ORGANIC LETTERS

2005
Vol. 7, No. 19
4229−4232

Synthesis of a Double Spiro-Polyindenofluorene with a Stable Blue Emission

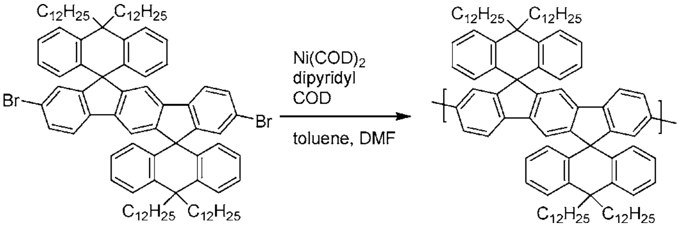
Doojin Vak,[†] Bogyu Lim,[†] Soo-Hyoung Lee,[‡] and Dong-Yu Kim*,[†]

*Center for Frontier Materials, Department of Materials Science and Engineering,
Gwangju Institute of Science and Technology, 1 Oryong-dong, Buk-gu,
Gwangju, Korea, and Opto Electronic Materials Research Center, Korea Institute of
Science and Technology, 39-1 Hawolgok-dong, Seongbuk-gu, Seoul, Korea*

kimdy@gist.ac.kr

Received July 14, 2005

ABSTRACT



A novel polyindenofluorene containing a double spiro-anthracene structure with solublizing alkyl groups was synthesized. Enhanced spectral stability of the polymer was investigated by heat treatment and photoirradiation in air. The EL spectrum of the polymer showed an enhanced sensitivity to the human eye and good color purity as a blue-emitting material.

Conjugated polymers have received a great deal of attention for use in organic light-emitting diodes (OLEDs).[1] In particular, blue-emitting polymers such as poly-*p*-phenylenes (PPPs), polyfluorenes (PFs), polyindenofluorenes (PIFs), and ladder-type PPPs (LPPPs) have been studied extensively.[2] This is because there are fewer efficient and stable blue-emitting materials compared to green- and red-emitting materials. Among the blue-emitting polymers, PFs are regarded as the most promising candidates for OLED because PFs have several merits with regard to both synthetic strategy and intrinsic characteristics such as a high photoluminescence (PL) efficiency and a high thermal stability.[3] However, recent research has focused on blue-emitting materials with a longer conjugation length due to the sensitivity of the human eye.[4] The intrinsic emission of PFs has an emission maximum at a very low sensitive region to the human eye. In comparison, PIFs and LPPPs have emission maxima in regions two or three times as sensitive.[5] On the other hand, color purity is also one of the essential elements of emitting materials of OLEDs. Therefore, PIFs were regarded as one of the ideal materials and were recently studied intensively.

Although the intrinsic emission of PIFs satisfies both relative eye sensitivity and color purity, not only PFs but also PIFs suffer from degradation of emission spectra. The

---

[†] Gwangju Institute of Science and Technology.

[‡] Korea Institute of Science and Technology.

(1) (a) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D. B.; Stocking, A. *Science* **1996**, *273*, 884. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Loglund, M.;; Salaneck, W. R. *Nature* **1999**, *397*, 121.

(2) (a) Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog. Polym. Sci.* **2000**, *25*, 1089. (b) Sherf, U. *J. Mater. Chem.* **1999**, *9*, 1853.

