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Blue-Light-Emitting Poly(arylene ethynylenes) Containing Alternating Sequences of Biphenylene or Fluorenediyl and *p*-Phenylene Moieties Linked Through Triple Bonds

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ABSTRACT: Two new poly(arylene ethynylenes) were synthesized by the reaction of 1,4-diethynyl-2,5-dioctylbenzene either with 4,4'-diiodo-3,3'-dimethyl-1,1'-biphenyl or 2,7-diiodo-9,9-dioctylfluorene via the Sonogashira reaction, and their photoluminescence (PL) and electroluminescence (EL) properties were studied. The new poly(arylene ethynylenes) were poly[(3,3'-dimethyl-1,1'-biphenyl-4,4'-diyl)-1,2-ethynediyl-(2,5-dioctyl-1,4-phenylene)-1,2-ethynediyl] (PPEBE) and poly[(9,9-dioctylfluorene-2,7-diyl)-1,2-ethynediyl-(2,5-dioctyl-1,4-phenylene)-1,2-ethynediyl] (PPEFE), both of which were blue-light emitters. PPEBE not only emitted better blue light than PPEFE, but it also performed better in EL than the latter when the light-emitting diode devices were constructed with the configuration indium–tin oxide/poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonic acid) (50 nm)/polymer (80 nm)/Ca:Al. The device constructed with PPEBE exhibited an external quantum efficiency of 0.29 cd/A and a maximum brightness of about 560 cd/m², with its EL spectrum showing emitting light maxima at $\lambda = 445$ and 472 nm. The device with PPEFE exhibited an efficiency of 0.10 cd/A and a

maximum brightness of about 270 cd/m², with its EL spectrum showing an emitting light maximum at $\lambda = 473$ nm. Hole mobility (μ_h) and electron mobility (μ_e) of the polymers were determined by the time-of-flight method. Both polymers showed faster μ_h values. PPEBE revealed a μ_h of 2.0×10^{-4} cm²/V·s at an electric field of 1.9×10^5 V/cm and a μ_e of 7.0×10^{-5} cm²/V·s at an electric field of 1.9×10^5 V/cm. In contrast, the mobilities of the both carriers were slower for PPEFE, and its μ_h (8.0×10^{-6} cm²/V·s at an electric field of 1.7×10^6 V/cm) was 120 times its μ_e (6.5×10^{-8} cm²/V·s at an electric field of 8.6×10^5 V/cm). The much better balance in the carriers' mobilities appeared to be the major reason for the better device performance of PPEBE than PPEFE. Their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were also a little different from each other. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 299–306, 2006

Key words: films; fluorescence; light-emitting diodes (LED); UV–vis spectroscopy

INTRODUCTION

Since the Cambridge group's report¹ on the electroluminescence (EL) properties of poly(*p*-phenylenevinylene) (PPV), interest in the EL phenomena of a wide variety of polyconjugated polymers^{2–7} has intensified due to the possible development of new display devices based on those polymers. PPV and its derivatives^{8–11} are representative green-light-emitting materials, and polyfluorenes (PFs)¹² are blue-light-emitting polymers. The performance of polymer light-emitting diode (PLED) devices not only depends on the chemical structure of the polymers but also on many other

factors, such as the nature of the electrodes and the use of additional carrier transporting layers.¹³ More recently, phosphorescent emission by complexes of transition metals,^{14–16} such as iridium and platinum, and also by polymers¹⁷ bearing those complexes have been reported.

We recently reported on highly efficient green-light-emitting PPV derivatives bearing carbazole,⁸ phenyloxadiazole,⁹ and fluorene pendants¹⁰ directly bonded to the PPV backbone. In general, they revealed¹¹ better balance in the mobility of the carriers. Moreover, some of the polymers formed new intragap states on contact with the calcium electrode, which appeared to be the reason for the lowered threshold electric field for some of the polymers.¹⁸

Among the polyconjugated polymers, different poly(*p*-phenylene ethynylene) (PPE) derivatives also have been studied in PLED applications.¹⁹ One may be able to reduce the wavelength of the emitted light

