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Synthesis of New Fluorene-Based Copolymers Containing an Anthracene Derivative and Their Applications in Polymeric Light-Emitting Diodes

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We report the synthesis of copolymers containing fluorene and highly soluble anthracene derivatives, of general formula, poly{9,9'-bis-(4-octoloxy-phenyl)-fluorene-2,7-diyl-co-9,10-bis-(decy-1-vnvl)-anthracene-2.6-divl}s (PFAnts). The PFAnts were svnthesized via Suzuki coupling and the feed ratios of the anthracene derivative (Ant) were 1, 5, 10, 30, and 50 mol % of the total amount of monomer. PFAnts showed well-defined high molecular weights and were more soluble in conventional organic solvents. The photoluminescence spectra of PFAnts shifted to longer wavelengths with increases in Ant proportion and the PFAnts emitted various colors varying from greenish-blue to orange. The highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels trended toward enhanced hole and electron recombination balance as the Ant proportion increased, due to the better electron-accepting ability of the anthracene moiety compared to the fluorene moiety. Polymeric light-emitting diodes with the configurations ITO/PEDOT:PSS(40 nm)/polymer(60 nm)/Ca(10 nm)/Al(100 nm) (Device A) and ITO/PEDOT:PSS(40 nm)/polymer(60 nm)/Balg(40 nm)/LiF(1 nm)/Al(100 nm) (Device B) were fabricated using the polymers as emissive layers. Especially, Device B with PFAnt01 exhibited the highest measured maximum brightness of 1760 cd/m² at 14 V, a maximum current efficiency of 1.66 cd/A, and a maximum external guantum efficiency of 0.70%.

Keywords: Conjugated Polymers, Light-Emitting Diodes (LED), Polyfluorenes, Anthracene.

1. INTRODUCTION

Conducting polymers have been extensively developed since the time doped polyacetylene was first used as a metallic conducting organic material in 1977.¹ Such conjugated conducting polymers are very important as active materials in polymeric electronic device applications. Examples are polymeric light-emitting diodes (PLEDs), photovoltaic cells, photodetectors, biosensors, and thinfilm transistors.^{2, 3} The polymers permit rapid and low cost fabrication because film-forming polymer solutions can be employed. In recent years, enormous interest and effort has driven the synthesis and characterization of conducting polymers for PLEDs.

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Polyfluorenes (PFs) have typically been used as polymer backbones for PLEDs because of their large band gaps, high photoluminescence (PL) and electroluminescence (EL) quantum yields, excellent chemical and thermal stability, good solubility and film-forming properties, and prompt availability from high-yielding synthetic routes, such as Suzuki coupling, of well-defined high molar-mass polymers.^{4,5} Recently, Hwang and colleagues reported that PF derivatives with bulky alkoxyphenyl groups at the 9-position showed more stable blue emission and better device performance than did alkyl-substituted fluorenes.⁶ However, PFs and derivatives thereof differ in charge carrier mobility, and hence in the relative proportions of holes and electrons because holes are usually faster than electrons. This poor charge balance can lower EL performance.

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Anthracene is one of the well-known fused aromatics used in organic electronic device applications. In 1963, Pope and co-workers reported the first use of anthracene in this context. They applied a high voltage to an anthracene single crystal, used as an organic electroluminescent material, causing blue light to be emitted.⁷ Moreover, single-crystal anthracene shows charge carrier mobility up to 3 cm²/Vs at 300 K.8 Several oligomers and polymers of anthracene derivatives, such as poly(anthrylene)s, poly(anthrylenevinylene)s, and poly(anthryleneethynylene)s, have been reported.9,10 Despite good conducting properties, polyanthrylenes and their derivatives have some drawbacks in that anthracene derivatives show low solubility and polymerization reactivity because of their rigid planar structures.¹¹ Recently, several attempts have been made to deal with these problems. Yang and colleagues synthesized a novel soluble poly(9,10-bis(p-(2ethylhexyloxy)phenyl)-2,6-anthracenevinylene) (2,6-PAV) for EL applications, but EL performance was not impressive.¹²

Here, we report the synthesis of a highly soluble anthracene (Ant) derivative, and poly(fluorene-*co*-anthracene)s, specifically poly{9,9'-bis-(4-octoloxy-phenyl)-fluorene-2,7-diyl*co*-9,10-bis-(decy-1-ynyl)-anthracene-2,6-diyl}s (PFAnts). To improve EL properties, we copolymerized the fluorene and Ant, with control of relative proportions of these materials, to minimize problems associated with the poor charge balance of PFs and the low solubility and reactivity of poly(anthrylene)s. In this paper, we systematically investigate the synthesis, thermal stability, and optical properties of the resulting polymers using PL tests. Finally, we study EL applications with or without an electron transport layer.

