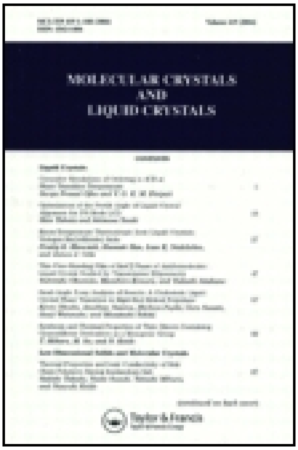

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Polarized Emission from Donor-Acceptor Liquid-Crystalline Polymers Containing Oxadiazole and Carbazole Moieties

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We have synthesized a class of blue-emitting polymers based on a donor-acceptor architecture composed of oxadiazole and carbazole moieties containing various substituted groups in the same side chain. Depending on the substituted group at carbazole, they showed different thermodynamic properties: two polymers containing N-methylcarbazole showed liquid-crystalline behavior. The single-layer polymer light-emitting diodes using these polymers exhibited blue emission with peaks from 430 to 440 nm. The device using the liquid-crystalline polymer with an alignment layer emitted polarized blue light with a dichroic ratio of 5.1.

Keywords: donor-acceptor; electroluminescence; liquid-crystalline polymer; polarized emission; polymer light-emitting diodes

INTRODUCTION

Polymer light-emitting diodes (PLEDs) have been studied intensively since the innovative discovery because they can be fabricated by solution processes with active materials [1]. PLEDs provide much less expensive manufacturing processes than those of LEDs which are prepared with small molecules by high vacuum deposition [2]. Light-emitting polymers, so far, are rarely good conductors for both electrons and holes, whereas PLEDs require a good charge balance. With a goal of balancing the charge injection and transport, a modulation of the polymer structure so as to contain both electron- and hole-transporting units is a reasonable approach to achieve a high performance in single-layer PLEDs [3].

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Anisotropy of liquid-crystalline polymers (LCPs) and their good processability allow direct preparation of well-aligned thin films, leading to PLEDs exhibiting polarized light [4]. It also has been reported that the LC self-organization process is useful to improve charge transport in aligned films [5,6].

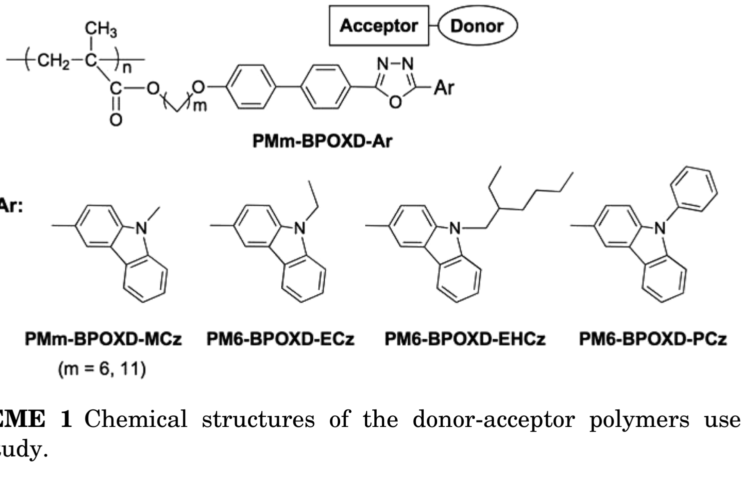
In the previous works, we have focused on the synthesis of bipolar polymers based on a donor-acceptor architecture containing both electron- and hole-transporting units in the side chain, and already observed polarized emission from PLEDs using LCPs [7–9].

Herein, we synthesized a class of bipolar polymers containing oxadiazole (OXD) as an electron transporter and carbazole (Cz) as a hole transporter in the same side chain. We modified chemical structures of the polymers so as to show intense blue emission, bipolar charge-transporting property and good film formation to achieve high performance in PLEDs. We also introduced various alkyl groups at the Cz moiety to give the polymers LC behavior and to obtain polarized electroluminescence (EL).

EXPERIMENTAL

Material

Scheme 1 shows the chemical structures of the donor-acceptor polymers used in this study. The polymers were prepared as reported previously and identified by means of ^{1}H NMR spectroscopy, elemental analysis and mass spectroscopy [7]. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were



SCHEME 1 Chemical structures of the donor-acceptor polymers used in this study.

determined by gel permeation chromatography (GPC; JASCO model DG-980-50; columns, Shodex K802 + K804 + K805; eluent, chloroform) calibrated with polystyrene standards.