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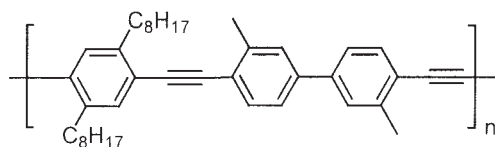
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by replacing the double bonds in, for example, PPV, with triple bonds, which increases the bandgap energy (E_g). In fact, there are several reports^{19–21} claiming that a proper design of PPE derivatives leads to blue-light emission. PFs are the most widely used blue-light emitters, but the color of the emitted light of the PLEDs made from PFs shifts from the desired blue to green, and even to yellow,^{22–24} under various operating conditions. This undesired phenomenon has also been observed in PL, but it is generally more common in EL.²³ Many possible causes^{23–27} have been suggested for the observations. Among them, most often mentioned are the so-called green band brought about by excimer emission and the oxidation of the nine-position carbon in the fluorene structures.²⁴ Many attempts have been made to mitigate these problems and to stabilize blue color emission from PFs.^{25–27}

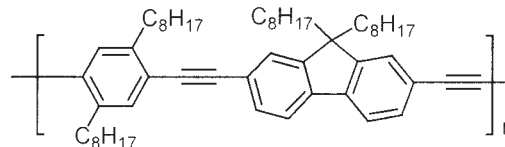
In this investigation, we prepared two new PPE derivatives, and their charge carrier mobility characteristics and EL properties were studied. The EL devices had a configuration of indium–tin oxide (ITO)/

poly(3,4-ethylenedioxythiophene) doped with polystyrenesulfonic acid (PEDOT; 50 nm)/polymer (80 nm)/Ca:Al ($\sigma = 10$ S/cm; Bayer, Leverkusen, Germany) and ITO for a glass coated with ITO (anode: $\rho = 20$ Ω /cm).

The first polymer, poly[(3,3'-dimethyl-1,1'-biphenyl-4,4'-diyl)-1,2-ethynediyl-(2,5-dioctyl-1,4-phenylene)-1,2-ethynediyl] (PPEBE), was an alternating copolymer containing phenylene and biphenylene moieties linked through acetylenic bridges. The second polymer, poly[(9,9-dioctylfluorene-2,7-diyl)-1,2-ethynediyl-(2,5-dioctyl-1,4-phenylene)-1,2-ethynediyl] (PPEFE), contained substituted fluorene rings instead of the biphenylene moieties present in PPEBE. The fluorene moiety in PPEFE, due to its conjugated ring structure, was of more of planar geometry than the biphenylene moiety in PPEBE, which was expected to have a twisted geometry. Therefore, it was interesting to study how such structural differences would influence the electronic structure and fluorescence properties of the polymers:



PPEBE



PPEFE

RESULTS AND DISCUSSION

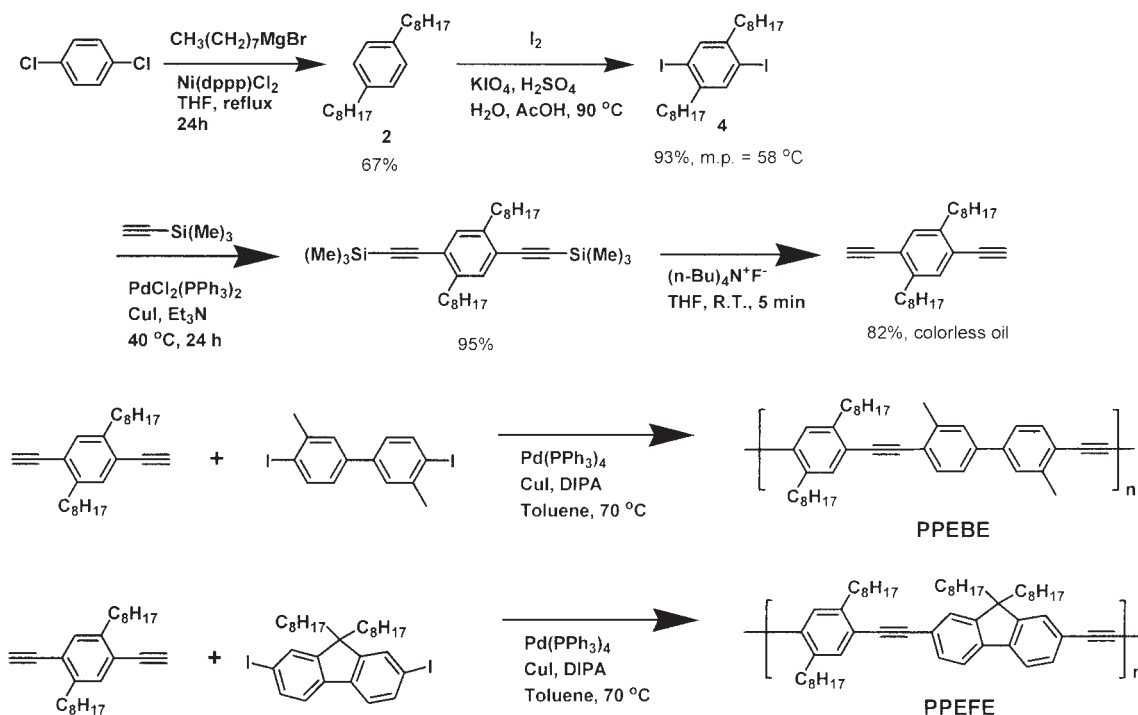
Synthesis and general properties of the polymers