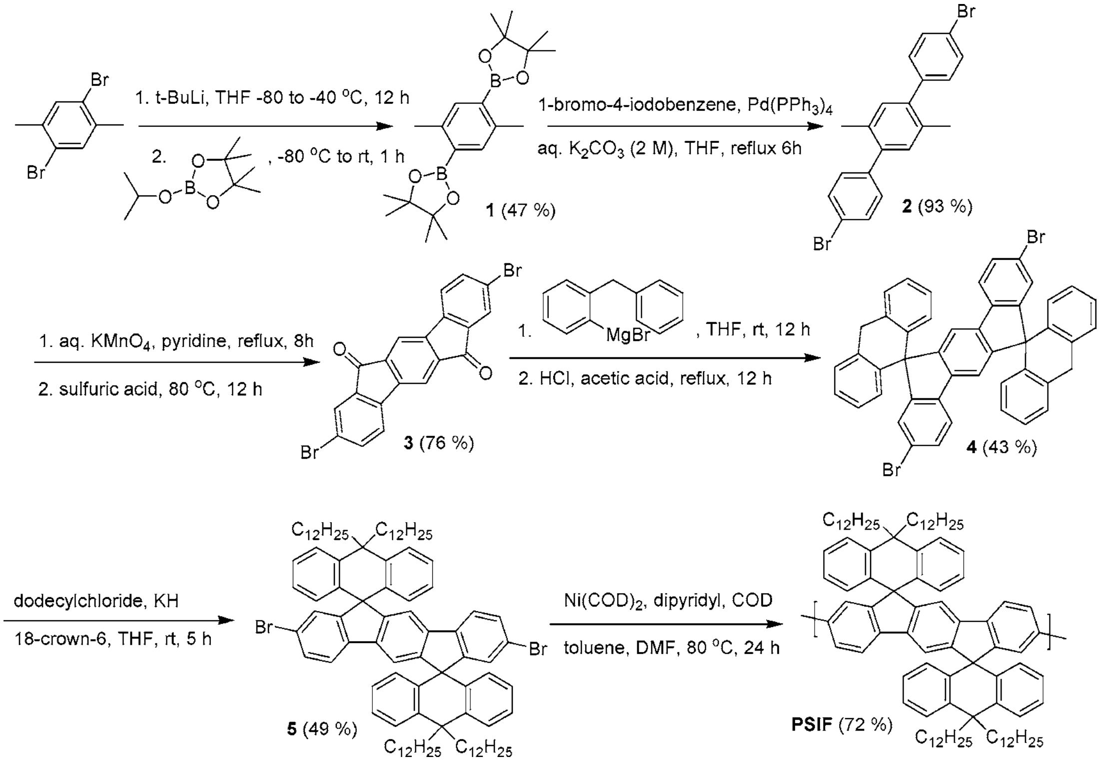
(3) (a) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686. (b) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D. Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099. (c) Bernius, M. T.; Inbaskaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737.

(4) (a) Setayesh, S.; Marsitzky, D.; Müllen, K. *Macromolecules* **2000**, *33*, 2016. (b) Jacob, J.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Gaal, M.; E. J. W. *Macromolecules* **2003**, *36*, 8240. (c) Sonar, P.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; Surin, M.; Lazzaroni, R.; Leclère, P.; Tierney, S.; Heeney, M.; McCulloch, I. *Macromolecules* **2004**, *37*, 709.

(5) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987.

10.1021/ol051661+ CCC: $30.25

Scheme 1



emission spectra of polymers were altered by the appearance of a troublesome broadband emission (around 540 nm region) during device operation, heat treatment, and photoirradiation. This phenomenon was explained by a physical degradation model, i.e., aggregate formation,[6] and chemical degradation model, i.e., keto-defect formation.[7] Although the two models attributed the degradation to issues of completely different origin, most previous reports concluded that the introduction of bulky phenyl side groups instead of long alkyl chains can effectively suppress the degradation.[8] Among various bulky phenyl structures, spirobifluorene structure appears to be one of the most promising solutions.[9]

Recently, we reported poly[10,10-bis(2-ethylhexyl)-10*H*-spiro(anthracene-9,9′-fluorene)-2′,7′-diyl] (PEHSAF), which contains a spiroanthracenefluorene (SAF) rather than a spirobifluorene.[10] The SAF structure still contains the useful spiro structure and, at the same time, permits the facile functionalization at the C-10 position of the dihydroanthracene unit, where solubilizing side chains can be easily introduced. The polymer showed not only stable photoluminescence (PL) spectra after thermal treatment and photoirradiation but also showed excellent characteristics as an organic laser material. The polymer showed amplified spontaneous emission up to 250 °C (limited by the apparatus) with very low optical loss (loss coefficient $= 0.8\ \mathrm{cm}^{-1}$) and higher PL efficiency than PFs.[11]

In this paper, we report on the synthesis and characterization of a new spiroanthracene-configured PIF derivative for both optimized emission spectra and enhanced stability.