Characterization

Glass transition and phase transition temperatures of the synthesized polymers were determined by differential scanning calorimetry (DSC; Seiko I & E models SSC-5200 + DSC220C) at a heating rate of 10°C/min under a nitrogen atmosphere. At least, three scans were performed for each sample to inspect its reproducibility. Phase transition behavior was also evaluated with a polarizing optical microscope (POM; Olympus model BX50) equipped with hot stages (Mettler, FP-90 + FP-82) and an X-ray diffractometer (Philips, PW1830) equipped with a thermal controller (Philips, HTK-2-HC), Absorption and photoluminescence (PL) spectra were measured at room temperature with a UV-vis spectrometer (JASCO, V-550) and a fluorescence spectrophotometer (Hitachi, F-7010), respectively. Cyclic voltammetry (CV) was carried out on an electrochemical analyzer (ALS, Model 600 A) with 0.1 mol/L tetra-*n*-s as a supporting electrolyte (a scan rate = 100 mV/s). A platinum wire was used as a counter electrode, and a saturated Ag/$AgNO_3$ solution (0.01 mol/L in acetonitrile) was used as an electrolyte. Potentials of the molecules were referenced to Ag/$AgNO_3$ and the oxidation potential of ferrocene/ferrocenium (FOC). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the polymer films were calculated from the onset potential of oxidation and reduction waves by assuming that the absolute energy level of FOC is 4.8 eV.

Polymer Light-Emitting Diodes

Single-layer PLEDs were fabricated using the polymers as an emitting layer. The polymer solutions were spin-coated onto ITO glass substrates and annealed at 160°C. In case of polarized LEDs, PEDOT-PSS (Bayer, EL grade) films were built up onto ITO glass substrates, and then polymer solutions in 1,1,2,2-tetrachloroethane (1.5 wt%) were spin-coated onto mechanically rubbed PEDOT-PSS films to give thin films of less than 100 nm. On a top of the polymer film, a thin layer of magnesium and silver (Mg:Ag = 10:1) as a cathode was deposited by thermal vacuum evaporation at a vacuum pressure less than 10^{-5} torr. Thickness of each film was measured with a Dektak surface profiler. EL spectra were measured with the fluorescence spectrophotometer at room temperature. Current density and luminance characteristics of the devices were measured with a power supply (Advantest, R6243) and a luminance meter (Minolta, LS-500). The emitting area was $2 \times 3\,\mathrm{mm}^2$. All measurements were performed under an ambient atmosphere.

RESULTS AND DISCUSSION

Thermodynamic Properties

DSC thermograms and POM images of the polymers are shown in Figure 1. Depending on the substituted groups at the Cz moiety, the polymers showed different thermodynamic properties. Molecular weights and thermodynamic properties of the polymers are detailed in Table 1.

Two polymers containing *N*-methylcarbazole (MCz) showed LC behavior. We observed nematic phases above glass transition temperatures and nematic to isotropic phase transitions at 223°C and 210°C for **PM6-BPOXD-MCz** and **PMll-BFOXD-MCz**, respectively. The other polymers containing ethyl, ethylhexyl and phenyl groups at the Cz moiety exhibited no LC phase even though their monomers showed LC phases. In the previous study, we reported that the LC