The two polymers were prepared as described in the Experimental section (Scheme 1). Polymerization proceeded homogeneously, and insoluble particles, diisopropylammonium iodide, palladium, and copper compounds, formed as the reaction progressed were removed by filtration. Both polymers were readily soluble at room temperature in chloroform and tetrahydrofuran (THF). Their number-average molecular weights determined by GPC against polystyrene standards were 15,500 and 14,700, respectively. Their polydispersity indices were 1.5 and 1.7, respectively.

Ultraviolet–visible (UV–vis) absorption and PL spectra

Figure 1 compares the UV–vis absorption and PL spectra of the two polymers in thin films. The absorption over the 375–450-nm region corresponded to $\pi \rightarrow \pi^*$ transitions of the backbone of the polymers. The absorption peaks of the films (80 nm thick) of the two polymers were composed of two major peaks overlapping with each other whose absorption maxima were located at 390 and 421 nm for PPEBE and 391 and 413

nm for PPEFE. The PL spectrum of the PPEBE polymer film (80 nm thick) exhibited finer vibronic details, with one maxima located at 464 nm and with distinct shoulders discernible at about 445 and 496 nm and another weaker shoulder at a longer wavelength (ca. 516 nm). Similarly, the PL spectrum of PPEFE showed a dominant peak maximum at 478 nm with weaker shoulders at about 461, 486, and 519 nm. The PL spectrum of PPEFE shifted only slightly compared with that of PPEBE. Huang et al.²¹ reported the optical properties of poly(2,5-dioctyl-1,4-phenylene ethynylene). The UV–vis absorption maximum of poly(2,5-dioctyl-1,4-phenylene ethynylene) film was located at 384 nm, and the PL maximum was at 502 nm. Regular inclusion of a biphenylene or fluorene moiety in the PPE derivatives showed a reduction in the PL λ_{\max} position by 30–40 nm. This was due to less efficient π -conjugation of the backbone by the presence of the comonomer units. The important point to be noted is that no green band²⁴ appeared in the PL spectrum of PPEFE, which implies that the formation of excimers was suppressed by copolymerization. The optical E_g estimated from the absorption edge (ca. 450 nm) for both polymers was 2.8 eV, which was higher than that of PPV (2.4 eV)¹ and lower than that of dioctyl-substi-



Scheme 1 Synthetic routes of the polymers.

tuted PF (3.1 eV).^{12(a)} As alluded to in the Introduction, the replacement of C=C double bonds in the conjugated polymers with C≡C triple bonds reduced the effective π -conjugation length and increased E_g values. Table I compares the relative PL quantum efficiencies (QEs) of the polymers in solution (5×10^{-5} mol/L of the repeating unit) in chloroform and in thin films (60 and 45 nm thick for PPEBE and PPEFE, respectively). In both cases, PPEBE exhibited a higher PL QE than PPEFE. The PL QEs of the films were in line with the external QEs of the light-emitting diode (LED) devices fabricated with them, which is discussed later. Both polymer films, however, exhibited poorer PL QEs compared with that of poly(9,9-dioctylfluorene), which was reported to reveal a PL efficiency of 0.9 in film.²⁸

tylfluorene), which was reported to reveal a PL efficiency of 0.9 in film.²⁸

EL device performance

We constructed PLED devices with the configuration ITO/PEDOT (50 nm)/polymer (80 nm)/Ca (10 nm)/Al (150 nm).