2. EXPERIMENTAL DETAILS

2.1. Measurements

¹H and ¹³C NMR spectra were recorded on Bruker AVANCE 300 and 400 spectrometers, respectively, with tetramethylsilane as an internal reference. Elemental analyses were performed by the Seoul Branch Analytical Laboratory of the Korea Basic Science Institute. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument, using THF as eluent and polystyrene as standard. Mass spectra were obtained with an Autospec ultra spectrometer. Thermogravimetric analysis (TGA) measurements of the polymers were performed under nitrogen atmosphere at a heating rate of 10 °C/min using TA Q500 instrument, and the differential scanning calorimetric (DSC) measurements were made using TA Q100 instrument and operated under nitrogen. UV-vis spectra were measured on a Jasco V-530 UV/Vis spectrometer and photoluminescence (PL) spectra of the polymers were measured at room temperature

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on a Spex Fluorolog-3 spectrofluorometer (model FL3-11) using spin-coated films. And PL measurements were prepared by spin-coating with the molecules dissolved in chloroform solution (1 wt%). Cyclic voltammograms were recorded at a scan rate of 50 mV/s at room temperature in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in acetonitrile. A Pt wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The oxidation potentials were calibrated using the ferrocene (Fc) value of -4.8 eV as the standard. A film of each polymer was coated onto a Pt wire electrode by dipping the electrode into a solution of the polymer. Film thickness was measured with a TEN-COR alpha-step 500 surface profiler. EL spectra of the devices were obtained using a Minolta CS-1000. Currentvoltage-luminance (I-V-L) characteristics were recorded simultaneously with the measurement of the EL intensity by attaching the photospectrometer to a Keithley 238 and a Minolta LS-100 as the luminance detector. All measurements were carried out at room temperature under ambient atmosphere.

2.2. Fabrication of EL Devices

In this study, single layer EL devices were fabricated on glass substrates patterned with indium-tin oxide (ITO). The device configurations of Device A: ITO/PEDOT: PSS/polymer/Ca/Al and Device B: ITO/PEDOT: PSS/polymer/Balq/LiF/Al. A hole injection layer of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonicacid) (PSS) (PEDOT:PSS, Bayer Al 4083) was spincoated onto each ITO anode from a solution. Each polymer solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution for spin coating was prepared by the dissolution of the polymer (2.0 wt%) in chlorobenzene. In the Device A, calcium and aluminum contacts were formed by vacuum deposition at pressures below 10⁻⁶ Torr. In Device B, a bis(2-methyl-8-quinolinolate)-4-(phenylphenolata)aluminum (Bala) electron-transporting layer (ETL), lithium fluoride and aluminuim were deposited in the same condition.

2.3. Materials

Acetic anhydride, chromium oxide, zinc chloride, 1-bromooctane, *t*-butyllithum, 2-isopropoxy-4,4,5,5tetramethyl-1,3,2-dioxaborolane, *n*-butyllithum, copper bromide, *t*-butyl nitrite, tetrakis(triphenylphosphine)palladium, toluene, aliquat[®]336, 1-decyne, tin chloride dehydrate were purchased from Aldrich Co. hydrochloric acid, potassium iodide (KI), acetonitrile, magnesium sulfate anhydrous (MgSO₄) were purchased from Junsei Co. potassium carbonate (K_2CO_3), sodium carbonate (Na₂CO₃) were purchased from Daejung Co. All reagents purchased commercially were used without further purification except for tetrahydrofuran (THF) dried over sodium/benzophenone. 2,6-Dibromoanthraquinone (1) and 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (3) were synthesized according to procedures outlined in the literature.¹³