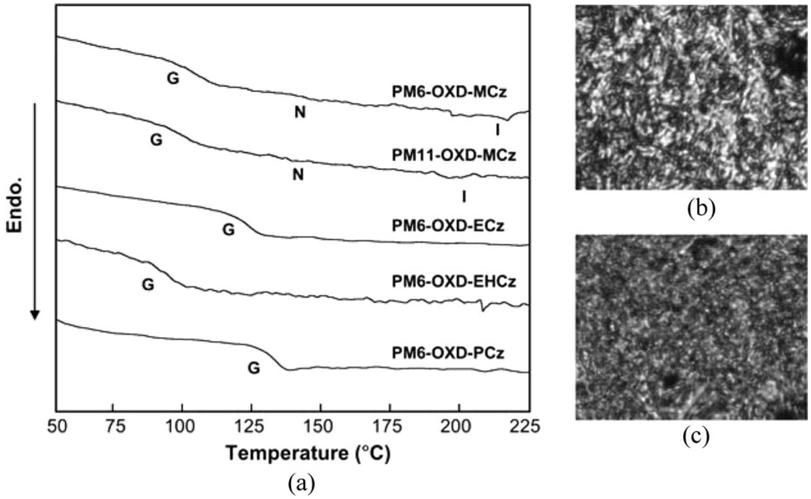


FIGURE 1 DSC thermograms on the second heating at a rate of 10°C/min for the polymers (a) and the textures of **PM6-BP0XD-MCz** (b) and **PMll-BPOXD-MCz** (c) at 160°C (on cooling) observed with a polarizing optical microscope.

TABLE 1 Intrinsic Properties of the Donor-Acceptor Polymers

Polymer	Phase transition temperature[a]	M_n $(M_w/M_n)^b$	$\lambda_{PL}{}^c$ nm	$\Phi_{PL}{}^d$ %	IP[e] eV	$E_g{}^f$ eV
PM6-BPOXD-MCz	G 105 N 223 I	25,000 (1.5)	425	72	5.60	3.22
PMll-BPOXD-MCz	G 100 N 210 I	28,000 (1.9)	430	72	5.60	3.20
PM6-BPOXD-ECz	G 120 I	38,000 (1.8)	421	72	5.78	3.26
PM6-BPOXD-EHCz	G 90 I	30,000 (2.1)	417	78	5.82	3.28
PM6-BPOXD-PCz	G 130 I	23,000 (1.4)	410	73	5.74	3.31

[a] G, glassy; I, isotropic; N, nematic.

[b] M_n, the number-average molecular weight (M_w/M_n, the molecular weight distribution).

[c] The peak wavelength of the PL spectrum in a film.

[d] The PL quantum yield of the polymer in dichloromethane.

[e] Determined from the onset of the oxidation wave of the polymer film.

[f] Determined from the band edge of the absorption spectrum.

properties of the polymers were strongly influenced by the molecular structures of the amine derivatives at the end groups [7].

Furthermore, solubility of the polymers was improved by introducing longer alkyl groups. These lateral substituents at the end Cz moiety give rise to a larger intermolecular distance, compared with a short group, and could increase the solubility.

Optical Properties

Absorption and PL spectra of the polymers were measured both in solutions and films at room temperature. The results are summarized in Table 1. The polymers showed absorption with peaks at 303 and 336 nm and emission peaks in the region of 410–430 nm (Fig. 2). The PL spectrum of the polymer film containing a methyl group at Cz was red-shifted compared with those of other polymer films with longer alkyl groups.

The quantum efficiency (Φ_{PL}) of the polymers was measured in a 10^{-6} mol/L dichloromethane solution by comparing emission with that of a standard solution of quinine sulfate ($\Phi_{PL} = 0.546$) in sulfuric acid. The polymers emitted intense blue light with high Φ_{PL} values over 70% in dichloromethane (Table 1).

Electrochemical Properties

CV measurement was performed to evaluate redox behavior and stability of both cation and anion radicals. In addition, the results were used to calculate both the HOMO and LUMO energy levels and the band gaps of the polymers (Table 1).

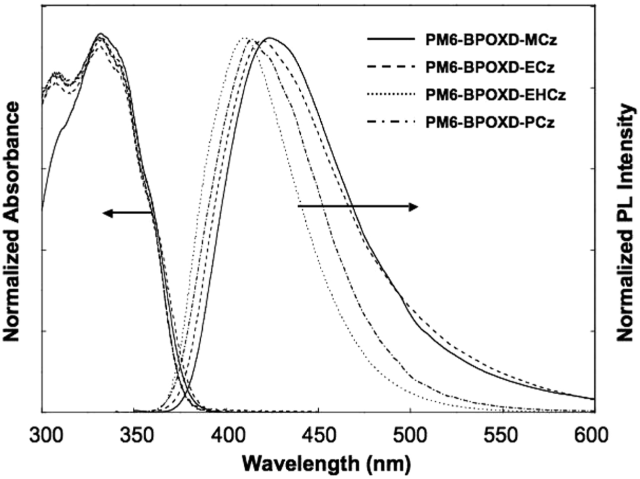


FIGURE 2 Absorption and PL spectra of the polymer films.