Figure 2 shows the EL spectra of the two devices obtained at operating voltages of 0.7 and 0.9 MV/cm, respectively. The overall features of the spectra were similar to their corresponding PL spectra, given in Figure 1, although there were some differences in the details. The LED device fabricated with PPEBE showed a broader EL spectrum than that fabricated with PPEFE. Moreover, the PPEBE device exhibited a much broader peak with a rather flat EL emission

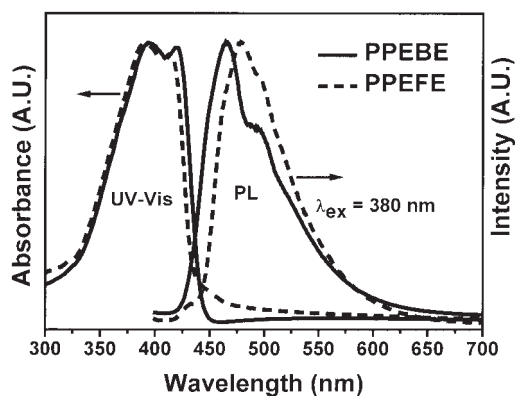


Figure 1 Film absorption and emission spectra of PPEBE and PPEFE (film thickness = 80 nm).

TABLE I
PL QE Values of the Solution (in Chloroform) and the Film (on a Quartz Plate)

	Solution QE ^a (%; 5×10^{-5} mol/L) ^b	Relative film QE ^c (%); (thickness)
PPEBE	81	95 (60 nm)
PPEFE	63	87 (55 nm)

^a Coumarin 307 was used as a standard material (QE = 73%).

^b Concentration of repeating units.

^c Relative value [normalized by the QE value of poly(9,9-dioctylfluorene)].

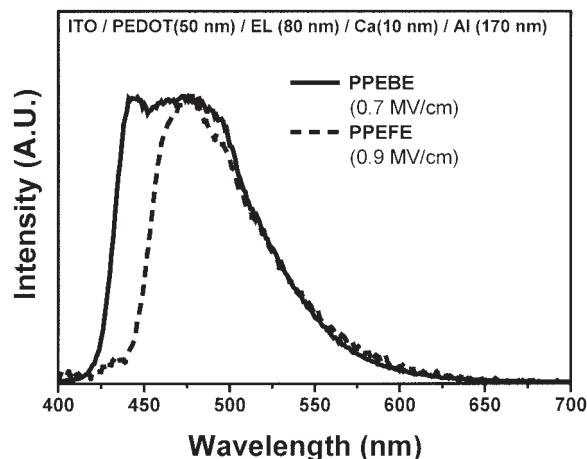


Figure 2 EL spectra of PPEBE and PPEFE.

maximum, which could be resolved to three maxima each, located at 440, 455, and 481 nm, all related to vibronic modes. On the other hand, the EL spectrum of the PPEFE device was significantly narrower and had a maximum light emission at 481 nm with a couple of discernible shoulders. The two polymers revealed practically the same feature in the tail part. PPEBE emitted more blue light of the desired wavelength than PPEFE. Weder et al.¹⁹ fabricated EL devices with dialkoxy PPE derivatives, and they were reported to be green-light emitters (EL λ_{max} = 540 nm) with an external QE of 0.03% (ITO/polymer/Al) and a maximum light brightness of 80 cd/m².

Figure 3 compares the characteristics of the devices fabricated with the polymers. We noted several important differences:

1. The threshold electric field of the PPEBE device was slightly lower (0.37 MV/cm) than that (0.41 MV/cm) of PPEFE.

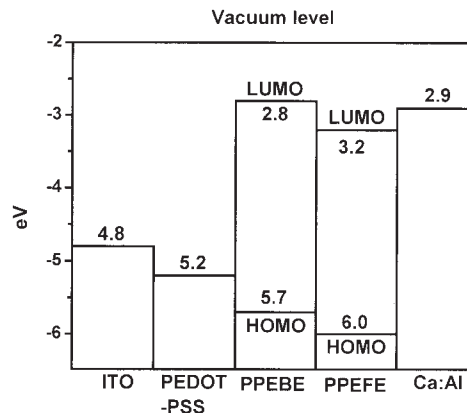


Figure 4 Electronic structures of PPEBE and PPEFE [PEDOT-PSS = polyethylenedioxythiophene doped with poly(styrene sulfonate)].