The synthetic scheme for the polymer is shown in Scheme 1. Compound **1** was synthesized by the addition of an excess amount of *tert*-butyllithium to dibromoxylene in a tetrahydrofuran (THF). The reaction mixture was stirred at -40 °C for 12 h after the addition of *tert*-buthyllithium at -80 °C. An addition of 2-isopropoxy-4,4,5,6-tetramethyl-1,3,2-dioxaborolane at -80 °C provided compound **1**. For the synthesis of compound **2**, we used 1-bromo-4-iodobenzene. Due to the higher reactivity of the iodine group compared to that of the bromine group for the Suzuki coupling, the coupling reaction of 1-bromo-4-iodobenzene with compound **1** occurred only at the iodine position of 1-bromo-4-iodobenzene, and we found only compound **2** by GC/MS

---

(6) (a) Weinfurtner, K. H.; Fujikawa, H.; Tokito, S.; Taga, Y. *Appl. Phys. Lett*. **2000**, *76*, 2502. (b) Grell, M.; Bradley, D. D. C.; Ungar, G.; Hill, J.; Whitehead, K. S. *Macromolecules* **1999**, *32*, 5810 (c) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854. (d) Zeng, G.; Yu, W. L.; Chua, S. J.; Huang, W. *Macromolecules* **2002**, *35*, 6907.

(7) (a) Gong, X.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S. *Adv. Funct. Mater*. **2003**, *13*, 325. (b) List, E. J. W.; Guentner, R.; de Freitas, P. S.; Scherf, U. *Adv. Mater*. **2002**, *14*, 374. (c) Scherf, U.; List, E. J. W. *Adv. Mater*. **2002**, *14*, 477. (d) Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *J. Chem. B* **2004**, *108*, 8689.

(8) (a) Yu, W. L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater*. **2000**, *12*, 828. (b) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, R. R. *J. Am. Chem. Soc*. **2001**, *123*, 6965. (c) Pogantsch, A.; Wenzl, F. P.; List, E. J. W.; Leising, G.; Grimsdale, A. C.; Müllen, K. *Adv. Mater*. **2002**, *14*, 1061. (d) Wu, Y.; Fu, Y.; Bo, Z. *Org. Lett*. **2004**, *6*, 3485.

(9) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829.

(10) Vak, D.; Chun, C.; Lee, C. L.; Kim, J.-J.; Kim, D.-Y. *J. Mater. Chem*. **2004**, *14*, 1342.

(11) Xia, R.; Heliotis, G.; Campoy-Quiles, M.; Stavrinou, P. N.; Bradley, D. D. C.; Vak, D.; Kim, D.-Y. *J. Appl. Phys.* Submitted.

analysis. Compound **3** was synthesized by a modified literature procedure for the synthesis of indenofluorene.[12] Two methyl groups of **2** were oxdized by $KMnO_4$ to form carboxylic acids. The compound was cyclized in hot sulfuric acid. After reaction for 12 h at 80 °C, the solution poured into an ice bath and a violet powder was precipated. The precipitates were nearly insoluble in various organic solvents. Therefore, the precipitates were purified by a solvent washing process using water, methanol, and boiling THF. Because only compound **3** in the reaction mixture was insoluble in the solvents, there was nearly no other material remaining. The purity of the compound was confirmed by elemental analysis.

Compounds **4** and **5** were synthesized in nearly the same manner as for synthesis of the mono-spiro-configured structure.[10] A Grignard reagent was formed by addition of 1-bromo-2-benzylbenzene to flame-dried Mg, and then **3** powder was added to the Grignard reagent solution. Because **3** was nearly insoluble in THF, reaction could occur only on the surface of **3** powders. Therefore, more reaction time was required for the reaction of **3** with the Grignard reagent. After the reaction complete, we obtained a soluble intermediate. The compound was cyclized via typical conditions for the synthesis of spiro compounds. Four dodecyl groups were attached to **4** in situ using KH and 18-crown-6 as a phase-transfer catalyst. Compound **5** was polymerized via a nickel-mediated polymerization to form PSIF. 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 PSIF showed a monomodal distribution with a number-average molecular weight (M_n) of 24 000 g/mol and weight-average molecular weight (M_w) of 80 000 g/mol. The polymer was soluble in common organic solvents such as toluene, THF, chloroform, and chlorobenzene.