2.4. Synthesis of Fluorene Derivative Monomers

2.4.1. 2, 6-Dibromo-9, 10-bis(decy-1-ynyl) anthracene (2)

To a solution of 1-decyne (6.35 mL, 31.75 mmol) in dry tetrahydrofurane (150 mL) at $-78\ ^\circ C$ was added by syringe, 21.9 mL (38.35 mmol) of n-butyllithium (2.6 M in hexane). The mixture was stirred at -78 °C for 2 hours. 2, 6-dibromoanthraquinone (1) (5 g, 13.65 mmol) was added to the solution, and the resulting mixture was stirred at 0 °C for 1 hour and warmed to room temperature slowly and stirred for 5 h. The mixture was extracted with petroleum ether (PE)/brine and then dried over MgSO₄. After the solvent being evaporated, the residue was dissolved in tetrahudrofuran (20 mL), and then dropwised into SnCl₂ · 2H₂O (15.4 g, 68.35 mmol, in 50 mL of 50% acetic acid). The mixture was stirred at room temperature overnight, and poured into water and extracted with ethyl ether. The organic layer was washed with brine and dried over anhydrous MgSO₄. Solvent was removed and the crude product was purified with column chromatography on silica with PE as eluent, and the residue was purified by several reprecipitation in PE to provide yellow solid. (6.34 g, 73%) ¹H NMR (CDCl₃, ppm) 8.66 (d, 2H), 8.36 (d, 2H), 7.57 (dd, 2H), 2.73 (t, 4H), 1.78 (m, 4H), 1.59 (m, 4H), 1.34 (m, 16H), 0.87 (m, 6H). ¹³C NMR (CDCl₃, ppm) 132.72, 130.61, 130.10, 129.17, 129.02, 121.34, 118.05, 104.33, 76.55, 31.89, 29.31, 29.22, 28.92, 22.70, 20.25, 14.12. Calcd for C₃₄H₄₀Br₂:C, 67.11; H, 6.63. Found:C, 66.53; H, 6.55.

2.4.2. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxyphenyl)-fluorene (4)

To a solution of 2,7-Dibromo-9,9-bis-(4-octyloxy-phenyl)fluorene (**3**) (5.00 g, 6.83 mmol) in dry tetrahydrofurane (150 mL) at -78 °C was added by syringe, 24.7 mL (27.3 mmol) of *t*-butyllithium (1.7 M in hexane). The mixture was stirred at -78 °C for 2 hours. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.18 mL, 20.5 mmol) was added to the solution, and the resulting mixture was stirred at -78 °C for 1 hour and warmed to room temperature slowly and stirred for 40 h. The mixture was extracted with dichloromethane/brine and then dried over MgSO₄. The solvent was removed by solvent evaporation, and the residue was purified by several reprecipitation in methanol to provide white solid. (3.6 g, 63%) ¹H NMR (CDCl₃, ppm) 7.75 (m, 6H), 7.10 (dd, 4H), 6.70 (dd, 4H), 3.86 (t, 4H), 1.71 (m, 4H), 1.38 (m, 4H), 1.27 (m, 40H), 0.85 (m, 6H). ¹³C NMR (CDCl₃, ppm) 157.71, 151.86, 142.61, 137.62, 134.04, 132.21, 129.39, 119.74, 113.98, 83.67, 67.85, 64.16, 31.79, 29.33, 29.29, 29.21, 26.04, 24.88, 22.63, 14.07. Anal. Calcd for $C_{53}H_{72}B_2O_6$: C, 77.00; H, 8.78. Found : C, 78.91; H, 8.93.

