To increase the yield of this polar complex hexane, which is one of the most non-polar solvents, was added. The precipitate was filtered, washed with hexane and dried. The resulting precipitate had a high purity, as confirmed by chromatography and was used without any other purification. To a solution of **2** in acetic acid, a few drops of concentrated HCl was added. At rt, **2** in acetic acid remained as an insoluble powder. As the temperature was increased, the solution became clear. After refluxing for 1 h, the solution was slowly cooled to rt. As the temperature was decreased, white crystals formed. The crystals were dissolved in chloroform and methanol was added dropwise to the solution until the transparent solution became turbid. After cooling for a few hours in the refrigerator, pure **3** was obtained as crystals in a 77% yield.

Ethylhexyl groups were introduced into **3** through a crown ether catalyzed reaction. Due to the low reactivity of the proton at the C-10 position of dihydroanthracene, we were not able to introduce alkyl chains by conventional methods. The pK_a of a dihydroanthracene is about 30, while that of fluorene is about 22.[40] The proton at the C-10 position of **3** could be abstracted by a very strong base, potassium hydride. Because the base was reactive, it was used in an emulsion state, and as a result it was not possible to measure the exact amount of the base. Although the proton could be removed by an excess of potassium hydride under reflux, the reaction time and reaction temperature could be reduced when the crown ether catalyst was used. The reaction was complete after 5 h at room temperature. After the reaction was complete, methanol was added dropwise to deactive the remaining active potassium hydride. The reaction mixture was extracted, dried and the solvent evaporated. The reaction mixture was purified by column chromatography and **4** was obtained as a white powder in 80% yield.

The Ni(0)-mediated polymerization was carried out following a procedure described in the literature.[41] About 2.5 eq. of bis(2,5-cyclooctadiene)nickel(0), dipyridyl and cyclooctadiene was dissolved in anhydrous DMF and stirred at 80 °C for 30 min. The mixture became a dark blue color and a solution of **4** in anhydrous toluene was added. The reaction mixture was stirred at 80 °C for 48 h and poured into a mixture of 250 ml of methanol and concentrated HCl (methanol : HCl = 8 : 2). The obtained yellowish powder was filtered and redissolved in hot chloroform and added dropwise to stirred methanol. The precipitation process was repeated several times. PEHSAF was obtained as a yellowish white powder in 61% yield.

The molecular weight of the polymer was determined by gel permeation chromatography (GPC) analysis in a THF solution calibrated against polystyrene standards. The GPC analysis of the PEHSAF showed a monomodal distribution with a number-average molecular weight (M_n) of 14000 g mol^{-1} and a weight-average molecular weight (M_w) of 43000 g mol^{-1}. The polymer was soluble in common organic solvents such as toluene.

Thermal properties

The thermal properties of the synthesized PEHSAF were characterized. TGA showed a 5% weight loss at 367 °C. No clear phase transition including T_g was observed before the decomposition from DSC. Due to the very bulky and rigid spiro-anthracene structure nearly no segmental motion of the polymer backbone would be possible even at an elevated temperature and, therefore, the polymer would be expected to possess enhanced thermal resistance to aggregate formation.

Optical properties

The optical properties of the polymer are shown in Fig. 1. The absorption onset and absorption maximum in solution appeared at 423 nm (the corresponding optical band-gap is 2.94 eV) and 399 nm, respectively. The PL spectrum of a PEHSAF solution showed an emission maximum at 425 nm with a vibronic feature at 446 nm. The emission peaks of the PEHSAF nearly coincide with those of PFs, indicating that the introduction of the spiro-structure does not disturb the conjugation of the phenyl groups. The emission spectrum of the PEHSAF film showed emission maximum at 418 nm with a slightly broader shape. This phenomenon has been attributed to a higher degree of disorder in the case of bulky group

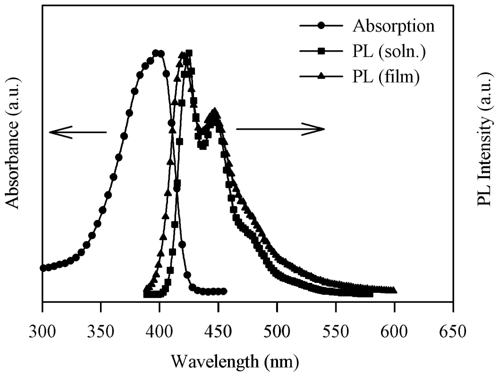


Fig. 1 Optical properties of PEHSAF.