The absorption and photoluminescence (PL) spectra of the polymer were also measured. The absorption maximum and emission maximum of the polymer solution appeared at 419 and 433 nm, respectively. These values are nearly identical to tetraoctyl substituted PIF.[4a] In comparison, the emission maximum of the polymer film appeared at 445 nm, which is slightly red-shifted from that of tetraaryl-substituted PIF,[4b] with a slightly broader shape. This phenomenon is probably due to the higher degree of disorder of the bulky structured polymer, called inhomogeneous broadening,[13] and/or the partial overlap of spiro phenyl rings with conjugated polymer backbone, called spiro-conjugation.[14] However, the wavelength of the polymer is nearly ideal as a blue emitter, since 440−450 nm is the preferred emission maximum to satisfy both color purity and relative eye sensitivity.[5]

To determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level, cyclic voltammetry measurements were carried out. The oxidation potential of the polymer was measured against that of a silver electrode and calibrated by comparison of the half-wave potential of ferrocene/ferrocenium redox couple. The HOMO level appeared at 5.72 eV, and the LUMO was determined by subtracting the optical band gap, 2.83 eV (which corresponds to absorption onset at 438 nm).

Thermal properties were characterized by means of TGA and DSC. The curves are shown in Figure 1**.** PSIF showed a 5% weight loss at 399 °C which is a typical value for PFs. In contrast, no significant phase transition including Tg was detected from DSC. We attempted several times to detect Tg using DSC several times. However, Tg was not detected even after super cooling of the sample using liquid nitrogen at 300 °C. We observed a similar behavior for the spiroanthracene configured PF, PEHSAF. This phenomenon is probably due to the very bulky and rigid spiro-anthracene structure. Almost no segmental motion of the polymer backbone would be possible even at an elevated temperature. Therefore, the polymer would be expected to possess an enhanced thermal resistance to aggregate formation.

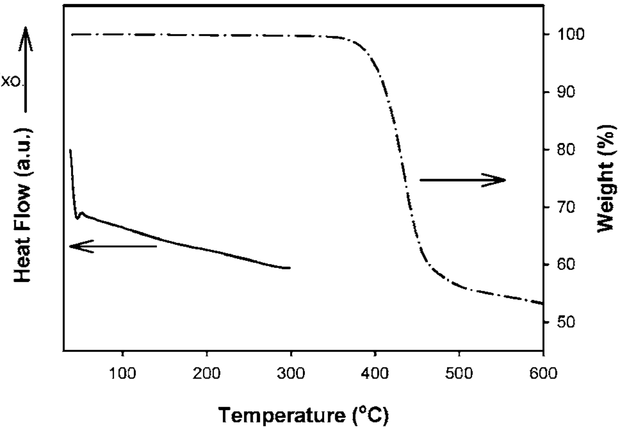


Figure 1. TGA (dash dot line) and DSC (solid line) curves of PSIF.

To investigate the stability of the polymer toward aggregate formation and oxidation, heat treatment and photoirradiation of the polymer film were carried out. Figure 2a shows the PL spectra of the PSIF film after annealing at 200 °C in air for 1 and 4 h, respectively. Although the polymer was annealed at a high temperature, only a small change was found. The inset is the PL spectra of PF before and after annealing 4 h at 200 °C for comparison. The result clearly shows the enhancement of stability of the polymer with respect to aggregate formation and/or thermo-oxidation.

Figure 2b shows the PL spectra of PSIF after photoirradiation for 3 min in air, almost no change was observed after photoirradiation while PL spectra of PF obviously changed. The inset shows the PL spectra of PF before and after photoirradiation. This result also shows the enhanced stability of the polymer.

We fabricated an OLED using PSIF. The electroluminescence (EL) spectra of PSIF and PEHSAF with a relative eye

---

[12] Merlet, S.; Birau, M.; Wang, Z. Y. *Org. Lett*. **2002**, *4*, 2157.

[13] Lupton, J. M.; Schouwink, P.; Keivanidis, P. E.; Grimsdale, A. C.; Müllen, K. *Adv. Funct. Mater*. **2003**, *13*, 154.

[14] Simmons, E.; Fukunaga, T. *J. Am. Chem. Soc.***1967**, *89*, 5208.

