Poly[(3,3'-dimethyl-1,1'-biphenyl-4,4'-diyl)ethynediyl(2,5-dioctyl-1,4-phenylene)ethynediyl] and a Related Copolymer – New Blue EL Polymers

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Summary: Electroluminescence (EL) properties of a new poly(aryleneethynylene) and a related copolymer were studied. They are poly[(3,3'-dimethyl-1,1'-biphenyl-4,4'-diyl)ethynediyl(2,5-dioctyl-1,4-phenylene)ethynediyl] (PPEBE) and related copolymer (PPEBE-*co*-mP) containing 20 mole % of 1,3-phenylene units. Both polymers are blue-light emitters; the former was found to perform better than the latter when the light-emitting diode (LED) device had the configuration of ITO/PEDOT/polymer/Li:Al. The device constructed with the former polymer exhibited the external quantum efficiency of 0.05 and the maximum brightness higher than 400 cd/m^2 with its EL spectrum showing maxima at λ = 445 and 472 nm. The performance of the device constructed with the copolymer was about one fifth of the device fabricated with the homopolymer.

Keywords: blue emitter; EL; PLED; poly(phenyleneethynylene)

Introduction

Since the Cambridge report[1] on the electroluminescence (EL) properties of poly(*p*-phenylenevinylene) (PPV), interest in the EL phenomena in a wide variety of polyconjugated polymers[2] has been intensified due to the possible development of new display devices based on those polymers. PPV is a green-light-emitting material and polyfluorenes[3,4] are blue-light-emitting polymers. The performance of polymer light-emitting diodes (PLED) devices not only depends on the chemical structure of the polymers but also on many factors such as the nature of electrodes, utilization of additional carrier transporting layers, and so on.

We recently reported highly efficient green-light-emitting PPV derivatives bearing carbazole[5], phenyloxadiazole[6], and fluorene pendants[7] directly bonded to the PPV backbone. They, in general, revealed[8] a better balance in the mobility of the carriers. Moreover, some of the polymers were found to form new intragap states upon contact with the calcium electrode, which appears to be the reason for a lowered threshold electric field for the polymers[9].

Among the polyconjugated polymers, various poly(*p*-phenyleneethynylene) (PPE) derivatives

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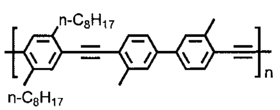
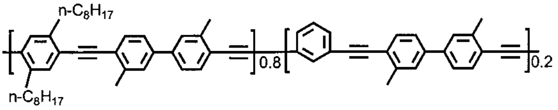
also have been studied in PLED applications[10]. We find the possibility that one may be able to reduce the wavelength of the emitted light by replacing the double bonds in, for example, PPV with triple bonds, which increases the bandgap energy. In fact, there are several reports[11,12] claiming that a proper design of a PPE derivative exhibits blue emission.

In this investigation we prepared the following new PPE derivatives and their EL properties were studied by examining the device performance of ITO/PEDOT/polymer/Li:Al.



PPEBE



PPEBE-*co*-mP

Experimental

Polymer Synthesis

PPEBE: 1,4-diethynyl-2,5-dioctylbenzenene (428 mg, 1.22 mmol), 4,4'-diiodo-3,3'-dimethyl-1,1'-biphenyl (580 mg, 1.34 mmol), $[Pd(PPh_3)_4]$ (84 mg, 0.07 mmol), and CuI (29 mg, 0.15 mmol) were combined in toluene (30 mL) and diisopropylamine (8 mL). The reaction mixture was then stirred at 70 °C. Ammonium iodide salts were formed immediately after starting the reaction and the mixture became highly fluorescent. After a total reaction time of 28 h, the reaction mixture was cooled to room temperature and added dropwise to rapidly stirred acetone (500 mL). After stirring for 2 h, the precipitate was collected and washed with acetone, hot ethanol, and then dissolved in chloroform and filtered through Florisil®(60-100 mesh) to remove residual palladium. The filtrate was dropwise added to cold acetone. The fluorescent precipitate was filtered off and dried overnight in vacuo. PPEBE was obtained as a greenish yellow solid (400 mg, 96 %), ^{1}H NMR ($CDCl_3$, δ ppm) 0.88-2.86 (m, 40H, Ar-CH_2-(CH_2)-CH_3, Ar-CH_3), 7.41-7.60 (m, 8H, Ar-*H*), Anal. Calcd for $C_{26}H_{38}$: C 90.85, H 9.15 %. Found : C 91.60, H 8.40 %

