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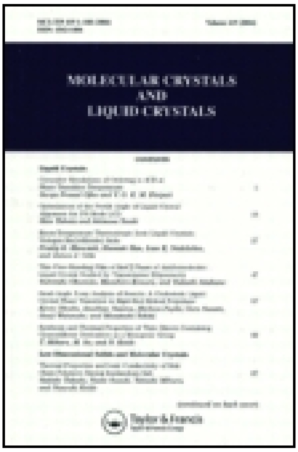

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Synthesis and Characterization of Violet Light Emitting Polymer based on Fluorene and Dimethylsilane

Dong-Soo Bae [a] , Dong-Hyun Lee [a] , Don-Eon Eim [a] , Seung-Eun Hu [a] , Shihaw Jung [a] , Ran Kim [b] , Jaeyoung Hwang [c] & Yun-Hi Kim [b]

[a] Gyeongnam Science High School , Jinseong , Jinju , Korea

[b] Department of Chemistry and Engineering Research Institute , Gyeongsang National University , Chinju , Korea

[c] School of Materials Science & Engineering and Engineering Research Institute , Gyeongsang National University , Chinju , Korea

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DONG-SOO BAE,[1] DONG-HYUN LEE,[1] DON-EON EIM,[1]
SEUNG-EUN HU,[1] SHIHAW JUNG,[1] RAN KIM,[2]
JAEYOUNG HWANG,[3,*] AND YUN-HI KIM[2,*]

[1]Gyeongnam Science High School, Jinseong, Jinju, Korea
[2]Department of Chemistry and Engineering Research Institute, Gyeongsang National University, Chinju, Korea
[3]School of Materials Science & Engineering and Engineering Research Institute, Gyeongsang National University, Chinju, Korea

*New fluorene based light emitting polymer, poly[(4-(9,9-didecyl-9*H*-fluoren-2-yl) phenyl)dimethyl(phenyl)silane] (PFDPS), was synthesized by palladium-catalzed Suzuki coupling reaction. The obtained copolymer was characterized by ^{1}H-NMR, and IR-spectroscopy. The polymer showed good solubility in common organic solvents and weight average molecular weight of 16,300 with polydispersity index of 1.4. The maximum photoluminescence of the solution and film of the polymer was observed at 392 nm and 410 nm, respectively.*

The double-layered device with the configuration, ITO/PEDOT/PFDPS/LiF/Al structure has a turn-on voltage at about 5.5 V and maximum brightness of 9.40 cd/m^2, and emitted violet light at 414 nm.

Keywords Dialkylfluorene; dimethylsilane; PLEDs; violet light emitting polymer

Introduction

Polymeric light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene (PPV) were first realized in the 1990s [1]. PLEDs have been the subject of academic and industrial research in recent years due to their potential applications in large area displays, flexible display and general lighting [2–6]. For full color OLEDs display, it is very important to develop wide-band gap materials for achieving high color pure and efficient blue emission.

Recently, the blue light emission is particular importance in the development of PLEDs. Blue electroluminescence has been demonstrated in polycarbazoles, polyfluorenes, polyoxadiazoles, and polythiophenes [7–13]. Especially, poly(fluorene)s are attractive as active components of organic light emitting diodes because of their thermal and chemical stability

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*Address correspondence to Jaeyoung Hwang, School of Materials Science & Engineering and Engineering Research Institute, Gyeongsang National University, Chinju 660-701, Korea, E-mail: jaeyoung@gnu.ac.kr and Yun-Hi Kim, Department of Chemistry and Engineering Research Institute, Gyeongsang National University, Chinju 660-701 Korea, E-mail: ykim@gnu.ac.kr

and their exceptionally high solution and solid state fluorescence quantum yields (0.6–0.8) [14–18].

Moreover, the facile substitution at the 9-position of the fluorene monomer allows control of polymer properties such as solubility, processability, and morphology. In this regard, polyfluorenes are particularly promising for various optical applications. On the other hand, the emission color of these polymers can be easily tailored by modifying the molecular design of an organic material used in the polymer structures [16–21].