2. The maximum light output of the PPEBE device was much higher than that of the PPEFE device. The maximum brightness observed for the PPEBE device was 560 cd/m², and it was 270 cd/m² for PPEFE. Both values were higher than the values reported for other PPE derivatives,¹⁹ and they were comparable with those reported for PFs.²⁹
3. The efficiency of PPEBE was higher (0.29 cd/A) than that of PPEFE (0.10 cd/A).
4. HOMO–LUMO (Fig. 4) energy levels, as measured by cyclovoltammetry and optical bandgap, of the PPEBE (5.7 and 2.9 eV) were higher than those of the PPEFEs (6.0 and 3.2 eV). The HOMO and LUMO levels of the two polymers shown in Figure 4 imply that hole injection from the anode to the polymer layer was easier for PPEBE, whereas electron injection from the cathode was easier for PPEFE. However, the fact that not only

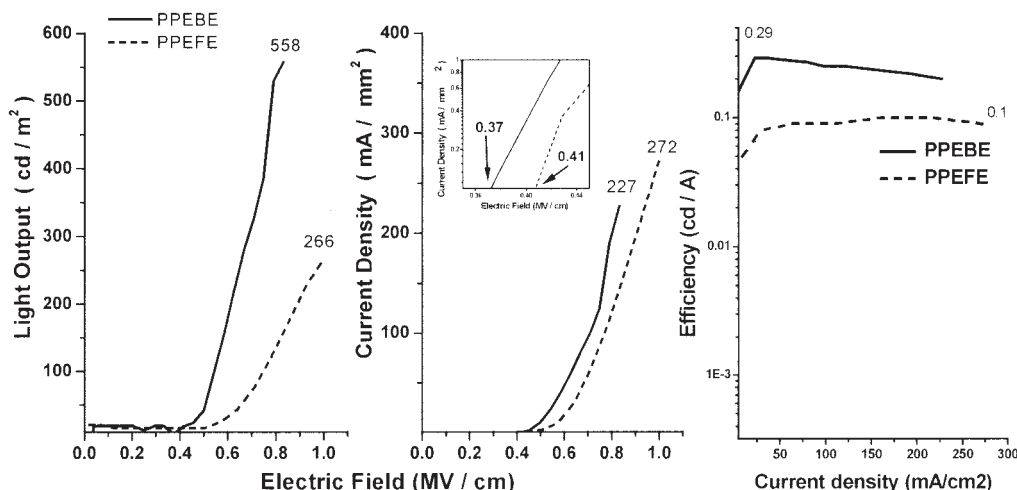


Figure 3 Luminescence versus electric field, current density versus electric field, and current density versus efficiency (cd/A) curves for the EL devices [ITO/PEDOT (50 nm)/polymer (80 nm)/Ca (10 nm):Al (170 nm)].