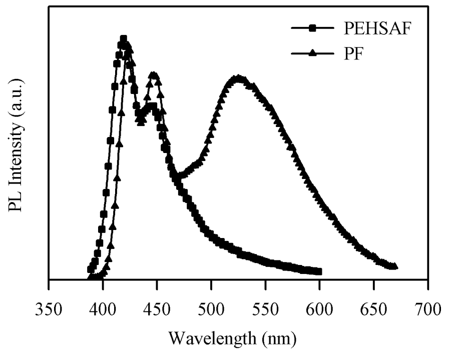


Fig. 2 PL spectra of PEHSAF and PF after annealing at 200 °C for 15 and 4 h, respectively.

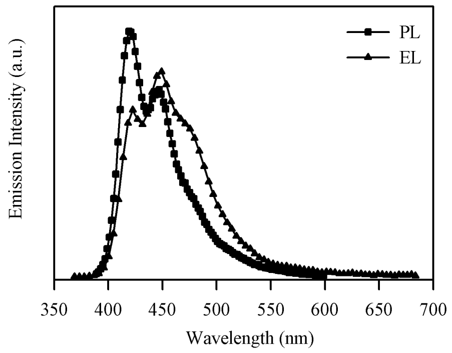


Fig. 4 PL and EL spectra of PEHSAF.

substituted PFs, which leads to a larger inhomogeneous broadening.[42]

Fig. 2 shows the PL spectra of PEHSAF and dihexyl substituted PF (PF6), for comparison, after heat treatment. From the DSC measurement we expected that the polymer should have an enhanced thermal resistance to aggregate formation and an enhanced spectral stability. Therefore, we annealed the polymer film under very severe conditions, 200 °C in air. In the case of the PEHSAF film that was annealed for 15 h, nearly no change was observed, while the emission of PF6 film changed within 4 h. In the case of the PF film, the broad band emission centered at 530–540 nm gradually increased and after 15 h of annealing, the orignal feature of the emission spectrum nearly disappeared. There are two reasons for this enhanced spectral stability. The first is that the spiroanthracene structure of the PF backbone efficiently protected the conjugated polymer backbone from other polymer backbones. Therefore, π-stacking and aggregate formation would be minimized even at high temperature due to its bulky and rigid structure. The second is the high resistance toward oxidative degradation. In the case of PF6, oxidative degradation occurs at the C-9 position of fluorene. However, the C-9 position of spiro-structured fluorenes consists of only stronger C_{sp^2}–C_{sp^3} bonds therefore would be more stable toward oxidative degradation.[38] The C-10 position of dihydroanthracene may be degraded as well. However, as already mentioned, the low reactivity of the C-10 reaction site could provide an enhanced stability toward oxidative degradation compared to the C-9 position of fluorene structures.

To investigate the stability of PEHSAF with respect to photo-oxidative degradation, we compared the PL spectra of PEHSAF and PF films after UV irradiation as shown in Fig. 3. The polymer films were irradiated using a 500 W xenon lamp directly in air for 3 min. The PL spectrum of PEHSAF film showed almost no change, while that of the PF film lost its original features. The intensity of the low energy PL features in the solid state could also be affected by the mobility of the excitons and the bulky spiroanthracene substituent could cause an increased interchain distance and a hindered transport of excitons to defects leading to the reduced intensity of the low energy PL features. However, the result, nearly no change, implies that the polymer not only has a high resistance to aggregate formation but also has high resistance to oxidative degradation.

Device characterization

PEHSAF-based EL devices were fabricated with the configuration ITO/PEDOT (60 nm)/PEHSAF (70 nm)/LiF (5 nm)/Ca (10 nm)/Ag (150 nm). The devices were fabricated on ITO coated glass cleaned by a conventional process. The PEDOT layer was used as a hole injecting layer and PEHSAF as the emitting layer. A LiF/Ca cathode which is one of the most efficient for electron injection was used.[43] The reactive Ca layer was capped by a Ag protecting layer. The EL spectrum of the device is shown in Fig. 4. The EL spectrum of PEHSAF in Fig. 4 is somewhat different from its PL spectrum. This phenomenon has been attributed to self absorption of the emitting material.[44] Due to the overlap of the 0–0 transition emission band and the absorption band, self absorption occurs and the relative intensity of the 0–0 transition band decreased. Therefore, the relative intensity of 0–1 and 0–2 transition emission band increased. When we fabricated a PEHSAF-based EL device with a thinner PEHSAF layer (40 nm), the EL spectrum of the device was nearly the same as the PL spectrum (not shown). This indicates that the difference between EL and PL spectra is due to self absorption. However, the decreased thickness of emitting layer led to a decreased efficiency. Although the EL spectrum of the device was different from its PL spectrum, the emission spectrum remained in the deep blue region with CIE 1931 color coordinates of $x = 0.17$ and $y = 0.12$. More importantly, the emission remained unchanged over the entire operating voltage range and under continuous operation with a high current passage. The I–V–L characteristics of the device are shown in Fig. 5. The device showed a turn on voltage at 6 V and a maximum luminance of over