PPEBE-*co*-mP: This polymer was prepared by the same procedure. A mixture of 1,4-diethynyl-2,5-dioctylbenzene (470 mg, 1.34 mmol), 1,3-diethynylbenzene[13] (43 mg, 0.34 mmol), 4,4'-diiodo-3,3'-dimethyl-1,1'-biphenyl (803 mg, 1.85 mmol), $[Pd(PPh_3)_4]$ (115 mg, 0.10 mmol), and CuI (38 mg, 0.20 mmol) were combined in toluene (35 mL) and diisopropylamine (8.5 mL). PPEBE-*co*-mP was obtained as light yellow solid (410 mg, 97 %), ^{1}H NMR ($CDCl_3$, δ ppm) 0.87-

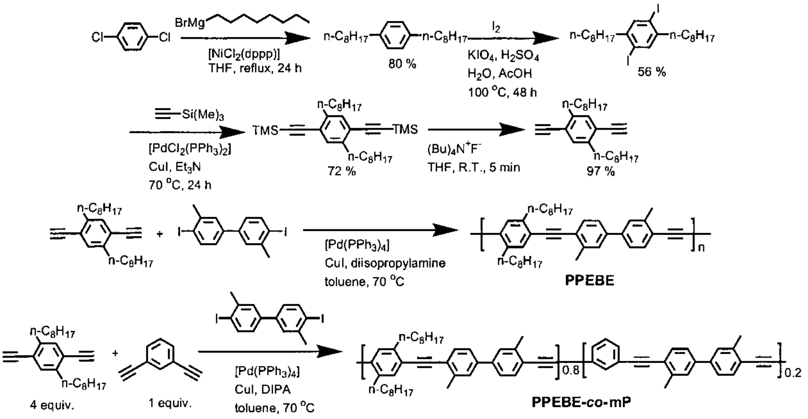
2.86 (m, 40H, Ar-C*H*$_2$-(C*H*$_2$)-C*H*$_3$, Ar-C*H*$_3$), 7.41-7.60 (m, 8H, Ar-*H*), 7.76 (s, 0.01H, Ar-H), Anal. Calcd for $C_{26}H_{38}$: C 92.26, H 7.74 %. Found : C 92.95, H 7.05 %

Measurements

GPC analysis was conducted with a Wyatt Dawn EOS system equipped with Ultra-I-stragel columns using THF at a flow rate of 0.5 mL/min at 40 °C with polystyrene as the calibration standard. The luminescence spectra for the polymers were recorded on an AMINCO-Bowman Series 2 luminescence spectrometer at room temperature. The current and luminescence intensity as a function of applied field were measured using an assembly consisting of PC-based dc power supply (HP 6623A) and a digital multimeter (HP 34401). Also a light power meter (Newport Instruments, model 818-UV) was used to measure the device light output in microwatts. Luminance was measured with a Minolta LS-100 luminance meter.