Thus, we designed new UV-violet light emitting polymer derived from fluorene and dimethydiphenylsilane. The introduction of δ-silicon interrupts the π conjugation to achieve UV-violet emission and inhibits intermolecular interaction because of its tetrahedral structure [22]. It is expected that the polymer can be deep blue material as well as host material for blue OLED because of its high band gap. Furthermore, the polymer will have amorphous nature due to its tetrahedral structure by introduction of dimethylsilane moiety.

The polymer was synthesized by well-known Suzuki coupling reaction. The thermal, optical, and electrochemical properties of poly[(4-(9,9-didecyl-9*H*-fluoren-2-yl)phenyl) dimethyl(phenyl)silane] (PFDPS) were investigated. The electroluminescence (EL) performances of PFDPS were evaluated using device configurations: ITO/PEDOT:PSS/ PFDPS/LiF/Al.

Experimental

Materials

All reagents and solvents were purchased from Sigma-Aldrich Chemical Co. and TCI Chemical. Tetrakis(triphenylphosphine)palladium($Pd(PPh_3)_4$) was purchased from Strem. Spectroscopic grade THF (Aldrich) was used for all absorption and emission experiments. PEDOT was purchased from Bayer. All other compounds were used as received.

Bis(4-bromophenyl)dimethylsilane (1). 1,4-Dibromobenzene (10.0 g, 42.4 mmol) was dissolved in dry Et_2O (300 mL) and cooled to −78°C under nitrogen. n-BuLi (2.5 M in hexanes, 17.0 mL, 42.4 mmol)was added into this solution dropwise and stirred for another 1 h at −78°C. Dichlorodimethylsilane (2.74 g, 21.2 mmol) was then added dropwise at this temperature. After the end of the addition, the solution was warmed slowly to room temperature and then stirred overnight. The reaction mixture was quenched with H_2O and extracted with Et_2O. The organic extracts were washed with brine and H_2O, and then dried over $MgSO_4$. After the solvent was evaporated, the crude product was purified by column chromatography (eluent = hexane/dichloromethane; 10:1 v/v). Yield: 29.8%. IR (KBr, cm^{-1}): 3100 (aromatic C—H str), 2900 (aliphatic C—H str), 1172(C-Br str): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.55 (s, 6H), 7.38 (m, 4H), 7.49 (m, 4H).

2,7-Dibromo-9,9-didecylfluorene (2). The compound was obtained by reported method [18]. Yield: 39.7%. FT-IR (KBr, cm^{-1}) 3100 (aromatic C—H str), 2900 (aliphatic C—H str): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.18 (m, 6H), 1.24 (m, 32H), 2.01 (m, 4H), 7.76 (m, 6H).

2,2′-(9,9-Didecyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3). The compound was obtained by reported method [23]. Yield: 64%. FT-IR (KBr, cm^{-1}) : 3100 (aromatic C—H str), 2900 (aliphatic C—H str), 1345(B-O str), 1420(C-O str): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.18 (m,6H), 1.41 (s, 24H), 1.24 (m, 32H), 2.01 (m, 4H), 7.76 (m, 6H).

Poly[(4-(9,9-didecyl-9H-fluoren-2-yl)phenyl)dimethyl(phenyl)silane] (PFDPS). The pol ymer was prepared from palladium catalyzed Suzuki coupling reaction. Tetrakis (triphenylphosphine) palladium(0) ($Pd(PPh_3)_4$) (0.14 g, 10 mol%) was added to the mixture of bis(4-bromophenyl)dimethylsilane (1) (0.53 g, 1.43 mmol) and 2,2′-(9,9-didecyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3) (1.0 g, 1.43 mmol), 2M K_2CO_3 (3.0 mL) and anhydrous THF (4.0 mL) under nitrogen atmosphere. After the reaction mixture was heated at 80°C under nitrogen atmosphere for 24 hr, bromobenzene was added, and then phenyl borate was added with small amounts of catalysts for end-capping. Then the reaction mixture was poured into the solution of 2N HCl. Finally, the crude polymer was dissolved in chloroform followed by the addition of methanol to afford the desired polymer. Yield: 26.7%. FT-IR (KBr, cm^{-1}) : 3100 (aromatic C—H str), 2924 (aliphatic C—H str): ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.66 (s, 14H), 0.67 (m, 6H), 2.05 (m, 4H), 0.78 (m, 32H), 0.85 (m, 6H).