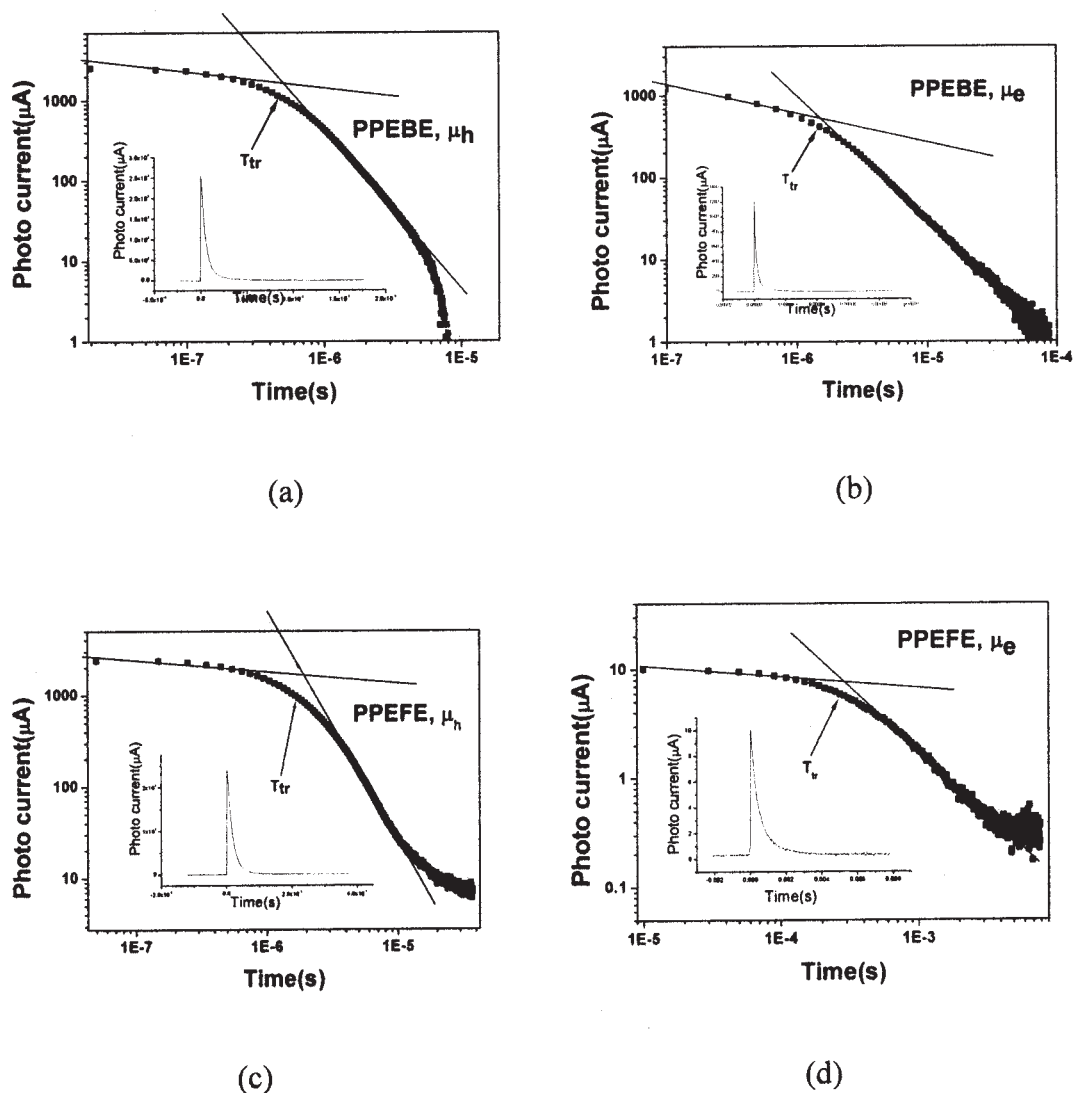


Figure 5 Double-logarithmic plots and double-linear plots (insets) of current versus time for the PPEBE (a) μ_h and (b) μ_e and PPEFE (c) μ_h and (d) μ_e . T_{tr} values are marked on each double-logarithmic plot by an arrow.

the major carriers were holes but also the faster mobility of both carriers in PPEBE than in PPEFE was believed to be the reason for the lower threshold field for the PPEBE device.

The maximum QE observed for the PPEBE device was 0.29 cd/A, which decreased slowly as the current density increased (Fig. 3). The maximum efficiency attainable for the PPEFE device was 0.10 cd/A, which was lower than the maximum efficiency of the PPEBE device.

Charge carrier mobility measurements

Figure 5 shows the double-logarithmic curves of photocurrent versus time obtained from the time-of-flight (TOF) experiments³⁰ conducted for the spin-coated films of the two polymers. They clearly show the

well-defined transit time (T_{tr} ; Fig. 5), from which we estimated the mobilities of carriers. The thicknesses of the PPEBE and PPEFE films were 174 and 215 nm, respectively. Table II compares the mobilities of photogenerated holes (μ_h) and electrons (μ_e) for the two polymers and their balance values, that is, μ_h/μ_e . According to the values given in the table, μ_h of PPEBE ($2.2 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ at 0.19 MV/cm) was about 3 times μ_e ($7.5 \times 10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$ at 0.19 MV/cm). In the case of PPEFE, μ_h ($7.9 \times 10^{-6} \text{ cm}^2/\text{V}\cdot\text{s}$ at 1.7 MV/cm) was more than 100 times μ_e ($6.6 \times 10^{-8} \text{ cm}^2/\text{V}\cdot\text{s}$ at 0.9 MV/cm). Bradley et al.²⁹ reported the μ_h value of ordered poly(9,9-dioctylfluorene) to be $\mu_h = 8.5 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$ at 10^4 V/cm . They observed that hole carriers were found to be nondispersive, but electrons were too dispersive to get carrier mobility. This value was faster than that of PPEBE. The presence of the $\text{C}\equiv\text{C}$ triple bonds and also of the two nonequivalent

TABLE II
Typical μ_h and μ_e Values of the Polymers

Polymer	Thickness (nm)	μ_h (cm ² /V s) (at electric field (V/cm))	μ_e (cm ² /V s) (at electric field (V/cm))	μ_h/μ_e
PPEBE	215	2.2×10^{-4} (1.9×10^5) 7.9×10^{-6}	7.5×10^{-5} (1.9×10^5) 6.5×10^{-8}	2.9
PPEFE	174	(1.7×10^6)	(8.6×10^5)	120

structures in the repeating units of the two polymers appeared to lower μ_h . We believe that the balance in the mobilities of the charge carriers observed for PPEBE was a major contributor in the better performance of its LED devices compared to those of PPEFE. The latter showed not only a much greater imbalance in charge carrier mobilities but also much slower mobilities of both carriers.