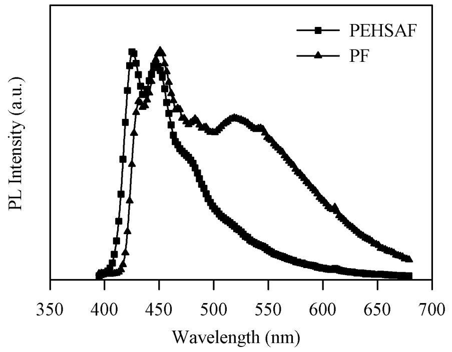


Fig. 3 PL spectra of PEHSAF and PF after irradiation for 3 min (500 W xenon lamp under air).

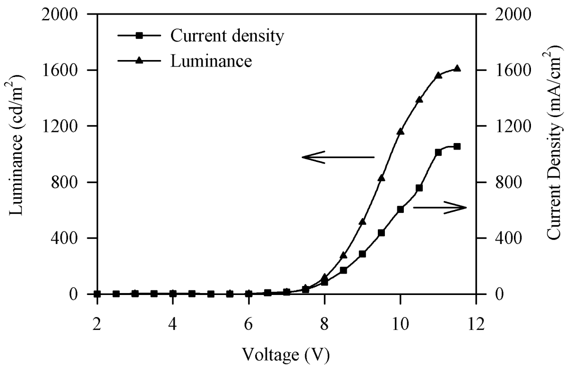


Fig. 5 I–V–L characteristics of a PEHSAF based EL device.

1600 cd m^{-2} at 11.5 V. The maximum efficiencies were 0.20% of external quantum efficiency, 0.06 lm W^{-1} of power efficiency, and 0.19 cd A^{-1} of luminance efficiency at 10 V with 1156 cd m^{-2} luminance.

Conclusion

A novel fully spiro-functionalized PF derivative containing a spiroanthracenefluorene unit has been synthesized. The bulky spiroanthracenefluorene structure improved the thermal and optical properties of the resulting polymer. The polymer showed a deep blue emission with a high spectral stability against heat treatment, UV irradiation, and high current passage. An EL device based on the polymer showed good color coordinates with CIE 1931 $x = 0.17$ and $y = 0.12$ and a maximum luminance over 1600 cd m^{-2}. These favorable thermal and optical properties suggest that polymers containing spiroanthracenefluorenes represent promising candidate materials for commercial PLED applications.

Acknowledgements

The authors would like to thank Dr. Soo-Hyoung Lee of Samsung Advanced Institute of Technology for helpful discussion.