Instruments for Characterization

^{1}H-NMR spectra data were expressed in ppm relative to the internal standard and were obtained on a Bruker Avance DRX 500 MHz NMR spectrometer. FT-IR spectra were obtained with a Perkin-Elmer FT-IR spectrometer, and the UV-vis absorption spectra obtained in chloroform on a Shimadzu UV 3100 spectrometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model M590 pump μ-styragel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Elemental analysis was performed by Leco Co. CHNS-932. TGA measurements were performed on a Perkin-Elmer series 7 analysis system under N_2 at a heating rate 10°C/min. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluoremeter utilizing a lock-in power meter (Newport 818-SL).

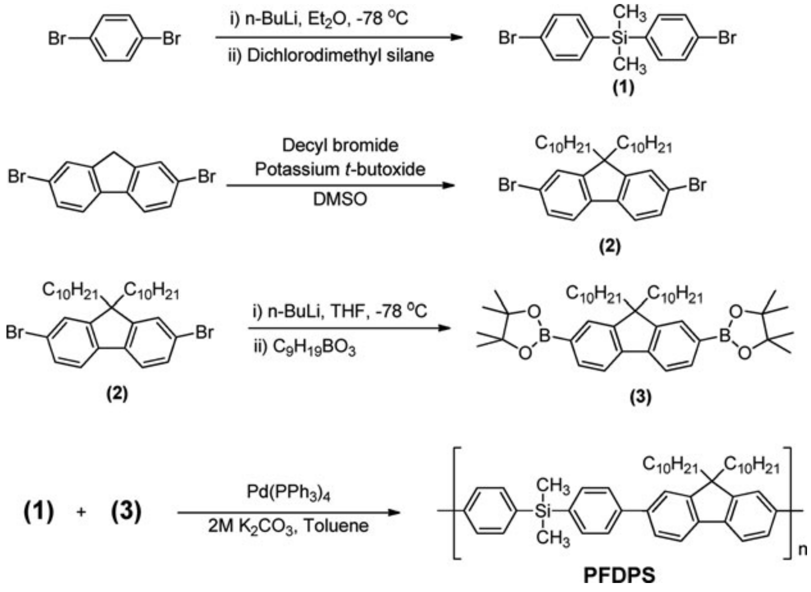
The cyclic voltammetry (CV) was performed using a CV-50W voltammetric analyzer (Bioanalytical System Inc. (BAS, USA)). A glass carbon working electrode, a platinum wire counter electrode and $Ag/AgNO_3$ reference electrode were used in the three-electrode system.

Fabrication of the LED. Poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) for a conducting polymer hole-injection layer was coated on an indium-tin oxide (ITO) coated glass substrate which had been washed with water, acetone, and isopropyl alcohol sequentially. A thin polymer film was spin-coated (3000 rpm, 50 s) from a filtered (0.2 m filter) 1.0 wt% polymer solution in chlorobenzene on a PEDOT:PSS layer. A thin layer of LiF (0.5 nm) and subsequently a 100 nm layer of Al were evaporated subsequently on the top of the emissive layer under a high vacuum (below 1×10^{-5} Torr). All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

Results and Discussion

The chemical structures and synthetic routes of monomer and polymer are shown in Scheme 1. The polymer was synthesized by the Pd-catalyzed Suzuki coupling reaction of the bis(4-bromophenyl)dimethylsilane and 2,2′-(9,9-didecyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). The molecular structures were verified by FT-IR and

^{1}H-NMR. The structure of polymer is consistent with the spectroscopy data from IR and ^{1}H-NMR. In the ^{1}H-NMR spectrum, PFDPS is confirmed by integration ratio of aromatic protons and aliphatic protons. In the IR spectra, the C—H stretching of aromatic and aliphatic protons appeared at 3100 and 2920 cm^{-1} and Si-C stretching appeared at 1450 cm^{-1}. In the ^{1}H NMR, aromatic protons appeared at 7.28–7.80 ppm, and Si-dimethyl and other aliphatic protons appeared at 0.60–2.05 ppm, respectively. PFDPS was soluble in common organic solvent such as chloroform, chlorobenzene, dichlorobenzene, and toluene at room temperature. PFDPS has a weight average molecular weight (M_w) of 16,300 with a polydispersity index (PDI) of 1.4 by a gel permeation chromatography (GPC) analysis relative to polystyrene standards.