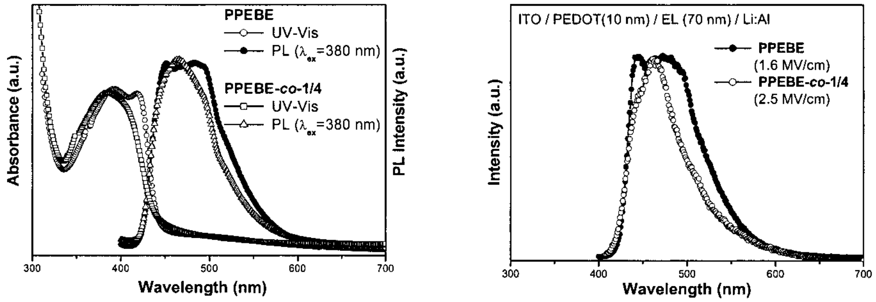
Results and Discussion

Synthesis of polymers: PPEBE and PPEBE-*co*-mP were prepared as described in Experimental (Scheme 1) Polymerization proceeded homogeneously and insoluble particles, diisopropylammonium iodide, were formed as the reaction progressed. Both polymers are readily soluble at room temperature in chloroform and tetrahydrofuran. Their number-average molecular weights ($\overline{M_n}$) determined by GPC were found to be 15500 and 10200, respectively. Polydispersity indices were 1.5 and 1.6.



Scheme 1. Synthesis of PPEBE and PPEBE-*co*-mP.

UV-vis absorption and photoluminescence (PL) spectra: Figure 1(a) compares the UV-vis absorption and PL spectra of the two polymers in thin films. We note that as we include the meta-phenylene unit in the copolymer, UV-vis absorption as well as PL spectra in the longer wavelength region is shifted toward blue side. The absorption in 375-450 nm corresponds to $\pi \rightarrow \pi^*$ transitions of the polymers. The PL spectrum of the PPEBE polymer exhibits finer vibronic details with two distinct maxima located at 451 and 485 nm with a weaker shoulder at about 525 nm. In contrast, the PL spectrum of the polymer, PPEBE-*co*-mP, shows a dominant peak maximum at 465 nm with two weaker shoulders in the longer wavelength region. The optical bandgap (E_g) estimated from the absorption edge (450 nm) for both the polymers is 2.7 eV, which is higher than that of PPV (2.4 eV).



a b

Figure 1. (a) Absorption and emission studies of PPEBE and PPEBE-*co*-mP, (b) their EL spectra (film thickness 70 nm).

EL device performance

We constructed PLED devices having the configuration of ITO/PEDOT (10 nm)/polymer (70 nm)/Li:Al. Here, PEDOT stands for poly[3,4-(ethylenedioxy)thiopene-2,5-diyl] doped with sulfonated polystyrene obtained from Bayer. The room temperature conductivity of the polymer was 10 S/cm. Figure 1b shows the EL spectra of the two polymers obtained at the operating voltages 1.6 and 2.5 MV/cm, respectively. The overall feature of the spectra is very similar to their corresponding PL spectra given in Figure 1a, although there are some differences in details.

The copolymer emits a better blue light of the desired wavelength. Figure 2 compares the characteristics of the devices fabricated with the polymers. We note several important differences: (1) The threshold electric field of PPEBE is significantly lower (1.4 MV/cm) than that (2.5 MV/cm) of the copolymer. (2) Maximum light output of the PPEBE device is much higher than that of the PPEBE-*co*-mP device. (3) HOMO-LUMO energy levels, measured by cyclovoltammetry and optical band gap of the homopolymer (5.9-3.1 eV) are higher than those of the copolymer (6.1-3.3 eV). (4) Device stability is much greater for the PPEBE device than for the other. Needless to say, the phenomena described in (1) – (4) are correlated.