References

1 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
2 J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. B. Roitman and A. Stocking, *Science*, 1996, **273**, 884.
3 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Loglund and W. R. Salaneck, *Nature*, 1999, **397**, 121.
4 M. Rehaln, A.-D. Schlüter, G. Wegner and W. J. Feast, *Polymer*, 1989, **30**, 1054.
5 Y. Yang, Q. Pei and A. J. Heeger, *J. Appl. Phys.*, 1996, **79**, 934.
6 N. Tanigaki, H. Masuda and K. Kearlyama, *Polymer*, 1997, **38**, 1221.
7 M. Rehahn, A. D. Schlüter and G. Wegner, *Macromol. Chem.*, 1990, **191**, 1991.
8 M. T. Bernius, M. Inbasekaran, J. O'Brien and W. Wu, *Adv. Mater.*, 2000, **12**, 1737.
9 M. T. Bernius, M. Inbaskaran, J. O'Brien and W. Wu, *Adv. Mater.*, 2000, **12**, 1737.
10 M. Leclerc, *J. Polym. Sci. Part A: Polym. Chem.*, 2001, **39**, 2867.
11 M. Kreyenschmidt, G. Klaerner, T. Fuhrer, J. Ashenhurst, S. Karg, W. D. Chen, V. Y. Lee, J. C. Scott and R. D. Miller, *Macromolecules*, 1998, **31**, 1099.
12 M. Ranger, D. Rondeau and M. Leclerc, *Macromolecules*, 1997, **30**, 7686.
13 A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu and E. P. Woo, *Appl. Phys. Lett.*, 1998, **73**, 629.
14 W. Yu, Y. Cao, J. Pei, W. Huang and A. J. Heeger, *Appl. Phys. Lett.*, 1999, **21**, 3270.
15 M. Grell, D. D. C. Bradley, G. Ungar, J. Hill and K. S. Whitehead, *Macromolecules*, 1999, **32**, 5810.
16 K.-H. Weinfurtner, H. Fujikawa, S. Tokito and Y. Taga, *Appl. Phys. Lett.*, 2000, **76**, 2502.
17 W.-L. Yu, J. Pei, W. Huang and A. J. Heeger, *Adv. Mater.*, 2000, **12**, 828.
18 G. Klärner, J.-I. Lee, M. H. Davey and R. D. Miller, *Adv. Mater.*, 1999, **11**, 115.
19 J.-I. Lee, G. Klaerner and R. D. Miller, *Chem. Mater.*, 1999, **11**, 1083.
20 C. Xia and R. C. Advincula, *Macromolecules*, 2001, **34**, 5854.
21 S. Setayesh, A. C. Grimsdale, T. Weil, V. Enkelmann, K. Müllen, F. Meghdadi, E. J. W. List and G. Leising, *J. Am. Chem. Soc.*, 2001, **123**, 946.
22 X. Gong, P. K. Iyer, D. Moses, G. C. Bazan, A. J. Heeger and S. S. Xiao, *Adv. Funct. Mater.*, 2003, **13**, 325.
23 U. Scherf and E. J. W. List, *Adv. Mater.*, 2002, **14**, 477.
24 E. J. W. List, R. Guentner, P. S. de Freitas and U. Scherf, *Adv. Mater.*, 2002, **14**, 374.
25 J. M. Lupton, M. R. Craig and E. W. Meijer, *Appl. Phys. Lett.*, 2002, **80**, 4489.
26 G. Zeng, W.-L. Yu, S.-J. Chua and W. Huang, *Macromolecules*, 2002, **35**, 6907.
27 M. Gaal, E. J. W. List and U. Sherf, *Macromolecules*, 2003, **36**, 4236.
28 J. Pei, X.-L. Liu, Z.-K. Chen, X.-H. Zhang, Y.-H. Lai and W. Huang, *Macromolecules*, 2003, **36**, 323.
29 F.-I. Wu, R. Dodda, D. S. Reddy and C.-F. Shu, *J. Mater. Chem.*, 2002, **12**, 2893.
30 G. Klärner, M. H. Davey, W.-D. Chen, J. C. Scott and R. D. Miller, *Adv. Mater.*, 1998, **10**, 993.
31 G. Klärner, J.-I. Lee, V. Y. Lee, E. Chan, J.-P. Chen, A. Nelson, D. Makiewicz, R. Siemens, J. C. Scott and R. D. Miller, *Chem. Mater.*, 1999, **11**, 1800.
32 D. Marsitzky, J. Murray, J. C. Scott and K. R. Carter, *Chem. Mater.*, 2001, **13**, 4285.
33 A. P. Kulkarni and S. A. Jenekhe, *Macromolecules*, 2003, **36**, 5285.
34 D. Marsitzky, R. Vestberg, P. Blainey, B. T. Tang, C. J. Hawker and K. R. Carter, *J. Am. Chem. Soc.*, 2001, **123**, 6965.
35 A. Pogantsch, F. P. Wenzl, E. J. W. List, G. Leising, A. C. Grimsdale and K. Müllen, *Adv. Mater.*, 2002, **14**, 1061.
36 C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker and K. Meerholz, *Nature*, 2003, **421**, 829.
37 H. Becker, S. Heun, K. Treacher, A. Büsing and A. Falcou, *SID Digest Tech. Pap.*, 2002, **33**, 780.
38 K.-T. Wong, Y.-Y. Chen, R.-T. Chen, C.-F. Wang, Y.-T. Lin, H.-H. Chiang, P.-Y. Hsieh, C.-C. Wu, C. H. Chou, Y. O. Su, G.-H. Lee and S.-M. Peng, *J. Am. Chem. Soc.*, 2002, **124**, 11576.
39 R. G. Clarkson and M. Gomberg, *J. Am. Chem. Soc.*, 1930, **52**, 2881.
40 F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish and X. Zhang, *J. Am. Chem. Soc.*, 1991, **113**, 9790.
41 S. Setayesh, D. Marsitzky and K. Müllen, *Macromolecules*, 2000, **33**, 2016.
42 J. M. Lupton, P. Schouwink, P. E. Keivanidis, A. C. Grimsdale and K. Müllen, *Adv. Funct. Mater.*, 2003, **13**, 154.
43 T. M. Brown, R. H. Friend, I. S. Millard, D. J. Lacey, J. H. Burroughes and F. Cacialli, *Appl. Phys. Lett.*, 2002, **79**, 174.
44 S. Tasch, A. Niko, G. Leising and U. Scherf, *Appl. Phys. Lett.*, 1996, **68**, 1090.