M6-BPOXD-MCz (monomer) showed very similar oxidation behavior to that of *N*-methylcarbazole as shown in Figure 3 [10]. Upon scanning in a positive direction, two radical oxidation waves were observed at 0.9 V (a half-wave potential) and 1,5 V vs SCE, corresponding to the formation of the radical cation and dication, respectively. The higher oxidation potentials of the monomer, compared with those of MCz at 0.7 V and 0.9 V, are caused by an electron-withdrawing effect of the directly attached OXD group. Upon negative scanning to −3.0 V, two separated irreversible reduction potentials were observed at −1.4 V and −2.3 V vs SCE. The latter corresponds to a reduction potential of the OXD moiety at −2.3 V vs SCE [11,12].

The oxidation and reduction waves of both the monomer and the polymer resembled those of MCz and OXD, respectively. As a result, the polymers show a bipolar charge-transporting ability to transport both holes and electrons injected from electrodes in single-layer PLEDs.

Single-Layer Polymer Light-Emitting Diodes

The single-layer devices, ITQ/polymer/MgAg, were fabricated to investigate EL property of the polymers. The single-layer PLEDs could be operated at the driving voltage higher than 8 V. The EL spectra of the polymers containing different alkyl groups at Cz are shown in Figure 4. The devices exhibited blue emission originated from the singlet emission of the polymers. The emission bands from 420 to 450 nm correspond to the PL spectra of the polymer films. The device

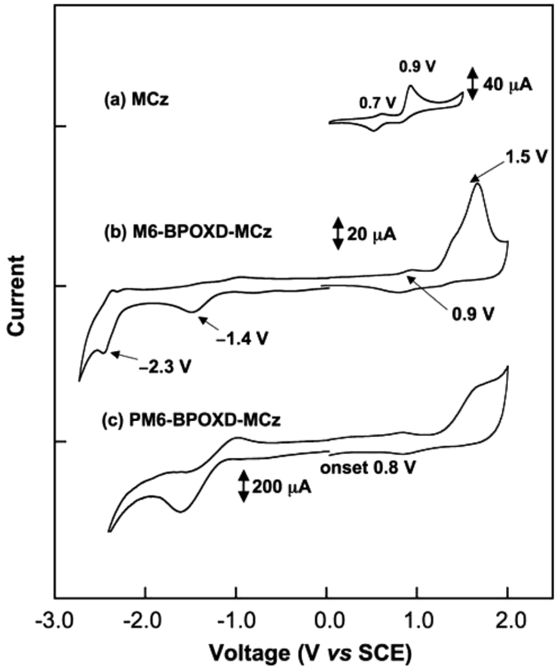


FIGURE 3 Cyclic voltammograms of MCz (a) and **M6-BPOXD-MCz** (monomer) (b) in solutions and **PM6-BPOXD-MCz** (polymer) in a film (c) (a scan rate = 100 mV/s).