EXPERIMENTAL

General

All reagents and solvents were purchased from Strem Chemicals, Inc. (Newburyport, MA), Aldrich Chemical Co. (Milwaukee, WI), Tokyo Kasei Kogyo Co. (Tokyo, Japan), or Merck (Frankfurt, Germany). Spectroscopic-grade chloroform was used for all of the spectroscopic studies. THF was dried over sodium benzophenone³¹ and distilled under an argon atmosphere before use. Triethylamine and diisopropylamine were dried over KOH, and toluene was dried over CaH. These solvents were then distilled under a nitrogen atmosphere and deoxygenated by being purged with argon for 30 min before use. All polymerizations were conducted with standard vacuum-line techniques.

Preparation and purification of monomers

4,4'-Diiodo-3,3'-dimethylbiphenyl (Tokyo Kasei Kyogo) and 2,7-diiodo-9,9-di(*n*-octyl)dofluorene (Aldrich) were purified by recrystallization from ethanol. 1,4-Dioctyl-2,5-diethynylbenzene was prepared following a published procedure.²¹

Synthesis of the polymers

PPEBE

1,4-Dioctyl-2,5-diethynylbenzene (500 mg, 1.43 mmol), 4,4'-diiodo-3,3'-dimethylbiphenyl (621 mg, 1.43 mmol), Pd(PPh₃)₄ (34 mg, 0.03 mmol), and CuI (11 mg, 0.06 mmol) were mixed in toluene (8 mL) and diisopropylamine (2 mL).³² The reaction mixture was then stirred at 70°C for 48 h. The mixture became highly fluorescent. Insoluble solids were filtered off after the

reaction mixture was cooled to room temperature. The filtrate was added dropwise to acetone (500 mL). After the reaction was stirred for 2 h, the precipitate was collected and washed with acetone and hot ethanol and then dissolved in chloroform. The solution was filtered through Florsil (60–100 mesh) to remove residual palladium. The filtrate was added dropwise to cold acetone. The fluorescent precipitate was collected on a filter. Low-molar-mass oligomers were removed from the product by Soxhlet extraction with acetone. The resulting polymer was dried overnight *in vacuo*. PPEBE was obtained as a light green solid (recovered yield = 680 mg, 90%):

¹H-NMR (CDCl₃, δ , ppm): 0.88 [s, 6H, Ar—CH₂—(CH₂)₆—CH₃], 2.85–2.62 (m, 10H, Ar—CH₂—, Ar—CH₃), 1.28–1.73 [m, 24H, Ar—CH₂—(CH₂)₆—CH₃], 7.41–7.60 (m, 8H, Ar—H). ANAL. Calcd for (C₄₀H₄₈)_n: C, 90.85%; H, 9.15%. Found: C, 90.60%; H, 9.40%.

PPEFE

This polymer was prepared by the same procedure as described previously for the preparation of PPEBE. A mixture of 1,4-dioctyl-2,5-diethynylbenzene (500 mg, 1.43 mmol), 9,9-di(*n*-octyl)-2,7-diiodofluorene (919 mg, 1.43 mmol), Pd(PPh₃)₄ (34 mg, 0.03 mmol), and CuI (11 mg, 0.06 mmol) were mixed in toluene (8 mL) and diisopropylamine (2 mL). The reaction and separation conditions were the same as described for the synthesis of PPEBE. PPEFE was obtained as a yellow solid (recovered yield = 840 mg, 80%):

¹H-NMR (CDCl₃, δ , ppm): 0.66–2.00 [m, 30H, (Ar—)₂C[—CH₂(CH₂)₆CH₃]₂], 2.87 [m, 4H, (Ar—)₂C[—CH₂(CH₂)₆CH₃]₂], 7.36–7.71 (m, 8H, Ar—H). ANAL. Calcd for (C₅₁H₆₈)_n: C, 89.94%; H, 10.06%. Found: C, 89.80%; H, 10.20%.