2.4.3. Poly(9,9'-bis-4-octoloxy-phenyl-fluorene) (PBOPF)

Into a 150 mL two-neck flask were added 0.5 g (0.817 mmol) of the dibromo compounds, 2,7-Dibromo-9,9-bis-(4octyloxy-phenyl)-fluorene (3) and 0.675 g (0.817 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (4) in 8 mL of anhydrous toluene. The air-sensitive and water soluble Pd(0) complex, tetrakis(triphenylphosphine)palladium (2 mol%), was transferred in a dry box. Subsequently, 2 M aqueous sodium carbonate deaerated for 30 min and the phasetransfer catalyst, Aliquat®336 (several drops), in toluene purged under nitrogen for 1 h was transferred via cannula. The reaction mixture was stirred at 80 °C for 3 days, and then, the excess amount of bromobenzene, the end-capper, dissolved in 1 mL of anhydrous toluene was added and stirring continued for 12 h. The reaction mixture was cooled to about 50 °C and added slowly to a vigorously stirred mixture of 200 mL of methanol. The polymer fibers were collected by filtration and reprecipitation from methanol and acetone. The polymers were purified further by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues, and column chromatographied with a chloroform solution of the polymer. The reprecipitation procedure in chloroform/methanol is then repeated several times. The resulting polymers were soluble in common organic solvents. (0.64 g, 67.9%) ¹H NMR (CDCl₃, ppm) 7.74-7.72(2H), 7.54-7.49(4H), 7.15-7.10(4H), 6.75-6.71(4H), 3.88-3.85(4H), 1.75-1.68(4H), 1.41-1.36(4H), 1.29-1.25(4H), 0.87-0.83(6H). Element Anal. Found: C, 87.98; H, 8.78.

2.4.4. Poly{9,9'-bis-(4-octoloxy-phenyl)-fluorene-2,7diyl-co-9,10-bis-(decy-1-ynyl)-anthracene-2,6-diyl} (PFAnt01)

The procedure was the same as the preparation of PBOPF but 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**3**) (0.98 equiv, 0.434 g), 2, 6-Dibromo-9, 10-bis(decy-1-ynyl) anthracene (**2**) (0.02 equiv, 7.36 mg) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (1 equiv, 0.5 g) (**4**) were used in this polymerization. (0.39 g, 55.6%) ¹H NMR (CDCl₃, ppm) aromatic; 7.76–6.71 (14H), aliphatic; 3.92–3.76 (4H), 1.75–0.86 (~22H). Element Anal. Found: C, 85.99; H, 8.55.

2.4.5. Poly{9,9'-bis-(4-octoloxy-phenyl)-fluorene-2,7diyl-Co-9,10-bis-(decy-1-ynyl)-anthracene-2,6diyl} PFAnt05)

The procedure was the same as the preparation of PBOPF but 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**3**) (0.9 equiv, 0.399 g), 2, 6-Dibromo-9, 10-bis(decy-1-ynyl) anthracene (**2**) (0.1 equiv, 0.368 g) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (1 equiv, 0.5 g) (**4**) were used in this polymerization. (0.39 g, 55.9%) ¹H NMR (CDCl₃, ppm) aromatic; 7.74–6.72 (14H), aliphatic; 3.87–3.86 (~4H), 2.74–2.73 (~0.15H), 1,74–1.68 (4H), 1.40 (4H), 1.28–1.25 (16H), 0.87–0.84 (6H). Element Anal. Found: C, 84.8; H, 8.45.

2.4.6. Poly{9,9'-bis-(4-octoloxy-phenyl)-fluorene-2,7diyl-co-9,10-bis-(decy-1-ynyl)-anthracene-2,6-diyl} (PFAnt10)

The procedure was the same as the preparation of PBOPF but 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**3**) (0.8 equiv, 0.354 g), 2, 6-Dibromo-9, 10-bis(decy-1-ynyl) anthracene (**2**) (0.2 equiv, 0.0736 g) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (1 equiv, 0.5 g) (**4**) were used in this polymerization. (0.42 g, 61.7%) ¹H NMR

 $(CDCl_3, ppm)$ aromatic; 7.78–6.72 (13H), aliphatic; 3.86–3.85 (~4H), 2.74–2.73 (~0.33H), 1,73–1.68 (4H), 1.39 (4H), 1.27–1.25 (16H), 0.87–0.83 (6H). Element Anal. Found: C, 85.32; H, 8.47.