Scheme 1. Synthetic schemes of monomers and PFDPS.

The thermal properties of PFDPS were investigated through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), as shown in Fig. 1. The 5% weight loss occurs at 436°C for PFDPS, which indicates good thermal stability of the polymer

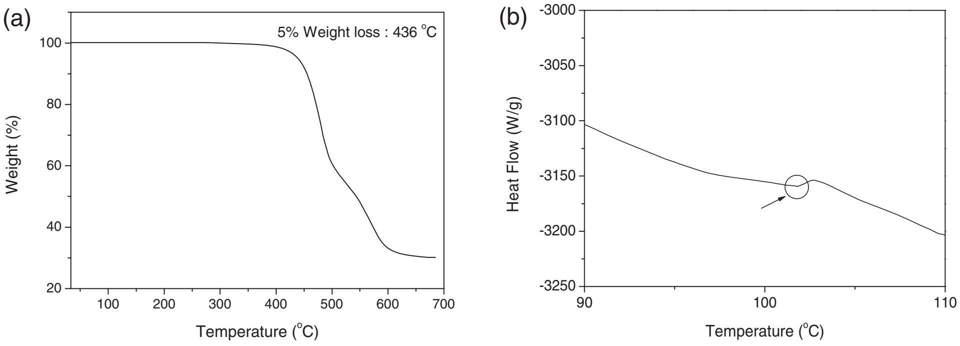


Figure 1. TGA and DSC thermograms of PFDPS.

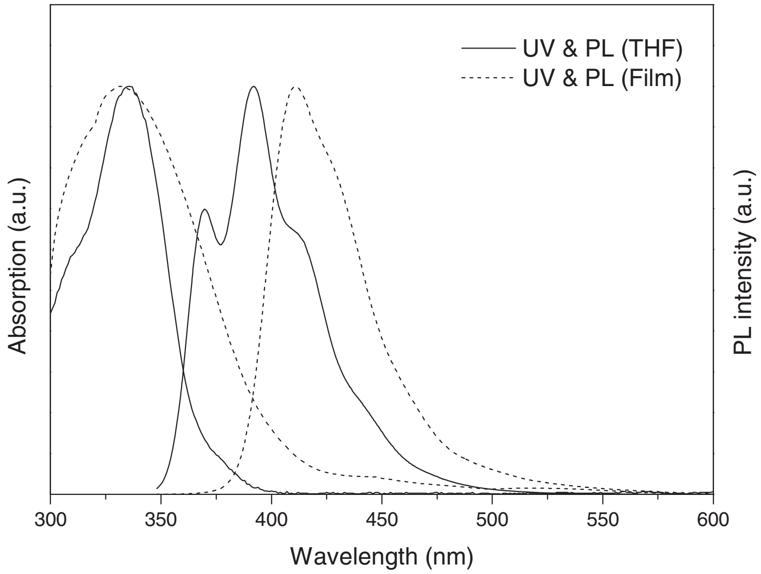


Figure 2. Absorption and photoluminescence spectra of PFDPS in solution and film.

(Fig. 1(a)). From the DSC curve, a distinct glass transition is observed at 101°C, and no other crystallization and melting peaks are found (Fig. 1(b)). The high thermal stability with amorphous nature of the polymer prevents the deformation of the polymer morphology and degradation of the polymer light emitting device by applied electric field of the LED.

UV-visible absorption and photoluminescence (PL) spectra of the polymer are presented in Fig. 2. Typical absorption spectra of dilute solutions of poly(9,9-dialkylfluorenes) show with absorption maxima at about 375 nm. In THF solution, the absorption maxima of PFDPS in blue-shifted to 335 nm compared to typical poly(9,9-dialkylfluorenes), due to the presence of diphenylsilane moiety. The absorption edge of the film sample is at 403 nm, which corresponds to the optical band gap (E_g) of 3.08 eV.