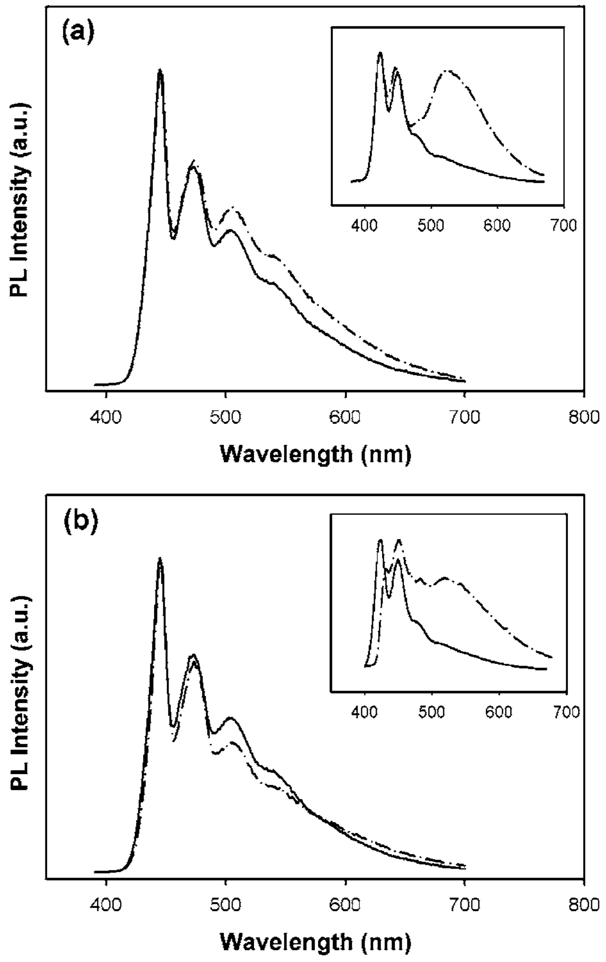


Figure 2. (a) PL spectra of PSIF (solid line) and PL spectra of PSIF after 4 h of annealing at 200 °C in air (dash dot line). The inset shows PL spectra of PF before and after annealing with the same conditions for comparison. (b) PL spectra of PSIF (solid line) and PL spectra of PSIF after photo irradiation by a 500 W xenon lamp in air for 3 min (dash dot line). The inset shows PL spectra of PF before and after photoirradiation with the same conditions.

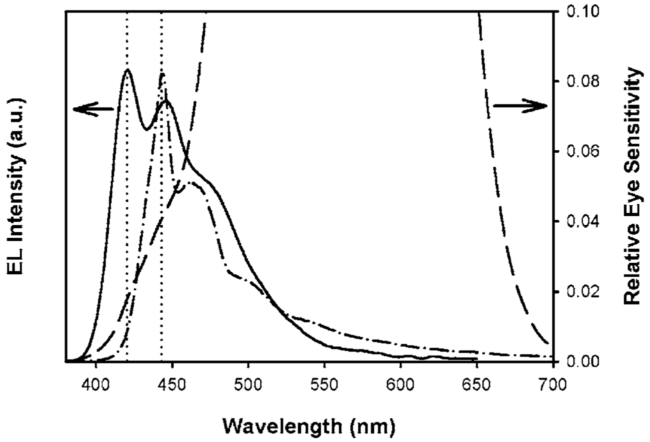


Figure 3. EL spectra of PSIF (dash dot line) and PEHSAF (a spiro PF, solid line) device with a relative eye sensitivity curve (long dash line).

sensitivity curve are shown in Figure 3. As shown in the figure, the EL spectrum of PSIF has a narrower shape with nearly the same peak positions as the PL spectrum. The emission maximum of PSIF is 445 nm and relative eye sensitivity, i.e., the photopic luminous efficiency, in the wavelength appeared about 2.3 times of that of PEHSAF, a single spiro PF, which has nearly the same emission wavelength as typical PFs. Although the emission maximum of the EL spectrum was red-shifted from that of typical PF, the CIE color coordinate was still in the deep blue region with $x = 0.18$, $y = 0.16$ due to its narrow spectrum shape.

In summary, we synthesized a new spiro-configured polyindenofluorene. The polymer showed an enhanced stability toward aggregate formation and thermo/photooxidation. The emission maximum of the polymer appeared in the 2.3 times more eye sensitive wavelength region compared to a spiro PF, while the emission was still in the deep blue region with the CIE 1931 color coordinate of $x = 0.18$, $y = 0.16$.

Acknowledgment. We gratefully acknowledge Samsung Advanced Institute of Technology, the Ministry of Science and Technology, and the National Laboratory program of KOSEF for their financial support.

Supporting Information Available: Detailed experimental procedures, characterization of the compounds, and NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL051661+