2.4.7. Poly{9,9'-bis-(4-octoloxy-phenyl)-fluorene-2,7diyl-co-9,10-bis-(decy-1-ynyl)-anthracene-2,6-diyl} (PFAnt30)

The procedure was the same as the preparation of PBOPF but 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**3**) (0.4 equiv, 0.0885 g), 2, 6-Dibromo-9, 10-bis(decy-1-ynyl) anthracene (**2**) (0.6 equiv, 0.11 g) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (1 equiv, 0.25 g) (**4**) were used in this polymerization. (0.10 g, 32.2%) ¹H NMR (CDCl₃, ppm) aromatic; 8.73–6.74 (~12H), 3.88 (4H), 2.73 (~1.7H), 1,77–1.58 (8H), 1.39–1.26 (30H), 0.84 (12H). Element Anal. Found: C, 84.15; H, 8.59.

2.4.8. Poly{9,9'-bis-(4-octoloxy-phenyl)-fluorene-2,7diyl-co-9,10-bis-(decy-1-ynyl)-anthracene-2,6-diyl} (PFAnt 50)

and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (1 equiv, 0.5 g) (4) The procedure was the same as the preparation of PBOPF but 2, 6-Dibromo-9, 10-bis(decy-1-ynyl) anthracene (2) were used in this polymerization. $(0.42 \text{ g}, 61.7\%)^{-1}$ H NMR log (1 equiv, 0.23 g) and 2,7-bis(4,4,5,5-tetramethyl-1,3,



Scheme 1. Synthetic routes for monomers.

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2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (1 equiv, 0.2659 g) (4) were used in this polymerization. (0.32 g, 82.5%) ¹H NMR (CDCl₃, ppm) aromatic; 8.73–6.73 (20H), 3.86 (4H), 2.74–2.73 (4H), 1,81–1.69 (8H), 1.60(4H), 1.39–1.23 (36H), 0.86–0.82 (12H). Element Anal. Found: C, 85.34; H, 8.50.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

We introduced the decyne group to 2,6-dibromoanthraquinone (1) at the reactive 9,10-positions and the synthesized Ant showed enhanced solubility because of the long alkyl chain. Five fluorene-based copolymers containing Ant were synthesized using the Suzuki coupling reaction. For comparison, a well-known typical polyfluorene homopolymer, poly[9,9-bis(4'-n-octyloxyphenyl)]fluorene-2,7-diyl] (PBOPF),⁶ was also synthesized under the same

conditions. 2-Bromobenzene was used as an end-capping reagent to remove monomer residues containing boronic acid. The solubility of synthesized polymers decreased slightly with increasing proportion of Ant, but all PFAnts were soluble in common organic solvents including chloroform, chlorobenzene, and toluene. The syntheses of all monomers and polymers are outlined in Schemes 1 and 2, respectively. Chemical structures were verified by ¹H- and ¹³C-NMR spectroscopy and elemental analysis. The actual mass fractions of Ant in PFAnts, as determined by NMR spectra after integration of copolymer peaks as shown in Figure 1, were somewhat lower than the feed ratios. The feed ratios were 5, 10, 30, and 50 mol% of the total amount of monomer, and the resulting proportions of Ant units in PFAnts were 3.67, 7.78, 29.30, and 47.68 mol%, respectively. Unfortunately, it was not possible to calculate the resulting proportion of PFAnt01, because of the very low Ant intensity on NMR. The number-average molecular weights (M_n) of the synthesized polymers were



Scheme 2. Polymerizations of PBOPF and PFAnts.



Fig. 1. ¹H NMR spectra of the polymers.

 $5,100 \sim 12,000$ (PDI = $1.63 \sim 2.99$). Because of long decyne chain, the solubility of the Ant monomer in organic solvents, and Ant reactivity therein, were dramatically enhanced compared with the properties of ordinary poly(anthrylene)s; as a result, the PFAnts had higher molecular weights. PBOPF and anthracene-containing PFAnts exhibited very good thermal stabilities, losing less than 5% of weight on heating to approximately 400 °C as evaluated by TGA under a nitrogen atmosphere. Data on the synthesized copolymers are summarized in Table I.