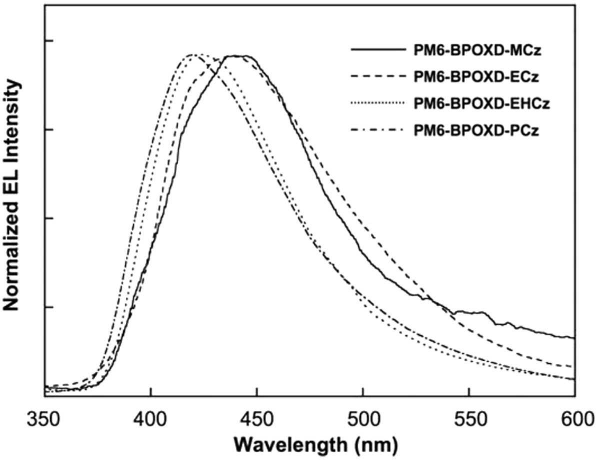
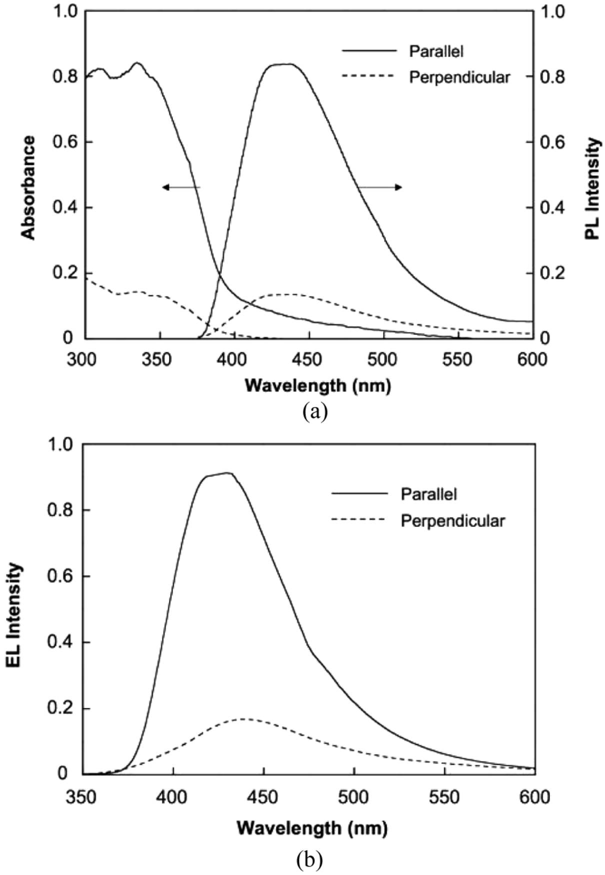


FIGURE 4 EL spectra of the single-layer PLEDs (ITO/polymer/MgAg) at an applied voltage of 15 V.

using **PM6-BPOXD-MCz** showed a red-shifted spectrum by about 20 nm compared to that of the device using **PM6-BPOXD-PCz**. This red-shifted emission might arise from densely packed chromophores in the side chain, where they are located closely enough to interact between neighboring chromophores in the **PM6-BPOXD-MCz** films.

The substituted alkyl groups at Cz led the polymers to show high solubility enough to give a good film as well as an amorphous structure, which makes them good candidates for application in PLEDs.



(a)

(b)

FIGURE 5 Polarized absorption and PL spectra of the **PMll-BPOXD-MCz** film spin-coated onto a rubbed PEDOT-PSS layer (a) and polarized EL spectra of the devices (b): parallel (solid line) and perpendicular (dashed line) to the rubbing direction.

Polarized Electroluminescence

An aligned LCP film was obtained by using an alignment layer of a mechanically rubbed PEDOT-PSS film on an ITO glass substrate. The LCP film on the rubbed PEDOT-PSS layer was annealed at 160°C where the polymer shows a nematic phase, then quenched by lowering the temperature below the glass transition temperature. The alignment of the LCP film was evaluated by absorption and PL spectra as shown in Figure 5(a). The polarized absorption spectrum of **PMI1-BPOXD-MCz** parallel to the rubbing direction was 4.5 times larger than that perpendicular to it, indicating uniaxial alignment of chromophores. The PL spectra of the LCP film showed a corresponding dichroic ratio of 4.5.

The device, ITO/rubbed PEDOT-PSS/**PMI1-BPOXD-MCz**/MgAg, exhibited polarized blue EL with a dichroic ratio of $R_{EL} = 5.1$ at 440 nm, which is slightly higher than the PL anisotropy as shown in Figure 5(b). This result indicates that the well-aligned **PMI1-BPOXD-MCz** films are obtained with a rubbed PEDOT-PSS layer by the following annealing treatment. The polarized EL spectrum showed a maximum peak at 440 nm and Commission Internationale de L'Eclairage (CIE) color coordinates of $(x,y) = (0.17, 0.04)$ at 15 V.

CONCLUSIONS

In this study, we synthesized a class of bipolar polymers containing OXD and Cz moieties to investigate polarized EL using the LCPs as efficient light-emitting materials in single-layer PLEDs. LC behavior, electro-optical properties and device performance were controlled by the alkyl groups at the Cz moiety. The synthesized polymer possessed bipolar charge-transporting properties, the LCPs showed lower HOMO levels comparing to the amorphous polymers. Intense blue emission was observed from the polymers and they showed high PL quantum efficiency over 70%. Using the LCP, polarized blue emission with a dichroic ratio of 5.1 was obtained in PLED.

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