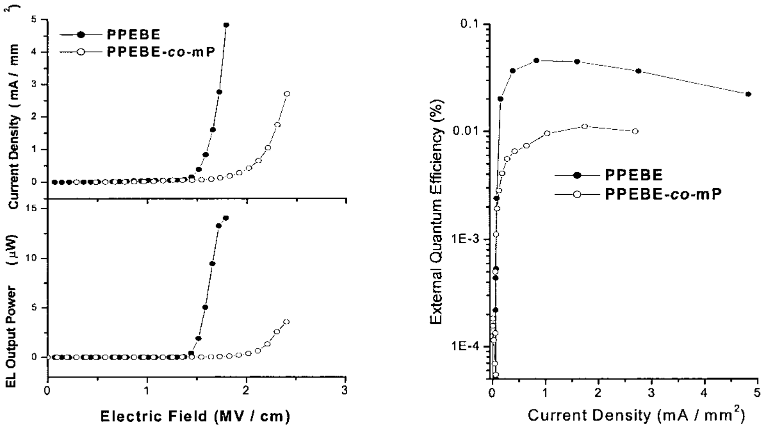


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Figure 2. Current density vs. electric field, EL intensity vs. electric field, and external quantum efficiency vs current density curves for EL devices (ITO/PEDOT (10 nm)/polymer (70 nm)/Li:Al).

The maximum brightness observed for the PPEBE device was 410 cd/m^2, which is much higher than the values reported for other poly(*p*-phenyleneethynylene) derivatives[10] and comparable with those reported for polyfluorenes[3].

The external quantum efficiencies of the two devices are shown in Figure 2b. The maximum quantum efficiency observed for the PPEBE device was 0.05 %, decreasing steadily as the current density or the applied electric field increased. The situation for PPEBE-*co*-mP was similar. The maximum efficiency attainable was 0.01 %. Therefore, it is concluded that the inclusion of the *m*-phenylene unit lowers the device performance, although the wavelength of the emitted light is close to the ideal blue light. In the light of the very low current flow in the copolymer device, it is conjectured that inclusion of the *m*-phenylene unit reduces the carrier mobility, which has to be confirmed by future work.

Nevertheless, we believe that a proper modification of the structure of PPEBE and better construction of the PLED device may lead to a successful development of blue-light emitting displays based on poly(phenyleneethynylene)s.

Acknowledgement

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[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, A. B. Holmes, *Nature* **1990**, 347, 539.
[2] H.-K. Shim, J.-I. Jin, *Adv. Polym. Sci.* **2002**, 158, 193.
[3] A. W. Grice, D. D. C. Bradley, M. Bernius, M. Inbasekaran, W.W. Wu, E. P. Woo, *Appl. Phys. Lett.* **1998**, 73, 629.
[4] M. Bernius, M. Inbasekaran, J. O'Brien, W.Wu, *Adv. Mater.* **2000**, 12, 1737.
[5] K. Kim, Y.-R. Hong, S.-W. Lee, J.-I.Jin, Y.Park, B.-H.Sohn, W.-H. Kim, J.-K. Park, *J. Mater. Chem.* **2001**, 11, 3023.
[6] D. W. Lee, K. Y. Kwon, J.-I. Jin, Y. Park, Y. R. Kim, I. W. Hwang, *Chem. Mater.* **2001**, 13, 565.
[7] B.-H. Sohn, K. Kim, D.-Soo. Choi, Y.-K. Kim, S.-C. Jeoung, J.-I. Jin, *Macromolecules* **2002**, 35, 2876.
[8] J.-I. Jin, C.-E. Lee, J.-S. Joo, Y. Park, Ed. Sasabe, in *Nanotechnology toward the Organic Photonics*, GooTech Press, Chitose, **2002**, p. 253.
[9] V. E. Choong, Y. Park, R. Hsieh, Y. Gao, in *Photonic Polymer Systems - Fundamentals, Methods, and Application*, Marcel Dekker, New York, **1998**, Chap. 5.
[10] A. Montali, P. Smith, C. Weder, *Synth. Met.* **1998**, 97, 123.
[11] G. Brizius, N. G. Pschirer, W. Steffen, K. Stitzer, H.-C. Loye, U. H. F. Bunz, *J. Am. Chem. Soc.* **2000**, 122, 12435
[12] W. Y. Huang, W. Gao, T. K. Kwei, Y. Okamoto, *Macromolecules* **2001**, 34, 1570.
[13] M. Itoh, M. Mitsuzuka, K. Iwata, K. Inoue, *Macromolecules* **2001**, 27, 7917.
[14] A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, E. P. Woo, *Appl. Phys. Lett.* **1998**, 73, 629.