3.2. Optical Properties Delivered by Publishing Technolog

The UV-visible absorption and PL emission properties of the Ant monomer, and the polymers in both solution and film states, were investigated; the results are summarized in Table II. The normalized absorption and emission spectra of Ant are shown in Figure 2. The absorption spectrum of Ant showed the characteristic vibration pattern of the anthracene group in both solution and film states. The Ant thin film shows absorption onset at 491 nm. The optical band gap of Ant, determined from absorption onset, was calculated to be 2.52 eV. The emission spectrum of the Ant film was markedly red-shifted (by about 60 nm) compared to that of Ant in solution, and exhibited peak emission at 513 nm. This suggests that the aggregation of Ant units in

Table I. UV-visible absorption and PL emission spectra of Ant and polymers in chloroform and in films.

Polymer	Solution λ_{\max} (nm) ^{<i>a</i>}		Film λ_{\max} (nm) ^b		
	Absorption	Emission	Absorption	Emission	
Ant	283	455	276	513	
PBOPF	385	399	388	421	
PFAnt01	380	396, 454	382	477 (509)	
PFAnt05	375	405, 476	380	485 (517)	
PFAnt10	377	412, 477	380	487 (517)	
PFAnt30	373	478	371	541	
PFAnt50	374	479	369	560	

^aDilute solution in chloroform. ^bSpin-coated thin film on quartz plate from chloroform solution for 40s at 1000 rpm.

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Table II.	De II. Physical properties of the polymers.				
Polymer	$M^a_{ m n}$	$M^b_{ m w}$	PDI	$T_{\rm g}~(^{\circ}{\rm C})$	$T^c_{\rm 5d}$ (°C)
PBOPF	6,400	13,000	2.01	94	426
PFAnt01	5,100	8,300	1.63	93	411
PFAnt05	5,400	10,000	1.93	92	399
PFAnt10	5,300	12,000	2.23	97	407
PFAnt30	12,000	32,000	2.69	94	401
PFAnt50	9,300	28,000	2.99	92	389

^{a, b}Number and weight average molecular weight determined by GPC using polystyrene as the standard in THF. ^cDecomposition temperature determined by TGA in N₂based on 5% weight loss.

the film caused a red-shift of the spectrum because of the rigid film structure and the interaction of Ant molecules in the film state.

Figure 3 shows the normalized UV-visible absorption spectra of PBOPF and PFAnts. In chloroform solution, all polymers exhibited absorption maxima at about 380 nm. Slight blue shifts in absorption maxima were seen as the proportion of Ant increased, and vibration intensities also increased because the Ant monomer absorption maximum and vibration pattern contributed more to the copolymer properties. The UV-visible spectra of the films were almost identical to the corresponding solution spectra.

In the case of the PL spectra, by contrast, the solution and film spectra were dissimilar. In Figure 4(a), two maximal emission peaks (one in the blue region at about 390 nm, from the fluorene moiety, and one in the green region at about 515 nm, from the anthracene moiety) are seen. Blue peak intensity fell and green peak intensity rose with increasing Ant proportion. PFAnt30 and PFAnt50 emitted almost pure green light because energy transfers were complete, whereas energy transfers were partial in PFAnt01, PFAnt05, and PFAnt10. In Figure 4(b), the PL emission maxima of polymers used in films were dramatically red-shifted compared to those in solution and exhibited emissions ranging from blue to orange as the proportion of Ant increased. The extents of PL spectral red-shifts when solution and film states were compared were 22-81 nm. Especially, the PL maximum of PFAnt50



Fig. 2. UV-visible absorption and PL emission spectra of the Ant monomer in chloroform solution and in film.





Fig. 3. UV-visible absorption spectra of PBOPF and PFAnts (a) in chlo-

roform solution and (b) in film.

shifted from 479 nm to 560 nm. Such large changes in PL maxima probably arise not only from intramolecular energy transfer from fluorene to Ant but also due to intermolecular aggregations of PFAnt molecules. In solution, chloroform solvent molecules interrupt polymer aggregation, so that only blue and green peaks are seen, caused by energy transfer from fluorene to anthracene. Under film conditions, without solvent, polymer aggregation occurs more easily than in solution because of the rigid, planar structure of Ant, and emission from the aggregates becomes the major feature of the PL spectra as Ant content increases.

3.3. Electrochemical Properties

The electrochemical properties of the polymers were studied to investigate redox behavior and to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. Electrochemical processes probed by cyclic voltammetry (CV) are similar to those involved in charge injection and transport processes in LED (light-emitting diode) devices.