The emission maximum of the polymer in solution and solid film was 392 nm and 410 nm, respectively. The emission peak is only slightly broadened in the film state than that in the solution state, resulting in the splitting of the excited states and more complicated electron transitions. As a result, PFDPS showed a PL emission maximum at 410 nm, yielding violet emission.

Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior as well as the HOMO and LUMO energy levels of polymer. CV was performed on a film of polymer deposited on a carbon electrode measured in $AgNO_3$ (0.01 M)/Bu_4NBF_4 (0.1M)/acetonitrile with a platinium counter electrode and silver reference electrode, calibrated against ferrocene-ferrocenium. The highest occupied molecular orbital (HOMO) level of the polymer was calculated from their respective onset oxidation potentials according to the equation $\mathrm{HOMO} = -(E_{\mathrm{ox,onset}} + 4.4)$ eV with the ferrocene oxidation potential as the standard [24]; the lowest unoccupied molecular orbital energy (LUMO) levels could only be estimated from the corresponding HOMO energy levels and optical band gaps (E_g). The HOMO and LUMO energy levels for polymer is -5.83 and -2.75 eV, respectively.

The OLED device based on PFDPS with the configuration of ITO/PEDOT: PSS/PFDPS/LiF/Al was fabricated. Poly(3,4-ethylenedioxythiophene) (PEDOT) doped

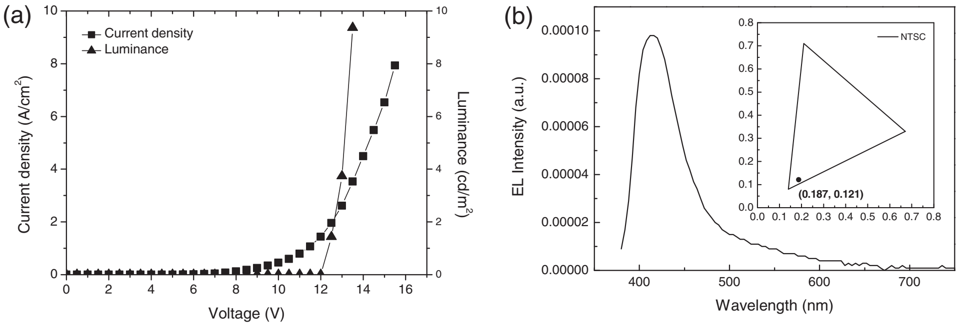


Figure 3. The current-luminescence-voltage characteristics (a) and EL spectrum (b) of the device of polymer. The inset shows the CIE chromaticity diagram with the coordinate of the spectra for the same device.

with poly(styrenesulfonic acid) (PSS) was used as the injection/transporting layer. Figure 3(a) showed the current-luminescence-voltage characteristics of the EL device, respectively. In the EL devices, the forward current increases with increasing forward bias voltage, and the curve has a shape that is typical diode. The device has a turn-on voltage at about 5.5 V and maximum brightness of 9.40 cd/m^2. The electroluminescence spectrum is displayed in Fig. 3(b). The device emitted violet light at 414 nm and a narrow full width at half-maximum (FWHM) of 51 nm. The emitting color of device showed the violet emission (x, y) = (0.187, 0.121) in CIE (Commission Internationale de l′Eclairage) chromaticity coordinates (inset of Fig. 3(b)). Bright violet electroluminescence was observed and the EL spectrum is similar to that of PL spectrum.

Conclusion

We have synthesized new soluble violet light-emitting polymer, which is composed of dialkylfluorene and dimethylsilane backbone by Suzuki coupling reaction. The polymer shows good thermal stability. The introduced dimethylsilane in the main backbone induced the polymer to have amorphous nature as well as to achieve UV-violet emission and inhibit intermolecular interaction due to δ-silicon interrupts the π conjugation. The OLED with the configuration of ITO/PEDOT:PSS/PFDPS/LiF/Al generated the maximum brightness of 9.4 cd/m^2 with a color violet emission of $\mathrm{EL}_{\lambda\max} = 414$ nm.

Acknowledgments

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