Measurements

¹H-NMR spectra of intermediates, monomers, and polymers were obtained on a Varian AM 300 spectrometer. ¹³C-NMR spectra of polymers were recorded on the same instrument in CDCl₃. Elemental analyses were performed by the Korea Basic Science Institute, Seoul, with a Flash EA 1112 series elemental analyzer (Milan, Italy). GPC analysis was conducted at 40°C

with a Wyatt Dawn EOS system (Santa Barbara, CA) equipped with Ultra-I-stragel columns with THF as the eluent at a flow rate of 0.5 mL/min and with polystyrene as the calibration standard. The UV-vis. absorption and luminescence spectra were recorded on an HP8452A diode array spectrophotometer (Hewlett Packard, Toronto, Canada) and an AMINCO-Bowman Series 2 (Thermo Spectronic, Rochester, NY) luminescence spectrometer, respectively, at room temperature. The cyclovoltammogram³³ was obtained on a Amagel 2049 potentiostat and a Power-Lab system (4 sp) (PAR EG&G model 273A, Princeton, NJ). The redox behavior of the compounds was investigated at room temperature under nitrogen with a standard three-electrode electrochemical cell at a scanning rate of 20 mV/s. in a 0.10M acetonitrile solution of tetrabutylammonium tetrafluoroborate. A platinum working electrode, counterelectrode, and Ag/Ag⁺ (0.01M in acrylonitrile) reference electrodes were used.

Charge carrier mobility measurements as done by the TOF method³³

To measure the charge carrier mobility, we first fabricated sample devices as follows:³⁴ an ITO-coated quartz plate with a sheet resistance of 20 Ω/cm^2 was patterned by the vapor of a mixed solution of HNO₃ and HCl in a volume ratio of 3:1. The patterned ITO-coated quartz plates were cleaned by sequential ultrasonication in distilled water, acetone, methanol, and 2-propanol for 30 min each and then dried in a stream of argon. Polymer layers were spin-coated on the ITO-quartz substrate. The thicknesses of the emitting layers of PPEBE and PPEFE were 174 and 215 nm, respectively. The semitransparent aluminum electrode was deposited at a deposition rate of about 2 $\text{\AA}/\text{s}$ to a thickness of 30 nm on the polymer layers under a pressure of 1×10^{-6} Torr with a VPC-260 vacuum coater (ULVAC, Kanagawa, Japan) and a CRTM-6000 thickness monitor (ULVAC). The active area of the device was 4.9 mm². The thickness of each layer was determined by a Tencor P-10 surface profiler (Tencor, Rocklin, CA).

To measure the mobility of charge carriers, a conventional TOF measurement technique^{30(a)} was used. For optical excitation, a 7-ns pulse at $\lambda = 355$ nm (a third-harmonic Q-switched Nd-YAG laser, 10 Hz, Continuum, Mountainview, CA) was used. The photocurrent transient was measured with a digital storage oscilloscope (LeCroy, 9361C, Dual 300 MHz, Chestnut Ridge, NY). Resistors from 50 Ω to 10 K Ω were used for photocurrent detection. The resistor's value was chosen by consideration of the magnitude of the signal and RC time of the total circuit of a sample device. At first, the transient photocurrent profiles of *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)-benzidine

(TPD) with a thickness of 900 nm [ITO/TPD (900 nm)/Al (30 nm)] was measured. The hole carrier transport appeared to be nondispersive with a clear plateau and a subsequent current drop. The measured μ_h (ca. $9 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$) was in a good agreement with the results of Naka et al.³⁰

CONCLUSIONS

We prepared two new copolymers by regularly inserting a 3,3'-dimethyl-1,1'-biphenylene unit or 9,9-diocetylfluorenylene unit in the PPE main chain, and we studied their PL and EL properties. The performance of the PPEBE device was better than that of PPEFE. Both polymers showed blue-light emission in PL and in EL with less green light than PFs.

PPEBE revealed a μ_h value on the order of $10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$, which belonged to the highest values known for simple polymeric materials, and the carrier balance was excellent ($\mu_h/\mu_e = 3$). It became clear that the inclusion of biphenylene comonomer units resulted in better EL performance than the inclusion of fluorenyl units, which must have resulted from their geometric differences. We believe that a proper modification of the structure of PPEBE and optimized construction of the PLED device may lead to the successful development of blue-light-emitting displays based on poly(phenylene ethynylenes).

This investigation demonstrated an important approach in the structural design of blue-light-emitting polymers for the achievement of balance in carrier mobilities.

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