In the anodic scan, the onsets of oxidation of PBOPF, PFAnt01, PFAnt05, PFAnt10, PFAnt30, and PFAnt50 were found to occur at 0.725, 0.724, 0.734, 0.708, 0.904, and

Fig. 4. PL emission spectra of PBOPF and PFAnts (a) in chloroform solution and (b) in film.

1.203 V (vs. SCE), respectively, corresponding to ionization potential (I_p) values of -5.40, -5.39, -5.40, -5.38, -5.57, and -5.87 eV, respectively, using a previously reported empirical equation.¹⁴ Usually, it is difficult to obtain LUMO energies for fluorene-based copolymers employing this technique; hence the LUMO values were estimated from the HOMO energies and optical band gaps taken from absorption onsets of polymer film UV-visible spectra.¹⁵ Energy levels of the polymers are summarized in Table III.

As shown in Figure 5, both HOMO and LUMO energy levels tended to fall as the proportion of Ant

 Table III.
 Electrochemical properties and energy levels of the polymers.

Polymer	$E^{a}_{\mathrm{g,optic}}$ (eV)	$E^b_{\mathrm{onset,ox}}$ (V)	HOMO (eV)	LUMO (eV)
PBOPF	2.95	0.725	-5.40	-2.45
PFAnt01	2.93	0.724	-5.39	-2.46
PFAnt05	2.53	0.734	-5.40	-2.87
PFAnt10	2.51	0.708	-5.38	-2.87
PFAnt30	2.50	0.904	-5.57	-3.07
PFAnt50	2.49	1.203	-5.87	-3.38

^{*a*}Eg,optic, calculated from the onset values of the absorption spectra of the spincoated films on quartz. ^{*b*}Eonset,ox, stand for onset potential (scan rate: 50 mV/s). ^{*c*}Calculated from the HOMO and $E_{g,optic}$.

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Polymers

PBOPF

PFAnt01

PFAnt05

PFAnt10

 $\lambda_{\rm max}$ (nm)

425, 449

481 (515)

487 (522)

527, 566

546

marized in Table IV.



Fig. 5. Schematic structure of the polymer energy band gaps.

increased. In other words, the Ant moiety of PFAnts showed better electron-accepting ability than did PBOPF. This indicates that electron injection from the electrode to PFAnts is much easier than to PBOPF. The good electron-accepting ability of PFAnts enhances EL performance, because polyfluorenes usually demonstrate electron-accepting problems arising from the abovementioned charge carrier mobility issues. In addition, the band gap of polymers decreased gradually with increasing Ant proportion. With PFAnt01, the band gap differed only slightly from that of PBOPF. However, the band gaps of other polymers, PFAnt05, PFAnt10, PFAnt30, and PFAnt50, were significantly smaller than that of PFAnt01. Such results are attributable to the rigid structure of Ant,

PFAnt30 22, 7.6 V (0.41, 0.50)PFAnt50 551 23, 4.4V 0.0012 0.0008 (0.42, 0.48)emitted orange light with an EL maximum at 551 nm and a broad peak. The quality of emission spectra is typically defined by Commission Internationale de L'Eclairage (CIE) 1931 chromaticity coordinates (x, y). The CIE coordinates and colors of the polymer EL spectra are sum-

Table IV. I-V-L characteristics of the polymers of Device A.

Maximum

luminance

 (cd/m^2)

193, 9.6 V

198, 12 V

101. 12.6 V

100, 13 V

Maximum

current

efficiency

(cd/A)

0.018

0.053

0.034

0.045

0.0012

Maximum

EQE (%)

0.014

0.027

0.018

0.02

0.001

CIE

coordinates

(0.20, 0.16)

(0.20, 0.43)

(0.31, 0.50)

(0.39, 0.50)

As shown in Figure 7, the PFAnts, especially PFAnt01, offered good EL performance. Moreover, as shown in Figure 7(b), the current efficiencies of PFAnt01, PFAnt05, and PFAnt10 were higher than that of PBOPF. However, PFAnt30 and PFAnt50 showed poorer performances than did the other PFAnts, because of intrinsic luminescence quenching after aggregation. When aggregation occurs, excitons spread out and dissociate into holes and electrons

which contributes to aggregation mediated by intermolecology to: Purdue University Libraries 500 ular interactions.

3.4. Electroluminescence Properties

To investigate the EL properties and current-voltageluminance characteristics of the synthesized polymers, PLED devices with the configuration of Device A were fabricated. EL spectra of PBOPF and PFAnts were similar to the PL spectra, as shown in Figure 6. The EL emission maxima of the polymers were red-shifted from 425 nm to 551 nm as Ant content increased. Whereas PBOPF emitted blue light with an EL maximum at 425 nm and a shoulder at 449 nm, PFAnt50, an alternating copolymer,



Fig. 6. EL spectra of the polymers of Device A.

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Fig. 7. (a) Voltage-luminance (V-L) and (b) voltage-current efficiency characteristics of the PBOPF and PFAnts forms of Device A.

 Table V.
 I–V–L characteristics of the PFAnt01, PFAnt05, and PFAnt10 polymers of Device B.

Polymers	$\lambda_{ m max}$ (nm)	Maximum luminance (cd/m ²)	Maximum current efficiency (cd/A)	Maximum EQE (%)	CIE coordinates
PFAnt01 PFAnt05	485, 516 524	1760, 14 V 280, 17 V	1.66 0.68	0.70	(0.22, 0.48) (0.35, 0.53)
PFAnt10	525	270, 16.5 V	0.64	0.26	(0.35, 0.53) (0.35, 0.53)

by π -orbital overlaps between adjacent molecules. The most interesting result is that PFAnt01 exhibited high PL/EL quantum yields. PFAnt01 exhibited the highest maximum brightness of 198 cd/m² at 12 V, a maximum current efficiency of 0.026 cd/A, and a maximum external quantum efficiency (EQE) of 0.024%. This is because the small Ant content minimized Ant-related problems. PFAnt01 is thus a promising material for PLED applications.

To improve EL performance, we developed three PFAnts, namely PFAnt01, PFAnt05, and PFAnt10, which showed good EL efficiencies, and fabricated Device B, with an electron transport layer (ETL). The data are summarized in Table V and Figure 8. Performance was much better than shown in Figure 7. PFAnt01 exhibited the



Fig. 8. (a) Voltage–luminance (V–L) and (b) voltage–current efficiency characteristics of the PFAnt01, PFAnt05, and PFAnt10 forms of Device B.

highest maximum brightness of 1760 cd/m^2 at 14 V, a maximum current efficiency of 1.66 cd/A, and a maximum EQE of 0.70%. Moreover, the EL performances of PFAnt05 and PFAnt10 also dramatically increased, as shown in Table V. These results show that PFAnts demonstrate improved EL performance compared with that of previously studied poly(anthrylene)s and offer high potential for use in PLED applications.

4. CONCLUSION

We synthesized new fluorene-based copolymers, poly{9,9'bis-(4-octoloxy-phenyl)-fluorene-2,7-diyl-co-9,10-bis-(decy-1-ynyl)-anthracene-2,6-diyl}s (PFAnts). The incorporation of the long alkyl chain at the 9,10-position of anthracene, and copolymerization with fluorene, afforded improved solubility in common organic solvents and increased film-forming molecular weight values, compared to common poly(anthrylene)s. Emission colors were easily controlled by adjusting the feed ratio of the anthracene derivative, exploiting useful Ant properties such as long conjugation length, small band gap, and a more rigid and planar structure compared to the fluorene derivative. Because of these properties, the polymers showed effective energy transfer and aggregation. Among the materials investigated, PFAnt01, PFAnt05, and PFAnt10 exhibited better EL efficiencies than PBOPF. Upon further investigation of devices made using these three PFAnts, greatly improved EL performance was noted. Especially, PFAnt01 exhibited the highest maximum brightness of 1760 cd/m² at 8 V, a maximum current efficiency of 1.66 cd/A, and a maximum EQE of 0.70%; the enhanced electron/hole balance led to improved device efficiency. These results suggest that copolymers containing anthracene derivatives show promise for use in PLED displays.

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